Boreskov Institute of Catalysis
Center of New Chemical Technologies BIC
Russian Mendeleev Chemical Society, Novosibirsk Department

6th International School-Conference on Catalysis for Young Scientists

Catalyst Design

From Molecular to Industrial Level

Novosibirsk, Russia
May 16-19, 2021

ABSTRACTS

Novosibirsk - 2021

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Сборник включает тезисы пленарных, устных и стендовых докладов.
Основные темы научной программы конференции:
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- Preparation of catalysts and adsorbents
- Characterization and *in situ* studies of the catalysts
- Mechanism and kinetics of catalytic reactions
- Catalysis for renewable sources
- Catalysis for fine organic synthesis, natural gas and petroleum chemistry
- Catalysis for environmental protection, photocatalysis, electrocatalysis

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PLENARY LECTURES

PL-1 ÷ PL-11

PL-1

Biomass Valorization Relying on Aldol Condensation and Deoxygenation

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The conversion of lignocellulose biomass to valuable chemical products, including high-quality transportation fuels, has been attracting an ever-increasing interest. While lignocellulose has a complex composition, it can provide relatively simple molecules which can be considered as starting building blocks for the construction of more complex compounds with tailored properties.

Aldol condensation of lignocellulose-derived aldehydes and ketones is a promising tool to produce compounds with increased molecular weight starting from relatively simple molecules. The (partial) deoxygenation of the condensation products results in the formation of various valuable products including alcohols or even fuel-range hydrocarbons.

This presentation discusses aldol condensation of furfural and acetone or cyclohexanone (used as model compounds) in presence of Mg-Al mixed oxides and the corresponding reconstructed hydrotalcites as solid basic catalysts. Their catalytic performance will be compared with zeolite-based catalysts (having either acidic or basic character). Finally, strategies for deoxygenation of the aldol-condensation products will be discussed as well.

PL-2

Heterogeneous Catalysis for Sustainable Chemical Conversion: On Metal Nanoparticles, Clusters, and Single Atoms at Interfaces

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Heterogeneous catalysis significantly shapes society, as it plays a crucial role in the production of fuels for mobility and base and speciality chemicals. C_1 chemistry is expected to be pivotal in the transition from the current fossil-based economy to a sustainable reality in which renewable feedstocks and energy are widely employed for the production of fuels and chemicals. Typical heterogeneous catalysts for the activation of small molecules like CO, CO_2 and CH_4 consist of "metal on a support". Structure sensitivity refers to the dependence of chemical reactivity of metal nanoparticles on size: whilst well understood for supported metal nanoparticles – even for a complex reaction as Fischer-Tropsch synthesis -, there is a lack of insight about how size and structure of supported metal clusters affect their catalytic performance. The latter systems require strong metal-support interactions to be stable and often exhibit unexpected catalytic reactivity at the metal – metal-oxide interface. I will highlight several examples of such systems in which metal – metal-oxide interfaces form the active sites. These include metal oxides on metal nanoparticles as well as ultra-dispersed metal phases for the activation of small molecules.

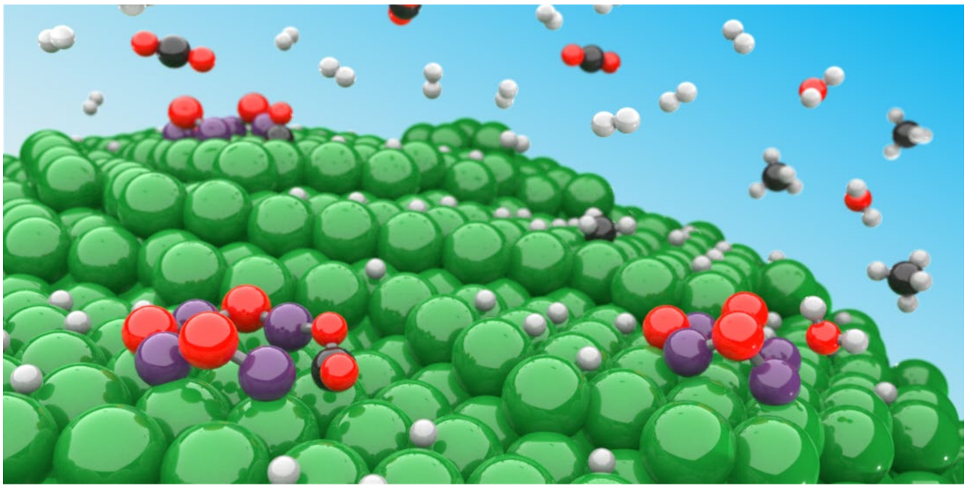

Figure 1: MnO clusters dispersed on Ni nanoparticles boost catalytic CO_2 hydrogenation through formation of oxygen defects in MnO, followed by facile C-O dissociation reactions of adsorbed CO and CO_2.

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PL-3

Creating Atomically Designed Catalysts by Gold Nanoclusters

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Catalysis is one of the key technologies that may finally enable a truly sustainable society. However, to understand and control catalytic performance of nanoparticles atthe molecular level remains a major challenge. Developing novel nanostructures withatomically controlled structural parameters is required, such as the number of atoms (size), elemental composition and surface modification by functional groups. This canbe achieved with metal nanoclusters, which have led to advances in nanoscience.

The application of monolayer protected metal nanoclusters is arising in several fields other than catalysis, like energy generation, sensing, electronics, bioimaging or medicaltherapy. Many of them involve the deposition of clusters on solid surfaces (supports),thus preserving the cluster properties is crucial. Particularly in heterogeneous catalysis, atomically precise gold nanoclusters open new opportunities for accurate studies of size-dependent properties, atomic structure effects and reaction mechanisms. However, a fundamental understanding of the cluster-surface interaction, control of the deposition and functionalization still needs to be improved.

We shed some light on this by in situ / operando spectroscopic studies (FTIR, XAFS, XPS), indicating a strong influence of the cluster structure/composition and support material on stability and catalytic properties. We studied the influence of Au systems,doped with metals such as Co, Ag, Pd, Pt or Cu, tuning the properties and reactivity in several reactions in gas and liquid phase. Further tuneability of the cluster propertieshas been achieved by ligand exchange reactions in solution and on supported clusters, inducing new properties like chirality. Furthermore, some of the cluster structures exhibit unexpected catalytic and intrinsically chiral properties, making thempromising asymmetric catalysts and providing ample opportunities to investigate chirality at a fundamental atomic level. First steps have been achieved on enhancing and understanding the chiral properties of clusters towards their application in heterogeneous enantioselective catalysis.

PL-4

Dispersed Catalysts for Refining, Natural Gas Chemistry and Renewables

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Industrial catalytic liquid phase processes traditionally used heterogeneous catalyst in reactors with insignificant motion of catalyst particles like fixed-bed or trickle bed reactors. The slurry bad reactors traditionally used in fine organic synthesis and its application in industrial process for refining and petrochemistry are limited. The advantages of slurry reactors deals with the high reaction rates and lower diffusion limitations for bulky substrate molecules, excellent heat and mass transfer characteristic for exothermic reactions like gas to liquid processes or hydrogenation. Other important advantages are the low pressure drop, the large catalyst area and lower catalyst consumption.

The traditional forms of catalysts for slurry reactors are micron-sized solid catalyst particles and an increase in the efficiency of the process can be associated with the use of nanosized particles (“nanoheterogeneous catalysis” [1-2]). The size of catalytic particles varied from nm to hundreds nm and the particles of catalyst are in dynamic equilibrium. Another approach for increase of efficiency of the process deals with the synthesis of catalyst in the reaction media with formation and a activation of catalytic active particles aggregates. Several hydrogenation processes for heavy oil processing using nanosized dispersed catalysts in slurry reactors have been scaled to the pilot, pilot-industrial and industrial levels [3] The formation of active catalyst in reactor media eliminate the stage of catalyst production and makes it possible to tune the catalyst to feedstock properties and reaction conditions.

We will discussed “nanoheterogeneous” approach for a number of industrially important processes as hydoconversion and hydrocracking of heavy oil feedstock and polymer wastes, hydrogenation of aromatics using sulfide based catalytic systems, hydrogenation of bio feedstock molecules. The features of catalytic systems based on molybdenum and tungsten sulfides for hydroprocessing of hydrocarbons with hydrogen or CO with water will be discussed. The data on the formation of nickel phosphide catalytic systems in situ for hydroproccesing of phenols, furfurol, levulinic acid will be presented. The application of dispersed catalysts based on iron and cobalt for transformation of syngas to hydrocarbons in bubble slurry systems and zeolites in liquid phase systems will be described .

Acknowledgement. This work was supported by the Russian Science Foundation, grant №17-73-30046

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PL-5

Cocktail-Type Catalytic Systems for Fine Chemicals Synthesis and Sustainable Development

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For a long time, development of catalytic systems provided outstanding driving force for the design of new industrial technologies. High demand in increasing molecular complexity focused in the area of fine chemical synthesis. Attempts to understand the nature of the catalytic reactions revealed a very complicated mechanistic picture, the concept of which underwent several “waves” from the simple molecular catalysis to complex dynamic nanoparticle systems (Figure 1) [1].

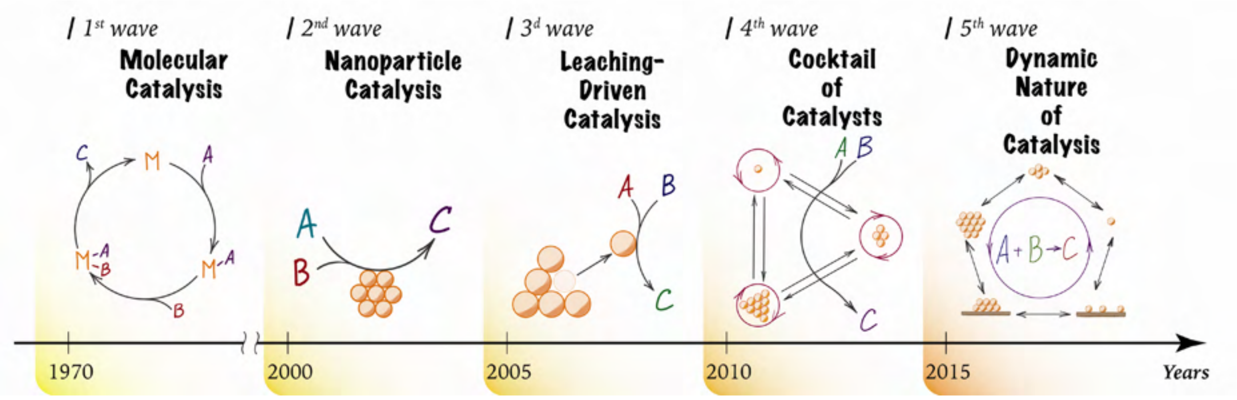

Figure 1. *Mechanistic studies of catalytic reactions [1].*

In the present lecture, the complexity of catalytic cycles will be discussed with the main emphasis on the problems of reaction mechanisms, which could be solved using modern powerful research methods [2]. Understanding complex reaction mechanisms in catalysis is urgently required to develop a new generation of chemical technologies with improved efficiency and selectivity, as well as particular attention on sustainability goals [3-5].

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PL-6

Correlating Structure and Reactivity on Energy Materials by In Situ Spectroscopy

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In heterogeneous catalysis surfaces decorated with uniformly dispersed, catalytically highly active particles are a key requirement for excellent performance. One of the main tasks in catalysis research is the continuous improvement or development of new catalytically active materials and the search for efficient catalyst synthesis routes.

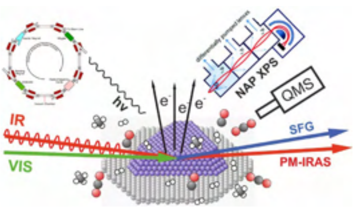

Fig. 1: Well-defined model catalysts were characterized in terms of structure, adsorbed molecules, and catalytic reactivity simultaneously.

Based on model catalysts we present different innovative approaches in catalyst design that allow precisely tuning the complexity of the surface structure. Furthermore, characterization under catalytically relevant reaction conditions (operando studies) with simultaneous gas analysis allows obtaining correlations between structure and reactivity.

Atomic layer deposition (ALD) can be utilized for controlled synthesis of catalysts with various surface structures (e.g. from small particles up to closed coatings) and the process can be easily scaled [1]. We present results on supported Pt model catalysts with different surface morphology and the resulting impact to catalytic reactivity.

Alternatively, an emerging concept in catalyst design is to selectively and reversibly tune and modify the surface chemistry by either electrochemical polarization or reductive treatment. Perovskite-type catalysts raise the opportunity to incorporate guest elements as dopants. Upon reduction (or in reducing reaction environment) these dopants emerge from the oxide lattice to form catalytically active clusters or nanoparticles on the surface (by exsolution). In consequence, this leads to a strong modification or enhancement of catalytic selectivity and activity.

Highlighted are studies for Pt/ZrO_2 model systems and different acceptor doped perovskite-type catalysts, which can be applied for CO2 utilization via rWGS or dry reforming. We show a direct correlation of surface chemistry with catalytic activity, selectivity.

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PL-7

Dynamic Structure of Active Sites in Ceria – Supported Pt Catalysts for the Water Gas Shift Reaction

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Determining the structure of active species and active sites, and their evolution in reaction conditions, are required step towards understanding catalytic mechanisms. In heterogeneous catalysts, multiple species of the same element: single atoms, larger clusters and nanoparticles may appear, disappear and coexist during the reaction. It is required therefore to monitor the charge and geometry of metal centers, as well as their dynamic changes, in reaction conditions. Even with that capability achieved, the reaction mechanism may not be understood until it is known which species are catalytically active, and which ones – spectators. One possible way to address that is to combine multiple in situ probes that can resolve between the heterogeneously distributed species with the online product analysis. This combination will correlate the changes in the spectra (and thus – in the structure) with the changes in activity and thus help identify the active species during the reaction. We used this multimodal approach to reveal the dynamic characteristics of a Pt/CeO_2 system at the atomic level for the WGS reaction and specifically reveal the synergistic effects of metal – support bonding at the perimeter region. We find that the perimeter Pt(0) − O vacancy−Ce(3+) sites are formed in the active structure, transformed at working temperatures and their appearance regulates the adsorbate behaviors. We find that the dynamic nature of this site is a key mechanistic step for the WGS reaction.

PL-8

Probing Kinetics of Electrocatalyst Transformations Using Synchrotron-Based *Operando* Techniques and Machine Learning

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The need to develop a sustainable energy economy together with environmental concerns have brought increasing attention to the studies of electrocatalytic processes, which might enable new cost-effective and environment-friendly routes for production of valuable chemicals and fuels. Our understanding of these processes, however, in many cases is still limited. In particular, our knowledge of the working mechanisms of electrocatalysts is still incomplete, which hinders the further improvement in the catalytic materials. The rapid developments in *operando* experimental characterization techniques and in theoretical methods during the last decades highlight the concept of catalysts being complex dynamic systems that actively transform and respond to the reaction conditions, rather than are just a static arrangement of atoms. This paradigm shift results in an even more pressing need for experimental tools that would allow one to probe the composition, structure and dynamics of catalysts in time-resolved manner under realistic reaction conditions. An additional challenge here is that catalysts are often heterogeneous, disordered systems with multiple species coexisting. In many cases the nature of the actual active site is still a matter of heated debate.

Synchrotron-based methods, such as *operando* X-ray absorption spectroscopy (XAS) and high energy X-ray diffraction (XRD) are well suited to provide key information from different perspectives about the identity of the active species and their activation/deactivation under reaction conditions, the reaction intermediates and preferred reaction mechanisms and the role of the reaction environment. However, in addition to experimental hurdles of tracking the structural changes in realistic working catalysts, one also needs to address the problem of data analysis. Indeed, the data treatment approaches that worked well for decades in the studies of well-defined samples under ambient conditions, can be inadequate for the characterization of dynamic processes in realistic heterogeneous and disordered samples in contact with diverse environments. A recently developed solution relies on applications of machine learning methods for deciphering experimental data. Here we illustrate the possibilities, enabled by synchrotron-based time-resolved *operando* investigations and machine learning methods, on example of studies of dynamic structural and compositional changes in copper-based catalysts for electrochemical reduction of CO_2.

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PL-9

Fischer-Tropsh Synthesis: an Old Reaction for New Perspectives

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PL-10
Catalysis for Energy Conversion

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The growth of civilization requires a lot of energy in many forms (Fig. 1). Different types of energy (electrical, chemical, light, etc.) are suitable for appropriate processes and in the case of insufficient amount of certain type of energy the process of its transformation is needed. In this way the development of the effective methods of energy conversion, transportation and storage is the vital task.

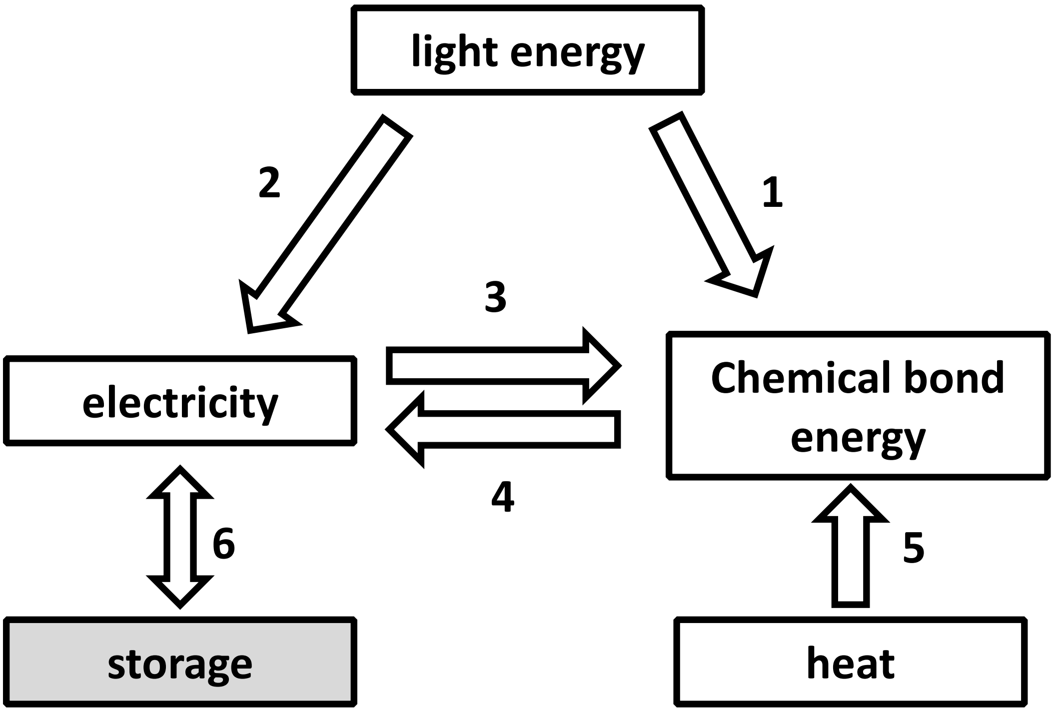

Fig. 1. Pathways for energy conversion and storage: 1. Photocatalytic water splitting, hydrogen evolution and CO_2 fixation; 2 – photo-electrochemical conversion; 3 – electro-synthesis; 4 – fuel cells; 5 – power to X conversion; 6 – super capacitors.

The catalytic approach allows to decrease the energy barriers and to increase the efficiency and selectivity of chemical reactions and physical processes of energy transformation and storage [1-5]. It should be noted that the energy transformation tasks frequently appear in the field of unconventional catalytic processes: artificial photosynthesis, hydrogen energy, photo-electrochemical light conversion etc.

The existing approaches for energy storage and transformation and the examples of their realization in the Boreskov Institute of Catalysis will be the subject of presentation.

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PL-11

In Situ/Operando Characterization of Electrocatalytic Materials by Bulk and Surface Sensitive X-Ray Spectroscopies

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An in depth understanding of the atomistic mechanism underlying different electrochemical processes requires recording large sets of data under *operando* conditions yielding key information of the electrified interface [1]. Thus, the desired parameters to be known include the chemical composition at the interface, chemical states of the atoms and their variation as a result of the electrochemical reactions as well as the structural evolution. Unfortunately the analytical techniques able to provide interface information are very limited and hardly compatible with liquids [2] allowing usually only *ex situ* characterizations leading to a loss of important information as in many cases the intermediates and electrocatalytic actives species cannot be "quenched" in post process analysis. X-ray spectroscopy techniques are able to provide relevant information of the electronic structure in an element specific manner but real electrochemical interfaces are buried and most of the time in presence of liquid electrolytes being inaccessible directly to the common surface sensitive techniques like photoelectron spectroscopy requiring new experimental strategies for their operation under these conditions [3]. In this talk I will present some of the new approaches developed in our laboratory which allow the investigation of the electronic structure variation of the electrocatalysts under reaction conditions using photoelectron spectroscopy, from gas phase up to bulk aqueous electrolyte [4-6]. These experimental setups based in photoelectron spectroscopy were used, among others, to investigated the not kinetically favored oxygen evolution reaction onto IrO_x catalysts which it is the study case in this presentation. Furthermore, their performance as well as the influence of the partial pressure in the operation will be compare with well established bulk sensitive approaches based in photon-in/photo-out techniques in flourescence yield mode [7] in order to validate these new approaches based in photoelectron detection.

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Catalyst Design

From Molecular to Industrial Level

MASTER CLASS

MC

AI Imaging Data Analysis in Material Science: Microscopy and Behind

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Advanced microscopy techniques, such as scanning probe microscopy, electron microscopy or optic microscopy are widely used in modern material science both at the stage of designing and investigation of materials. In heterogeneous catalysis, the catalyst usually consists of an active component deposited as nanoparticles on a support. To compare catalysts it is necessary to know the particle's parameters (size, amount, coverage of the surface, etc.). When microscopy is used for these purpose processing data on hundreds of particles from several points of the catalyst is required, the more the better [1]. So having available and simple in use tool for automatic object recognition, size measuring and statistical analysis can significantly lighten the work of researchers release the time for experiments.

In the present work two services for automatic image data processing based on the use of deep neural networks, or in other words artificial intelligence (AI), are presented:

- the web service ParticlesNN with a pre-trained neural network for online recognizing nanoparticles in scanning tunneling microscopy and transmission electron microscopy images;
- the cloud service DLgram based on the Telegram channel that allows a user to train the network on its own images and to use it in future work.

The results of recognition allow statistical analysis of obtained data (size, quantity and area, histograms).

The online service ParticlesNN

We have developed the online service ParticlesNN [1] (http://particlesnn.nsu.ru), which is based on the Cascade Mask-RCNN neural network. The online service ParticlesNN processes the results obtained by determining the size of the contours and their statistical parameters – the degree of coverage, concentration, average size, and object size distribution.

The ParticlesNN online service differs from other software products, such as ImageJ/Fiji [2], WSxM [3] or CellProfiler [4], in the following features [1]:

- it is possible to process images that contain significant noise and artifacts without pre-processing;
- the user can adjust automatically defined contours in order to refine the recognition results;
- the option of simultaneous statistical processing of several images is implemented;
- the processing results are displayed in the form of a histogram and tables, in which information on all identified objects is available – their coordinates, dimensions;
- the refinement of particle contours is implemented using the fitting procedure with a Gaussian 2D distribution;
- functions of correct accounting of objects on the image border are implemented.

The detailed text and video instruction for the use of the service is available on the web site of the service. The authors implement permanent support of the service work.

The cloud service DLgram

We implemented a revolutionary subshot learning approach that allows researchers to train a deep neural network using a handful of the instances of objects of interest. The trained network able to effectively recognize the rest of the object instances on the same image as well as correctly segment similar objects on other images. Training and inference can be implemented in no code mode and perform automated processing of scientific data using a cloud service in Telegram messenger group referred as t.me/nanoparticles_nsk [5].

The realized cloud service is especially user-friendly for the following reasons:

- no need to install special software;
- it is possible to train a neural network on any type of objects;
- for training only a few objects should be labelled;
- the trained neural network can be used for recognizing identical objects on other similar images;
- the user can adjust automatically defined contours in order to refine the recognition results;
- the statistical processing of the obtained data is implemented.

The cloud service works well with any microscopy images (transmission electron microscopy, scanning electron microscopy, scanning probe microscopy of any type, optic microscopy) for any applications (material science, catalysis, biology, etc.). User defines the quality of recognition by himself following the instruction presented in Telegram messenger group. Important, that the cloud service DLgram can be easily applied not just for microscopy image analysis, but for any images, for example, to measure size distribution of grains of catalysts by photo.

Proposed services are user-friendly and the accuracy of recognition and measurement are satisfactory for the requirements of research tool. Application of deep neural network approach allows broad possibilities for service improvement and adaptation for certain application.

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6th International School-Conference on Catalysis for Young Scientists

Catalyst Design

From Molecular to Industrial Level

ORAL PRESENTATIONS

Section 1. Preparation of catalysts and adsorbents
OP-I-1 ÷ OP-I-14

Section 2. Characterization and *in situ* studies of catalysts
OP-II-1 ÷ OP-II-13

Section 3. Mechanism and kinetics of catalytic reactions
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Section 4. Catalysis for renewable sources
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SP-1

OP-I-1

Oxidovanadium Complexes with Diimine Ligands: Synthesis and Catalytic Studies

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Oxidovanadium complexes containing the V=O group are the most common class of compounds in the chemistry of vanadium. They possess high catalytic activity in various oxidation reactions including alkane oxidation, olefin epoxidation, aromatization of α,β-unsaturated cyclohexanone derivatives, alcohol oxidation, C-C bond cleavage of glycols, naphthol coupling and α-oxidation of hydroxyl esters and amides, alkane oxidation [1-4].

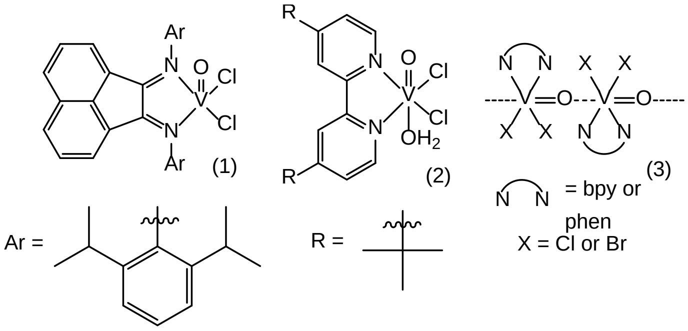

Fig. 1. The structure of complexes 1-3.

This work is devoted to the study of reactions of VX_3 (X = Cl, Br) or $VCl_3(thf)_3$ with diimine ligands, such as 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen), 4,4′-di-tert-butyl-2,2′-dipyridyl (dbbpy), bis(imino)acenaphthene (dpp-bian) in acetonitrile in air, which lead to the formation of molecular complexes $[VOCl_2(dpp\text{-}bian)]$ (1), $[VOCl_2(H_2O)(dbbpy)]$ (2), and polymeric compounds $[VOX_2(L_{NN})]$ (X = Cl, Br; L_{NN} = bpy, phen) (3). Magnetic and redox properties were investigated for the obtained compounds. Complexes 1-3 exhibit high catalytic activity in alkane oxidation reactions, and complex 2 catalyzes cyclooctene oxidation [1-2].

Acknowledgement. This work was supported by the Russian Science Foundation, grant 18-03-00155.

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OP-I-2

Phase Transformations Occurring During Mechanochemical Synthesis of the MgAl-Layered Double Hydroxides

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Layered double hydroxides (LDH) are one of the most studied materials. LDH, as well as the products of their calcination – mixed oxides – have large areas of application. They are used as adsorbents, catalysts, catalyst supports, materials for the delivery of drugs. Coprecipitation is a traditional method of LDH synthesis. The most serious disadvantages of this method are the duration, the large amount of alkaline rinsing water, and the difficulty of obtaining some types of LDH (for example, containing Li cations). In this regard, the search for new, fast and eco- friendly methods for LDH synthesis is an actual task. Mechanochemical synthesis is a perspective method of LDH preparation. It is waste-free and helps to reduce the amount of alkaline wash water.

The aim of this work was to study of the composition and structure of MgAl-LDH formed during mechanochemical synthesis at varying the acceleration of the milling bodies and the activation time. In addition, the effect of the conditions of mechanochemical synthesis on the structural properties of mixed oxides obtained after calcination of MgAl-LDH at a temperature of 550 ° C was investigated.

MgAl-LDH were synthesized by mechanochemical method in two stages. At the first stage initial reagents ($Mg(OH)_2$, $Al(OH)_3$ (gibbsite) and Na_2CO_3) mechanical activated in a planetary mill AGO-2C with steel drums and steel balls. At the second stage the aging of the mixture in distilled water at 65 °C with vigorous stirring were performed. The synthesis was conducted at acceleration of the milling bodies 500 or 1000 m s^{-2} at different activation time (5 – 90 min). Metals content (Mg, Al, Fe) in the solid MgAl-LDH after their calcination and dissolution were estimated by inductively coupled plasma atomic emission spectrometry on a Varian 710-ES instrument. Structural properties of the synthesized LDH were studied by means of X-Ray diffraction analysis (XRD). X-ray diffraction studies were carried out on a D8 Advance (Bruker) diffractometer using Cu-Kα radiation (λ=0.15406 nm).

Chemical and phase composition of the samples were studied both immediately after mechanical activation and after their aging in distilled water. Also structural properties of calcined LDH synthesized at 1000 m s^{-2} at different time were studied.

It was shown that the LDH phase didn’t form directly after mechanical activation regardless of the synthesis conditions. The invariability of the position of magnesium and aluminum hydroxides peaks at the diffractograms indicates the absence of any chemical interactions between them. The broadening of the peaks of metal hydroxides indicates decrease of the particle size and an increase in their X-ray amorphousness with increasing activation time. Moreover, the formation of the watered sodium carbonate occurred during mechanical activation. The formation of the MgAl-LDH phase took place even after 5 minutes of activation (acceleration 1000 m s^{-2}) and 15 minutes of aging water. However, the reaction between the initial reagents does not proceed completely, since the diffractogram also contains distinct peaks characteristic of the initial substances: magnesium and aluminum hydroxides (Fig. 1). The full transformation of initial components with the formation of single-phase MgAl-LDH occurred after 30 minutes of activation at acceleration of milling bodies 1000 m s^{-2}. A further increase in the activation time up to 60 minutes did not lead to the appearance of any additional phases except for the LDH phase. The acceleration of the milling bodies plays a primary role in the process, since single-phase MgAl-LDH formed for 30 minutes at acceleration of 1000 m s^{-2} and for 90 minutes at acceleration 500 m s^{-2}. In accordance to the data obtained in the present study, we can make the assumptions about the mechanism of MgAl-LDH formation in the process of mechanochemical synthesis.

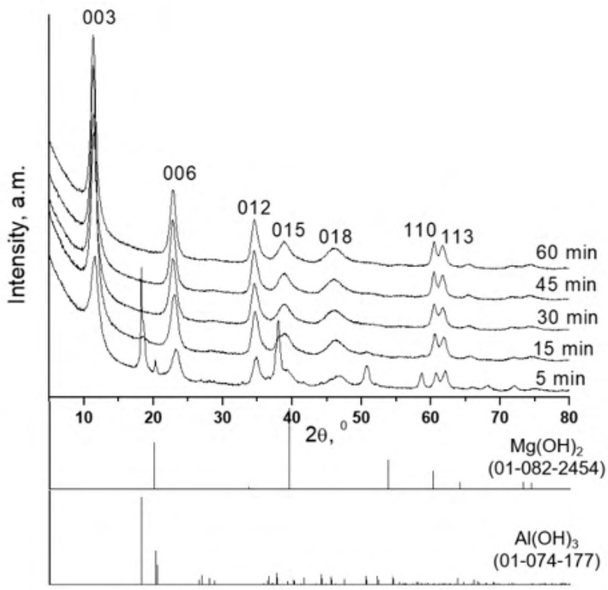

Fig. 1. Diffractograms of the samples prepared at mechanical activation of the mixture of initial reagents at acceleration of milling bodies 1000 m s^{-2} after water aging step.

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OP-I-3

Influence of the Preparation Conditions on Formation of Active Component Particles of Pt/Sibunit Catalyst

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The development of Pt on Sibunit catalyst has got significant attention due to its broad range of applications from the standpoint of active species of high catalytic activity and porous support with high surface area and low concentration of impurities [1]. As the preparation conditions during the widely used wet impregnation method of synthesizing supported catalysts play a critically important role in obtaining the desired final characteristics for targeted implementation of Pt/Sibunit catalyst, so an immense need for deep investigation about the influence of preparation conditions is essentially required.

The core aim of this research was to define the effect of preparation conditions, so in the present work different sets of Pt/Sibunit catalyst samples were prepared by varying preparation conditions such as pretreatment of carbon support with HNO_3, platinum precursor solution composition [2], and $NaBH_4$ and H_2 reductants.

To observe the effect of pretreatment on support, a BET - analysis of Sibunit was carried out before and after the interaction of 70% concentrated HNO_3 with Sibunit at room temperature, which showed a substantial increment in the volume of pores and surface area due to etching of the surface of a support. XPS (X-ray photoelectron spectroscopy) study revealed the appearance of $-NO_2$ groups and the increase of the amount of oxygen functional groups (C=O, C(O)O, and C-OH) [3,4] which serve as anchoring sites for active component precursor on the Sibunit support. Both original and pre-treated supports were used for Pt deposition using procedures similar to described in [2]. Platinum nitrate (IV) solution and the same solution modified with TMA (tetramethylammonium hydroxide) were used as active component precursor solutions.

The influence of support pre-treatment as well as precursor solution composition on chemical state of platinum just after impregnation as result of ‘active component – support’ interaction was shown by XPS. According to XPS analysis the depth of platinum reduction is higher when TMA - modified solution and HNO_3 pre-treated Sibunit are used. It can be expected that the difference in ‘active component – support’ interaction adjusted at preparation stage is important for the catalytic behavior and system stability under reaction conditions [2].

To study the influence of Pt reduction conditions H_2 and $NaBH_4$ were used as reductants. All the reduced catalysts with different preparation conditions were analyzed by transmission electron microscopy (TEM) to investigate the morphological characteristics. The migration and agglomeration of the Pt active specie on the surface of the support, led to wider particle size distribution, had been found out in case of using H_2 as reducing agent. The most uniform and narrow particle size distribution with mean particle size of 2.1 nm (original

Sibunit) and 2.5 nm (HNO_3 pre-treated Sibunit) was achieved when Pt nitrate solution modified with TMA and $NaBH_4$ as reductant were used.

The XPS/TEM/BET study of Pt on Sibunit at every stages of preparation depending on preparation conditions gave the keys to control chemical state and particle size distribution of the final catalysts.

This work was conducted within the framework of the budget project for Boreskov Institute of Catalysis SB RAS.

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OP-I-4

Comparison of Methods for Surface Modification of Hyper-Crosslinked Polystyrene for the Synthesis of Bifunctional Catalyst

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Reactions in the presence of catalysts on the polymeric support become more significant in the recent years. Hyper-crosslinked polymers represent a class of microporous polymeric materials obtained by the intensive crosslinking of linear or rarely crosslinked polymer-precursors. Hypercrosslinked polymers are characterized by a very high surface area, porosity, a low density, outstanding adsorption properties, and high chemical and thermal stability [1,2]. From this point of view, hypercrosslinked polymers are promising supports for metallic catalysts. In spite of high advantages of the hypercrosslinked polymers for the catalysts, their main drawbacks are hydrophobicity of the surface and the absence of acid-base sites [3]. One of the methods for the solution of these problems is the modification of the polymer surface to impart them specific properties. The strategy of coating hypercrosslinked polymers with nanostructured inorganic materials is of special interest. For example, a new category of HPS-based nanocomposites containing surface-modified carbon nanotubes, graphene nanosheets, and surface-modified graphene oxide was synthesized [4, 5]. This functionalization of the surface makes it possible to obtain new materials combining advantages of polymeric and inorganic supports.

HPS was chosen for the catalyst support because of its high surface area and rigid structure. Moreover, it is highly hydrophobic and has a good affinity toward the hydrocarbons [6-8]. Thus, the modification of the polymer was carried out to form the acid sites.

To form the silica-containing phase which is characterized by the high acidity, the polymer was treated with the TEOS and APTES. Two different methods for the silica deposition on the HPS surface were used: wet impregnation and hydrothermal deposition. The active phase was applied to the surface of the modified polymer using the hydrothermal method.

To evaluate the porosity of the synthesized catalysts and the influence of silica precursors and synthesis methods, the study was performed using the low-temperature nitrogen physisorption and also the analysis of the pore size distribution. Polymer impregnation with TEOS and APTES leads to a decrease in the surface area of the support and pore volume however, the form of isotherms does not change. This indicates that the structure of the support remains the same as that for the initial polymer. Silica deposition on HPS by the hydrothermal method leads to the changes in both the isotherm and hysteresis loop forms which correspond to the micromesoporous materials.

The deposition of metal phase on the surface of the modified polymer showed the changes in the porous structure that was confirmed by the shift of the form of the hysteresis loop to H4 typical for micromesoporous materials. These changes were observed for all studied samples. Besides, neither the surface area nor pore volume practically decreased during the metal incorporation. To compare the influence of the synthesis method and silica precursor type on the formation and distribution of the silica-containing phase, the samples were studied by the transmission electron microscopy. The hydrothermal deposition allows the SiO_2 particles to be distributed uniformly on the polymer surface in comparison with those obtained by the impregnation. Moreover, when the catalysts were synthesized hydrothermally, the silica-containing phase precipitated on both internal and external surfaces of HPS, while the impregnation leads to the formation of silica phase predominantly on the external polymer surface. It should be noted, that when the TEOS was used as a silica precursor, the better precipitation was observed in both impregnation and hydrothermal deposition methods in comparison with the use of APTES.

Analysis of the composition of the metal-containing phase was performed using the X-Ray photoelectron spectroscopy. The study of the silica-containing phase was performed by the X-Ray photoelectron spectroscopy and FTIR-spectroscopy. To estimate the silica-containing phase crystallinity, XRD patterns were obtained for the synthesized samples using Empyrean diffractometer. The measurements of catalyst acidity were carried out by the ammonia chemisorptions.

The use of TEOS as a silica precursor provides higher acidity of the synthesized catalysts. Hydrothermal deposition seems to be the most effective method for the polymeric support modification with silica. The synthesized bifunctional catalysts combine the advantages of highly porous polymer-based structure, a high acidity of SiO_2.

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OP-I-5

Application of Iridium(III) Aquanitrocomplexes for the Preparation of Supported Ir-Ni Catalysts for Selective Decomposition of $N_2H_4{\cdot}H_2O$

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The absence of safe and effective methods of hydrogen storage is the major threshold in the widespread application of hydrogen as an environmentally-friendly fuel. The hydrous hydrazine is a promising material for the chemical storage of hydrogen, containing 8.0 wt% of H and producing only nitrogen as the complete decomposition by-product. Noble metal-containing catalysts have proven themselves as very active systems of $N_2H_4{\cdot}H_2O$ decomposition, albeit having low H_2 selectivity. For example, Ir/Al_2O_3 is the most active catalyst for hydrazine decomposition, but its selectivity towards the H_2 generation is only 6%. The competitive process of $N_2H_4{\cdot}H_2O$ disproportionation leads to the production of ammonia which not only lowering the efficiency of the fuel but also might be harmful to the elements of the fuel system (fuel-cells and membrane). The addition of Ni or Co can significantly improve characteristics of catalysts, so that Ni-M (Ir, Rh, Pt) bimetal nanoparticles supported on metal oxides (Al_2O_3, CeO_2, etc.) are among the most active systems for the $N_2H_4{\cdot}H_2O$ decomposition and show the H_2 selectivity up to 100% [1].

Halogen-free precursors are generally utilized for the preparation of such systems as halogen-ions are known to cause poisoning and corrosion of the catalysts. However, while for Pt, Rh, Pd the halogen-free thermolabile precursors with aqua-, hydroxo- and nitrato-ligands (CAS: 18496-40-7, 10102-05-3, 21656-02-0, 34513-98-9), which can be easily removed from the surface, are commercially available, in case of iridium there are no analogous appropriate compounds.

As an alternative in this work, we consider aquanitrocomplexes of Ir(III) (Ir ANC), mainly *fac*-$[Ir(NO_2)_3(H_2O)_3]$ [2,3], as precursors for the preparation of supported Ir-Ni catalyst of hydrogen generation from hydrous hydrazine. The main advantage of the Ir ANC is a combination of thermolability along with high stability during the storage (compare to traditional counterparts Ir ANC are stable in water solutions in a wide range of pHs, do not undergo hydrolysis with formation of IrO_x sol [2,3]). Additionally, the high solubility of the ANC in water and organic solvents allows achieving high concentration of iridium on a support in a single deposition step. Meanwhile, deprotonation of aqua-ligands in ANC to hydroxo allow controllably charging the complexes for the processes of electrostatic sorption of the iridium precursor on a supports surface. This work reports the preparation techniques and investigation of the Ir-Ni bimetallic nanoparticles supported on different supports (Al_2O_3, MgO, layered double hydroxides) utilizing the Ir ANC as a new perspective iridium precursor.

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OP-I-6

Design of an Affordable and Efficient SAPO-34 Catalyst Based on Natural Halloysite Nanotubes

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Silicoalumophosphate molecular sieve of SAPO-34 type with topological structure of chabazite (CHA) is a subject of a large number of studies as one of the most effective catalysts for methanol to olefin process. However, the microporous structure of SAPO-34 is prone to rapid deactivation due to coke formation, which significantly reduces the catalyst's lifetime [1].

In recent years, various synthetic strategies have been developed to reduce the rate of coke settling. Among the proposed methods is the introduction of meso- or macropores into the SAPO-34 framework, which can significantly reduce coke formation by increasing the efficiency of mass transfer of reagents and products, thus extending the life of the catalyst [2].

In this work, a micro/mesoporous catalyst SAPO-34 was synthesized using halloysite nanotubes (HNT) as a co-template. Halloysite is a natural aluminosilicate material with a molecular formula $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ (n = 0, 2). HNTs are multilayer mesoporous nanotubes, the outer surface of which consists of silicon oxide, and the inner surface of aluminum oxide. Also, the application of halloysite as a source of SiO_2 and Al_2O_3, instead of traditional reagents, can reduce the cost of the final product.

The SAPO-34 samples were obtained according to the modified method described in [3] using tetraethylmonium hydroxide as the main template. To discover the regularities of the synthesis, the duration of hydrothermal treatment was varied from 24 to 48 h. The obtained materials were compared with a reference sample SAPO-34 synthesized on the basis of standard reagents - tetraethyl orthosilicate (TEOS) and aluminum isopropoxide (AIP). Table 1 presents the synthesized samples, the conditions of their synthesis, and the obtained texture characteristics.

Table 1. Synthesis conditions, compositions and textural properties of the SAPO-34 samples

Sample	Crystallization time, h	Source		Molar composition of obtained samples	S_{BET}, m^2/g	Pore volume, cm^3/g	
		Al	Si			V_{meso}	V_{micro}
S-1	24	AIP	TEOS	$0.3SiO_2/1.1Al_2O_3/1.1P_2O_5$	475	0.03	0.28
S-2	48			$0.3SiO_2/1.3Al_2O_3/1.3P_2O_5$	335	0.01	0.19
S-3	24	AIP + HNT	HNT	$0.3SiO_2/0.8Al_2O_3/0.5P_2O_5$	381	0.06	0.17
S-4	48			$0.3SiO_2/1.1Al_2O_3/1.1P_2O_5$	412	0.10	0.21

To confirm presence of the target structure, a complex of physicochemical analyzes was carried out: X-ray diffraction (XRD), X-ray fluorescence (XRF), low-temperature adsorption/desorption of nitrogen, scanning and transmission electron microscopy (SEM and TEM).

According to the results of XRD analysis (Fig. 1.), S-1 and S-2 samples had a target structure of chabazite, which is a characteristic of SAPO-34 formation. The XRD pattern obtained for S-3 did not reveal the presence of CHA, while S-4 had most of the desired peaks. However, in addition to the SAPO-34 phase S-4 also contained some amount of aluminum phosphate.

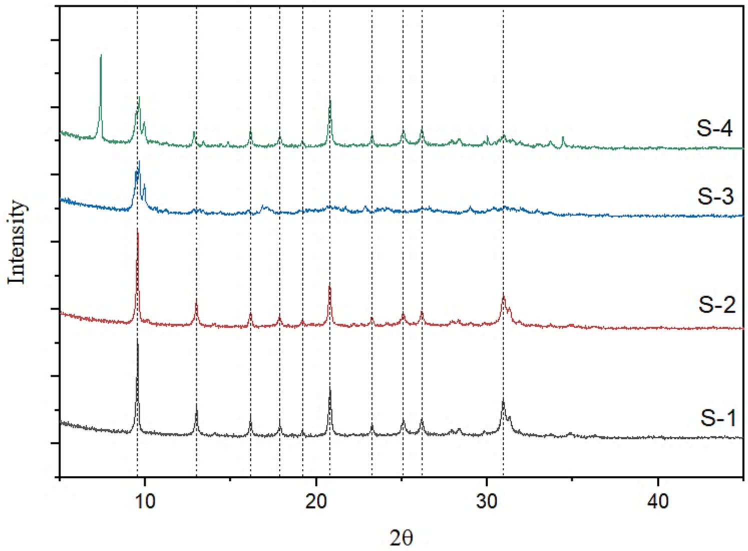

Fig. 1. Powder XRD patterns of SAPO-34 synthesized specimens (Dotted lines - characteristic peaks of SAPO-34)

As shown in the SEM images (Fig. 2.), the crystals of the samples had a cubic morphology, which is typical for SAPO-34 [4]. The average crystal size of the reference sample S-1 was 1.02 µm, and that of S-4 sample was 0.95 µm.

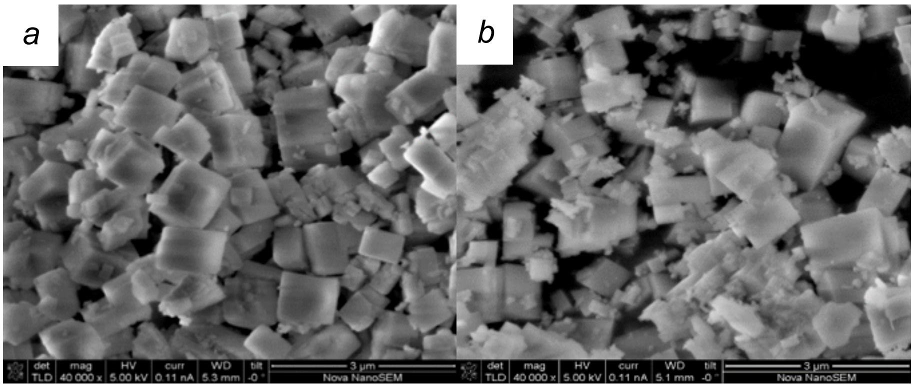

Fig. 2. SEM images of S-1 (a) and S-4 (b) samples

The studies carried out prove the possibility of synthesizing micro/mesoporous material SAPO-34 using natural aluminosilicate halloysite nanotubes as a co-template during hydrothermal treatment for 48 h. The sample synthesized on the basis of HNT for 48 h demonstrates a high purity of the SAPO-34 phase, has a large specific surface area (S_{BET} = 412 m^2/g) and a significant number of mesopores (V_{meso} = 0.10 cm^3/g).

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OP-I-7

Design of Pt-Ga Catalysts Supported on Hierarchical Silica Materials for Propane Dehydrogenation

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The CrO_x/Al_2O_3 (Catofin process) and $Pt\text{-}SnO_x/Al_2O_3$ (Oleflex process) catalysts are the major industrial catalysts used for direct propane dehydrogenation (PDH). The main disadvantage of the alumina support consists in high surface acidity that leads to a decrease in the selectivity and catalyst deactivation due to the coke formation. The growth of propylene market and abovementioned factors prove the need to designing new PDH catalysts. The bimetallic Pt-Ga combination is a promising catalyst system since both components are active in the PDH reaction [1]. Moreover, the gallium additions enhance both the dispersion of platinum particles and the stability of the catalyst system.

The silica support MCM-41 is one of the most studied mesoporous materials and is promising for the preparation of catalysts based on transition metal oxides and/or noble metals [2,3]. However, the PDH is a high temperature diffusion controlled process that requires specific catalyst structure that ensures efficient transport of reagents to the active sites of the catalyst and removal of products from the reaction zone. The materials with a hierarchical porous structure are promising to address this challenge by combining a wide pore transport system (mainly, above 50 nm) and mesopores providing high values of specific surface area of the catalyst [4].

The present study is devoted to development of silica support with a hierarchical structure based on the diatomite and MCM-41 as well as to designing of the Pt-Ga catalysts on the basis thereof for the propane dehydrogenation to propylene.

The MCM-41 was synthesized from sodium silicate in an alkaline medium (pH≈12) using cetyltrimethylammonium bromide (CTAB) as a template. The diatomite (LLC “Kvant”, Russia) was used to synthesize the composite MCM-41/diatomite supports [5]. The $Pt\text{-}Ga/SiO_2$ catalysts were prepared by impregnation method. 9 wt.% gallium and then 1 wt.% platinum were introduced by the incipient wetness impregnation of SiO_2 from the corresponding precursors, i.e., gallium nitrate and H_2PtCl_6 solution. After the impregnation, the catalyst was calcined at 500 °C under air. The structure and chemical properties of the synthesized materials were studied by low-temperature nitrogen adsorption, SEM, XRD, and TPR-H_2 methods.

According to the low-temperature nitrogen adsorption results (Fig. 1a), the sharp increase in the adsorption value in the relative pressure range of 0.3-0.38 is observed for MCM-41/diatomite composite indicating the presence of the ordered MCM-41 structure in the material. A hysteresis loop in the pressure range of 0.95-1.0 also indicates the preservation of the diatomite macroporous structure in the material [4]. Thus, the MCM-41/diatomite composite is characterized by the hierarchical porous structure. Fig. 1b represents the SEM image for diatomite. A layer of amorphous material that may be attributed to the MCM-41 is observed in the diatomite pores for the MCM-41/diatomite composite (Fig. 1c). The XRD results for Pt-Ga catalysts show that the samples are characterized by the amorphous silica and β-Ga_2O_3. The Pt-containing samples are characterized by the presence of metallic Pt particles.

The catalytic activity was investigated in the PDH reaction at 550 °C. According to the results obtained, the Pt-Ga catalysts show higher activity compared to Pt and Ga_2O_3 catalyst (Fig. 1d) that may be attributed to the synergy between Pt and Ga_2O_3 species in the dehydrogenation reaction. The Pt-Ga/MCM-Diatomite catalyst shows the highest activity due to both Pt-Ga synergy and increased surface area of the catalyst.

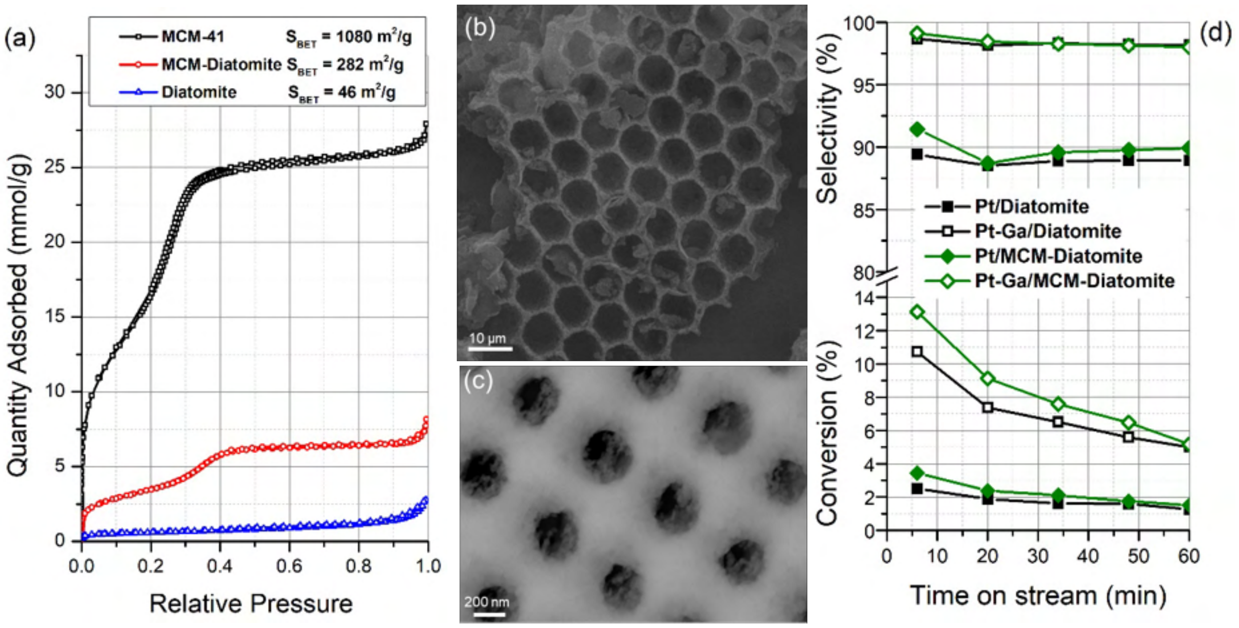

Fig. 1. Nitrogen adsorption-desorption isotherms for synthesized supports (a); SEM images for diatomite (b) and MCM-Diatomite composite (c); catalytic activity in PDH at 550 °C (d).

In summary, it was shown that the synthesized composite support MCM-41/diatomite is characterized by a hierarchical porous structure. The Pt-Ga catalysts supported on MCM-41/diatomite composite is characterized by high activity in the propane dehydrogenation reaction. The effect of Ga addition comprising the increase in the efficiency of Pt catalysts has been shown.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant No. 19-43-700008.

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OP-I-8

The Influence of Dopant, Modifier and Template Nature on the Catalytic Efficiency of Ceria in CO Oxidation

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Unique redox properties provide high efficiency of ceria-based systems in oxidation of CO and soot particles [1]. However, in terms of catalytic activity, they are inferior to widespread catalysts, including supported metals. Nowadays the development of new approaches to improve catalytic properties of relatively cheap CeO_2-based systems is a pressing task. Several methods have been proposed to improve the efficiency of catalytic systems based on cerium oxide, among them doping with the oxides of the other rare-earth or transition elements, addition of modifiers and promoters, and optimization of preparation conditions. In our work, we tried to reveal the combination of these ways which is the most effective to improve catalytic properties of CeO_2 in total oxidation of CO, alone or in the presence of hydrogen (PROX).

The series of $Ce_{0.8}Zr_{0.2}O_2$ (CZ) samples was synthesized by co-precipitation method using different template agents (cetyltrimethylammonium bromide, CTAB; Pluronic 123, P123; pine sawdust, SD) or without template by co-precipitation with ammonia solution (CP) [2, 3]. Then the CZ systems with the most promising catalytic properties in CO oxidation were modified with MnO_x or CuO (Mn-CZ and Cu-CZ). Mn and Cu loadings were about 8 wt.%. To compare catalytic efficiency of Zr and Sn-containing systems in CO oxidation and reveal an influence of dopant nature $Ce_{0.9}Sn_{0.1}O_2$ (CS) and $CuO/Ce_{0.9}Sn_{0.1}O_2$ (Cu-CS) were also produced by CTAB-templated method.

Catalytic properties in CO oxidation were tested in the fixed-bed microcatalytic set in a pulse regime (2 vol.% CO, 1 vol.% O_2 in He, 60 ml/min) at 100 to 400°C. PROX CO was performed in ULKat-1 (UNISIT, Russia) catalytic setup equipped with fixed-bed continuous-flow steal reactor (4 vol.% CO, 3 vol.% O_2, 13 vol.% N_2 and 80 vol.% H_2, 76 ml/min) at 50 - 450°C.

As we can see from catalytic results presented in Fig. 1(a) all types of templates provide an improvement of catalytic efficiency of double CZ systems in CO conversion, especially significant for CZ(SD) and CZ(CTAB). Despite the lower specific surface area (Fig. 1(b)), CZ (SD) exhibits much higher activity over the investigated temperature range than the other samples, possibly because of improved oxygen mobility. On the base of O1s XPS spectra, TPR data and the Raman spectra it was demonstrated that advanced oxygen mobility is characteristic for biomorphic samples in comparison with CP and CTAB-templated ones. In addition, according to XPS and SEM-EDA data, biomorphic CZ sample comprises ash impurities e.g. K and Ca, which can promote the catalytic activity in the oxidation reactions.

OP-I-8

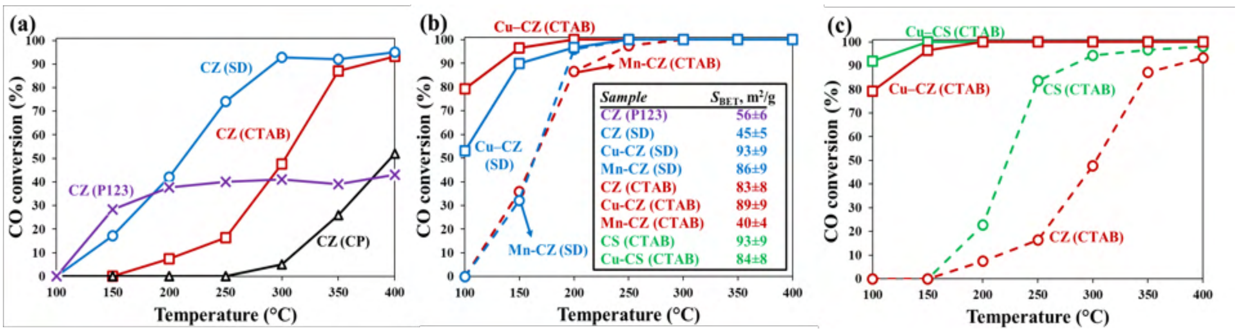

Fig. 1. CO conversion (%) vs reaction temperature for CZ (a), Cu or Mn-modified CZ systems (b) and CS-based catalysts

Modification by CuO and MnO_x leads to a significant enhancement of low-temperature catalytic activity due to the involvement of additional redox pairs Cu^+/Cu^{2+} or Mn^{2+}/Mn^{3+} into catalytic cycle, and the formation of mixed oxide phases. Copper addition helps to produce the most effective ternary oxide systems. However, Cu-CZ (CTAB) shows a bit higher CO conversion at low temperatures than biomorphic Cu/CZ(SD) sample due to the difference in interaction extent between CuO and CZ. Mn was less efficient dopant for CZ systems than copper Incorporation of manganese ions in the crystal lattice of CZ, however in small amounts, was detected by EPR. The weak interaction of MnO_x with CZ does not provide the formation of highly defective structure, and therefore causes no significant increase in the amount of active oxygen, in contrast with Cu-CZ systems.

Sn-containing samples showed the best catalytic properties in comparison with CZ-based counterparts (Fig. 1(c)) because of increased defectiveness.

We can conclude that the additional modification and the use of template synthesis methods allow improving CO to CO_2 conversion in the wide temperature range (100-400°C). It was confirmed that tin is a more effective dopant for CeO_2. Now, we are conducting additional catalytic tests of Cu-CS and Cu-CZ in PROX CO reveal the influence of dopant type (Zr or Sn) on catalytic properties.

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OP-I-9

Role of Texture and Acidity of SAPO-34 in Methanol to Olefins Conversion

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SAPO-34 is an important member of silicoaluminophosphate family, zeolite-like materials, with framework of zeolite CHA and possessing a three-dimensional pore system with small 8-ring channels with a pore diameter of 0.38 nm [1]. SAPO-34 attracted much interest because of its various applications in the chemical and petrochemical areas, such as CO_2/CH_4 separation, heat thermochemical storage, hydrogen purification, selective catalytic reduction of NO_x, and catalysts for the conversion of methanol to olefins (MTO reaction) [2].

This work is dedicated to SAPO-34 synthesis with different amount of structure-directing agent (tetraethylammonium hydroxide, TEAOH), its influence on physico-chemical properties of SAPO-34 and, as a result, its catalytic performance in MTO conversion.

SAPO-34 crystals were synthesized hydrothermally using aluminum isopropoxide, phosphoric acid and fumed silica as sources of aluminum, phosphorus, and silicon respectively; and tetraethylammonium hydroxide as structure-directing agent (template). Precursor mixture with composition of $0.6\ SiO_2 : 1Al_2O_3 : 1P_2O_5 : x TEAOH : 76H_2O$, where $x = 1–3$, was prepared by mixing the precursors using an overhead stirrer with simultaneous ultrasonication in an ultrasonic bath. Hydrothermal synthesis was carried out at 200°C for 48 hours. MTO conversion proceeded at 400°C and atmospheric pressure.

Obtained SAPO-34 crystals with ratios of $TEAOH/Al_2O_3 = 1, 2, 3$ differ significantly in acidic and textural properties. These differences in physico-chemical properties of SAPO-34 cause the corresponding changing in MTO product distribution. Figure 1 represents the main parameters of MTO process on the catalysts SAPO-34.

There is no direct correlation between template amount and acidity and texture of the catalysts and catalytic performance, however, we found out the linkage of acidity and texture with selectivity and yield of olefins [3].

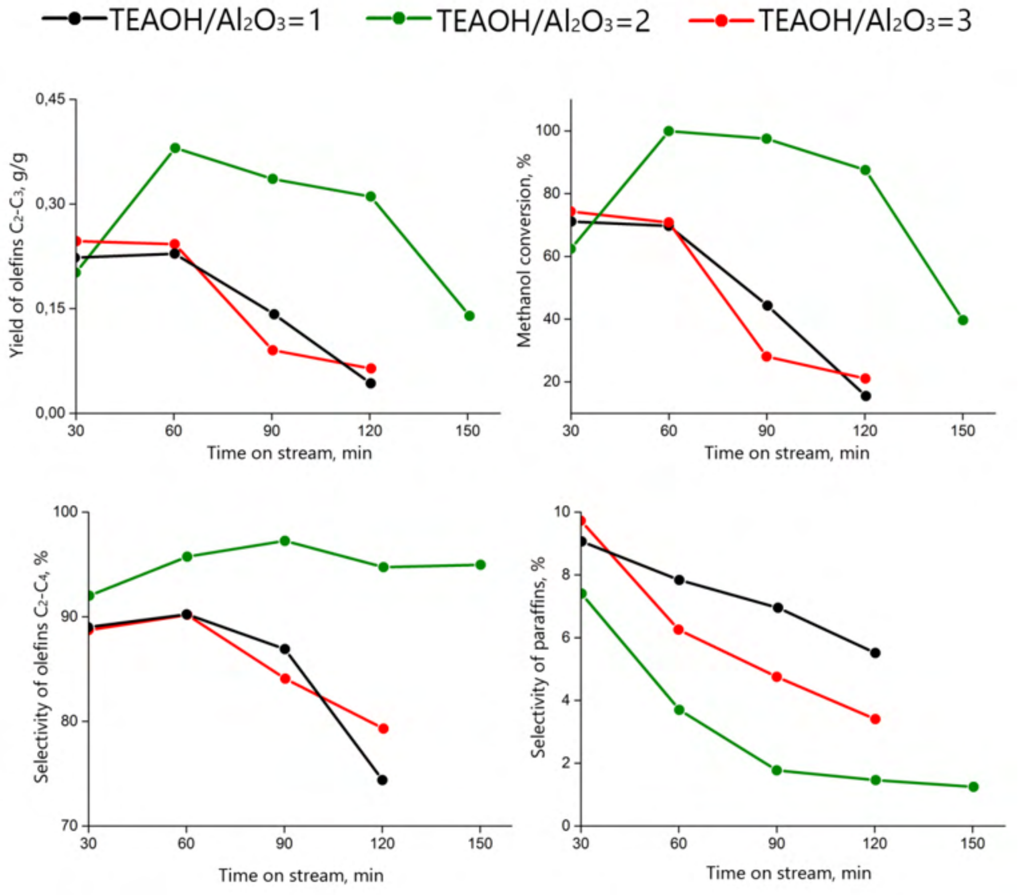

Fig. 1. The key parameters of the MTO process

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OP-I-10

Synthesis Parameters Effect on the Kinetics of Platinum Nanoparticles Formation and Pt/C Catalyst Structure

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Nanostructured platinum-containing catalysts are widely used in devices for chemical synthesis and energy conversion [1]. The properties of nanostructured materials depend on the size and shape of the Pt-nanoparticles. That is especially important in catalysis, where an increase in the activity and selectivity of the catalyst can be caused by a change in the number of active sites because of surface modification [1]. Understanding the kinetics of nucleation and particle growth helps to optimize synthesis and control the catalysts structure. At the same time, the processes of nucleation and growth of particles depends on the reaction conditions and even a small change in the synthesis parameters can lead to significantly different mechanism.

The influence of controlled synthesis parameters, such as temperature, composition of the atmosphere and liquid phase, on the kinetics of the formation of the platinum colloidal solution was studied. Important results were obtained using methods for controlling the colour of solutions during the synthesis and spectrophotometry. It was previously found [2] that the atmosphere of carbon monoxide makes it possible to slow down the growth of nanoparticles and complicates the subsequent aggregation. We have shown that the CO atmosphere affects to the duration of the induction period, the stage of nucleation and particle growth and, as result, on the size of obtained nanoparticles. The multifactorial temperature effect on the rate of nanostructures formation was also determined. The role of homogeneous and heterogeneous nucleation in the synthesis of Pt/C catalysts by introducing a carbon support at different stages of the synthesis was also studied. Based on a comparison of structural characteristics (mass fraction of platinum, average crystallites size in according to XRD, the electrochemically active surface area (ESA), degree of particles aggregation) was determined the range of values for liquid-phase synthesis parameters that allow to control the size and size distribution of platinum nanoparticles in synthesized Pt/C catalysts.

As a result of this study, Pt/C catalysts were obtained, which ESA and mass activity were significantly higher than that of commercial analogs.

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OP-I-11

Effect of Synthesis Methods on the Structure and Properties of Pd-Zn/Sibunit Catalysts for Acetylene Hydrogenation

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High selectivity for the target product is one of the main requirements for modern catalysts. One of the approaches to increase the acetylene hydrogenation selectivity to ethylene is the application of catalysts containing bimetallic particles as an active component [1]. Pd-Zn catalysts are of particular interest. Palladium, interacting with zinc, can form both solid solutions and ordered intermetallic compound PdZn. Zinc atoms in the bimetal structure “dilute” neighboring palladium atoms, effectively isolating them from each other, so active centers are formed on the catalyst surface [2–4].

Since the structure of active sites, determined by the method of synthesis, plays an important role in achieving the specified parameters of the catalytic process, the goal of this work was to establish the correlation between the method of synthesis of supported Pd-Zn catalysts, the structure of the active component, and the catalytic properties in the gas-phase hydrogenation of concentrated acetylene mixtures with hydrogen.

Carbon material Sibunit was used as a catalysts support. The choice of the support was stipulated, first of all, by absence of strong surface acid sites responsible for acetylene oligomerization [5]. In addition, Sibunit, in contrast to traditional oxide supports (for example, Al_2O_3), is not able to interact with the modifier (Zn) to form various compounds (for example, spinels), which should increase the likelihood of contact between palladium and zinc precursors to form bimetallic nanoparticles [6]. The samples were obtained by an incipient wetness impregnation method by varying the sequence of palladium ($Pd(NO_3)_2$) and modifier ($Zn(NO_3)_2$) precursors deposition. At the first stage, one of the precursors was deposited, then the sample was dried at 120°C (3 h), and reduced in a hydrogen stream at 500°C (3 h). At the next stage the second precursor was added, followed by drying and heat treatment under the same conditions. Also one more bimetallic Pd-Zn sample was prepared by co-deposition of palladium and zinc nitrates, drying at 120°C (3 h), and reduction in H_2 at 500°C (3 h). The palladium and zinc contents were 0.5 and 0.31 wt.%, respectively. Catalytic tests were carried out in flow reactor, in a stream of gas mixture containing 4 vol.% C_2H_2 and 96 vol.% H_2 at 25-95 °C.

The obtained catalysts were studied using a set of instrumental methods (EXAFS, XRD, TEM). It was found that the sequential addition of palladium and zinc precursors with an intermediate stage of reduction in hydrogen flow ensures the closest contact between the metals. As a result, dispersed

(d_{av} = 5.3 nm) intermetallic PdZn particles with a tetragonal structure are predominantly formed, which, as can be assumed, provide a high ethylene selectivity up to 74%.

Acknowledgement. This work was conducted within the framework of the budget project for Boreskov Institute of Catalysis.

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OP-I-12

Target Synthesis of N-Doped Carbon Nanofibers on Self-Organizing Nickel-Containing Catalysts

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Carbon nanomaterials (CNM) belong to the most attractive and promising materials, which can be used as supports for catalysts, adsorbents, or modifying additives in various composites. CNMs are highly resistant to most of the aggressive media that make them applicable in various processes. One of the advantageous features of carbon materials is the unlimited possibility of their physicochemical modification. Variations in the synthesis conditions allow fine-tuning both the CNM texture (porosity, defectiveness) and the surface chemical composition (the presence of functional groups and heteroatoms). The controlled synthesis of nanostructured and functionalized materials widens the range of their practical application [1].

The introduction of heteroatoms into the CNM structure affects the interaction between the carbon surface and the supported component. Due to this fact, it is possible to control its morphology, dispersion, stability, and catalytic characteristics. Doping of the support with nitrogen is a relevant way to modify the catalyst properties. Nitrogen is adjacent to carbon in the periodic table and has some similarities with the latter. Close atomic radius and number of electrons allow a relatively easy substitution of atoms in the carbon matrix. Besides, the introduction of nitrogen promotes the formation of electron-donor centers. It increases the hydrophilicity of carbon materials and makes them water-dispersible, thus expanding their application areas [2].

There are two approaches to obtaining N-doped carbon materials: 1) synthesis via one-pot pyrolysis of nitrogen- and carbon-containing precursors; 2) post-functionalization of preliminary prepared carbon materials by treatment with N-containing compounds. The first method is simpler to implement, but the second one allows more precise tuning of the content and configuration type of heteroatoms in the final material. In the general case, the synthesis is based on pyrolysis of a carbon-containing precursor (e.g., ethylene) in the presence of metal catalysts that induce CNM growth. Several studies have shown that the method based on the self-organization of bulk Ni-M (M = Cu, Mo, Pd, etc.) alloys during the decomposition of a carbon-containing precursor in an H_2 atmosphere can be efficiently used to obtain carbon nanofibers (CNFs) [3,4]. Under the reaction medium, the initial alloy undergoes disintegration to form the sites for the carbon fibers' growth. Materials resulting from the *in situ* N-functionalization according to the bi-substrate approach (ethylene + acetonitrile) have a segmented structure reflecting the graphite density fluctuations (Fig. 1).

A similar structure can also be observed in non-functionalized CNFs obtained via the decomposition of ethylene. Due to their morphology with a rough surface, they can be easily post-functionalized with nitrogen further. In most cases, the postmodification procedure consists of such stages as impregnating the initial carbon material with an N-containing precursor and its subsequent thermolysis.

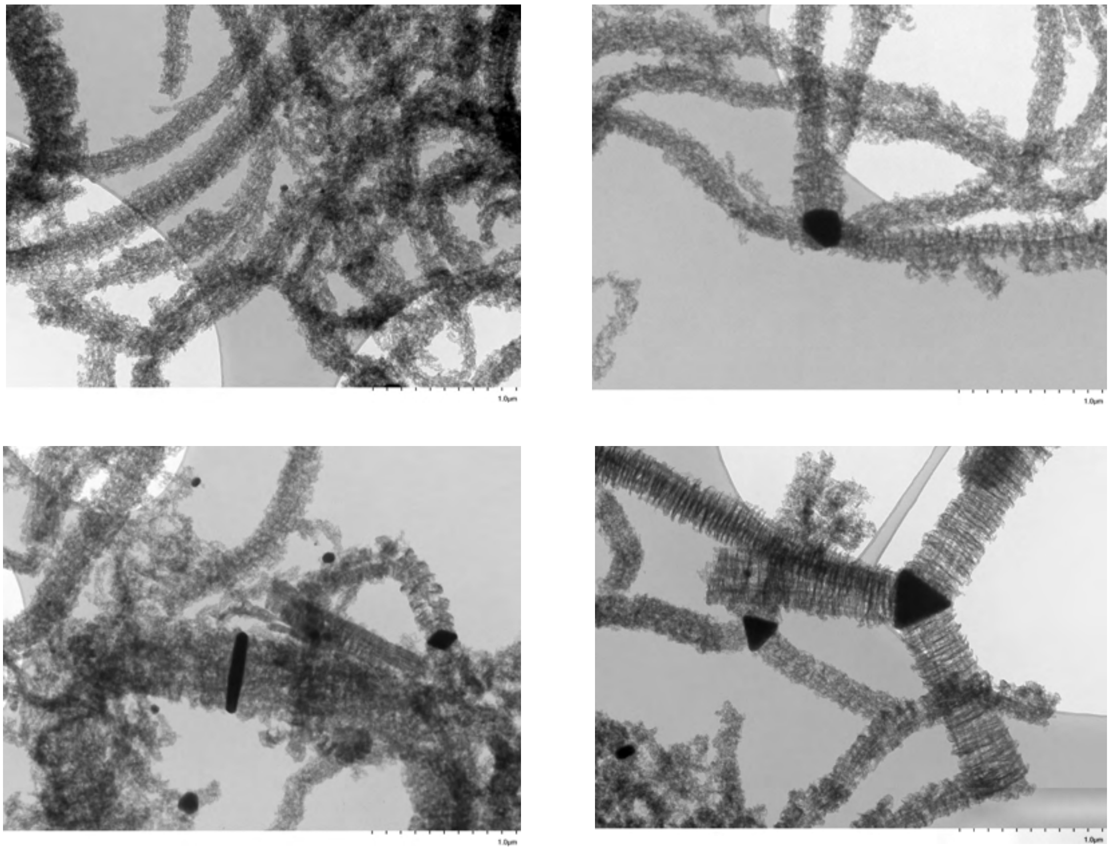

Fig. 1. TEM micrographs of the segmented CNF sample produced by the combined H_2-assisted decomposition of {C_2H_4 + CH_3CN} mixture on Ni-Cu catalyst at 550°C.

In the present work, we have carried out a comparative study of the nitrogen precursor effect (pyridine, 1,10-phenanthroline, pyrrole, aniline, ethylenediamine, and melamine) on the properties of the N-doped CNFs obtained by the postmodification route. Indicative material properties, including the content of the nitrogen introduced, its configuration type, as well as morphological and textural characteristics, are to be reported. Moreover, the advantages and drawbacks of the two methods (one-pot synthesis and post-functionalization) have been disclosed. Finally, the possibility of using the functionalized CNFs as adsorbents for chlorine-substituted aromatic compounds (as an example of the hazardous wastewater pollutants) has been studied. In the sorption experiments, the 1,2-dichlorobenzene was used as a model water contaminant.

Acknowledgment. This work was supported by the Russian Foundation for Basic Research, grant 18-29-19053_mk.

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OP-I-13

Effect of the Preparation Method and the Chemical Composition of Co-Containing Catalysts Based on Layered Hydroxides on Their Properties in the Furfural Hydrogenation

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The products of the catalytic hydrogenation of furfural are widely used in industry. However, industrial catalysts for this process are environmentally unsafe. Therefore, it is important to create highly efficient and environmentally friendly catalysts. Layered double hydroxides (LDHs) are widely used as catalyst precursors due to the unique possibility of introducing metals into the layer structure at the stage of synthesis. This provides a high dispersion of the active metal and high catalytic activity. Promising environmentally friendly mechanochemical method will be used for the synthesis of LDH as an alternative to the traditional coprecipitation method.

The aim of this work was to study the effect amount of Co in the composition of MgAl-LDH (Co/Al and Co/(Co+Mg) ratios) and the method of LDH synthesis (coprecipitation and mechanochemical synthesis) on their structural properties and catalytic activity in the hydrogenation of furfural.

In this work, two types of cobalt-containing catalysts were synthesized: bimetallic systems CoAl and trimetallic systems Co-MgAl with different Co content. The synthesis of catalysts was carried out by two methods: coprecipitation (c) and mechanochemical synthesis (m).

Coprecipitation was carried out by gradually adding of a solution containing $Co(NO_3)_2$, $Mg(NO_3)_2$, and $Al(NO_3)_3$ to Na_2CO_3 solution while maintaining 60 °C and pH = 10. The synthesis of Co-MgAl-LDH with a different ratio of metals in the composition of LDH by the mechanochemical method was carried out in two stages. At the first stage, metal hydroxides taken in calculated ratios were subjected to mechanochemical activation in an AGO-2C ball planetary mill. In the second stage, the samples were aged in distilled water.

Study of structural properties of synthesized LDH was carried out by X-ray diffraction (XRD) analysis on a D8 Advance (Bruker) diffractometer. Temperature-programmed reduction of Co was examined by H_2-TPR using an AutoChem II 2920 (Micromeritics) chemisorption analyzer equipped with a thermal conductivity detector (TCD). The thermal analysis of catalysts samples was performed in the range of 0– 900 °C using a DTG-60 instrument (Japan). The study of catalytic activity was carried out on the installation for liquid-phase hydrogenation of furfural at elevated pressure. The reaction was carried out at a temperature of 90°C, a hydrogen pressure of 2.0 MPa and a concentration of furfural in an aqueous solution of 5 wt%. The reaction products were analyzed by gas chromatography with capillary VB-WAX column.

The phase composition of all obtained catalysts was studied. It is shown that the structure of the samples obtained by the coprecipitation method corresponds to the structure of the LDH. The samples obtained by the mechanochemical method, along with the formed LDH phase, have phases of the original hydroxides.

The process of decomposition of the samples was studied by thermal analysis. Two pronounced peaks of the decomposition of the LDH phase were observed for all synthesized samples. The peak at low temperatures (below 200 °C) corresponds to the decomposition of interlayer water, and the peak at high temperatures (in the region of 300 °C) corresponds to dehydroxylation of the layers and decomposition of interlayer anions. For the systems obtained by the mechanochemical method, the weight loss was less than for the samples obtained by the coprecipitation method.

According to the TPR data, the number of peaks on the TPR profile of the samples is determined by their cationic composition. The TPR profile of CoAl-c has three sharp and one diffuse peak. Apparently, they correspond to the reduction of various cobalt oxides, which can be simultaneously present in the calcined sample. The 0.3Co-MgAl-c sample is characterized by the presence of one diffuse peak with a maximum at 379 °C and a shoulder at 257 °C. The complete reduction of cobalt occurs at 550 °C.

All obtained catalysts were tested in the liquid-phase hydrogenation of furfural. Furfural conversion is largely determined by the amount of cobalt contained in the LDH. The LDH synthesis method has less effect on the activity of catalysts. Therefore, mechanochemical synthesis can be used as a fast alternative method for preparing catalysts based on LDH without deteriorating their activity.

Table 1. Catalytic characteristics of Co-containing catalysts based on layered hydroxides

Sample	Furfural conversion, %	Reaction rate	Selectivity, %		
			Furfuryl alcohol	Tetrahydrofurfuryl alcohol	Tetrahydrofurfural
CoAl(4)-c	44	0.0059	99.9	–	–
0.3Co-MgAl(4)-c	34	0.0061	99	0.5	0.2
CoAl(4)-м	86	0.0353	99	1	–
0.3Co-MgAl(4)-м	21	0.004	98	1.5	0.5

M^{II}/Al=4, indicated in brackets

It was found that a unique feature of Co-containing catalysts based on LDH is their high selectivity for the formation of furfuryl alcohol (above 98%), regardless of the composition of the original LDH (Table 1).

Acknowledgement. This work was carried out within the state task of the Boreskov Institute of Catalysis (Project AAAA-A17-117021450095-1). The research was performed using equipment of the Shared-Use Center "National Center for the Study of Catalysts" at the Boreskov Institute of Catalysis.

OP-I-14

The Effect of pH During the Sol-Gel Synthesis of NiO-MgO Systems on Their Textural and Redox Properties

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Due to its diverse properties, nickel oxide is widely used in various industrial catalytic processes. One of the possible directions of nickel oxide usage is oxygen acceptance in chemical looping technology. The essence of the technology lies in the fact that oxygen acceptors, most often metal oxides, are used as a source of oxygen capable of giving off oxygen to the substrate under reaction conditions, transforming into a reduced form with a lower oxidation state of the metal. This allows avoiding the use of oxygen mixtures with nitrogen and argon for oxidation, which facilitates the isolation of the final product. The use of pure oxygen also comes with additional costs. In the second stage, the oxygen acceptor enters the second reactor, where it is regenerated with atmospheric oxygen and can be used again as the oxygen source.

Since oxidation processes often require high temperatures, the oxygen carrier must be resistant to the sintering at high temperatures. Therefore, inert textural promoters or supports are commonly applied. One of the possible inert matrices is magnesium oxide, which has a high melting point and, hence, good thermal stability. As known, magnesium oxide with the highest possible textural characteristics can be obtained via a sol-gel approach.

In our previous works, a number of systems based on magnesium oxide were investigated: CoO_x-MgO, Fe_2O_3-MgO, CuO-MgO, and others [1]. The NiO-MgO system seems to be the most promising one [2]. Figure 1 shows the transmission electron microscopy images of the NiO-MgO system. As seen, the sample is represented by nanocrystals of the MgO matrix with distributed NiO particles (dark areas).

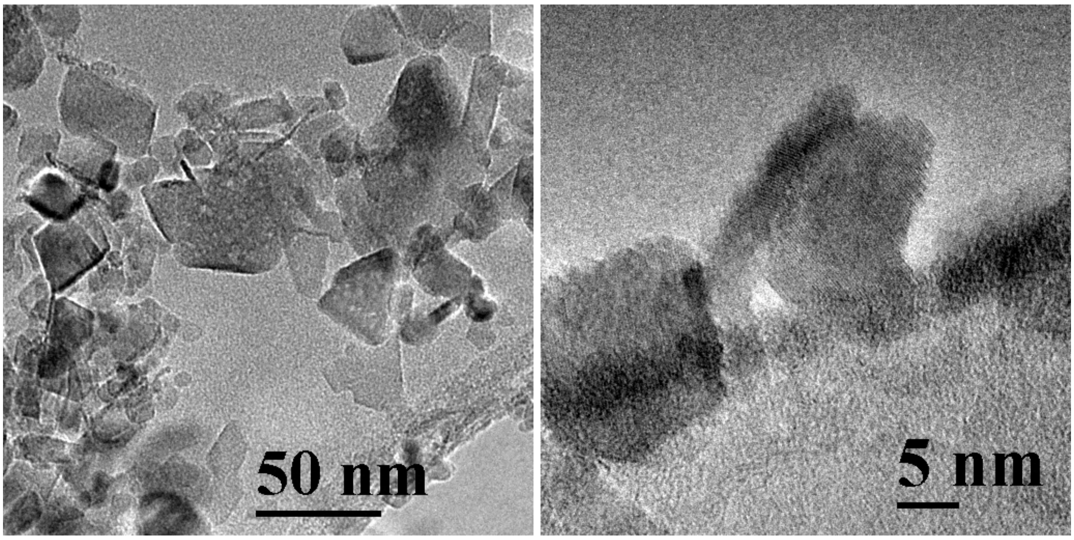

Fig. 1. TEM micrographs of the nanocrystalline NiO-MgO system obtained via a sol-gel method at neutral pH value.

The alkoxide sol-gel method was used in all these cases. Generally, magnesium was dissolved in methanol, toluene was added, and hydrolysis was carried out with an aqueous solution of the second component. In this case, the solution pH values affecting the resulting oxide materials' properties were not taken into account. Meanwhile, it is known that pH has a significant effect on the rates of hydrolysis and condensation processes. Usually, the rate of hydrolysis is the highest in the high and low pH ranges and the lowest in the neutral range. For the condensation rate, the dependence on pH is usually more complex.

Thus, in the present work, the goal was set to study the effect of pH on the properties of produced NiO-MgO materials obtained via the sol-gel method. So, a number of samples were synthesized using the solutions with pH of 1, 3, 5, 7, and 9. All prepared oxide samples were studied by low-temperature nitrogen adsorption. The thermo-programmed reduction with hydrogen was performed in the 9 reduction/oxidation cycles. In the first cycle, a low-temperature peak is observed, corresponding to the reduction of weakly bound forms of nickel oxide; at a high temperature, nickel is reduced from a NiO-MgO solid solution. In subsequent cycles, similar reduction profiles are observed; thus, the system exhibits high stability and reproducibility.

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OP-II-1

Near Ambient Pressure XPS and MS Study of CO Oxidation over Model Pd-Au/HOPG Catalysts: The Effect of Metal Ratio

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The ability of bimetallic supported catalysts to overperform their monometallic counterparts has induced a great deal of interest to these systems within scientific community. However, despite a large number of investigations of various bimetallic catalysts published in the last decade, the structure of catalytic active sites therein is still under debate. The reason for that is the proneness of bimetallic particles to transformations under the influence of temperature and reaction mixture. PdAu system is among the most studied ones due to its enhanced catalytic properties for a number of reactions, such as vinyl acetate synthesis, low temperature CO oxidation, NO reduction, direct formation of hydrogen peroxide from an H_2+O_2 mixture and others. However, the structure of catalytic active sites even in this prototypic system remains elusive since the actual ratio of the metals on the surface of a working catalyst is not determined unambiguously by the amount of initially introduced metals, but is also strongly affected by the calcination temperature. Moreover, a redistribution of the metals in the particle can occur directly during the course of a catalytic reaction, under the influence of temperature and reaction mixture. To address the problem, *operando* studies have to be performed. In our recently published papers [1, 2], the model bimetallic Pd–Au/HOPG catalysts have been investigated towards the CO oxidation reaction using a combination of NAP XPS and MS techniques. The samples have shown an onset of catalytic activity at temperatures above 150°C. CO adsorption on the bimetallic nanoparticles under reaction conditions has been shown to induce segregation that manifested itself as an enrichment of the surface with Pd. It has been shown that heating of the sample under reaction conditions above 150°C gives rise to the decomposition of the Pd–CO state due to the CO desorption immediately followed by oxidation and simultaneous Pd–Au alloy formation on the surface. Thus, it was clearly demonstrated that it is exactly the alloyed surface that is responsible for the CO oxidation. This conclusion is in line with the Goodman’s mechanism which suggests that gold atoms are responsible for the CO adsorption, whereas contiguous Pd sites are responsible for the O_2 dissociation and a further spillover of O_{ads} to Au and/or to isolated Pd sites followed by the oxidation of activated adsorbed CO. However, according to this mechanism, CO oxidation should occur at relatively low temperatures when weak interaction between CO and Au can provide an appropriate concentration of adsorbed CO molecules. But significant surface segregation of Pd atoms induced by CO adsorption can destroy the alloy structure and inhibit the metal surface completely thus effectively deactivating the catalysts. We suggested that such a situation was indeed realized for the samples studied in [1]; the initial Pd/Au ratios at the surface exposed to the reaction mixture were quite large ~ 1.4 and 3.5 for the studied model bimetallic Pd-Au/HOPG catalysts. In that case, the mechanism of the CO oxidation reaction could switch to that typical of monometallic Pd nanoparticles due to a prominent shortage of Au atoms on the topmost surface layer. In a full agreement with this consideration, both the Pd-Au/HOPG catalysts were inactive towards the CO oxidation in the low-temperature mode, the activity ignited only at temperatures above 150°C. Finally, it was suggested that the use of bimetallic model Pd-Au/HOPG samples with a lower Pd/Au ratio would lead to increased activity below 150°C.

In the current work, we have compared the results obtained in the previously published paper [1] with ones obtained for the Pd-Au/HOPG model bimetallic catalyst with a lower Pd/Au ratio on the particles surface. The key goal of this investigation was to find a correlation between the catalytic activity of those model catalysts towards the CO oxidation reaction and the Au/Pd atomic ratio on the surface of bimetallic particles. A systematic elucidation of electronic properties of the elements in bimetallic palladium-gold particles and their depth profiles as well as their transformation induced by the reaction environment of CO oxidation was performed using a combination of NAP XPS and MS techniques for different reaction conditions and initial Pd/Au ratios.

The activities of Pd-Au/HOPG model catalysts towards the CO oxidation reaction are different for the two samples with different initial Pd/Au atomic ratios. More specifically, the PdAu-2 sample with a lower Pd/Au surface ratio (~ 0.75) is already active starting from 100°C, while the PdAu1 with a higher Pd/Au surface ratio (~ 1.0) becomes active only at temperatures above 150°C. The exposure to reaction mixture at RT induces the palladium surface segregation accompanied by an enrichment of the surface of bimetallic Pd-Au particles with palladium due to the fact that CO adsorption on Pd atoms lowers the nanoparticle total energy. The segregation extent depends on the initial Pd/Au surface ratio. The difference in activity of these two catalysts is determined by the presence and/or higher concentration of specific Pd active sites on the surface of bimetallic particles, i.e., by the ensemble effect. The reverse redistribution of the surface composition observed after cooling down to RT converts the catalysts back to the inactive state, which strongly suggests that the optimum active sites emerge under reaction conditions.

Acknowledgement. This work was supported by the Ministry of Science and Higher Education of the Russian Federation (within the budget project of the Boreskov Institute of Catalysis).

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OP-II-2

Operando Study of Mono- and Bimetallic PdPt Catalysts for Methane Oxidation by XAS and XRD

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The relevance of the study is determined by the widespread use of PdPt catalysts in the reactions of complete oxidation of hydrocarbons, in particular for the additional oxidation of exhaust gases of gasoline internal combustion engines and internal combustion engines operating on a methane-butane-propane mixture, as well as in gas turbine plants operating at temperatures of 1000-1100C. Although these systems have been studied for a long time, nevertheless, there is currently no unified point of view on the nature of the catalytic action of PdPt catalysts, and questions about the synergistic effect of platinum and palladium and their thermal stability and deactivation during the catalytic process are also open.

A series of Pd/Al_2O_3, Pt/Al_2O_3, $PtPd/Al_2O_3$, catalysts was synthesized with a metal content of 1% and 3%. The catalysts were characterized by X-ray diffraction, transmission electron microscopy, XPS, XANES, and EXAFS. It has been shown that the proposed methods make it possible to synthesize metallic catalysts with a narrow distribution of supported particles. The catalysts 3%Pt/Al_2O_3 and 3%Pd/Al_2O_3 with a particle size of about 2 nm exhibit the maximum activity in the methane oxidation. A decrease in the content of noble metal from 3 to 1% leads to a decrease in the activity of catalytic activity due to the decrease of surface concentration of active centers (nanoparticles).

The aim of this work was to study in situ the chemical and phase composition of Pt, Pd, and PdPt catalysts. The studies were carried out both in a stream of pure methane and in a stream of methane and oxygen in a wide temperature and ratio range using X-ray absorption spectroscopy (XANES and EXAFS) and X-ray diffraction. A distinctive feature of the XANES / EXAFS methods is the possibility of their application for the analysis of the chemical state and structure of nanoparticles and amorphous phases. XANES in situ allows you to determine the chemical state of platinum and palladium in the bulk of the catalyst under reaction conditions. The EXAFS method makes it possible to determine the structure of the local environment of platinum and palladium atoms even at low concentrations (1-3 wt.%). XRD gives the information about the deactivation of catalysts due to formation of large particles detected by XRD (size > 3-5 nm).

The XANES / EXAFS X-ray spectra at the Pd K absorption edge and the Pt L3 edge were measured at the EXAFS spectroscopy station of the Siberian Center for Synchrotron and Terahertz Radiation (INP SB RAS). The local spatial structure of bimetallic catalysts was investigated. It was found that under reaction conditions, there is a partial reduction of platinum and palladium to the metallic state (even in exceed of oxygen). It is assumed that the active component is the metal oxide state.

Acknowledgement. The reported study was funded by RFBR, project number 20-33-70124.

OP-II-3

The Application of Aromatic Probe Molecules EPR Spectroscopy for Studying the Acidic Properties of the Catalysts for Vegetable Oil Hydrodeoxygenation Based on Anion-Modified Alumina

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Aromatic compounds (anthracene, perylene, toluene, etc.) are capable of forming stable radical cations upon adsorption on the surface of calcined acidic oxides, which are easily detected by EPR [1]. The mechanism of the reactions occurring has not yet been unambiguously established; nevertheless, the most significant concepts assumes the participation of Brønsted acidic sites (BAS) in the oxidation of probe molecules to the corresponding radical ions [2,3]. The concentration of perylene, anthracene, or other aromatic radical cations formed reflects the number of BAS on the catalyst surface.

Previously we applied this approach for the study of a series of borate-modified alumina and supported catalysts for the oligomerization of butenes and the hydroisomerization of a heptane/benzene mixture, and later the technique was significantly improved both experimentally and in terms of the results interpretation [4,5]. It was proposed to carry out the adsorption of probe molecules from a solution in hexane and to determine the initial concentration of radical cations. This made it possible, on the one hand, to avoid side probe interaction with the solvent, and, on the other hand, to reduce the consumption of probe molecules without losing informativeness. Current work is aimed at expanding the type of the studied alumina catalytic systems and determining the effect of various modifying oxides (B_2O_3, WO_3) and supported metals (Ni-Mo, Pt) on the acidic properties of catalysts supports of vegetable oil hydrodeoxygenation [4-6] on the basis of the developed EPR techniques.

EPR measurements were performed on Bruker EMXplus X-band (~9.7 GHz) spectrometer at 25°C. Each sample of the support and catalyst was activated at 500°C and 380°C respectively. Then it was treated by probe solution with further radical cations registration.

As the main result, in current study we obtained the dependences of the concentration of perylene and anthracene radical cations on the content of modifier oxide for the supports of the following compositions: (0–30 % wt) B_2O_3–Al_2O_3 (BA), (0–30 % wt) WO_3–Al_2O_3 (WA), as well as for supported Ni-Mo and Pt catalysts on their basis. From the analysis of the obtained results, the concentration of “weak” and “medium” strength BAS was calculated (Figure 1) for both series of alumina samples. Generally, it was found that the introduction of the oxide modifier promotes an increase in the acidity of the samples under study. The BA and WA series demonstrate identical dependences of the concentration of each strength BAS on the modifier content: their growth in the range from 0 to 20–25 wt. % modifier. Then there is a slight decrease in the concentration of “medium” strength BAS, while the trend of “weak” strength BAS remains the same. A similar trend is characteristic for supported Ni-Mo and Pt catalysts.

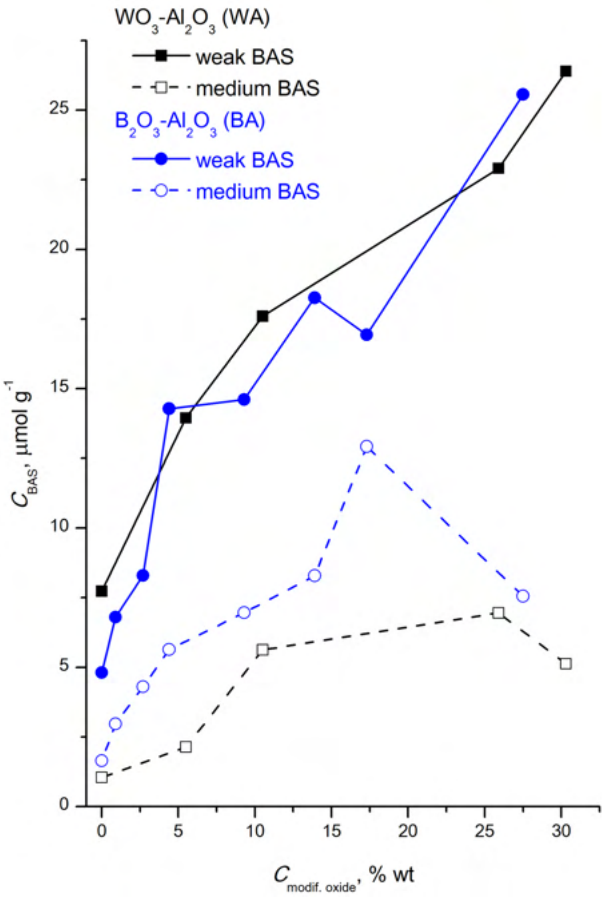

Figure 1. The concentration of “weak” and “medium” strength BAS depending on the modifier oxide content for B_2O_3–Al_2O_3 and WO_3–Al_2O_3 supports (calculated from probe EPR results).

It should be noted that the supporting of 0.5 wt % of Pt did not affect the concentration of radical cations in BA and WA supports, in contrast to the supporting of 4 % wt of Ni and 12 % wt of Mo, leading to a decrease in the amount of BAS [4,5]. The adsorption of metals on the oxide surface leads to the blocking of acidic sites. It was also found that the isomerization activity of the catalysts increases with increasing the concentration of determined BAS [4]. The approach proposed in this work is of significant interest as a promising method for studying the surface acidic properties of various series of new catalytic systems.

Acknowledgement. This work was conducted within the framework of the budget project for Boreskov Institute of Catalysis.

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OP-II-4

Evaluating Number of Basic Centers in Zr-MOFs by Liquid-Phase Adsorbtion of Isobutyric Acid

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Metal-organic frameworks (MOFs) are a class of porous crystalline materials characterized by an extremely high surface area, which suggests their widespread use for storage and separation of gases [1]. The presence of metal centers in the structure makes MOFs promising materials for catalytic transformations [1]. Stability, surface area, porosity, adsorption and catalytic properties of Zr-MOFs (UiO-66, UiO-67, MIP-200, and Zr-abtc) are associated with the presence of defects in their structure [2]. In addition, the number of defects is related to the number of acidic and basic sites which affect the catalytic properties. Several approaches based on TGA, XRD, and N_2 adsorption have been developed for assessing the number of defects of the MOF structure [2]. The presence of acidic and basic centers in MOFs was also probed using IR spectroscopy with $CDCl_3$ adsorption [3]. However, no reliable methods have yet been proposed for quantification of the number of basic centers in the MOFs.

In this work, we suggested a new approach for evaluating the number of basic centers in Zr-MOFs based on the liquid-phase adsorption of isobutyric acid (IBA). The acid concentration during the adsorption was measured by GC with an internal standard. Various Zr-MOFs, including MIP-200, Zr-abtc and a number of UiO-66 and -67 samples were investigated. The samples were characterized by IR spectroscopy, N_2 adsorption, SEM, XRD, and TGA. The number of basic sites evaluated by the IBA adsorption correlates with the number of defects determined by TGA. We also studied how the activation process (heating in a vacuum at 150°C) affects the number of basic centers. It was shown that activated samples adsorb less IBA than hydrated samples. This may indicate that the basic centers in Zr-MOFs are Zr-OH groups, which undergo dehydration under the activation conditions.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 18-29-04022.

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OP-II-5

Palladium Supported on *N*-Heterocyclic Carbene in Dynamic Catalysis

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Since the Herrmann group first demonstrated in 1995 the possibility of efficient application of NHC transition metal complexes in homogeneous catalysis [1], this field has become one of the most rapidly developing in organometallic chemistry [2].

The M/NHC system undergoes significant transformations during catalytic reactions. In terms of stability, the NHC as a stronger donating ligand would bind to the NPr through a covalent bond. It is shown that NHCs in solution can interact with the solvent, stabilize metal nanoparticles and clusters in solution, and participate in the molecular type of catalysis.

We studied the model Heck reaction (figure 1) and assumed to trace the entire path of catalyst transformations.

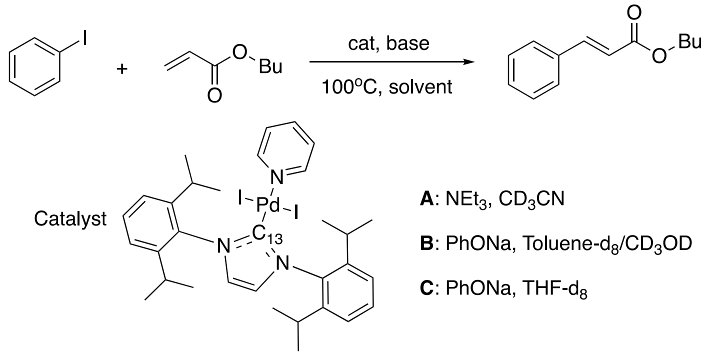
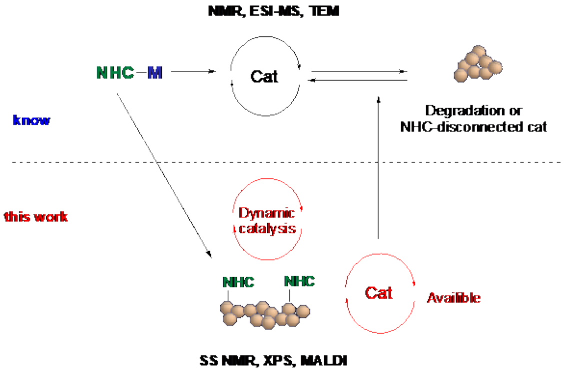


Fig. 1. Model Heck reaction

Based on the previously obtained data [3], a number of substances were synthesized, which, as we expected, can be formed during the reaction. In addition to the expected substances, it was found that NHC is involved in the dynamic catalytic system, being deposited on palladium nanoparticles, and can also catalyze the cross-coupling reaction.



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OP-II-6

Parahydrogen and ^{129}Xe for *In Situ* Studies of Heterogeneous Catalytic Reactions

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Heterogeneous catalytic hydrogenation processes are the cornerstone of chemical industry, and optimization of the catalytic performance requires studies under *operando* conditions. Nuclear magnetic resonance spectroscopy (NMR) and magnetic resonance imaging (MRI) were proven to be powerful tools for such studies due to their non-invasive nature and versatility. However, their application to catalysis is challenging due to their intrinsically low sensitivity, and is further hampered by distortions of the magnetic field homogeneity, associated with the presence of solid catalyst beads inside the spectrometer. All these problems are even more pronounced in the gas-phase studies, where the spin density of reactants and products is particularly low. Nevertheless, implementation of hyperpolarization techniques, such as parahydrogen-induced polarization (PHIP) or spin-exchange optical pumping (SEOP), can increase the NMR (and MRI) signal intensity by orders of magnitude, helping to overcome the obstacles outlined above. PHIP is based on the introduction of parahydrogen (spin isomer of H_2 with total nuclear spin I=0) into the hydrogenation reaction. If two hydrogen atoms from one parahydrogen molecule are added to the same product molecule (i.e. the catalytic reaction proceeds *via* pairwise hydrogen addition route), ^{1}H NMR signals of hydrogenation reaction products become significantly enhanced. On the other hand, SEOP technique allows to polarize noble gases, among which ^{129}Xe is of particular interest, because its chemical shift is extremely sensitive to the external conditions. In this work we've combined the two hyperpolarization techniques to acquire different information about hydrogenation reactions inside a working catalytic reactor.

Firstly, we've studied a new type of model catalytic reactors that minimize the perturbation of the magnetic field homogeneity and are thus suitable for MRI investigations. These reactors were glass tubes with a thin layer of titania, that was impregnated with the Rh precursor solution, and in situ reductive treatment of impregnated reactors yielded the catalytically active porous Rh/TiO_2 coating. These reactors were found to be both active in hydrogenation of propylene and selective to the pairwise addition route to some extent, allowing to perform ^{1}H MRI visualization of a working catalytic layer during propylene hydrogenation with parahydrogen. Secondly, for the first time it was shown that ^{129}Xe, hyperpolarized by SEOP technique, can be used as a non-invasive temperature probe inside a working catalytic reactor. Using xenon chemical shift, we have monitored the temperature changes of Pt/Al_2O_3 catalyst pellets during the start-up of propylene hydrogenation reaction. It was estimated that the temperature directly inside the reactor reached 106 °C within only 30 seconds after the start of reaction and increased to 200 °C within 70 seconds. Importantly, this information cannot be obtained by invasive methods, such as, for instance, the use of a thermocouple. Moreover, we have supplemented this study by obtaining ^{1}H MR images of the catalyst pellet during the hydrogenation with selective visualization of either the reactant or the product. Therefore, it is reasonable to expect that combination of both hyperpolarization methods can bring us closer to the possibility to directly visualize the processes happening inside the catalytic reactors.

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OP-II-7

Developing of New SAXS Technique for Metal Supported Catalysts Study

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The precise determination of particle sizes for supported catalysts is an actual task because catalytic properties can dramatically depend on the small changing of metal particle sizes. For providing information on the size, size distribution, and shape of the nanocrystals with size ranging from 1 to 100 nm, Small Angle X-ray Scattering (SAXS) is more perspective. The use of SAXS for particle sizes determination in supported catalysts can provide better accuracy for obtaining particle sizes distributions. Also SAXS is more sensitive to the large particles and can detect even their small amount in the presence of high content of small particles. However, SAXS has very limited application due to the problem of distinguishing a weak scattering signal originating from supported metal particles from the strong background scattering signal of a porous support. Thus, simply subtraction of the support SAXS pattern from the catalyst SAXS pattern is ineffective and requires more complex approaches for precise determination of particle sizes. Moreover, even a small change in the support porous structure due to the catalyst preparation can have a greater effect on the SAXS signal compared to the presence of metal nanoparticles in the initial porous matrix.

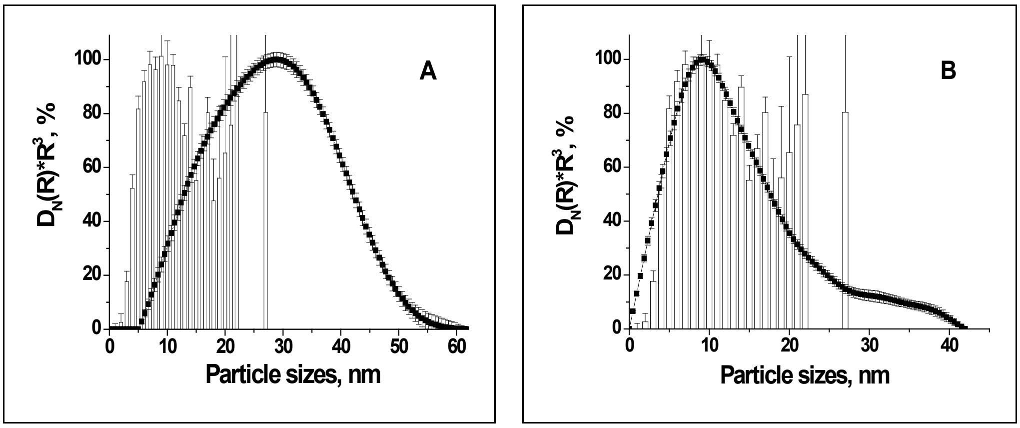

Fig. 1 TEM and SAXS data for supported Pd a) standard SAXS technique b) new STS technique.

In this work has been offered a new simple technique STS (from solids to sols) for removing parasitic scattering signal from porous matrix. Efficiency of STS technique was demonstrated on three different supported catalysts. A good agreement between TEM, XRD and SAXS data was found. The noticeable advantage of STS technique is possibility to study supported catalysts with high dense supports. STS technique can be an expansion of SAXS application for analysis of a wider range of solid functional materials with poly-phase composition.

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OP-II-8

O_2-Induced Segregation as an Efficient Tool for Fine-Tuning the Intermetallic Pd-In/HOPG Surface Structure

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Nowadays, bimetallic catalysts attract considerable attention from many researchers because their properties may significantly differ from monometallic ones, with the mixtures often exhibiting enhanced catalytic activity, stability and selectivity. Despite significant efforts origins of synergistic effects occurring upon the introduction of a second metal into monometallic catalysts in different systems are still under debate. The addition of a second metal is known to lead to active sites with a specific geometry and modified electronic properties. Therefore, the formation of specific surface configurations of bimetallic particles is primarily responsible for the synergistic effect. Due to this reason, many researchers believe that detailed study of their surface is a key for the comprehension of such effects.

The chemical composition and structure of active sites are determined at the preparation step (relative amounts of two metals being deposited, the order of deposition, temperature, etc.). However, it can spontaneously change under reaction conditions or get deliberately tuned by a specific treatment of the surface sample in the reactive gas atmosphere. Enrichments of the nanoparticle surface by one of the components upon adsorption under catalytic reaction conditions, which are referred to as adsorption-induced segregation effects, are being paid ever augmenting attention by researchers dealing with heterogeneous catalysis. Though attempts of deliberate using these effects for the modification of surface composition are still rather rare, we believe the adsorption-induced segregation effects are greatly promising for fine surface composition tuning and consequent rational optimization of catalytic properties in low-temperature reactions [1, 2]. The use of model systems, where metal particles are deposited on a planar support, together with *in situ* techniques can increase the information content and reliability of the results regarding the surface structure and chemical composition of active metal particles and their evolution in response to different treatment modes and reaction conditions.

In this work, a series of model bimetallic Pd–In catalysts with different ratios of metals and size distributions of supported particles has been prepared by successive metal deposition onto a modified surface of highly oriented pyrolytic graphite (HOPG). X-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM) were used to characterize the electronic and structural properties, as well as the morphology of nanoparticles at all stages of catalyst preparation. It was revealed that indium deposition onto Pd/HOPG sample led to spontaneous formation of intermetallic Pd-In nanoparticles or at least partial indium diffusion into palladium particles with emergence of In-Pd surface alloy. It was found that an additional cycle of oxidation-reduction treatment is necessary in order to form the uniform Pd-In alloy species. It was found that the prepared model Pd-In/HOPG catalysts were stable against sintering up to 500 °C in UHV and at least up to 100 °C under «realistic» conditions (200 mbar O_2).

Using the synchrotron radiation-based XPS, it was demonstrated that long-term contact of Pd-In/HOPG samples with air led to partial decomposition of intermetallic particles with the formation of Pd^0 homogeneously distributed over their bulk, and the formation of surface indium oxide and bulk indium oxide. Mild oxidative treatment (0.25 mbar O_2, 150˚C) leads to indium surface segregation and formation of indium oxide predominantly localized in the interior and metallic Pd^0 uniformly distributed over the depth. The indium oxide is distributed homogeneously at further temperature increasing to 200˚C. It was also demonstrated that surface composition could be tuned using the O_2-induced segregation phenomenon by varying both O_2 partial pressure and exposure temperature. Thus, reversible oxidative-reductive transformation $PdIn_{IMC} \rightleftarrows Pd^0 + InO_x$ can be efficiently used to deliberately tune the nanoparticles surface composition/structure and respective catalytic characteristics.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 19-13-00285.

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OP-II-9

New Model Supports and Catalysts Based on Thin $N_xAl_yO_z$ Films

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The improvement of existing as well as developing of new effective heterogeneous catalysts require a detailed study of the features of the interaction of reaction mixture both with the active component and with the support material. The interaction of catalyst surface with the reaction mixture components can be either a side process accompanying the catalytic reaction or it can be carried out purposefully to modify the catalytic system properties. Aluminum oxide is one of the most common catalyst supports, which attracts the interest of researchers [1,2]. To find the ways of alumina modification to improve catalysts made on its base is very promising for the practical applications.

In the present work, the procedure of nitrogen doping of thin film of alumina [3] formed on the surface of a polycrystalline foil of the FeCrAl alloy is proposed. To determine the mechanism of NO interaction with the surface of the primary AlOx film, the samples were studied by *in situ* X-ray photoelectron spectroscopy (XPS) in the presence of NO in the gas phase. According to the XPS data, under the used conditions, nitrogen has been introduced into the oxide support due to the formation of aluminum oxynitrides, compounds with the general formula $N_xAl_yO_z$ [4]. The influence of sample temperature, treatment duration and NO gas pressure on modified film growth were investigated. It was shown, that the amount of nitrogen introduced into the film is controlled by the NO pressure during sample annealing at 670°C. It is shown that the obtained systems are stable under heating in a vacuum up to 700°C. Based on the obtained data, a mechanism of modifying the forming AlOx film by nitrogen introduction due to the activation of NO on the metal components of the substrate alloy is proposed. Modified and clean systems were studied by scanning tunneling microscopy (STM). It was found that the morphology of the both original and modified supports is the same and controlled by the polycrystalline foil of the substrate.

To study the effect of the proposed modification of the alumina film on the behavior of the catalysts, the set of Au/AlOx/FeCrAl and Au/N-AlOx/FeCrAl samples were prepared by vacuum vapor deposition of gold nanoparticles on the surface of model supports [5]. Using XPS, it is shown that the sintering process on the unmodified support starts at the temperature of 300°C, while for the Au/N-AlOx/FCA systems this process starts at 400°C, which shows better resistance to sintering in the vacuum of samples on N- doped alumina film. According to STM data mean particle size for studied samples was less than 3 nm. Particles of this size are the most interesting for the gold nanoparticle catalysis and, at the same time, such particles are the most sensitive to the sintering. So the 100 degree shift in thermal stability is very important to preserve catalytic activity of gold catalysts. The similarity of support morphology showed by STM means that sintering resistance effect arises from chemical composition of the support rather than morphology features.

Thus, the procedure of N- doping of the AlOx/FeCrAl film, used as model supports of the catalysts, based on NO treatment of the primary AlOx with formation of $N_xAl_yO_z$ film is proposed. It is shown that procedure affects the sintering resistance of supported catalysts, which is very promising for practical applications.

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OP-II-10

The Investigation of “Cocktail”-Type Origin of Platinum Species Catalyzing Hydrosilylation Reaction

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The concept of “cocktail” of catalysts (or dynamic catalytic systems) was first proposed in our laboratory and is widely developing nowadays. It states the interconversion of metal species (such as molecular complexes, clusters, nanoparticles) contributing to catalytic activity separately [1], therefore the homogeneous and heterogeneous paths are present simultaneously (fig.1). Palladium catalytic systems were proved to be dynamic [1, 2]. In our opinion platinum catalytic systems should also possess dynamicity and we challenged to show that in this work.

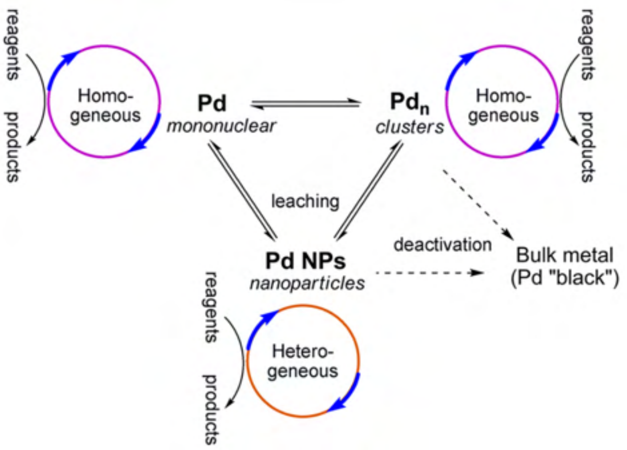
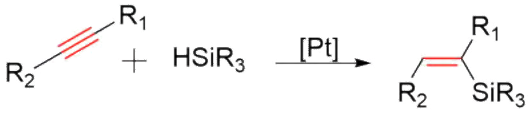


Fig. 1. Plausible pathways of the palladium species transformation during the catalytic reaction (L for ligand, S for solvent and X for heteroatom) [2]

The hydrosilylation reaction of acetylene derivatives was taken as a model reaction and transformations of species from supported platinum catalysts was investigated. Obtained results will be discussed.



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OP-II-11

Effect of Hybridization Method on Bifunctional Catalysts for Direct Synthesis of Dimethyl Ether Based on Cu-ZnO(Al) and Supported Heteropolyacids

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Introduction

Currently, the direct synthesis of DME from syngas (STD) is a relevant topic in the research of alternative fuels since DME is a direct and cleaner alternative to diesel [1]. Furthermore, DME is an important raw material to produce many chemicals [2] and it is used as a propellant in aerosols.

Industrially, DME is produced in two-steps: first, methanol is obtained from hydrogenation of CO/CO_2; and in another reactor, DME is produced through the dehydration of methanol. In addition, it is important considering the (reverse) water gas shift reaction [3]. High thermodynamic limitation in the methanol synthesis step is the main problem of this system that leads to a low gas conversion per pass (15-25%), high recirculation ratios and costs. In this sense, STD reaction is studied to avoid this limitation, where both reactions are coupled *in situ* ($2CO/CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O$) [4]. The synthesis of methanol industrially uses a catalyst based on $Cu/ZnO/Al_2O_3$ (CZA) and zeolite HZSM-5 is the main acid component [5]. However, such hybrid catalysts undergo deactivation.

In this work, we use an alternative acid component for hybridization, heteropolyacids (HPAs). HPAs with Keggin-type structures are widely studied for DME synthesis from methanol, but few studies have focused on their hybridization with CZA in STD. Consequently, our aim is to study the performance of bifunctional hybrids based on HPA supported on TiO_2 combined with CZA in STD reaction. Taking into account that physicochemical characteristics and performance of bifunctional catalysts depends on the interaction stablished between them even during hybridization process, we have studied specifically the effect of four different methods to hybridize both functionalities.

Materials and Methods

The CZA catalyst (Cu/Zn/Al = 68/29/3) was prepared by co-precipitation and then was calcined in air at 340 °C. The supported HPA catalyst was prepared by incipient wetness impregnation on TiO_2. The solids were thermally treated at 150 °C. Finally, the hybrid catalysts were prepared by four mixing methods in a mass ratio of 2:1 (w/w). The four methods to hybridize were: simple mixing (SIMP), which consists in manual mix of both catalysts with a spatula; mixture in an agate mortar by milling (MILL); mixture in rotary evaporator in a round bottom flask with hexane as solvent (HEXA); and finally, mixture by pressure (PRES) and milled again in an agate mortar. The final hybrid catalysts were obtained from the thermal reduction under diluted hydrogen flow (2.2 vol% H_2) at 200 °C. All samples were characterized by different techniques: XRD, DRIFTS (Pyridine), H_2-TPR, N_2-isotherms, N_2O chemisorption and NH_3-TPD; and their catalytic activity was measure in a fixed-bed reactor at 250 °C and 30 bar under syngas.

Results and Discussion

The hybridization process produces several alterations in both components of the bifunctional catalyst and depends on the chosen method. The main physicochemical changes are summarized below: (i) some splittings and shifts of IR bands in the Keggin structure region; (ii) high loss of total porosity as well as a modification of its pore size distribution; (iii) significant alteration of Cu-ZnO reducibility, as well as a large decrease of Cu surface area; (iv) significant increment of crystallite size (Cu^0 and ZnO) which becomes evident in reduced state; and (v) almost disappearance of contribution at high temperature in NH_3-TPD experiments and significant decrease of ratio Brønsted/Lewis sites according Py-DRIFTS results. All these modifications are attenuated as the hybridization process is less severe. Probably, they are due to the cation exchange of Cu^{2+}/Zn^{2+} species from CZA and acid H^+ or addenda atoms from HPA. Likewise, it could be possible that higher contact between both catalysts leads to some physical blockage of active sites from CZA by acid catalysts particles.

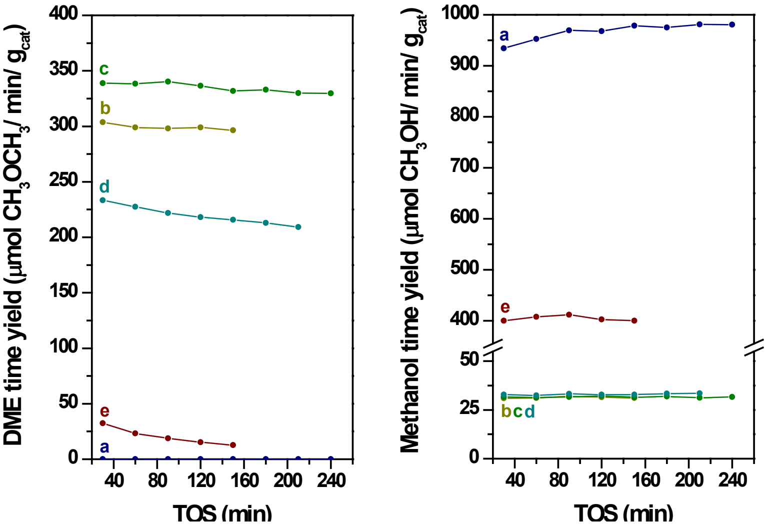

Fig. 1. DME and methanol time yield from syngas over CZA (a) and SIMP (b), HEXA (c), MILL (d) and PRES (e).

Regarding the catalytic behaviour (Fig. 1), the hybrid catalyst prepared by pressure (PRES) shows minimum DME time yield which is almost zero (19.4 μmol/min·g_{cat}) compared to the other catalysts (≈205-335 μmol/min·g_{cat}). In addition, its methanol synthesis does not reach by far the pristine CZA methanol production (404.3 and 967.3 μmol/min·g_{cat}, respectively). Due to all these reasons, we can affirm that properties and catalytic performance of hybrid catalysts are clearly conditioned by hybridization method and strongly depends on contact degree, which has to be modulate accurately to find a compromise that allow both functions be active.

Conclusions

Remarkable differences in STD were found depending on the hybridization method used to combine CZA and the acid function (supported HPA). The possible interactions were studied through the modulation of the proximity between both active sites for characterize their physicochemical properties and test their activity. Effectively, some interactions occur and they are intensified with a closer contact. The hybrid catalyst prepared by pelletizing, which represents the closest contact, shows many alterations in both functions. Hence, these effects should be carefully considered in STD, which reveals that further advances in research are necessary to reach a catalyst optimization. In this sense, future lines that research alternative hybridization process, that maybe include physical barriers, will be necessary.

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OP-II-12

Investigation of the Limits of Applicability of Hyper-Cross-Linked Aromatic Polymers in Heterogeneous Catalysis

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Over the past decades, microporous materials, having pore sizes less than 2 nm in diameter, gained great attention from both the academic and the industrial communities due to their wide range of potential applications in gas storage [1], molecular separation [2] and catalysis [3]. Besides the consolidated use of microporous inorganic materials (typically zeolites and silica) as supports for catalytically active metal nanoparticles, in recent years new classes of micro-(and meso-)porous organic materials useful for catalysis have been developed. They are: metal-organic frameworks, crystalline covalent-organic frameworks, and amorphous microporous organic polymers.

Porous polymers are being synthesized since fifty years ago [4] by incorporating di/multitopic monomers into well-known step-growth and chain-growth polymerization processes to provide cross-links between propagating polymer chains, yielding three-dimensional network materials. Until today the most popular class of these materials is that based on the polystyrene-divinylbenzene (PS-DVB) system [5]. Nowadays, highly porous hyper-cross-linked aromatic polymers (HAP) are available commercially with different organic functionalities which possess promising mechanical, thermal and chemical stability [6]. Such amorphous microporous organic polymers can be successfully used in catalysis due to the high specific surface area (SSA), porosity and double hydrophilic-hydrophobic character. At the same time, functional groups in the polymer enhance the metal dispersion, and the porous structure provides better diffusion of reagents in the pores and facilitates interaction with active centers.

HAP has become a new generation of polymers with high microporosity. During the last decade, the interest of the scientific community and many manufacturers to hyper-cross-linked polystyrene (HPS) adsorbing materials increased steeply, because their advantages over traditional macroporous resins and activated carbons, in terms of higher sorption power and simpler regeneration, have become evident [7]. HPS networks and sorbents, for the first time described in scientific literature in the early 1970s, substantially came into routine practice by the end of 1990s [8].

This work is devoted to the study of HPS and HPS-based catalysts containing precursors of Pd, Pt and Ru via liquid nitrogen physisorption, X-ray photoelectron spectroscopy (XPS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), thermogravimetric analysis (TGA) and thermogravimetric analysis-mass spectrometry (TG-MS). The following properties of HPS were addressed:

i) thermal stability (for initial polymer, during the synthesis of metal-containing catalytic systems, during the catalysts activation procedure with moleccular hydrogen, and also during their operation);

ii) ability to effectively stabilize the forming active phase;

iii) abrasion resistance during exploitation as catalytic support.

At elevated temperatures, polymers are subject to degradation as a result of tarring, destruction of the polymeric network and depolymerization. The data of low-temperature nitrogen physisorption, TG, TG-MS, XPS and DRIFTS revealed that HPS samples can be used in non-oxidative atmosphere at a temperature lower than 400^{o}C. In the case of HPS-based catalytic systems, the observed changes in composition of the polymers is accompanied by transformation of precursors of catalytically active phase. At the same time the behavior of active metal precursors during the catalyst synthesis and activation strongly depends on the precursor nature (hydrophobicity, amount of oxygen, mechanism and rate of ageing) and properties of used HPS (relative hydrophylicity/hydrophobicity, oxygen content in the polymeric network, existence of functional groups).

The possibility of HPS to retain metal precursors was found to be dependent on the metal and precursor nature as well as on the solvent properties. For example, it was found that HPS allows retaining palladium effectively in different medium, while in the case of platinum slight decrease of metal content can be observed.

Moreover, HPS as a support is limited in its ability to control metal nanoparticles formation, which obviously depends on metal content. Thus some recommendations regarding to the optimal metal (Pd, Pt, Ru) content can be also proposed for HPS-based catalytic systems.

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OP-II-13

Investigation of Heterogeneous Gas Phase Hydrogenation Using Spatially Resolved NMR Spectroscopy and Parahydrogen

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Operando studies of working catalytic reactors are essential for improvements of overall reactor performance. However, the main limitation of heterogeneous gas phase reactions investigations using NMR is low sensitivity of the method, which arises from the small spin level populations difference. Amenable technique to resolve this problem is parahydrogen-induced polarization (PHIP). It uses parahydrogen (pH_2) spin order as a source of spin hyperpolarization. The previous study [1] demonstrated possibility of operando MRI studies of heterogeneous gas phase hydrogenation using model catalytic reactors. In this study [2], 16 glass tube reactors containing Pd, Pt, Rh or Ir nanoparticles dispersed on a thin layer of TiO_2, CeO_2, SiO_2 or Al_2O_3 were tested for the hydrogenation of 1,3-butadiene using parahydrogen.

For each reactor, ^1H NMR spectra were acquired. Analysis of NMR spectra showed that the catalytic coatings of Ir and Rh gave hydrogenation products with the highest nuclear spin polarization while the coatings with Pd are the most selective ones for the semihydrogenation of 1,3-butadiene to 1- and 2-butenes. Therefore, for the experiments using spatially resolved ^1H NMR spectroscopy Ir/SiO_2 and Rh/CeO_2 catalysts were chosen. The spatial distribution of the reactants and products of heterogeneous hydrogenation was visualized for these catalysts using spin-echo pulse sequence (Fig. 1).

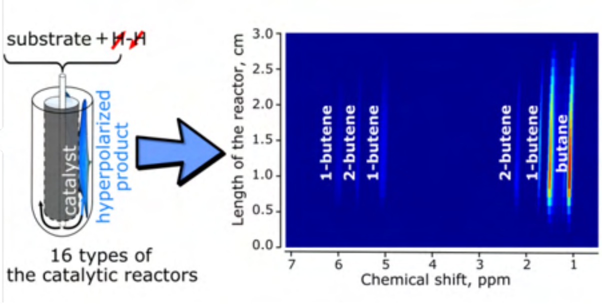

Fig. 1. The spatial distribution of ^1H NMR signal intensities in the working reactor along its Z-axis during 1,3-butadiene hydrogenation over Ir/SiO_2 catalyst with parahydrogen (1,3-butadiene:pH_2 ratio = 1:4, 5.1 $mL{\cdot}s^{-1}$ flow rate, 130 °C)

The results of spatially resolved NMR spectroscopy provided mechanistic insights into the reaction under operando conditions

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OP-III-1

Methane Joint Conversion with Higher Alkanes on Zn-Modified BEA Zeolite: Kinetic and NMR evidences for the Reaction Occurrence in Nonoxidative Conditions

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Methane joint conversion with higher alkanes on Zn-modified zeolites was first studied few decades ago [1-3], and the possibility of methane involvement into the aromatization reaction was demonstrated. Later on, the pathway of methane transformation to aromatic products was established with the aid of advanced ^{13}C MAS NMR method [4, 5]. It is suggested that this process occurs through the alkylation of aromatic hydrocarbons, formed exclusively from the higher alkanes, by methoxy surface species originated from methane. It is also shown that methane activation on the Zn sites follows the "alkyl" pathway that leads to zinc-methyl species, whereas the only way for the methoxy species to be formed is through zinc-methyl oxidation with O_2 impurities [6]. Thus, it was clear that methane conversion to aromatics in nonoxidative conditions is hardly possible considering the established mechanisms.

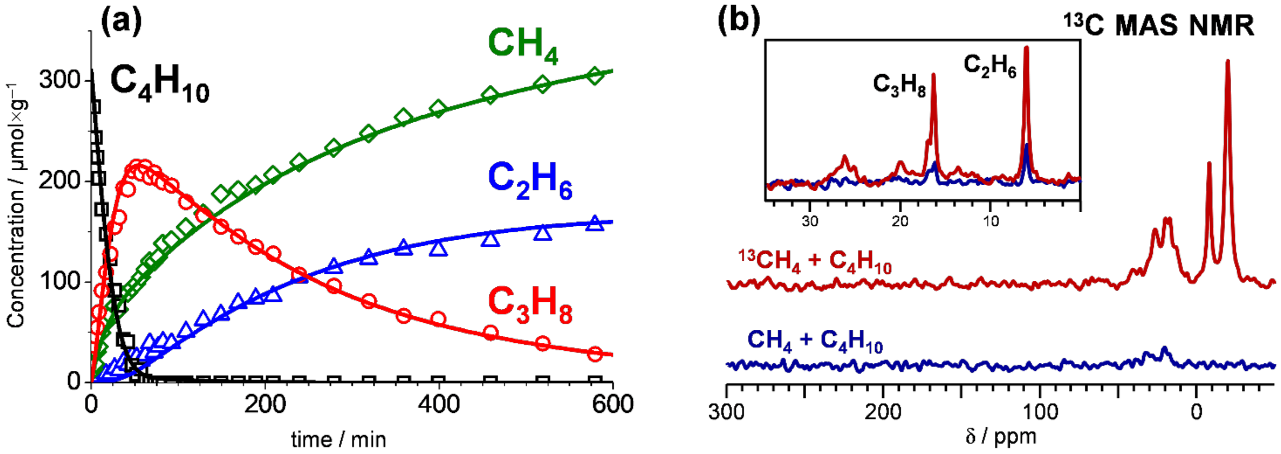

Fig. 1. The kinetics of n-butane transformation on Zn/H-BEA at 573 K (a). ^{13}C MAS NMR spectra of the products of n-butane conversion on Zn/H-BEA jointly with either methane or methane-^{13}C (b).

Our recent studies on the properties of Zn-modified BEA zeolite, containing either Zn^{2+} sites or ZnO clusters, with respect to C_3–C_4 alkanes aromatization [7, 8] have revealed an interesting peculiarity. During the initial period of n-butane conversion kinetics (Fig. 1a), the amount of methane formed is lower than that of propane. This is unusual observation if one assumes methane and propane are the products of n-butane hydrogenolysis only. To explain such experimental finding, we reasonably suggested there was a rout of methane consumption. It is observable at the initial stage of the alkane conversion (propane and n-butane) and can be described as a complex reaction involving surface intermediates formed from both the alkane and methane and yielding smaller alkanes (ethane and propane, respectively). Importantly, we have obtained spectroscopic evidences of the occurrence of such reaction (Fig. 1b). It was monitored with ^{13}C MAS NMR method that ^{13}C atoms of methane-^{13}C penetrated into the products of n-butane transformation on Zn/H-BEA zeolite to both smaller alkanes and olefins/aromatics.

In this report, we present our recent experimental data and discuss this finding in terms of possible mechanism of methane and higher alkanes joint conversion in nonoxidative conditions on Zn-modified zeolites.

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OP-III-2

Inverse Dependence of Turnover Frequency on Palladium Precursor Concentration in Hydrogenation of Unsaturated Compounds

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Since the beginning of the 21st century, transition metal phosphides have been postulated as a promising new class of hydroprocessing catalysts, which proved to be more resistant to deactivation than metals, carbides and metal sulfides [1, 2]. The report presents the results of a study of the catalytic properties of Pd-P nanoparticles in the hydrogenation of representatives of various classes of unsaturated compounds. The properties of Pd-P nanoparticles have been studied in the chemoselective liquid-phase hydrogenation of alkynes, alkynols, and alkenes under mild conditions (303 К, $P(H_2) = 2$ atm). High selectivity (95-98%) at 96-98% substrate conversion and activity in the hydrogenation of model compounds were obtained: 2-methyl-3-butyn-2-ol (TOF = 2380 min^{-1}), phenylacetylene (TOF = 1118 min^{-1}) and styrene (TOF = 2620 min^{-1}). An inverse dependence of the apparent turnover frequency on the concentration of the palladium precursor was found. The combination of kinetic methods and electron microscopy made it possible to discriminate hypotheses about the reasons for the inverse dependence of the hydrogenation rate of unsaturated compounds (alkyne, alkynol, alkene) on the catalyst concentration: dissociation of polycrystalline Pd-P nanoparticles, the equilibrium shift (stabilized cluster - cluster + stabilizer), and aggregation - disaggregation of Pd- P nanoparticles. It has been shown that the main reason for the effect of the catalyst concentration on the apparent turnover frequency in the range of 0.125 - 1 $\text{mmol}\cdot\text{L}^{-1}$ is the dissociation of aggregates of Pd-P particles upon dilution as a result of the adsorption of solvent molecules and/or substrates. Depending on the substrate nature, the effect of this factor on the activity is different. A kinetic model was proposed that describes the effect of the association of Pd-P particles in solution with an increase in their concentration on the TOF of unsaturated compound hydrogenation. It includes a stage of reversible aggregation and subsequent hydrogenation of unsaturated compounds by the Langmuir–Hinshelwood mechanism. The correspondence of the proposed kinetic model to experimental data was shown by the example of styrene hydrogenation, the aggregation constant and rate constants of individual stages were determined. Hypotheses about the nature of catalytically active species in Pd-P particles were discriminated by the method of phase trajectories under conditions of competition between two alkynols.

Acknowledgement. This work was supported by the Government Assignment for Scientific Research from the Ministry of Science and Higher Education of the Russian Federation, project FZZE-2020-0022.

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OP-III-3

Theoretical Design of Self-Assembling Monolayers on the Platinum Surface for Stereoselective Adsorption and Catalysis

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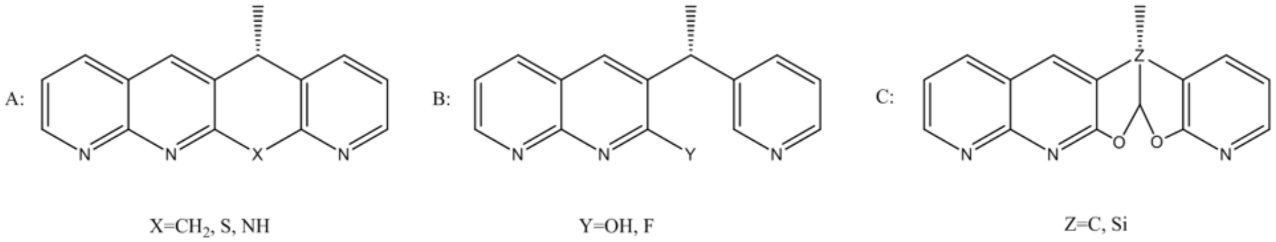
The development of stereoselective catalytic systems is one of the key problems of modern physical chemistry. Particularly, actual direction in it is stereoselective hydrogenation of unsaturated bifunctional compounds, which could be very useful in pharmacology, cosmetology and fragrance industry. Designing of the special orienting covering on the catalyst surface, which will guide the reaction in the right way, with the only one of stereoisomers, might be one of the approaches to solve this problem. This work is devoted to the theoretical design of such coverings and verification of their orienting action in the adsorption of chiral amino acids and ketones. Seven variations of the pyridine condensed derivatives (Fig. 1) were considered as the orienting ligands (OL).



X=CH$_2$, S, NH

Y=OH, F

Z=C, Si

Fig. 1. Orienting ligands types A,B,C with substitutes X,Y,Z

The structure of the OL has been optimized using the DFT (B3LYP/6-31G(d,p)) and PM6 methods. The catalyst surface was modeled by clusters Pt_{36} and Pt_{64} corresponding to tetragonal fragments (6x6) and (8x8) of face (100) of the platinum monocrystal. Two OL were placed on the cluster surface modeling the orienting monolayer. The resulting model of catalytic system has been partially optimized by PM6 with fixed platinum atoms of the bottom layer and side atoms. Adsorption energies of different OL were estimated as 34-57 kcal/mol. The highest adsorption energy and the most stable layer geometry corresponded to OL type A, X=S. Modeling of coadsorption of catalytic reaction reagent was carried out for the system "cluster Pt_{64} + two molecules of OL + adsorbed chiral molecule". L- and D-proline **1**, alanine **2**, pantolactone **3** and unsaturated ketone 3-methylhex-4-en-2-on $C_7H_{12}O$ **4** (Fig. 2) were considered as chiral reagents.

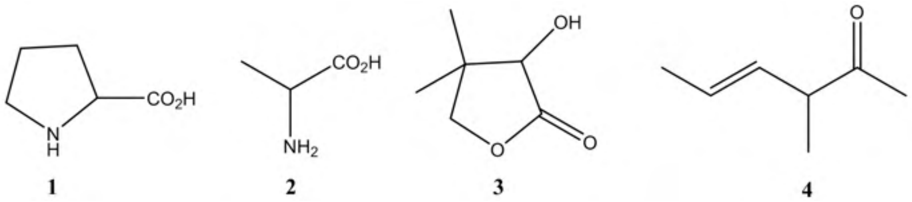


Fig. 2. Chiral reagents

It was found that the adsorption energy of ketones is too low to form stable adsorption complexes in the presence of dense ligand layers. Thus, the catalytic reaction with these reagents should slow down significantly. At the same time, proline and alanine form stable adsorption complexes, the adsorption energy of which substantially depends on the configuration of the asymmetric center. For proline, the adsorption energy of D-isomer varies within 8-23 kcal/mol, depending on the relative position of the OL and the chiral molecule (PM6 calculations) (Fig. 3). At the same time, the adsorption energy of L-proline is only in the range of 6-13 kcal/mol (Fig. 3).

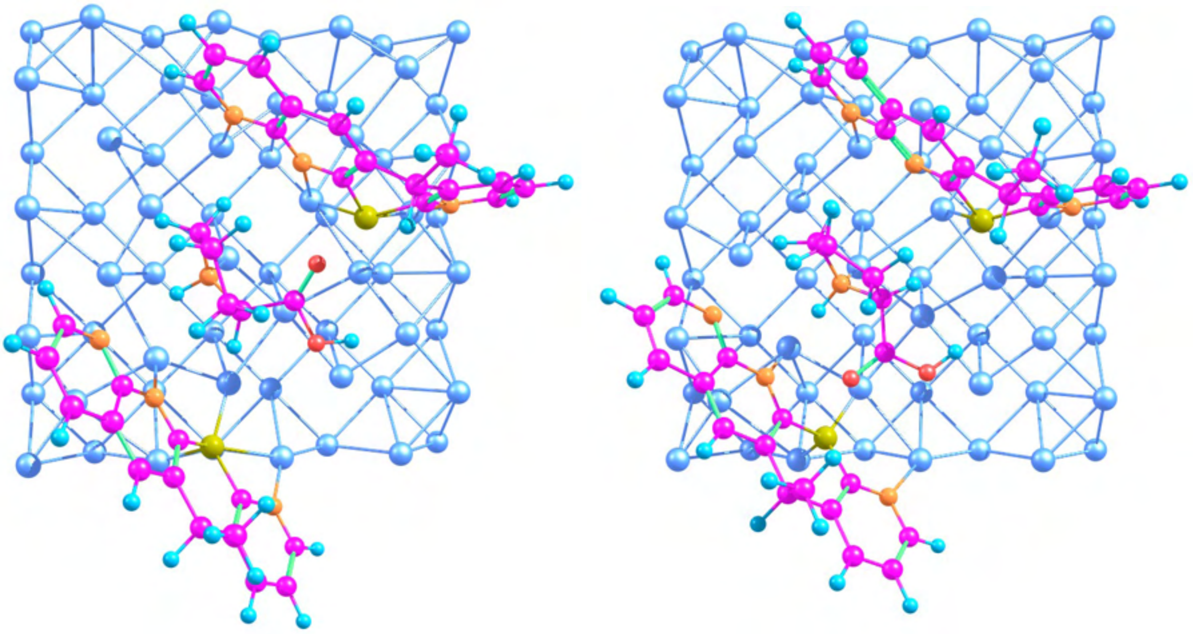


Fig. 3. Optimized systems "cluster Pt$_{64}$ + two molecules of OL + D-proline" (on the left, E$_{ads}$ = 23 kcal/mol) and "cluster Pt$_{64}$ + two molecules of OL + L-proline" (on the right, E$_{ads}$ = 13 kcal/mol)

The significant difference of adsorption energies demonstrates that the proposed OL structures ensures the effective discrimination of different enantiomers and can be prospective for the development of stereoselective catalysts for the reactions of bifunctional amino derivatives.

In order to simulate the more realistic reaction environment, the molecular dynamic study of the monolayers formed by the proposed OLs augmented with long aliphatic chains ensuring their vertical orientation on a Pt surface was carried out using the ReaxFF force fields. The results of this modeling allow estimating the temperature ranges within which the structure of the OL monolayers keeps their orienting action.

Acknowledgement. The study was carried out with financial support of the Russian Foundation for Basic Research (projects № 20-03-00282 and 18-43-520012).

OP-III-4

DFT Prediction of the ^{13}C NMR Chemical Shifts of the Adsorbed Zeolite Species: a Methodological Study

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High resolution solid- state ^{13}C MAS NMR is a very efficient tool for studying the of hydrocarbon species in zeolites. [1] In particular, this method allows one to obtain information on the pathways of hydrocarbon transformation, the reaction intermediates and products adsorbed on zeolite surface and establish various factors influencing the pathways of catalytic transformations. Detection and correct identification of surface hydrocarbon species based on the analysis of the specific chemical shifts in the ^{13}C NMR spectra is crucial step of the mechanistic studies by NMR method. One of the ways to ensure the molecular assignment of the observed signal to a particular specie is a DFT calculations of the NMR chemical shift for the alleged surface species. However, there are a number of issues that could limit the accuracy of the calculated chemical shifts should be studied. First, the uncertainties could be caused by the calculation technique. Secondly, there is a problem of a model selection to represent local zeolite structure of the alleged species. [2]

We present a study on the accuracy of the various DFT calculations for rationalizing the ^{13}C NMR spectra of ZSM-5 zeolite adsorbed reaction intermediates. Both model- and methodology-related uncertainties have been examined by calculating ^{13}C NMR chemical shifts of the Si–O(CH$_3$)–Al methoxides with well-known chemical shift of 59 ppm, placed at the different locations within the zeolite framework.

Firstly, the periodic structures of the Si–O(CH$_3$)–Al methoxides were calculated (PBE-D3BJ/450 eV). Then cluster models from the periodic structures were constructed. Two different approaches were used for the chemical shift calculations on the cluster models namely, (i) single-point chemical shift calculation (SP) directly on the geometry from periodic DFT or (ii) full optimization (OPT) of the cluster followed by chemical shift calculations. 6 DFT functionals were employed: GGA-level PBE-D3 functional and hybrid GGA-level PBE0-D3, HSE06, wB97xD, B3PW91-D3, mPW1PW91 functionals. In total, 12 calculation protocols were examined.

The accuracy of the computational protocols assessment was carried out for the Si–O(CH$_3$)–Al methoxide species with well-known experimental chemical shift values of 59 ppm. To analyze the how the chosen model affects the chemical shift calculations we studied 12 zeolite models with locations of the Si–O(CH$_3$)–Al species. These models are further denoted as "T(Al)-site–T(Si)-site".

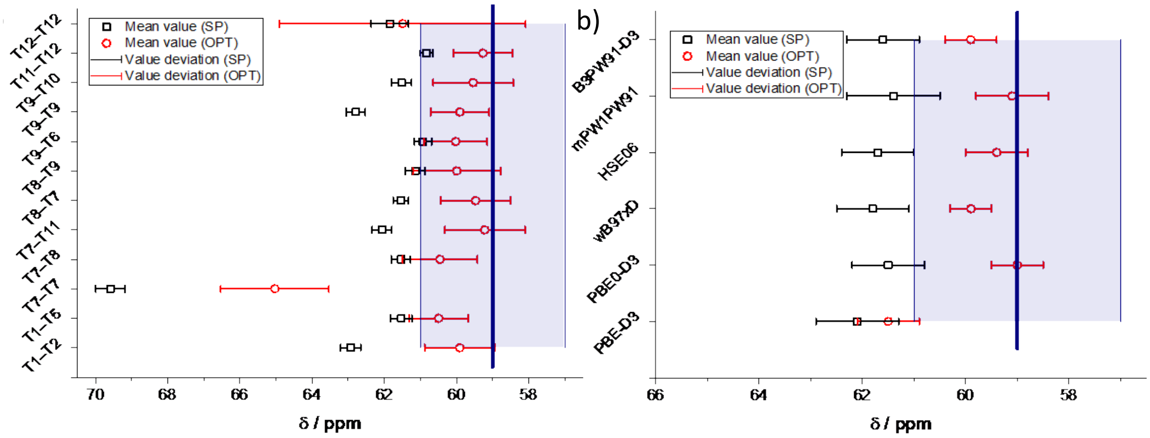

***Figure 6.** a) Mean calculated ^{13}C chemical shifts of the Si–O(CH_3)–Al methoxides calculated by various calculation techniques and method-related uncertainties. b) Mean calculated ^{13}C chemical shifts of the Si–O(CH_3)–Al methoxides placed in the different locations throughout the ZSM-5 zeolite framework and the chemical shift value deviations. The filled area indicates the half-width of the experimentally observed signal at 59 ppm.*

Figure 1a presents the method-related uncertainty on the mean ^{13}C chemical shift values for each calculated methoxide. It is clearly seen that the obtained chemical shifts are not significantly influenced by the chosen calculation DFT functional in case of SP calculations. The value deviations are in the range of 0.2–0.5 ppm. Concerning mean ^{13}C chemical shits calculated using cluster OPT procedures, it is clearly seen that XC-related uncertainties are larger compared to single point calculations. The results obtained demonstrate the deviation of the chemical shifts calculated using cluster optimization model is in the range of 0.8–1.5 ppm. The exceptionally high chemical shift of the T7-T7 methoxide is due to its low relative stability: 80 kJ/mol vs. 0-20 kJ/mol for other methoxides. OPT Chemical shift deviation of T12–T12 methoxide (±3.7 ppm) is so high because of conformational change due to the cluster geometry optimization.

Placing the methoxide species into various locations of zeolite framework influences the computed chemical shift by up to ±0.8 ppm due to local confinement differences (Figure 1b). The observed differences between the experimental chemical shifts and the values predicted for different methoxide configurations are attributed to the fact that the experimental data can be viewed as a statistical average over various methoxides locations, whereas the calculations deal with one model for one specific configuration.

The results obtained indicate that geometry optimization of the active site local environment at an H-GGA level of theory is critical to obtain chemical shift values close to experimental ones. Our analysis indicates that the full geometry optimization of a zeolite cluster at PBE0-D3/6-311G(d,p) level of theory followed by GIAO/PBE0-D3/aug-cc-pVDZ calculations is the most suitable approach for the calculation of ^{13}C chemical shifts of zeolite surface intermediates.

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OP-III-5

Propylene Oxidation on Ag Single Crystal: In Situ Study by Polarization Modulation Infrared Reflection Absorption Spectroscopy

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Nowadays, the process of ethylene epoxidation over silver catalysts is of great industrial importance. This reaction was being intensively studied 30 years ago and now high active Ag-based catalysts which provide selectivity toward ethylene oxide exceeding 90% are developed [1, 2]. Propylene oxide is a very valuable precursor in the chemical polymer industry [3]. The epoxidation of propylene by oxygen over silver catalysts is also attractive reaction because of it is a more environmentally friendly method compared to the processes involving chlorohydrin and peroxides. However, the selectivity of this reaction is 2-4 % only [4, 5]. To develop more effective catalysts for the propylene epoxidation it is necessary to perform mechanistic studies using in situ methods. The knowledge about active cites and reaction intermediates will be useful to improve the characteristics of the catalysts and achieve higher selectivity.

Surface-sensitive in situ techniques for studying heterogeneous catalysts are now widely developing since it is impossible to find out the exact characteristics of the “active phase” of the catalyst during ex situ studies of the surface before or after reaction. A number of methods used to study the kinetics of reactions on model catalysts are carried out under UHV conditions. This is the reason for the "pressure gap" between surface science and applied catalysis.

In this work we present the results of our studying the oxidation of propylene by oxygen on the surface of a silver single crystal. Propylene oxidation was investigated at temperatures from 30 to 300°C in the pressure range from 1 to 10 mbar by polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). By this method it is possible to carry out research at pressures ranging from UHV to 1 bar and simultaneously observe both the reaction products in the gas phase and the reaction intermediates adsorbed on the surface directly during the reaction. Thus, through such research we obtain information about the reaction intermediates and elementary stages of the heterogeneous catalytic process [6].

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OP-III-6

In Situ DRIFTS Study of the Reactivity of Hydrides in the Gas-Phase Hydrogenation of Acetic Acid on a Pt-ReOx/TiO_2 Catalyst

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In view of the limited reserves of the petroleum resources, more and more attention is being drawn to use of the renewable raw materials (biomass) to obtain valuable chemical products. Carboxylic acids are one of the main products of biomass conversion. The catalytic hydrogenation of carboxylic acids is a very promising method for the production of alcohols - substances valuable from the industrial point of view. Recently, highly selective metal-oxide supported catalysts have been actively developed, where the metal is usually Pt, Pd, Ir, Ru, and the oxide part is low-valent oxides ReOx, WOx, MoOx [1-2]. However, the hydrogenation mechanism on these catalysts has not yet been established. For example, the interaction of hydrogen with the catalyst has not been studied, and there is also no data on reactive particles on the catalyst surface.

In this work, we have studied the interaction of a Pt-ReOx/TiO_2 catalyst with hydrogen and the reactivity of the formed hydrides with acetic acid vapor by in situ DRIFTS. The catalyst has been characterized by HAADF-STEM, EDX, BET and XPS methods.

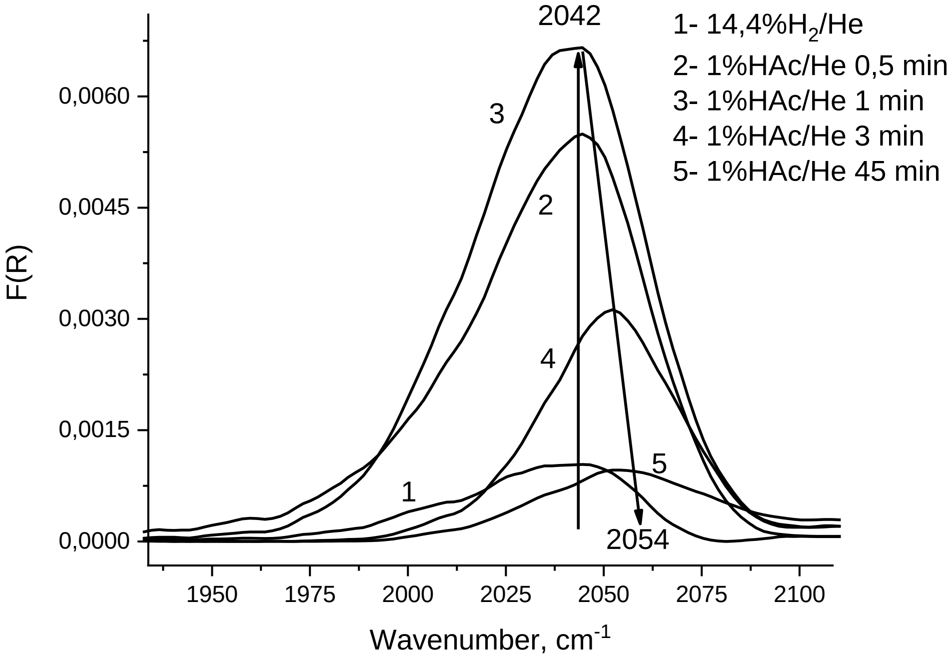

Fig. 1. IR spectra of diffuse reflectance of the Pt-ReOx/TiO_2 catalyst in the region, sequentially treated at $T = 200^oC$ with gas mixtures.

It was shown that the average size of the deposited Pt-Re particles is ~ 1 nm. Despite the high dispersion, platinum atoms are in the Pt^0 state due to the transfer of electron density from neighboring low-valent rhenium ions. When Pt-ReOx/TiO_2 catalyst interacts with mixture of 14.4% H_2/He, the absorption band at 2042 cm^{-1} appeared, which can be attributed to platinum hydride (Fig. 1) [3]. When the catalyst interacts with acetic acid, the platinum hydride band sharply increases in intensity, presumably due to the effect of the formed acetates on the Pt-H bond energy. Upon further treatment of the catalyst with acetic acid vapor, the intensity of the platinum hydride band decreases due to acid hydrogenation.

With the reverse replacement of the reaction flow with reducing 14.4%H_2/He, the appearance of intense bands at 1918 and 2025 cm^{-1} is observed, which, as we assume, refer to the hydrides. The high intensity of the bands, in our opinion, is also explained by the influence of neighboring acetates on the Pt-H bond energy. It was found that acetates are not desorbed in an inert gas flow. It was shown that when the catalyst was treated with mixture of 14.4%H_2+He, no decrease in the intensity of the acetate bands was observed. This indicates their high reactivity in the hydrogenation of acetic acid. The surface acetates with bidentate bridging structure do not completely disappear, which indicates that only acetates that are in close proximity to Pt-H particles are involved in the reaction. In turn, the acetates located on the support's surface without close contact with Pt-Re particles remain inaccessible; that is, do not take part in hydrogenation.

Acknowledgement. The reported study was funded by RFBR and National Research Foundation of Korea according to the research project № 19-53-51002

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OP-III-7

Aromatization of n-Butene on Zn/H-BEA Zeolite: ^{13}C MAS NMR Study of the Reaction Mechanism and the Role of Zn^{2+} and ZnO Species

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Light alkenes (C_2–C_4) are the main products of steam cracking of naphtha and liquefied natural gas. While ethylene and propylene are then mostly used for the production of polymers (packaging, fibers, films etc.), the demand for butenes seems to be lower, and the approaches for the effective industrial utilization of butenes are needed. Zinc-modified zeolites represent promising catalytic systems for converting small alkanes and alkenes to more valuable aromatic hydrocarbons [1].

Ono et al. [2] investigated the process of n-butene conversion over H-ZSM-5 and Zn-ZSM-5 zeolites. It was found that the modification of H-ZSM-5 zeolite with zinc leads to a drastic increase in the selectivity towards simple aromatics and simultaneous decrease of the yield of light alkanes (C_1–C_3) as compared to unmodified H-ZSM-5. Based on the observation of butadiene among the reaction intermediates, the authors proposed the aromatization mechanism to be different from the carbenium ion pathway typical of H-form zeolites and to involve the formation of carbanionic allyl-like species. However, the studied Zn-ZSM-5 sample was prepared via the traditional procedure of ion exchange, which leads to the appearance of the mixture of various Zn species (Zn^{2+} cations and ZnO clusters) located inside the zeolite pores [3]. A few recent studies have shown that cationic species and small clusters of zinc oxide have their own peculiarities and different activities in the processes of the alkanes and alkenes activation and transformation on Zn-containing zeolites [4–6]. Hence, the goal of the given study was to establish how the nature of Zn species affects n-butene transformation mechanism and to clarify if allylic species are indeed the intermediates for n-butene aromatization on Zn-modified zeolites.

To reveal the peculiarities of n-butene transformation on zeolites with different Zn species (isolated Zn^{2+} cations and ZnO clusters) the method of solid-state NMR spectroscopy (MAS NMR) was applied. Selectively ^{13}C-labeled in either $=CH_2$ or $=CH–$ groups n-but-1-ene was used to unequivocally identify the structures of the reaction intermediates by ^{13}C MAS NMR and gain insight into the aromatization mechanism.

It is inferred that the aromatization of n-but-1-ene on zeolite selectively modified with isolated zinc cations (Zn^{2+}/H-BEA sample) proceeds with the involvement of Zn^{2+} sites (Fig. 1). The following intermediates were detected: π-complex of n-but-2-ene, methylallylzinc and delocalized carbanionic oligomeric (polyene) species stabilized on zinc cations. Desorption of highly unsaturated polyene chains from Zn^{2+} sites and subsequent protonation and dehydrocyclization on Brønsted acid sites (BAS) results in final reaction products – aromatic hydrocarbons such as toluene and xylenes.

For the zeolite sample containing small clusters of zinc oxide (ZnO/H-BEA), n-but-1-ene transformation was found to occur via two pathways: (1) aromatization with the assistance of ZnO species similar to the case of Zn^{2+}/H-BEA zeolite; (2) conjunct polymerization with the involvement of BAS. The latter process is indicated by the presence of the signals from methyl-substituted cyclopentenyl and cyclohexadienyl cations in the obtained ^{13}C MAS NMR spectra. Conjunct polymerization contributes notably to n-butene transformation on ZnO/H-BEA and results in the formation of the noticeable quantity of C_1–C_4 alkanes.

The difference in the performances of the two zeolite samples, Zn^{2+}/H-BEA and ZnO/H-BEA, was explained by the different stability of n-butene π-complex on Zn^{2+} and ZnO sites, which was confirmed by related DFT calculations. It is concluded that Zn-modified zeolite containing exclusively Zn^{2+} cationic species and small quantity of BAS should exhibit higher efficiency as the catalyst for small alkanes and alkenes aromatization rather than the zeolite with ZnO species and high concentration of BAS.

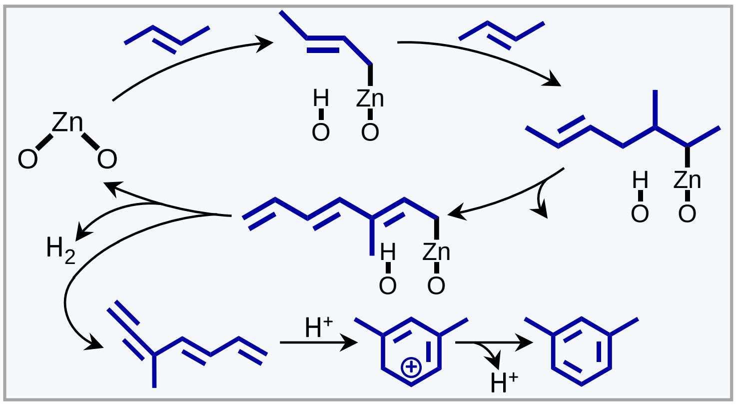

Figure 1. Possible mechanism of n-butene aromatization on Zn-modified zeolites performed with the assistance of the Zn sites, Zn^{2+} cations or ZnO clusters.

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OP-III-8

CO Oxidation on Copper-Doped Gold Thiolate Clusters Supported on CeO_2: DFT Study

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Gold nanoparticles have obtained much attention due to their promising catalytic activity in different chemical reactions including CO oxidation [1]. However, catalytic activity of gold nanoparticles strongly depends on particles size and structure [2]. Thus, it is important to study catalytic activity of gold nanoclusters of a certain size and composition. One of the methods for preparing size-selected and structure-selected nanoparticles catalysts is the impregnation of an oxide support (for example, CeO_2) with a solution containing gold clusters stabilized by organic ligands, in particular, $Au_n(SR)_m$. Many aspects of the preparation and use of $Au_n(SR)_m/CeO_2$ in catalytic reactions have not been established yet, including the preparation details, reaction mechanism, structure of the active site, and effect of the support and the promoting metal.

Here we present a quantum chemical simulation of CO oxidation on $Au_{19}Cu(SCH_3)_{16}/CeO_2$ to study the effect of copper on the catalytic properties of a gold cluster stabilized with thiolate ligands. Previously, we found that $Au_{20}(SCH_3)_{16}$ is chemically inert and does not react with CO and O_2 without heating and degradation of the ligand shell [3]. The study has several calculation steps: (i) structure of $Au_{19}Cu(SCH_3)_{16}$ in gas phase and on CeO_2; (ii) adsorption energy of O_2 and CO on clusters; (iii) energy path-way of CO oxidation on the cluster supported on CeO_2. Calculations in the gas phase were carried out by the DFT PBE in the Priroda program; support effects were considered in periodic approach using VASP program code. This work has been carried out using computing resources of the federal collective usage center Complex for Simulation and Data Processing for Mega-science Facilities at NRC “Kurchatov Institute”.

Different position of copper on gold protected cluster were considered including position in the cluster core or on staple fragment. According to the energy calculation of six possible isomers of $Au_{19}Cu(SCH_3)_{16}$, copper can be located both in cluster core and in outer ligand shell. Next, we simulated the adsorption of O_2 and CO on $Au_{19}Cu(SCH_3)_{16}/CeO_2$. The CO molecule is coordinated on the copper atom of the cluster, O_2 can be coordinated on CeO_2 and on the copper atom. A further mechanism includes the oxidation of CO with oxygen via Mars-van-Krevelen and Langmuir-Hinshelwood mechanisms.

It is shown that the introduction of copper into the $Au_{20}(SCH_3)_{16}$ cluster creates new sites for the adsorption of CO and further oxidation. It is predicted that bimetallic gold-copper clusters protected by thiolate ligands supported on CeO_2 can be used as catalysts for CO oxidation.

Acknowledgement. This work has been carried out using computing resources of the federal collective usage center Complex for Simulation and Data Processing for Mega-science Facilities at NRC “Kurchatov Institute”, http://ckp.nrcki.ru/.

OP-III-8

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OP-III-9

Oligomerization of Propylene over TON, FER and MFI Zeolites

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Oligomerization of light alkenes is an important process for the production of high-octane fuel additives, plasticizers, oils and surfactants [1]. Currently, oligomerization is carried out over molecular sieve catalysts with Brønsted acid sites. It is known that over wide pore molecular sieves, such as BEA, MOR, rapid deactivation of the catalyst occurs owing to the formation of heavy alkenes and aromatics that block the transport pores of the catalyst. This drawback can be avoided by running the process on zeolites smaller in pore diameter, typically on zeolites of MFI structure. In turn, little attention is paid to oligomerization over narrow-pore molecular sieves, which are interesting due to the difficulty in the formation of heavy alkenes and aromatics over them.

A series of zeolites with MFI, TON and FER structural types were tested in propylene oligomerization to study their textural properties and peculiarities. Acid sites in these zeolites are located in pores of different sizes: from 3.5 to 5.6 Å, which can affect the course of the oligomerization process. In addition, TON, FER and MFI zeolites have 1, 2 and 3-dimensional channel systems, respectively. Zeolites were studied using a complex of physicochemical methods of analysis: TPD NH_3, IR (ads. CO), XRD, XRF, and low-temperature nitrogen adsorption-desorption. It was shown that all observed zeolites have a similar chemical composition and strength of acid sites, but different concentration of acid sites. Differences in the shape of crystals (needles, plates, spherical co-crystallisates) was due to the peculiarities of their crystal lattices.

It was found that the arrangement of acid sites in pores of different sizes directly affects both the conversion and the selectivity of the oligomerization process. Zeolite with FER structural type which has the smallest pore size shows the least catalytic activity. Comparison of the selectivity of the process at the same conversion level indicates that in the narrow pores of TON and FER zeolites predominantly di- and trimerization of propylene occur with the formation of olefins C_6 and C_9 (Fig. 1). In the MFI structural type zeolite, a wide product distribution is observed, which indicates a significant contribution from secondary reactions.

To study the features of the process in pores of different sizes, kinetic dependences of the yield-conversion on zeolites with FER and MFI structural types were plotted. They confirmed the differences in the mechanism of oligomerization on acid sites with different localization. It can be concluded that narrow-pore molecular sieves, such as FER and TON zeolites are more selective towards formation of propylene dimers and trimers and more stable to deactivation than MFI zeolite with its 3D porous system.

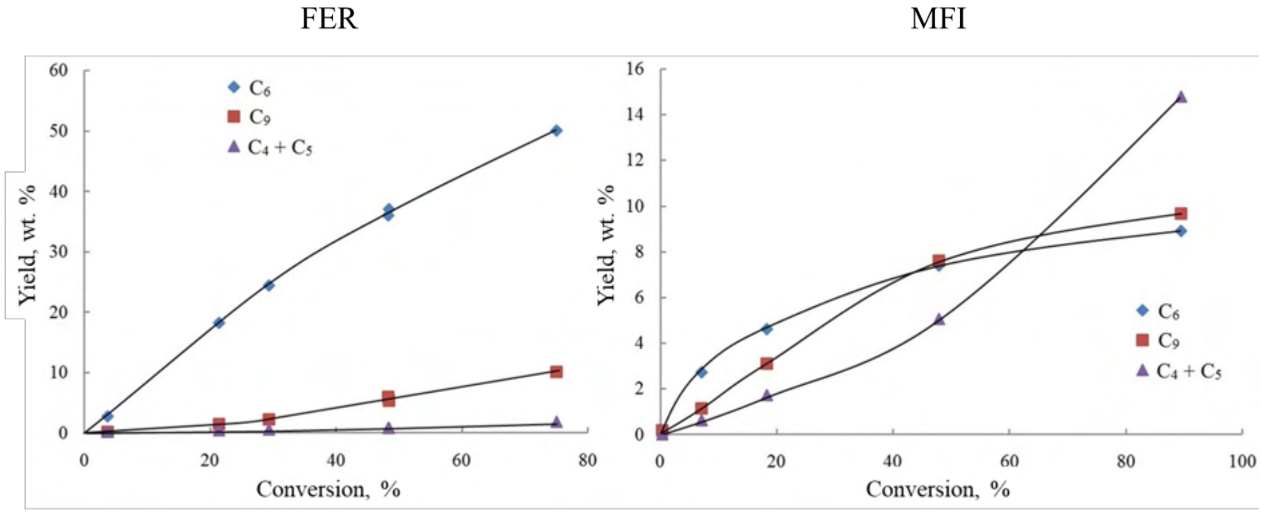

Fig. 1. Kinetic dependencies yield-conversion in oligomerization of propylene over FER and MFI zeolites (T = 300 °C, p = 15 atm). "C_6" stands for propylene dimers, "C_9" – for propylene trimers, "C_4+ C_5" – for products of side processes.

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OP-III-10

Quantum Chemical Simulation of Methanol Oxidation on Vanadium Oxide

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Small clusters formed by transition metal oxides are an interesting object of research due to the variety of structures and physicochemical properties [1]. Metal oxide clusters are studied using modern experimental and theoretical methods. Of particular interest are transition metal oxides, which are catalysts in many commercially important reactions. For example, vanadium oxide is active in the reactions of oxidation and dehydrogenation of organic compounds, in the oxidation of SO_2, and in the selective reduction of NO_x [2-4]. One of the catalytic processes taking place on V2O5 is the selective oxidation of methanol to formaldehyde. However, active centers and the structure of vanadium catalysts is still being actively studied by scientific groups around the world. The report is devoted to the search for a model of a vanadium-containing catalyst; atomic monometallic $(V_2O_5)_x$ and bimetallic clusters and the surface of vanadium oxide are considered.

The existence of a cluster with the composition V_4O_{10} was experimentally confirmed [5], and this is why the transformation of methanol into formaldehyde was considered and studied this via model. Various methods of quantum chemistry were used to optimize the structure of the cluster, and the energies and harmonic frequencies of vibration were calculated. Based on the testing performed, the most accurate method was selected. A quantum chemical simulation of the oxidation of methanol to formaldehyde on the $(V_2O_5)_2$ cluster and on the $(V_2O_5)_n$ surface was carried out. Modeling in the cluster approach included the following steps: calculating the structure of the $(V_2O_5)_2$ cluster, its complexes with methanol, finding the transition states, and plotting the potential energy surface cross section for individual stages using the PBE density functional theory in the Priroda program. The VASP quantum chemical program was used to carry out model calculations on the surface.

The V_3TiO_{10} cluster was found in the literature, which has a similar with V_4O_{10} adamantane structure [6]. The study of the reaction mechanism on both clusters helped to reveal the positive effect of the titanium atom on the catalytic properties.

The report will present the calculated kinetic and thermodynamic values of the stages of the considered mechanism of methanol oxidation to formaldehyde on different models and compare them with the available experimental and theoretical data.

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OP-IV-1

New Biodegradable Copolymers Based on Betulin, Organic Acids and Their Derivatives

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The production of plastics based on fossil fuels leads to environmental pollution and depletion of petroleum reserves in the world. The synthesis of new polymers based on renewable sources, such as biomass, has become a critical research focus of modern polymer science. Along with solving environmental problems, biopolymers pose less health risk than petroleum-based polymers.

Betulin is triterpene derivative, that contains a large amount of bark white birch (about 30%), also a waste product of the wood industry. Its molecule has three unique functional groups: primary and secondary OH moieties and a isopropenyl group. Importantly, as a diol, betulin can undergo polycondensations with organic acids and ring-opening copolymerization with cyclic ethers, hence it can become one of the promising petroleum based polymers replacements.

Betulin and its derivatives are safe for health and show great medical effects [1], particularly anti-cancer, hypolipidemic, anti-leishmania, bactericidal, fungicidal and antiviral properties, including against Epstein–Barr virus and HIV. In this case, copolymers based on betulin can be used as controlled drug delivery systems, in which the monomer will be active treat agent. On the other hand, in material science, betulin based polymers have high mechanical properties. They are promising materials for gas separation or storage. The large interest is evoked by the green house gas CO_2 separation.

Despite all the advantages that betulin-based copolymers have, there are only a few works in the scientific literature devoted to the creation and study of copolymers of this kind (about 20 works in total). In addition, in most of the works presented [2,3], despite good copolymer yields of 70-90%, carboxylic acid chlorides are used as a comonomers, and organotin compounds and pyridine act as copolymerization catalysts, which are toxic substances and, accordingly, require certain measures precautions in their use, and their separation and neutralization is a laborous and resource intensive process. In this regard, the aim of this study is to develop a method for producing copolymers of betulin with organic acids and their derivatives, based on the use of a catalyst that is safer for health and the environment.

In this work, we used γ-Al_2O_3 as the catalyst for copolymerization betulin with organic acids (adipic, lactic, glycolic) or their derivatives (butyllactate, glycolide, lactide). The copolymerization process was carried out with constant stirring at 180 °C in inert argon atmosphere at the presence of 0.1 wt.% catalyst for 3, 15 and 24 hours. In addition, we proposed to introduce tert-butyl hydroperoxide (TBHP) as an OH group initiator. The molecular weight and structure of the copolymers was confirmed by gel permeation chromatography (GPC) and ^{1}H, ^{13}C nuclear magnetic resonance (NMR). The results are shown in Table 1.

Table 1 – γ-Al_2O_3 catalysed copolymerization of betulin with organic acids or derivatives.

Comonomer	Time, h	M_n^{NMR}, g/mol	M_n^{GPC} , g/mol	M_w, g/mol
Adipic acid	3	1514	1581	1858
L-lactic acid	3	500	455	470
Glycolic acid	3	-	-	-
Lactide	3	1265	801	905
Glycolide	3	826	749	893
Glycolide	15	1013	993	1356
Glycolide	24	1610	1555	1579
Butyllactate	3	559	492	731
Butyllactate	15	3155	3043	4129
Butyllactate*	3	1225	1496	1861
Butyllactate*	15	5300	5331	11756

*-with TBHP initiator addition; M_n^{NMR} –number average molecular weight using 1H NMR; M_n^{GPC} – number average molecular weight using GPC; M_w – weight average molecular weight using GPC.

It should be noted that copolymerization with hydroxycarboxylic acids (lactic and glycolic) failed, since, in the case of lactic acid, a low molecular weight lactic acid oligomer was obtained, and no reactions with glycolic acid. Probably, the formation of water during polycondensation can cause inhibition of the copolymerization.

However, betulin copolymers were successfully obtained with dicarboxylic acid and oxycarboxylic acids derivatives. It can also be noted that with synthesis time growth, the molecular weight and the degree of polymerization increase. The maximum molecular weight was reached for the copolymer of betulin with butyl lactate in the presence of an Al_2O_3 catalyst after 15 h of synthesis, which was 4129 g/mol. With the TBHP as initiator, the molecular weight of the copolymer increased to 11756 g/mol. Molecular weight growth with TBHP initiator addition can define that copolymerization follows a radical-polycondensation mechanism.

The obtained copolymers molecular weights, as well as their yield (up to 90%), correspond to the results obtained using an organotin catalyst and pyridine [2,3], which shows the potential use of γ-Al_2O_3 as safety betulin copolymerization catalyst.

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OP-IV-2

Study of Mo-Ni-Based Catalysts in the Hydrotreatment of Sewage Sludge-Derived Pyrolysis Oils

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Nowadays, the world confronts a great necessity in efficient recycling of sewage sludge (SS). This is a semisolid by-product, being inevitably left over wastewater treatment plants. Moreover, production of sludge increases gradually, due to the growth of world population, urbanisation and industrialisation. This raises the global concerns of how to dispose sewage sludge in an efficient manner by recovering energy [1]. Recently, there has been an interest in thermal treatment of SS by fast pyrolysis as a promising option for handling this waste stream. In particular, fast pyrolysis offers opportunities for producing biofuels from SS via initial formation of pyrolysis liquids or pyrolysis oils (Py-SS). Importantly, such liquids contain water and high concentrations of heteroatomic (N-, O-, and S) compounds. As a result, catalytic hydrotreatment of sewage sludge-derived pyrolysis oils becomes extremely important, taking into account the existing engine fuel requirements. Besides, bearing in mind typically high concentrations of N-containing compounds in SS pyrolysis liquids, in contrast to those reported, e.g. for crude oil and lignocellulosic bio-oil, an effective hydrodenitrogenation (HDN) constitutes one of priority tasks for Py-SS processing. Recent research [2] has shown high activity and selectivity of molybdenum nitrides in HDN transformations, while the efficiency of the target process was further improved when promoting the catalyst with nickel [3]. At the same time, the effect of the catalyst support on the formation of nitride phase and the catalyst activity in HDN of Py-SS are not sufficiently covered in the literature, especially given the obstacles created by sulfur, oxygen, and water to HDN efficiency.

In the present study, a series of Mo-Ni-based catalysts supported on various oxides (SiO_2, γ-Al_2O_3, TiO_2, CeO_2, ZrO_2-La_2O_3, zeolite TPIC-02) were synthesized using appropriate techniques, including incipient wetness impregnation, co-precipitation and sol-gel method. Nickel was used as a promoter with a molar ratio Ni/(Ni + Mo) = 0.3, by analogy with conventional CoMo and NiMo hydrotreatment catalysts. In addition, a reference sulfided NiMo/P-γ-Al_2O_3 catalyst was prepared similar to those previously reported [4]. A number of physicochemical methods (TPR-H_2, XRD, XPS, BET, CO chemisorption and others) was applied in order to clarify the structural features of the considered catalysts. The activity of the catalysts was studied in HDN of indole, being a model compound of Py-SS. The process was carried out in a batch reactor (autoclave, V = 300 ml) at temperature of 350 °C and hydrogen pressure of 5.0 MPa (25 °C).

Maximum indole conversion (100%) and complete nitrogen removal were achieved (Fig. 1a) over the catalyst with γ-Al_2O_3 as a support; while the rest catalysts showed lower indole conversion (less than 60%) as well as low selectivity to nitrogen-free products.

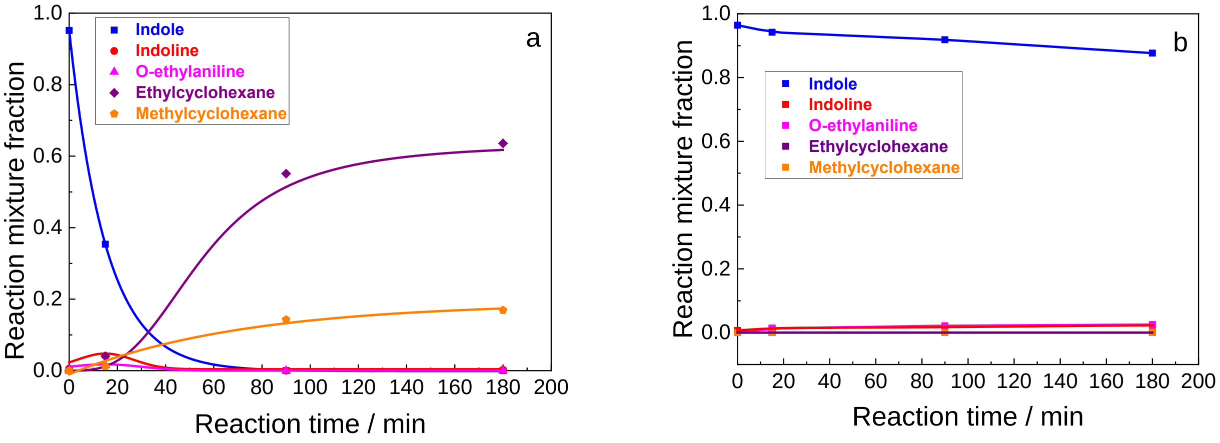

Fig. 1. Composition of the reaction mixture (fraction) vs reaction time (min) of indole hydroconversion over MoNiN/γ-Al_2O_3 catalyst: (a) in the absence of DBT; (b) after addition of DBT.

The study also revealed the importance of the ammonolysis treatment of the catalyst. Thus, the oxide precursor as well as the hydrogen-activated samples could not demonstrate as high activity and selectivity in indole hydroconversion as observed for the MoNiN/γ-Al_2O_3 catalyst. One of the distinctive work's features, being important both from a fundamental and practical point of view, was the stability studies of the catalysts under model hydrothermal conditions. The studies showed that the modification of γ-Al_2O_3 by phosphorus significantly increases the stability of the support in the presence of water and prevents its transition to boehmite. However, it also results in a significant decrease in the HDN activity of the catalyst. In addition, since Py-SS contains sulfur (up to 1 wt%) along with significant amounts of nitrogen and oxygen, the effect of the model S-compound dibenzothiophene (DBT) on indole transformations was studied in the presence of the selected catalysts. Thus, a sharp decrease in indole conversion was noted in the case of the MoNiN/γ-Al_2O_3 system after the addition of DBT (Fig. 1b). This could be due to the blocking of the catalyst sites, being active in hydrogenation and subsequent hydrodenitrogenation of indole, by the sulfur-containing agent. The obtained results may be also associated with the way of the phosphorus introduction into the catalyst; thereby its further modification is required.

The hydrotreatment of the original feed (Py-SS) was also studied using the chosen catalyst samples, the observations made will be discussed in more detail during the talk.

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OP-IV-3

Catalytic Oxidation of 5-Hydroxymethylfurfural over $Au_{1-x}Ag_x$ and $Pd_{1-x}Ag_x$ Catalysts

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At present, a large part of valuable organic compounds and fuels is produced from depleting and unsustainable fossil resources, primarily oil, characterized by constantly growing complexity of production technologies and negative environmental impact [1]. Currently, the use of biomass becomes promising due to the high renewability of the feed as well as opportunity to synthesize a wide spectrum of organic compounds and fuels. One of the main advantages of this direction is the presence of valuable side products formed during the refining, e.g., 5-hydroxymethylfurfural (HMF) [2]. The HMF is a multifunctional platform molecule used to synthesize various important compounds ranging from healthcare products to polymers. Among others, the 2,5-furandicarboxylic acid (FDCA) is an important product of the HMF oxidation (Fig. 1) serving as an alternative for terephthalic acid in the synthesis of metal-organic frameworks (MOFs) [3].

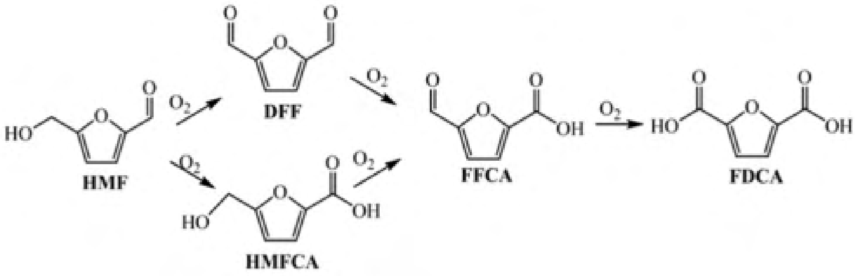

Fig. 1. The proposed scheme of HMF transformations.

Diverse catalytic systems were proposed for the HMF selective oxidation that influence the selectivity towards desired products in the oxidation process [4]. Nevertheless, the factors affecting the pathways of the HMF oxidation over different catalysts are still not clear and require additional studies.

The present work is devoted to the study of the catalytic HMF oxidation with molecular oxygen in water solutions over noble metal (Me = $Au_{1-x}Ag_x$, $Pd_{1-x}Ag_x$) nanoparticles (NPs) obtained by laser ablation in liquid (PLAL) and Me@UiO-66 composites. The influence of the catalytic experiment conditions such as substrate/catalyst and NaOH/substrate molar ratios, reaction temperature, oxygen pressure was studied.

Table 1 shows a selection of results of the study of catalytic properties under specified conditions (reaction temperature of 100 °C, oxygen pressure of 5 or 10 atm, substrate/catalyst ratio of 100, reaction time of 6 h). The $Au_{1-x}Ag_x$ NPs obtained by LAL show high catalytic activity in a neutral medium, but the main products of the HMF transformations are low-molecular compounds of oxidative decomposition. The $Pd_{1-x}Ag_x$ NPs were characterized by lower activity and relatively high selectivity towards DFF, but the main direction of the HMF transformation is the formation of the C–C oxidative cleavage products. The incorporation of $Pd_{1-x}Ag_x$ NPs into the UiO-66 matrix contributes to a noticeable decrease in the activity of bimetallic Me@UiO-66 composite catalysts towards the oxidative C-C cleavage.

Table 1. Catalytic properties of mono- and bimetallic NPs and corresponding UiO-66-supported composites in the HMF oxidation.

Sample	Experimental conditions					HMF conv., %	Selectivity, %			
	Time, h	T, °C	P_{O2}, atm	Molar ratio			FDCA	DFF	HMFCA	FFCA* + low molecular weight products
				Sub. /Cat.	NaOH /Sub.					
Pd (abl.)	6	100	5	100	0	24.2	1.0	28.7	4.4	65.9
PdAg (abl.) (0,5:0,5)	6	100	5	100	0	22.2	0.5	6.9	0.7	91.9
Au (abl.)	6	100	5	100	0	77.5	1.0	0.5	2.6	95.9
AuAg (abl.) (0,5:0,5)	6	100	5	100	0	50	1.5	2.2	0.8	95.5
1%Pd-Ag@UiO-66 (0,85:0,15)	6	100	5	100	0	30.8	2.2	66.9	3.5	27.5
1%Au@UiO-66	6	100	10	100	0	35.0	2.7	23.5	1.6	72.3
1%Au@UiO-66	6	100	10	100	2	58.2	0.2	1.1	10.8	87.9
1%AgAu@UiO-66 (0,5:0,5)	6	100	5	100	0	18.6	1.2	13.4	1.1	84.3

*Selectivity towards FFCA for all samples does not exceed 5% except for 1%Au@UiO-66 in alkali medium (FFCA selectivity is 12–29%).

The results obtained indicate that the main direction of the FDCA formation in the presence of the base is the oxidation of the carbonyl group of HMF to yield HMFCA followed by its consecutive oxidation to FFCA and FDCA (Fig. 1). In the neutral medium, the FDCA formation occurs through the oxidation of the both hydroxyl and carbonyl groups to yield the DFF and HMFCA, respectively, for the Me NPs. The incorporation of $Pd_{1-x}Ag_x$ NPs into the UiO-66 matrix facilitates the FDCA formation in a neutral medium mainly through the DFF, while the contribution of the parallel route through the HMFCA becomes insignificant.

The effect of modification of UiO-66 with NH_2- and SO_3-groups on the catalytic properties of the Me@UiO-66 composites and the role of the base agent and its nature in the HMF transformations will be discussed.

Acknowledgement. This work was supported by the Russian Science Foundation, project No. 19-73-30026.

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OP-IV-4
Syngas Conversion over Perovskite-Like $La_yCa_{1-y}Co_xTi_{1-x}O_3$/KIT-6 Catalysts

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Conversion of syngas, obtained by biomass gasification, into valuable chemical products is one of the important processes in green chemistry. Thus, higher alcohols and hydrocarbons can be synthesized on cobalt-containing perovskites (ABO_3). In this work, the dependences of the selectivity and activity of a series of $La_yCa_{1-y}Co_xTi_{1-x}O_3$/KIT-6 samples on the specific surface area samples and the extent of substitution of calcium for lanthanum in position **A**, and titanium for cobalt in position **B** are considered.

The samples were synthesized by the citrate method, calcined at 700°C, and washed to remove excess KIT-6 mesoporous silica with a NaOH solution. All synthesized samples had a perovskite-type structure. After hydrogen activation in all the samples Co-nanoparticles are formed on the surface of La-containing oxide. Hydrocarbons are the predominant products of syngas conversion. The alcohol selectivity to higher alcohols was 5-20%. No CO_2 formation was observed, indicating the removal of oxygen from the reaction in the form of water.

Table 1. The results of catalytic tests in the syngas conversion. Test conditions: 2 MPa, 240°C, reaction mixture $H_2/CO/N_2$ = 6/3/1, activation in hydrogen at 500°C. Designation: S_{sa} – surface area of sample (m^2/g), X – conversion of CO (%), ROH – alcohols, RH – hydrocarbons, S – selectivity (%), α – parameter for Anderson-Flory-Schulz distribution, Y – yield (mg/g_{cat}×h).

#	Sample	S_{sa}	GHSV, h^{-1}	X_{CO}	ROH, C_{1-6}			RH, C_{9-16}		
					S	α	Y	S	α	Y
1	$LaCoO_3$	7	830	6.5	-	-	-	-	0.82	-
2	$LaCoO_3$/KIT-6	117	2350	22.4	6	0.41	9	61	0.82	52
3	$La_{0.85}Ca_{0.15}CoO_3$/KIT-6	118	650	20.2	16	0.41	6	58	0.81	19
4	$LaCo_{0.7}Ti_{0.3}O_3$	12	830	1.6	-	-	-	-	-	-
5	$LaCo_{0.7}Ti_{0.3}O_3$/KIT-6	233	590	19.2	22	0.31	7	57	0.82	11
6	$La_{0.7}Ca_{0.3}Co_{0.7}Ti_{0.3}O_3$/KIT-6	175	560	13.5	11	0.32	2	64	0.80	8
7	$LaCo_{0.5}Ti_{0.5}O_3$	20	770	1.4	-	-	-	-	-	-
8	$LaCo_{0.5}Ti_{0.5}O_3$/KIT-6	225	500	16.0	12	0.31	3	57	0.79	9
9	$La_{0.5}Ca_{0.5}Co_{0.5}Ti_{0.5}O_3$/KIT-6	206	530	16.0	7	0.32	2	69	0.79	10

Modification of the samples with calcium (#5/6 and #8/9) reduces the selectivity for higher alcohols in favor of hydrocarbons, which may be due to a decrease in the effect of lanthanum oxide support on active cobalt nanoparticles. In addition, for samples #2/3, the effect of calcium is traced in a significant decrease in catalytic activity, despite the complete reduction of cobalt according to DTA data. The modification of the samples with titanium significantly reduces the activity of the samples. This is due to the preservation of the perovskite structure during sample reduction, which prevents sample amorphization and sintering of cobalt particles. As a result, a decrease in the selectivity for higher alcohols is observed. Bulky samples (# 1, 4, 7) turn out to be inactive in the conversion of synthesis gas due to the low specific surface area. XRD data of samples after catalytic tests indicate the presence of cobalt carbide CoC_x in the samples, which is responsible for the synthesis of higher alcohols on cobalt-containing samples. [1].

The results obtained show that the partial substitution of ions in positions **A** and **B** is an effective method for controlling the catalytic properties of catalysts based on Co-perovskites.

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OP-IV-5

Ethanol to Hydrocarbons Transformation over Modified and Unmodified Zeolite H-ZSM-5

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Increasing growth of ecological problems results in needs to develop new and reliable ecology friendly energy technologies to decrease greenhouse gas formation. Biofuel produced from not food substances can serve as possible alternative to fossil fuels[1]. Second and third generation bioethanol obtained from cellulose containing wastes does not contribute to greenhouse gas growth therefor its application for automobile transport can increase. However direct application of bioethanol as automobile fuel have some technological problems such as low ethanol vapor pressure at low temperatures, possibility of water adsorption from air, high corrosion of aluminum containing part in the presence of ethanol, beside wide availability of bioethanol can results in some social problems[2]. Therefor new technologies for methanol transformation in fuel components, applicable for automobile transport needs to be developed. Ethanol transformation to hydrocarbons (ETG) can be a perspective technology to obtain traditional fuel componentand decrease fossil fuel demand.

Typically, ETG process is provided using alumosilicates including zeolites, zeotypes and hydroxyapatite at temperature 300-400 ^{0}C and ethanol weight hourly space velocity (WHSV) 0.1-10 h^{-1}[3]. H-ZSM-5can be considered asone of promising catalyst for ETG process providing formation mainly of C4-C9 hydrocarbonsincluding paraffins, olefins and aromatic hydrocarbons. Formation of different types of hydrocarbons allows application of this process not only for automobile fuel component production but also for raw materials production of basic chemicals synthesis.

Here a study of H-ZSM-5 commercial samples HKC(China, Si/Al=12.5),CVN (Nigegorodskie sorbenty, Russia, Si/Al=20), CVM (Nigegorodskie sorbenty, Russia, Si/Al=40) and samples modified with sodium hydroxide solution is reported.Samples characteristics are presented in table 1. Initial samples with an average crystal diameter of 70 µm was calcined at 550 ^{0}C in air. Subsequently, the sample was suspended in a sodium hydroxide solution with a concentration of 0.1 Min shaker. Ethanol was introduced in reactor field with zeolite heated up to 350 ^{0}C by pump 0.1 ml/min. Then reaction mixture flows to condenser where gas and liquid phases were separated. Gas samples are taken at a frequency of once per hour by an automatic chromatograph dispenser. Liquid samples are taken in accordance with the experimental procedure, the mass, the proportion of the liquid water fraction and the composition of the hydrocarbon fraction are determined. The analysis of liquid hydrocarbons was provided using a Shimadzu HPMS2010 gas chromatography-mass spectrometer, chromatograph Krystal 2000M in accordance with GOST R 52714-2007.

Initial zeolites characterized by 248-303 m^2/g micropores surface area and 55-79 m^2/g mesopores surface area. Ammonia chemosorption shown presence of two types of Brønsted acid sites weak sitesat 310^{0}C and strong sites at 560^{0}C (Table 1).Treatment of zeolites with alkali solution result in decrease of micropores surface area and some increase of mesopores surface area that can favor mass transfer of ethanol and reaction products and therefor results in some increase of reaction rate. Beside decrease of Brønsted acid sites quantity take place that can lead to some decrease of reaction rate.

Table 1. Physicochemical characteristics of studied catalysts

Sample	Surface area, m^2/g		Ammonia chemosorption, mmol/g		Initial activity, $\frac{kg(EtOH)}{kg(Cat)\ h}$	Selectivity to liquid hydrocarbons, %
	Micropores	Mesopores	t=310^{o}C	t=560^{o}C		
ZSM-5-CVN	248	71	0.47	0.34	0.24	42
ZSM-5-CVN-0.1NaOH	234	79	0.42	0.29	0.31	36
ZSM-5-CVM	288	48	0.72	0.52	0.42	54
ZSM-5-CVM-0.1NaOH	254	52	0.65	0.48	0.48	50
ZSM-5-HKC	303	55	0.84	0.40	0.45	48
ZSM-5-HKC-0.1NaOH	261	67	0.72	0.34	0.52	42

Initial activity of unmodified zeolites follows with Brønsted acid sites concentration on zeolite surface, while after alkali modification initial activity increases for 10-15%, however process selectivity to liquid hydrocarbons decreases for 5-8%.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 20-08-00191.

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OP-IV-6

Schungite Based Catalysts for the Deoxygenation of Vegetable Oil and Bio-Oil

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The steadily increasing demand for motor fuel, depletion of crude oil sources, a decline in the quality of the produced oil, and the environmental problems associated with the emission of greenhouse gases make the producers replace fossil fuels with alternative environmentally friendly energy resources, e.g. biomass. The existing liquid fuels from biomass (including bio-oil and biodiesel) do not always have good miscibility with the petroleum and require additional modification to meet fuel standards. This modification involves the removal of oxygen and isomerization of the resulting hydrocarbons in the presence of hydrogen (so-called hydrotreatment processes) [1]. Deoxygenation of carboxylic acid and phenols is one of the widely studied reactions in hydrotreatment. The industrial hydrotreatment catalysts (sulfided CoMo and NiMo) are typically used in deoxygenation of oxygen-containing compounds of biomass [2]. The modern tendencies in the deoxygenation focused on the search of novel highly active and sulfur-free catalysts [3]. In the last decades, different Ni-, Pt- and Pd-containing catalysts were developed for deoxygenation [3-6].

However, the catalysts used often have high selectivity to the formation of alkenes. This leads to the need in the additional hydrogenation step. Moreover, the developed catalysts tend to the metal leaching and surface deactivation. These disadvantages strongly depend on the properties of the catalyst support. From this point of view, the search of the novel supports is one of the urgent tasks.

In this work we proposed the use of schungite as a catalyst carrier for the deoxygenation of oxygen-containing compounds of vegetable oils and bio-oil. Schungite is a mineral consisted of 90-95% of carbon, 2.5% of oxygen, 1% of hydrogen, about 1% of nitrogen and 0.5% of sulphur. The schungite structure is presented by the carbonaceous matrix with the implemented highly dispersed silicates. Moreover, this is a carbon-reach material that has high sorption ability and high reductive properties [7, 8]. Thus, it can be sufficiently used as a catalyst support for different reactions.

The catalysts were prepared by both impregnation method and hydrothermal deposition [9]. Co and Ni nitrates were used as metal precursors. The synthesized catalysts were studied by the low-temperature nitrogen physisorption, XPS, TEM, and TPR. Testing of the prepared catalysts was performed in the deoxygenation of model compounds (stearic acid, and guaiacol) in the medium of supercritical hexane. The catalysts showed high effectiveness in the oxygen removal, providing over 90% of the yield of hydrocarbons.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 19-79-10061. Catalyst characterization was supported by the Russian Foundation for Basic Researches, grant 19-08-00318.

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OP-IV-7

Plant of Fast Pyrolysis of Lignocellulosic Waste

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In the Russian Federation, as a result of the activities of industrial enterprises, enterprises of the timber industry complex, the communal and agricultural sectors, about a billion tons of lignocellulosic biomass wastes are generated annually, and a small part of them is used useful[1]. A significant problem in the technological use of these wastes is their dispersal, hygroscopicity, combined with biological activity. Therefore, an important aspect in organizing the local conversion of lignocellulosic biomass is its primary collection and transportation to processing sites. One of the cost-effective methods of processing (liquefaction) of lignocellulosic raw materials today is the technology of fast pyrolysis [2,3]. Fast pyrolysis technology is an effective method of biomass liquefaction, using which the negative properties of biomass (low density, biodegradability, unstable composition, variability of properties, low-tech use in the existing infrastructure, etc.) are leveled, and it is converted from a polymer form to a low molecular weight form [4]. The liquid products obtained during fast pyrolysis (pyrolysis liquid, PL) have a 12 times higher energy density compared to the original biomass and can be more efficiently transported for further concentration and processing, including using the equipment of the existing infrastructure of energy enterprises, chemical technology and oil refining [5].

We have developed an industrial technology for fast pyrolysis of lignocellulosic waste. This technology was implemented in the form of an industrial FPP02 plant with a capacity of 500 kg/h, the appearance of which is shown in Fig. 1.

In the course of work on this plant, tests were carried out on various types of raw materials: wood waste of hard, soft and mixed species, straw, elevator waste, chicken litter, peat, sewage sludge from housing and communal services and industrial enterprises, waste wooden sleepers, plastics, etc. Data on the material balance of the process for various types of raw materials are presented in Table 1.

Figure: 1. External view of the FPP02 plant

Table 1. Material balance of the process on various types of raw materials

Feedstock	Liquid, %	Solid, %	Gas, %
Brown coal	18	64	18
Peat	40	43	17
Wood	65	15	20
Straw	56	19	25
Chicken litter	57	20	23
Wood-litter mass	47	32	21
Elevator waste	52	23	25
Sewage sludge	39	40	21
Plastics	75	2	23

The obtained results have confirmed the stable operation of the plant using various types of raw materials. This plant can be the initial stage in the processing of renewable biological resources, including waste, into fuel and chemical products.

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OP-IV-8

Selective Hydrogenation of Furfural: Catalytic Performance by Pd-Cu Alloy Nanoparticles in Porous Polymer

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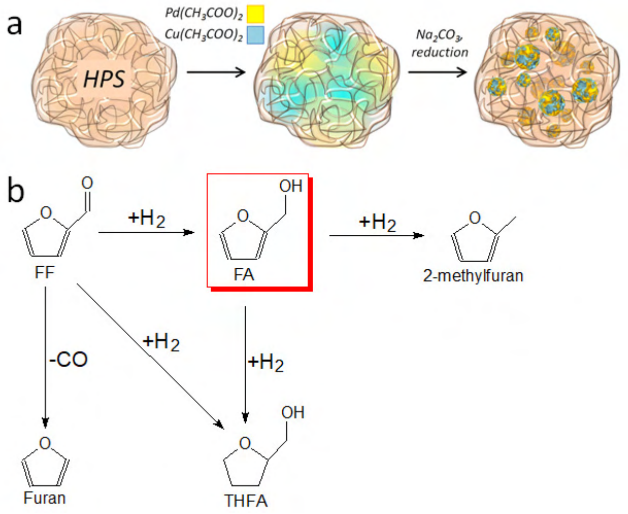
In recent years, a great deal of attention has been paid to the development of environmentally friendly processes using biomass ingredients as precursors for syntheses of value-added chemicals. Furfural (FF) is a high-output chemical obtained by dehydration of xylose (a byproduct of farming and wood processing) [1-3] and utilized for hydrogenation to furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), cyclopentanone, etc. [4]. FA is generally used in a paint production, as solvent and precursor in the production of glass fiber and polymer concrete. Heterogeneous catalysts are commonly employed in the FF hydrogenation due to their high stability, facile separation from the reaction medium, and recyclability [5-6].

The bimetallic catalyst synthesis was carried out by impregnation of hypercrosslinked polystyrene (HPS) with the solution containing both palladium and copper acetates, followed by the Na_2CO_3 treatment to precipitate metal nanoparticles (NPs) in the HPS pores (Scheme 1a). Earlier it was demonstrated that precipitation prevents metal species from falling out of the HPS pores during further treatment [7].



Scheme 1. *Schematic representation of the formation of Pd-Cu NPs in the HPS pores (a) and FF hydrogenation (b). The red rectangle in (b) shows the target product, FA.*

We developed a novel catalyst for the selective FF hydrogenation (Scheme 1b) based on Pd-Cu alloy NPs and the commercially available micro/mesoporous HPS support. The advantages of this inexpensive polymer support such as high porosity and mechanical robustness, were fully realized by forming well-defined 6-7 nm NPs in the pore junctions, providing a sufficient pore system (~60%

by volume) for transport of reacting and target molecules. XRD confirmed the formation of alloy Pd-Cu NPs, while XPS showed the enrichment of the NP surface with Cu atoms as well as the presence of both zerovalent and cationic Pd and Cu species, i.e., NP heterogeneity. Such a structure of Pd-Cu alloy NPs allowed for nearly 100% conversion and excellent selectivity to FA (95.2%) along with a significant activity of the catalyst (TOF_S= 1209 h^{-1}). This exceptional performance was attributed to the prevention of the furan ring adsorption on Pd due to neighboring Cu species and facilitated FA desorption, both leading to higher selectivity. Controlled hydrogen and FF adsorption due to mixed valence states of Pd and Cu species lead to higher conversion. These factors as well as remarkable catalyst reusability in ten consecutive reactions makes this catalyst promising for practical applications.

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OP-IV-9

Acetalization of Furfural Catalyzed by Zeolites Catalysts to Obtain Biofuels Additives

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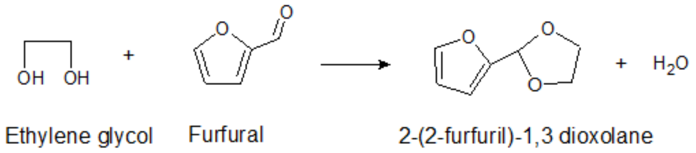
During the last decade, renewable fuels have become an important focus of research in the energy field, likewise the building block derived from biomass waste search for sustainable alternative due to the increasing world energy demand. In this sense, the catalytic valorization of glycerol, generated from biodiesel production, with carbonyl compounds, as molecules derived from lignocellulosic biomass waste, by the acetalization reaction has application as bio-additives for oil and biofuels industry [1,2]. Bio-additives improves the cold and antioxidant properties of biodiesel and diesel therefore enhancing engine performance, offering a sustainable alternative.

In this work, the acetalization reaction of ethylene glycol with furfural as molecules derived from biomass to obtain 2,2-furfuyl-1,3-dioxolane was investigated, in order to establish the reaction conditions with a simpler polyol molecule than glycerol (sch. 1).



Scheme. 1. Acetalization reaction of furfural with ethylene glycol.

For this purpose, two commercial zeolites (ZSM-5 and Mordenite) were modified in the laboratory with ammonium nitrate to convert in the acid form and then were calcinated at 500°C during 2 h. Both acid zeolites were characterized by several techniques (XRD, FTIR spectroscopy and potentiometric titration).

The acetalization reaction was carry out in a round-bottom flask with a reflux condenser and acetonitrile was used as a solvent reaction. For a typical reaction, the mixture was composed of ethylene glycol (EtGly) and furfural (FUR) were added in 1:1 molar ratio and heated to 100°C with magnetic stirring. Then, 10 wt.% of catalyst was loaded, and the reaction times were 1 and 2 hours.

At the end of each reaction, the liquid products were separated by filtration. The liquid samples were analyzed by gas chromatography with a flame ionization detector (FID) and a gas chromatograph/mass spectrometer to calculate the yields and selectivities.

The characterization results shown by XRD that both zeolites conserve the crystalline structures and with infrared spectroscopy technique was observed the typical band of alumina silicate in these materials. In the figure 1.a) shows the curves of the potentiometric titration by n-butylamine for both materials. The zeolite H-ZSM-5 have more total acidity than the H-Mor and contain a higher percentage of strong acid sites as observed in the bars chart (Fig. 1b).

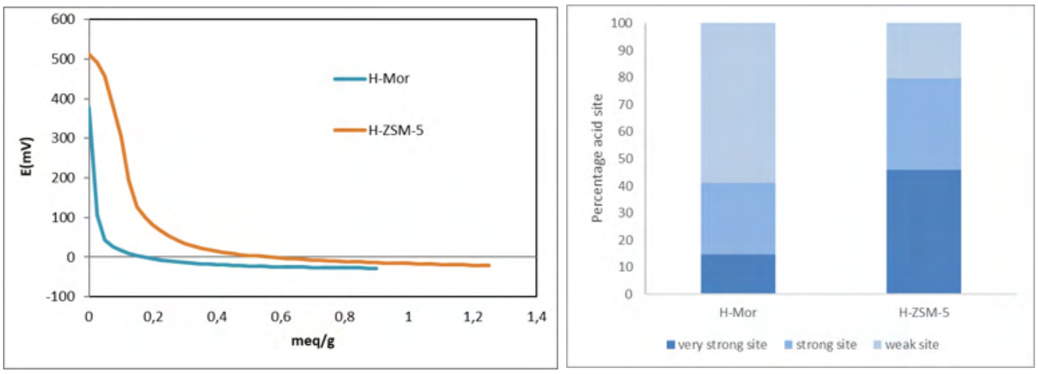


Fig. 1. a) Potentiometric titration n-butylamine of H-ZSM-5 and H-Mor, b) Acid site distribution

Figure 2.a) presents the catalytic results for both zeolites. The H-ZSM-5 obtained nearly 85% of dioxolane in hour, whereas the H-Mor exhibited less yield almost 43%. The decrease in the conversion after 2 hours is likely due to the presence of water for the H-ZSM-5 catalyst and the increase of yield to H-Mor due to that this material present low acidity and required more time in contact with the substrate. Besides, the yield increased with catalyst loading as expected (Fig. 2 b).

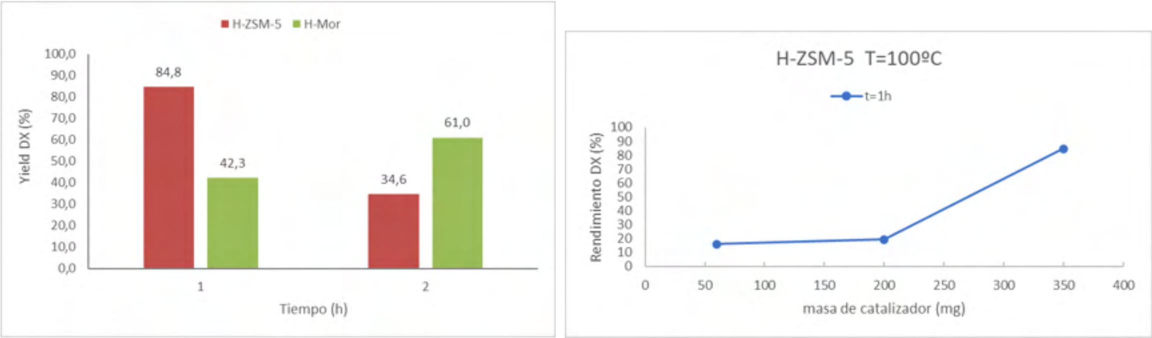


Fig. 2. Catalytic results: a) Yield DX, b) effect of catalyst load for H-ZSM-5.

In conclusion, the most promising result was obtained for H-ZSM-5 catalyst, achieving an 80% yield to dioxolane.

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OP-V-1

Influence of the Lewis Acidity of Functionalized Aryldifluoroboranes on Their Catalytic Activity

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Despite a vast number of recent research in catalysis for fine organic synthesis and diverse results obtained in this area, development of homogeneous catalysts with controlled Lewis acidity remains relevant. This necessity is due to the possibility of carrying out selective organic processes in fine organic chemistry field. Aryldifluoroboranes are one of the promising classes of homogeneous catalysts satisfying requirements for "fine" acidity tuning (Fig. 1_). Thus, an aromatic ring modification was shown to affect the Lewis acidity of compounds involved.[1]. Nevertheless, most of the works devoted to boron-containing Lewis acids are limited to comparison of their acidity by classical methods without their practical application. Consequently, one of the urgent problems in this area is the prediction of related compounds catalytic activity based on a relative acidity scale.

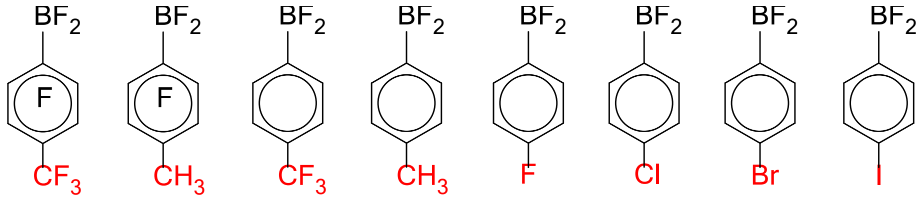

Fig. 1. Examples of some aryldifluoroboranes used in this work.

Previously, the authors demonstrated aryldifluoroboranes to be soft Lewis acids capable to selectively catalyze an alkylation of activated arenes [2]. Bentley et al suggested a mechanism including both Lewis and Brønsted acids in alkylation processes catalyzed by boron-based Lewis acids [3] . This assumption requires an additional proof since anisole and phenol were found to demonstrate opposite results in arildifluoroborane catalyzed alkylation processes (Fig. 2).

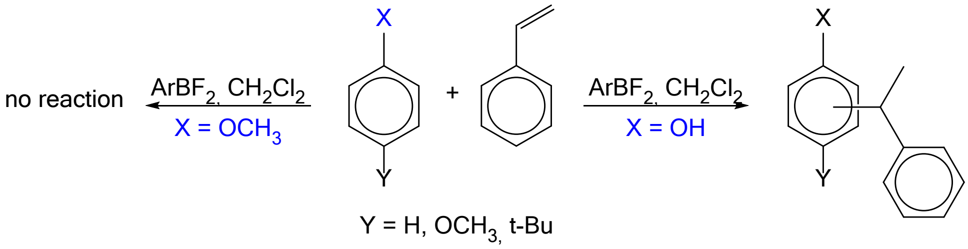

Fig. 2. Aryldifluoroborane-catalyzed alkylation processes.

Thus, the aim of the present work is to establish the activation mechanism for the soft Lewis acids-catalyzed alkylation of arenes using aryldifluoroboranes as an example, as well as to construct correlations between the acidity of aridifluoroboranes with their catalytic activity in model alkylation processes.

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OP-V-1

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OP-V-2

New Chromium-Carbon Catalytic Systems for Oxidative Propane Dehydrogenation in Presence of CO_2

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Nanostructured carbon materials are widely used in different areas of the chemical industry. Their high demand is explained by variety of demonstrated chemical and physical properties, as well as their high potential in terms of surface modification [1]. This is because carbon nanomaterials (CNMs) are actively studied in catalytic processes, one of which is the production of propylene. Over the past decade, the demand for propylene in the world has shown steady growth due to the increasing interest in polypropylene products. The industrial way for propylene producing is fluid catalytic or steam cracking. The disadvantages of this approach lie in the need to create high temperatures and, therefore, deactivation and coking of the catalyst. Oxidative propane dehydrogenation (ODP) in the presence of CO_2 is an alternative method for producing propylene. Its advantages are both decrease in the reaction temperature and prevention of catalyst deactivation because of coking [2]. Various transition metal oxides, such as CrO_x, VO_x, FeO_x, MoO_x, GaO_x, and InO_x, supported on mesoporous/microporous materials [3] are usually used as ODP catalysts.

This work is devoted to the study of chromium catalysts for the ODP process supported on carbon nanotubes (CNTs) and graphene nanoflakes (GNFs). The selected CNMs are considered as promising supports in heterogeneous catalysis, since they possess chemical inertness, high thermal conductivity, and variable texture. To increase the activity and introduce additional stabilization of metal particles on the surface, CNTs and GNFs are functionalized by oxidation or doping with nitrogen atoms. The incorporation of heteroatoms into the CNM structure changes its electronic properties and creates additional defects [4].

Undoped and doped CNTs and GNFs were synthesized by catalytic decomposition or template pyrolysis of hexane and acetonitrile, respectively. Oxidation of CNT and GNF was carried out by boiling in a concentrated solution of nitric acid. The resulting supports were examined by SEM, TEM, and XPS. The synthesis of catalysts was realized by impregnating them with a solution of chromium nitrate and subsequent annealing at 300°C. Catalysis was tested at atmospheric pressure and a temperature range of 500-750 °C in a flow-through catalytic set equipped with a steel reactor with an inner diameter of 4 mm.

It was found that the conversion of all catalytic systems increases with temperature and the maximum values are observed in the case of samples deposited on oxidized CNTs and undoped GNFs. Methane, propylene, ethane and ethylene are detected among the hydrocarbon fraction formed in the reaction. The formation of propylene at 600°C is observed only for systems based on GNFs and oxidized CNTs. With a further increase in temperature to 700°C, all systems have a selectivity of 40-50% to this product. The highest propylene yield is achieved on pristine GNF support. The highest selectivity for ethylene was demonstrated by systems based on N-CNM, which is apparently associated with the predominance of the thermal cracking process in them. Figure 1 shows a high-resolution micrograph of a catalyst based on N-CNTs, which demonstrates that metal particles are located not only on the external surface, but also inside the tube channels, which can affect the diffusion of reagents to active sites.

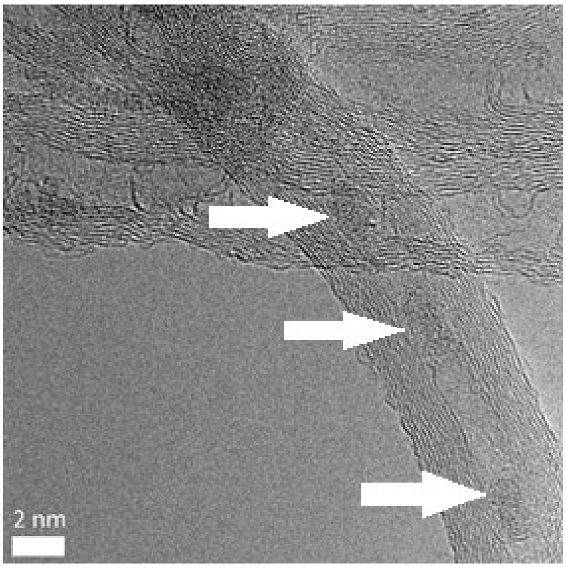

Fig. 1. HR-TEM micrograph Cr/N-CNT. Arrows point on the metal-based nanoparticles

It was shown that the most promising supports for ODP chromium catalysts in the presence of CO_2 to propylene and ethylene are GNFs, oxidized CNTs and nitrogen-doped CNTs; at the same time, the effect of the incorporation of nitrogen into the support structure requires a more detailed study in the future.

Acknowledgement. The reported study was funded by RFBR according to the research project
№ 20-33-90043.

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OP-V-3

Nickel Phosphide Catalysts for Diesel Fuel Hydroisomerization Processes

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Hydroisomerization of n-alkanes is an important process for obtaining fuels with improved low-temperature properties. It is generally carried out on bifunctional catalysts composed of metal sites for dehydrogenation/hydrogenation function and acidic support, which performs branching and C-C bond cleavage. The metal sites are usually provided by noble metals (platinum, palladium), but their cost and high sensitivity to sulfur poisoning restrict their industrial use. The low-cost nickel-based catalysts could be considered as promising candidates to replace noble metals if their hydrogenolysis activity was restrained. It was described in the literature that phosphorus modification of nickel to obtain Ni phosphides led to metal-like materials [1, 2] with excellent performance in HDS, HDN and HDO reactions and much lower activity for the C-C bond hydrogenolysis [3-5]. Based on the above considerations, we investigated the possibility of using Ni_xP_y/ZSM-23 materials as catalysts for diesel fuel isodewaxing.

In the course of this work, the influence of Ni phosphide source concentration and its reduction temperature on the isomerization performance of Ni_2P/ZSM-23/Al_2O_3 samples (zeolite/Al_2O_3 = 60/40) was studied. The synthesized samples were analyzed by temperature-programmed reduction, X-ray diffraction, H_2 chemisorption, high resolution transmission electron microscopy and IR spectroscopy of adsorbed pyridine. The catalytic properties of in-situ reduced samples were tested in the hydroisomerization of n-decane taken as a model compound.

Nickel hydroxide and an aqueous solution of hypophosphorous acid (H_3PO_2) were used to prepare the precursor of the active component with a P/Ni ratio of 2. Different concentrations of nickel hypophosphite were supported by incipient wetness impregnation to obtain samples with Ni_2P content from 2.5 to 15% after H_2 reduction. After impregnation, all samples were dried at 70 ° C for 24 hours.

According to TPR data, the formation of the phosphide phase in x-Ni_2P/ZSM-23/Al_2O_3 samples occurs in the temperature range of 500-630°C. The comparison of n-C_{10} conversion and iso-selectivity of catalysts reduced at different temperatures allows us to conclude that the hydro/dehydrogenating properties of the supported Ni phosphide phase do not change significantly in the range of 550-650°C. This conclusion is in accordance with the results of chemisorption experiments, which evidence no obvious change in the dispersion of Ni_2P particles with an increase in the reduction temperature up to 700°C, and a sintering of the active component at higher temperatures. Ni_2P/ZSM-23/Al_2O_3 sample reduced at 500°C exhibited an unstable behavior during catalytic run, namely a gradual decrease in n-decane conversion as well as in isomers yield with TOS.

The catalytic performance of the samples with different concentrations of nickel phosphide is presented in Fig. 1. These data reveal the drop in activity with increase in the content of supported phase that correlates well with the decrease in total amount of chemisorbed hydrogen and suggests the segregation of Ni2P particles. It should be noted that all catalysts, regardless of the phosphide phase concentration, exhibit maximum isomer yield in the range of 62-67%, which is comparable to or even slightly higher than that of the reference sample (Pt-based catalyst).

The results of the present study demonstrate a promising hydroisomerization performance of Ni_2P/ZSM-23-based materials and provide a basis for the use of nickel phosphide phase as a hydro-/dehydrogenation component of bifunctional isodewaxing catalysts.

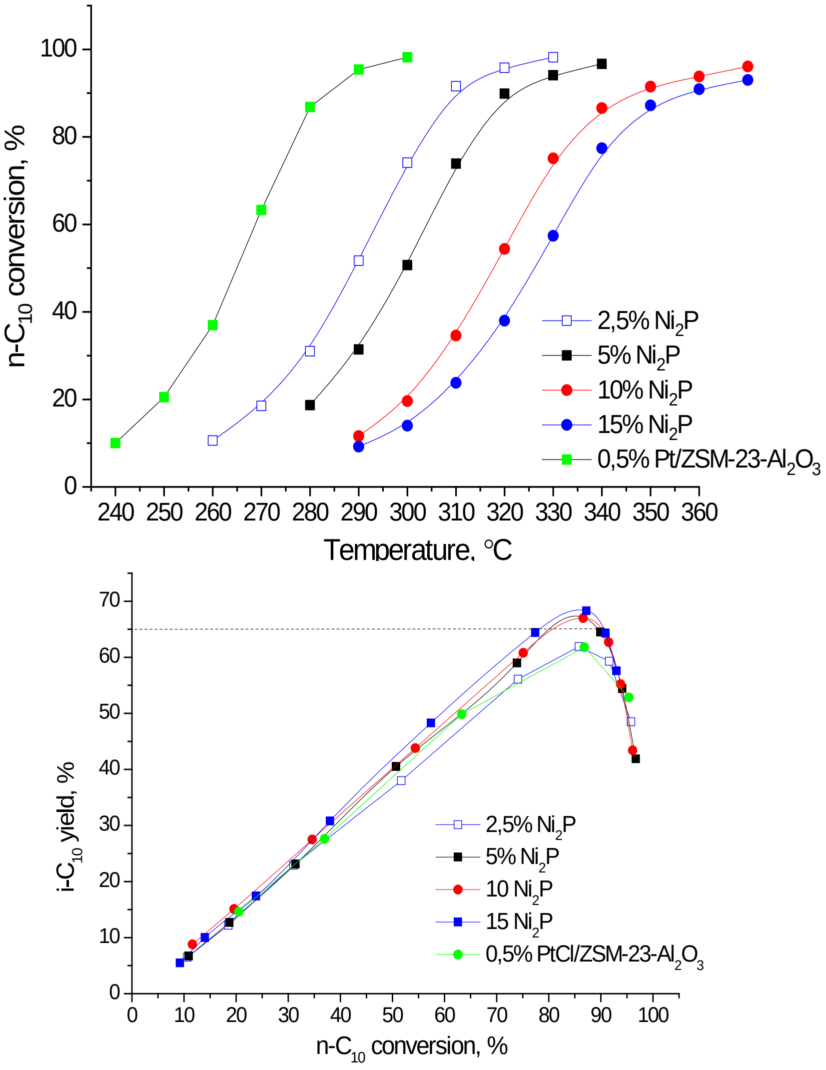

Fig. 1. Activity and isomers yields obtained over $Ni_2P/ZSM\text{-}23/Al_2O_3$ samples in n-decane conversion

Acknowledgement. The work was carried out with financial support from AO Gazpromneft-ONPZ.

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OP-V-4

Acid Sites Formation on P Doped ZSM-5 Zeolite Catalysts for Catalytic Cracking

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The acid ZSM-5 zeolite is the main component of ZSM-5 catalytic additives [1]. The last are widely used in Fluidized Catalytic Cracking units in refineries for processing heavy oil fractions in order to boost LPG olefins production as well as the quality of FCC gasoline [2]. The ZSM-5 zeolites are getting deactivated by steam presence like all the acidic zeolites [3-5]. In order to mitigate this phenomenon, Phosphorus (P) is introduced in ZSM-5 [6]. In this way, the ZSM-5 lifetime is prolonged significantly because Phosphorus acts as a stabilizer. The scope of this work was to investigate the effect of Phosphorus on acid sites formation and stabilization using Phosphorus free and Phosphorus doped ZSM-5 zeolites.

In order to simulate the zeolite deactivation on lab scale, we implemented an accelerated steaming/deactivation protocol. We performed steaming deactivation for two fresh samples; a) ZSM-5 zeolite b) P doped ZSM-5 zeolite (P/ZSM-5). The steaming procedure took place in a fixed bed reactor with 90% steam in He carrier gas for 20 hours at 788°C. After the deactivation half of the deactivated samples were studied immediately, and the other half was humidified by exposure to steam at 200°C for 5h. Therefore, four samples were prepared for the specific study.

All the samples were characterized by BET, XRD, XPS and pyridine adsorption/desorption FTIR techniques. Furthermore, the zeolites were subjected to catalytic testing in a short contact time MAT unit using as feed n-heptane (n-C7) [7].

The textural results showed that the steaming deactivation reduces the micropore area which is attributed to zeolite framework partial destruction forming defects. These defects are in mesopore range and consequently the mesoporosity of steamed zeolites is higher than the corresponding of parent samples. The steaming deactivation and the formation of defects in zeolite material did not cause significant changes in crystallinity. Despite the similarities for both ZSM-5 and P/ZSM-5 regarding the changes in textural properties and crystallinity, the acidities do not follow the same path. The acidity of fresh ZSM-5 was higher than the corresponding of P/ZSM-5. The P/ZSM-5 sample retained its acidity in much higher extent than the P free ZSM-5 sample. Furthermore, the exposure to humidity showed that the acidity of the P free steam deactivated sample was not altered, while there was a significant increase of Bronsted acid sites for P/ZSM-5. The FTIR spectrum revealed that OH groups of acidic character were formed on humidified P/ZSM-5 sample after the reaction with steam. Moreover, these OH groups are stable at 450°C (FTIR pretreatment temperature) showing that there is a reaction between water molecules and P/ZSM-5 and not a simple physisorption. The fact that this phenomenon takes place only on P/ZSM-5 zeolite suggests that Phosphorus plays a crucial role in the formation of new OH groups. The XPS analysis showed that the formation of these OH groups takes place on Phosphorus species rather than anywhere else.

The catalytic cracking of n-C7 showed that there are activity changes, which are in correlation to the acidity of the ZSM-5 samples. This fact verifies that the new OH groups are catalytically active and resistant to dehydroxylation at temperatures as high as 560°C. Despite the differences in activity/acidity, the selectivities towards LPG olefins did not changed.

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OP-V-5

The Use of Oxidoreductase Class Enzymes in the Synthesis of Vitamins

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In recent years, enzymes are widely used in pharmaceutical and food chemistry, wastewater treatment, obtaining highly effective biosensors, cosmetology, etc. [1-3]. The presence of enzymes makes it possible to work in environmentally friendly conditions without the use of aggressive chemicals at low temperatures. The immobilization of enzymes on various carriers ensures their stability and the possibility of their reuse. One of the promising directions in this area is the immobilization of horseradish root peroxidase (HRP) on magnetic nanoparticles. In this work, we studied the oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethylhydroquinone (an intermediate of vitamin E, TMHQ) using hydrogen peroxide.The enzyme on magnetic nanoparticles was immobilized. The effects of initial substrate concentration, temperature, and pH were studied.

Magnetic nanoparticles were obtained by the known polyol method [4]. $FeCl_3 \cdot 6H_2O$ (3mmol), succinic acid (1 mmol) and urea (30 mmol) were successively dissolved in 30 ml of ethylene glycol. The resulting mixture was kept at 200 ° C for 4 hours. Iron oxide nanoparticles were washed with ethanol and modified with 3-aminopropyltriethoxysilane (APTS) to provide reactive amino groups to the support surface. The separation of magnetic nanoparticles was carried out using a neodymium magnet. Then, HRP was immobilized onto the modified carrier. The oxidation of TMP was carried out in a glass reactor having a heating jacket. Analysis of the reaction mixture was carried out using high performance liquid chromatography.

The kinetic curves of the dependence of the product yield on the initial substrate concentration are shown in Fig. 1. The optimal concentration of TMP was 1.5 mmol / L both when using native HRP and HRP immobilized on Fe_3O_4, since at this concentration the maximum yield of the product is achieved. This may be due to the fact that the enzymatic reaction can be inhibited by a high concentration of the substrate.

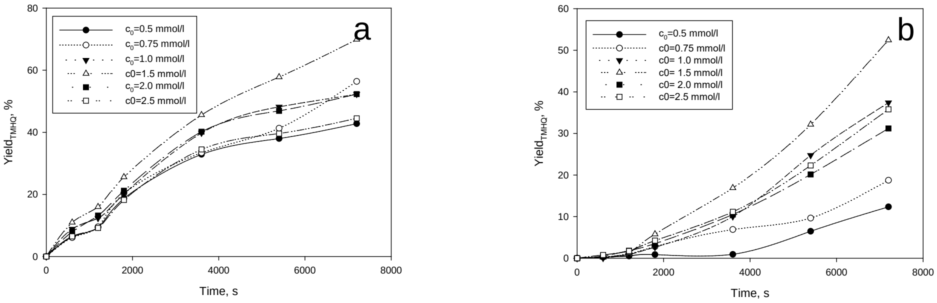

Fig. 1. Kinetic curves of the dependence of TMHC yield
a) native HRP; b) Fe_3O_4/APTS/HRP

To determine the optimum temperature for the oxidation of TMP in the presence of a synthesized catalyst, an experiment was conducted at temperatures of 30 ° C, 40 ° C, 45 ° C, 50 ° C, 55 ° C. The optimum temperature of the process of oxidation of TMP in the presence of immobilized

HRP was chosen at 40 ° C, because when conducting an experiment above this temperature value, a slight deactivation of the enzyme occurred. At temperatures above 40 ˚C, nanoparticles have a significant effect on the oxidation of TMP.

To determine the optimal pH, the experiments were carried out in the pH range from 6.0 to 7.4. The optimal pH for the oxidation of TMP in the presence of a HRP-based biocatalyst and native HRP is 6.5. This suggests that the immobilization of Fe_3O_4 onto magnetic nanoparticles did not cause a pH optimum shift, in comparison with the native HRP.

HRP immobilized on magnetic particles showed good results in the synthesis of TMHQ. In this work, the conditions for the oxidation of TMP in the presence of a synthesized biocatalyst were optimized, which is characterized by the ease of separating it from the reaction mixture with an external magnet.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 19-79-00134.

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OP-V-6
Vanadium-Loaded Faujasites as Catalysts for the Oxidative Dehydrogenation of Propane

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In recent years, the scientific community aims to exploit to the maximum compounds readily available or which are waste from existing industrial processes for energy and chemical production. One of the main objects of interest is the production of light alkanes, as they are in high demand by chemical industry. Production of light alkenes via oxidative dehydrogenation (ODH) of alkanes is becoming an alternative to olefin extraction by conventional methods. Vanadium based systems are the important class of ODH catalysts, but their performance depends strongly on vanadium dispersion. There is still a debate which types of vanadium canters are active in ODH: isolated vanadium canters in tetrahedral or octahedral coordination or polymeric V-O-V chains [1]. Vanadium catalysts were obtained by classical impregnation using FAU zeolite with Si:Al ratio of 31 as a support and desilicated FAU zeolie (FAU_{des}) with Si:Al ratio of 18. The preparation was conducted at pH = 2.5. These allowed for different catalysts with varying amounts and type of vanadium phase depending on the synthesis conditions. The nature of the introduced vanadium species was probed by ^{51}V MAS NMR, XAS and FT-IR spectroscopy. The catalysts are submitted to catalytic tests in ODH of 7.1 %vol. propane in air at temperature 420 – 500°C in gas-flow fixed-bed reactor coupled to GC. The results of the catalytic tests show that tetrahedral vanadium sites seem to be mainly responsible for selective ODH reaction, while octahedral vanadium sites are mainly responsible for total combustion.

Acknowledgement. This work was supported by the National Science Centre, Poland within project no 2016/23/B/ST4/02854.

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OP-V-7

Catalytic Methanol Synthesis from Syngas of Matrix Methane Conversion

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As known, methanol production contains three main steps: preparation of syngas, methanol synthesis and downstream separation [1]. The process of its obtaining seems to be investigated enough until source gas has a proper composition. It usually depends on the production method. Methane matrix conversion process based on partial oxidation mechanism is another technology we are developing. It allows us to burn the lean methane/oxygen mixtures to obtain synthesis gas with a high content of CO and H2 (excess oxidizer ratio $\alpha = 0,35 - 0,40$). In practice, the product gas mixture contains (% vol.) 55% of H2, 30% of CO, 4,3% of CO2 and 8,7% of CH4. This way of producing syngas shows advantages in decreasing capital costs with the same productivity. For this reason finding an appropriate catalyst is necessary for comprehending a process of methanol production under such conditions. Using a catalyst of low temperature CO conversion with different ratios of Cu/Zn active sites is a good opportunity to carry out the process under softer conditions.

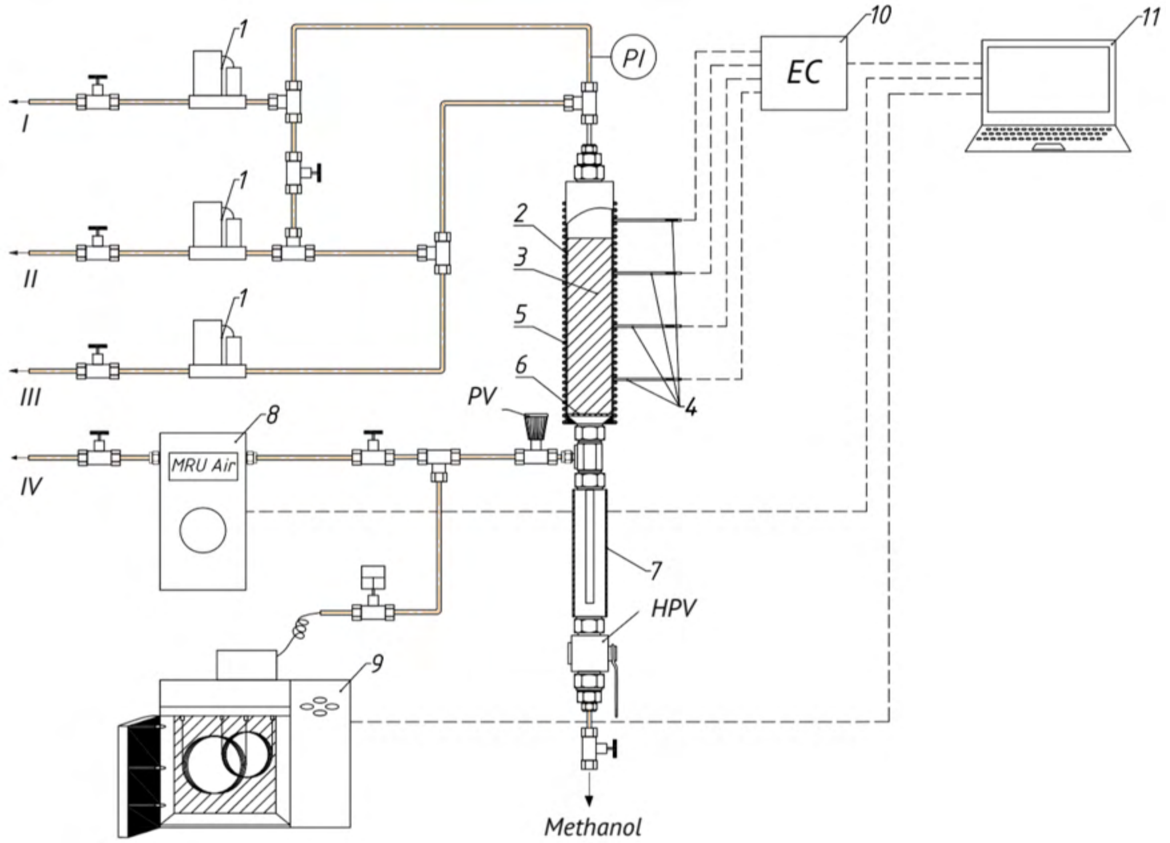

Fig. 1. Experimental stand of Methanol production

Streams: I - to syngas balloon, II - to hydrogen balloon, III - to nitrogen balloon, IV - abgas

Positions: 1 - gas flow meter, 2 - methanol synthesis unit, 3 - catalyst, 4 - thermocouple unit, 5 - thermal heat, 6 - catalytic mesh, 7 - pressure separator, 8 - gas detection analyzer, 9 - gas-liquid chromatography recorder, 10 - electronic inverter, 11 - PC

In addition, 2-3% of C2H2 usually known as a catalytic poison is endemic for matrix conversion syngas due to low temperature pyrolysis of methane.

Mentioned species of synthesis-gas display noninvestigated area that looks interesting to be explored. For these reasons an experimental stand has been designed which is shown in fig. 1. Experiments carried out under 40 atm pressure with stoichiometric number S = 2,8 of ongoing gas mixture. External gas mixture was diluted by nitrogen in amount of 65%. Conversion degree of carbon monoxide was about 20% during the whole experiment session. Liquid phase of the process contains from 2,5% of H2O and 97% CH3OH.

Acknowledgement. Mathematical and kinetic modeling were performed at IPCP RAS with financial support from Russian Science Foundation (project no. 19-73-00291).

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OP-V-8

Catalytic Performance of Glucose Oxidase Immobilized on Magnetic Zirconia

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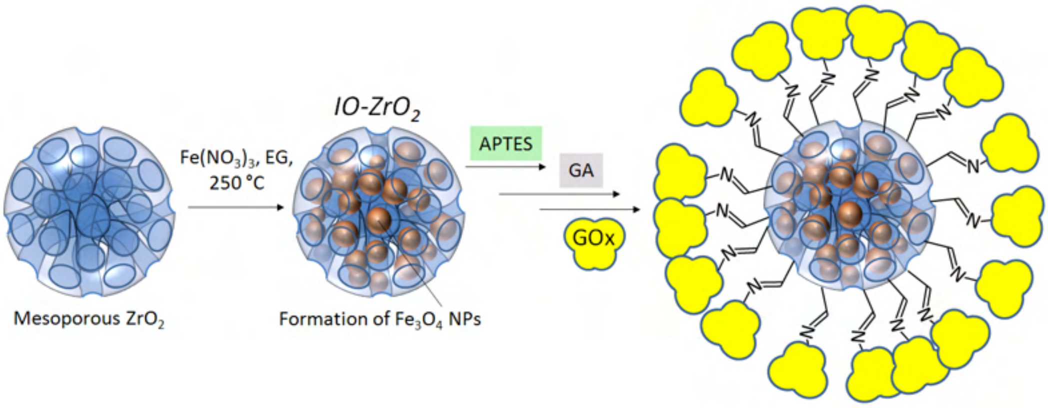
Biocatalysts based on immobilized enzymes received considerable attention, especially in the lastten years, due to higher stability of immobilized enzymes vs native enzymesat various pH and temperatures [1-5]. The major challenges in biocatalysis are preservation of native enzyme activity,high loading of enzymes on a support, and facilitated separation of catalysts to name a few [6]. It is reported that the support structure and morphology can strongly influence the enzyme properties.

The structures and properties of biocatalysts based on glucose oxidase (GOx) macromolecules immobilized on the mesoporous zirconia surface with or without magnetic iron oxide nanoparticles (IONPs) in zirconia pores were reported. Properties of these biocatalysts were studied in oxidation of D-glucose to D-gluconic acid at a wide range of pH and temperatures. We demonstrate that the calcination temperature (300 °C, 400 °C, or 600 °C) of zirconia determines its structure, with crystalline materials obtained at 400 °C and 600 °C. This, in turn, influences the catalytic behavior of immobilized GOx, which was tentatively assigned to the preservation of GOx conformation on the crystalline support surface. IONPs significantly enhance the biocatalyst activity due to synergy with the enzyme. At the same time, neither support porosity nor acidity/basicity shows correlations with the properties of this biocatalyst. The highest relative activity of 98% (of native GOx) at a pH 6-7 and temperature of 40-45 °C was achieved for the biocatalyst based on ZrO_2 calcined at 600 °C and containing IONPs. This process is green as it is characterized by a high atom economy due to the formation of a single product with high selectivity and conversion and minimization of waste due to a magnetic separation of the catalyst from an aqueous solution. These and an exceptional stability of this catalyst in ten consecutive reactions (7% relative activity loss) make it favorable for practical applications.

Immobilization of GOx macromolecules on IO-ZrO_2 was performed according to the protocol presented in Scheme 1. First, the support was modified with amino groups using (3-aminopropyl)triethoxysilane followed by the reaction with the glutaraldehyde (GA) linker. Next, aldehyde groups of GA was reacted with GOx amino groups.



Scheme 1. *Schematic representation of GOx immobilization on the magnetic support.*

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OP-V-9

Partial Oxidation of Ethane to Ethylene and Acetic Acid over MoVTeNbOx Catalyst

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Ethylene is one of the most important building blocks in the chemical industry. It is the feedstock employed in the production of a vast array of chemicals, including polymers, monomers, functionalized hydrocarbons and many other basic and intermediate products. Traditionally, ethylene is produced along with other light olefins by steam cracking or fluid catalytic cracking of higher hydrocarbons. The oxidative dehydrogenation of ethane makes it possible to carry out the reaction for producing ethylene under milder conditions. MoVTeNb mixed oxide catalysts are of the greatest interest for this process. Oxidative dehydrogenation of ethane on MoVTeNb mixed oxide catalysts allows ethylene and acetic acid to be obtained. The simultaneous production ethylene and acetic acid provides an additional generated value and a direct feed for downstream applications that require both ethylene and acetic acid. The processes requiring both ethylene and acetic acid include the production of vinyl acetate monomer, ethylene vinyl acetate copolymer, polyvinyl alcohol products, polyethylene terephthalate, ethyl acetate and similar derivatives. A special interest in this regard is to find out the dependence of the amount of acetic acid in products on the reaction conditions.

Bulk MoVTeNb mixed oxide catalysts were obtained by slurry method [1]. The gel with a composition $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$ was dried using a hot surface and heated firstly in air at 310 °C and secondly in Ar flow at 560 °C for 2 hours. The catalysts were characterized by low temperature nitrogen adsorption and XRD. The catalytic properties of catalysts were studied in oxidative dehydrogenation of ethane process in a fixed-bed reactor. The effect of temperature, the ratio of the initial reagents and the presence of water vapor in the reaction mixture were studied.

The specific surface area determined by the multipoint BET method is about 5 m^2/g. The XRD method revealed that the samples contain only the orthorhombic M1 phase with the general formula $(TeO)_xM_5O_{14}$ and the pseudo-hexagonal M2 phase with the general formula $(TeO)_xM_3O_9$, where M = Mo, V, Nb. Moreover, the contribution of the M1 phase is more than 93%.

Catalytic experiments have shown that the amount of acetic acid in the products may be increased by an increase of the water vapor content in the reaction mixture with decrease of reaction temperature. However, a change in the ratio of oxygen to ethane does not lead to a change in the amount of acetic acid in the products in a wide range of ratios.

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OP-V-10

Influence of the Si/Al Ratio in Pt-Containing Catalysts Based on Al-MCM-41 and Natural Halloysite Nanotubes on Xylene and Ethylbenzene Isomerization Activity

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The fraction coming from the reforming units is rich in C_8-aromatics (para-, ortho-, meta-xylenes and ethylbenzene). In order to increase the yield of a valuable para-isomer, the C_8 fraction is usually subjected to catalytic hydroisomerization.

Catalysts for this process have been widely studied. However, the task of developing and modifying catalysts for the isomerization of the C_8-fraction in order to achieve a high yield of para-xylene while simultaneously reducing the total xylenes loss, as well as of possibility of processing raw materials with a high content of ethylbenzene, remains urgent.

Within the current work, we have synthesized composite functional materials with a Si/Al ratio of 3, 10 and 40 based on ordered Al-MCM-41 aluminosilicates and natural halloysite nanotubes (HNT). Halloysite belongs to natural minerals of the kaolinite group with the chemical formula $Al_2Si_2O_5(OH)_4 * nH_2O$. In fact, HNTs are formed by rolled kaolinite layers separated by a water monolayer. Due to their origin, HNTs possess a negatively charged external surface consisting of silicon oxide and a positively charged internal surface formed by aluminum oxide. Application of halloysite allows to obtain various structures with enhanced thermal and mechanical stability, which makes them perspective catalysts supports. In this work, the materials obtained based on HNTs and mesoporous aluminosilicate Al-MCM-41 were used for synthesis of Pt-containing catalysts for isomerization of aromatic compounds.

Al-MCM-41+HNT materials were synthesized via hydrothermal template method at 180 °C during 48 h using cetyltrimethylammonium bromide as a structure-directing agent. Tetraethyl orthosilicate and aluminum isopropoxide were applied as silica and alumina sources for Al-MCM-41, respectively.

The obtained Al-MCM-41+HNT materials were mixed with a binder (boemite) in the mass ratio of 60/40 and formed using an extruder. The metal deposition on the formed support was carried out by a wet impregnation method using hexachloroplatinic acid as a source of platinum. (the calculated Pt content was 0.5 wt %). Finally, the samples were calcined to remove water and reduced in the hydrogen flow at 450 °C. The resulting catalysts had the following composition: Pt/Al-MCM-41+HNT(X)/Al_2O_3, where X denotes the Si/al molar ratio.

Elemental composition, structural and acidic properties of the synthesized catalysts were studied by X-ray diffraction, X-ray fluorescent spectroscopy, low-temperature nitrogen adsorption/desorption, transmission electron microscopy, temperature-programmed ammonia desorption, thermal gravimetric analysis and differential scanning calorimetry [1,2].

It was found that the functional material with Si/Al ratio = 10 had a larger specific surface area 1356 m^2/g) than the other materials (792 and 910 m^2/g) with lower synthesized using aluminum isopropoxide (table 1). However, the highest value of acidity was obtained for Al-MCM-41+HNT(3), which is most likely connected with higher concentration of Al in its composition.

Table 1. Parameters of Al-MCM-41+HNT materials and them-based catalysts

Sample		Si/Al mol.	Textural parameters			Acidity, μmol NH_3/g
			S_{BET}, $m^2 \cdot g^{-1}$	D_{pores}, Å	V_{pores}, $cm^3 \cdot g^{-1}$	
Al-MCM-41+HNT(3)	Material	3.1	792	26	0,43	859
	Catalyst		513	33	0,34	1131
Al-MCM-41+HNT(10)	Material	9.8	1356	24	0,67	737
	Catalyst		1270	28	0,43	1006
Al-MCM-41+HNT(40)	Material	38.6	910	27	0,59	739
	Catalyst		796	29	0,51	974

Catalytic experiments with the obtained samples were carried out in a laboratory flow-type unit with a fixed catalyst bed in the temperature range of 320 – 400 °C, LHSV of 1 – 6 h^{-1} under hydrogen pressure of 1 MPa and with the H_2:feedstock volume ratio of 1200. Meta-xylene and ethylbenzene were used as raw materials. Liquid and gaseous reaction products were analyzed by gas-liquid and gas chromatography.

It was proven that the Si/Al ratio in functional materials significantly affects the catalysts' textural and acidic parameters and reaction mechanism. The Al-MCM-41+HNT(3)-based catalyst provided higher substrates conversion, however, dealkylation also took place at higher temperatures giving undesirable toluene and benzene. The Al-MCM-41+HNT(40)-based catalyst decreased the amount of dealkylation products and demonstrated excellent selectivity to PX which is up to 15% higher than the same over the other catalysts.

The optimal temperature range providing high *p*-xylene selectivity and ethylbenzene and *m*-xylene conversion over Pt/Al-MCM-41+HNT(3)/Al_2O_3 was 320-340°C at LHSV = 1h^{-1}. Under these conditions the catalyst's stability was evaluated during 50 hours of of continuous operation and it decreaded only by ~1 %.

Acknowledgement. This work was financially supported by Russian science foundation (project № 19-79-10016).

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OP-V-11

Zn- and Co-Zeolite Imidazolate Frameworks as Effective Catalysts for the Cycloaddition of CO_2 to Propylene Oxide

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Propylene carbonate (PC) is one of the commodity cyclic carbonates, which is widely used as a solvent for Li-ion batteries and as a monomer for polycarbonate synthesis. A common methodology for the preparation of the PC is based on the reaction of phosgene with the 1,2-propanediol. An attractive alternative synthesis involves the reaction of propylene oxide (PO) with CO_2 to yield PC (Fig. 1).

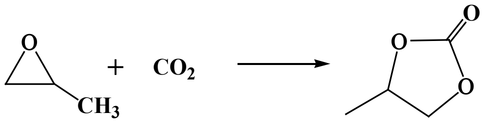

Fig. 1. Synthesis of propylene carbonate from propylene oxide and CO_2

This way possesses the advantages of high atomic economy and the use of inexpensive and relatively non-toxic reagents. Both homogeneous and heterogeneous catalysts were suggested for the epoxide carbonation, including metal-organic frameworks (MOFs) and a typical sub-family of MOFs, zeolitic imidazolate frameworks (ZIFs). Although many ZIFs have been applied in CO_2 conversion, the effects of structure and crystal size of ZIFs remain unclear. We investigated catalytic properties of Zn- and Co-zeolitic imidazolate frameworks based on 2-methylimidazole (ZIF-8/ZIF-67), 2-ethylimidazole (MAF-5 and MAF-6) linkers in cycloaddition between CO_2 and PO.

Effects of chemical composition, structure and crystal size of ZIFs on the reaction rate and yield of PC were investigated by a combination of catalytic and physicochemical methods, including X-ray powder diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption-desorption and Infrared spectroscopy using $CDCl_3$ as probe molecule. The catalytic performance of the ZIFs in the presence of tetrabutylammonium bromide as co-catalyst was investigated at 8-12 atm of CO_2 and 60-120^{o}C under solvent-free conditions. Amount of co-catalyst was demonstrated to be crucial for the formation of PC.

In the presence of all studied ZIFs selectivity towards PC was about 99%. Activity of Co-formed ZIFs was lower in compared with Zn-formed ZIFs (Fig. 2). Conversion of PO decreased after substitution of Zn^{2+} ions by Co^{2+} ions in framework of ZIF-8.

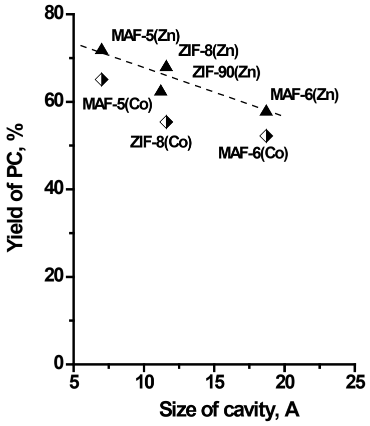

Fig. 2. Effect of cavity size on the yield of propylene carbonate

According to IR spectroscopy using $CDCl_3$ as probe molecule, basicity of Zn-ZIFs decreased in the order: MAF-5 > MAF-6 > ZIF-90 > ZIF-8. However, activity of ZIFs and yield of PC did not correlate with this order. A correlation was established between acid-base characteristics and catalytic activity.

Yield of PC was found to depend on the structural properties of ZIFs. The increasing cavity size of ZIFs led to the decreasing yield of PC (Fig. 2). The correlation between the crystal size of the MAF-6 material and the yield of PC was investigated. Yield of PC decreased with increasing crystallite size. 80.5% maximum yield of PC was observed in the presence of MAF-6 with crystal size in the region of 50-100 nm. This phenomenon was explained by the rising diffusion limitations due to the increasing microporosity of MAF-6. Another explanation of the dependence of yield of PC on the crystal size of the MAF-6 material was suggested to be related to varying localization of active sites.

OP-V-12

Research of the Process of Carbon Erosion of Nickel Alloys in an Ethylene Atmosphere to Produce Carbon Nanofibers

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Nowadays, one of the most important problems in the gas and oil industry is the processing of associated petroleum gas (APG), which combustion is recognized to be the main source of environmental pollution in the area of gas and oil production. On the one hand, the efficiency of the APG processing can be enhanced by its catalytic decomposition to produce hydrogen. Hydrogen is now believed to be the main fuel of the future; thereby, the challenge of its generation and subsequent use is of particular relevance for the industry. At the same time, there is an additional valuable product of hydrocarbon decomposition known as carbon nanomaterial (CNM). Due to a unique combination of physical and chemical properties, CNM can be applied in various fields of science and technology [1]. The search for novel areas of application for CNM seems to be of considerable interest due to the development the hydrocarbon processing technologies to produce hydrogen as the main product.

The carbon nanofibers (CNF), one of the types of CNM, are known to be widely used as a modifying agent for the improvement of physical and mechanical characteristics of composite materials based on cement stone, polymers, ceramics, lubricants, epoxy resins, etc. [1]. The addition of CNF in small amounts (less than 0.1 %) to the structure of composites can lead to a significant increase in their strength characteristics, crack resistance, as well as an enhancement of the anti-friction characteristics of lubricants [2].

The process of carbon erosion (CE) of catalytically active alloys can be used for the target synthesis of CNF materials [3,4]. As a result of CE occurring under the action of a reaction medium containing hydrocarbons, the rapid disintegration of alloys takes place, which ultimately results in a spontaneous formation of active particles catalyzing the growth of carbon filaments. This approach requires further development due to the search for optimal catalytic compositions, which would allow controlling the structural type, textural characteristics, and macroscopic properties of the CNF product.

In this research, we have studied the process of CNF production performed in a regime of the controlled carbon erosion of Ni-based alloys. Ethylene was used as a model hydrocarbon. The role of the catalyst's precursors was played by bulk $Ni_{1-x}M_x$ (M = Cu, Mo, etc.) alloys, which were represented, according to the XRD data, by the solid solutions based on the FCC (face-centered cubic) lattice of nickel. Ni-based alloys were synthesized by the mechanochemical alloying using the planetary mill 'Activator-2S' and then used as the catalyst's precursors. The kinetics of the carbon erosion process was examined in a flow reactor with McBain balances, which allow following the changes in the sample's weight directly during the decomposition of ethylene on the bulk nickel alloy samples in a real-time mode.

It was found that nickel-copper alloys are the most effective precursors of the catalyst in terms of CNF production. The yield of CNF obtained at T = 650 °C was 163 g/g for 30 min of the ethylene decomposition process in a presence of hydrogen. The influence of temperature on the occurrence of the CE process was studied, and the optimal 'operation window' for the catalysts was defined. For Ni-Cu alloy, a detailed study of the CE process at its early stages was performed at T = 600 °C. The influence of temperature on the duration of the induction period of the reaction was also investigated. It was shown that during the induction period the active dispersed particles are formed. These particles further catalyze the growth of the CNFs (Fig. 1).

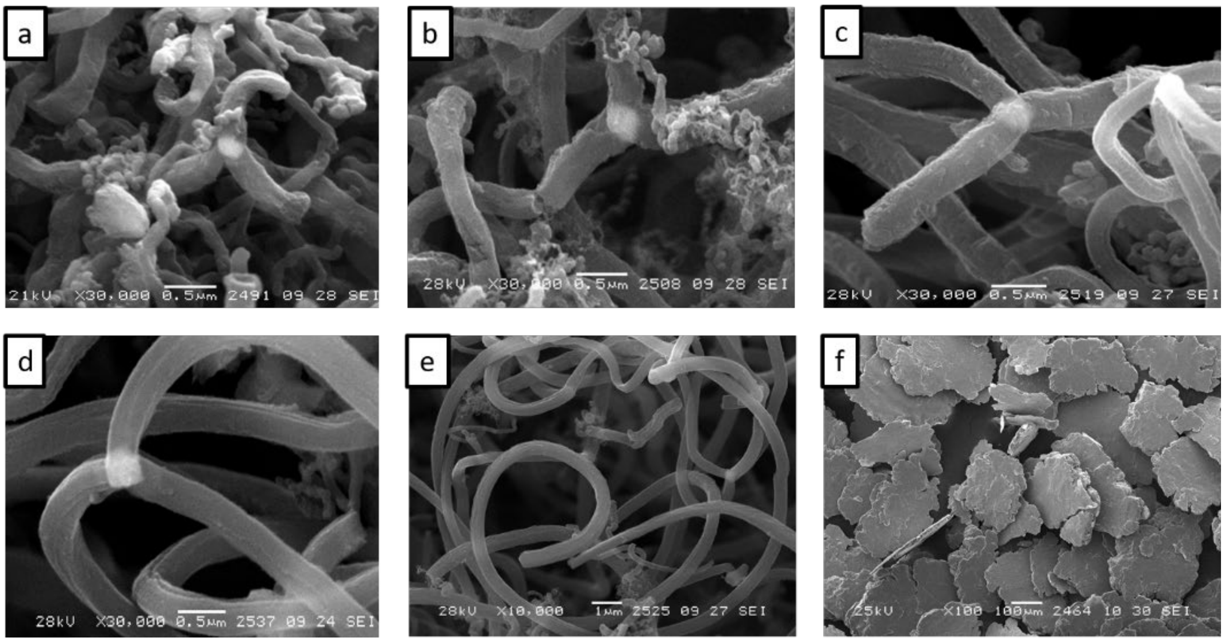

Fig. 1. Active particles of CNF growth resulted from a carbon erosion of Ni-Cu alloy exposed to a mixture of C_2H_4/H_2 at: ***a*** *– 475 °C;* ***b*** *– 500 °C;* ***c*** *– 600 °C;* ***d*** *– 650 °C;* ***e*** *– general view of CNF formed at T = 650 °C;* ***f*** *– pristine Ni-Cu alloy. SEM data.*

The report will present the results of the study on the effect of the promoting additives on the activity of Ni-based alloys and the kinetic characteristics of the process at the stages of the induction period and the growth of CNF. The physicochemical and textural characteristics of the obtained carbon nanomaterials will also be presented and discussed.

Acknowledgements: This work was supported by the Russian Science Foundation, grant number 18-29-19053_mk.

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OP-V-13

Effect of Indium Doping of the Pt-Sn/Al_2O_3 Catalysts in n-Heptane Reforming

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Naphtha reforming catalysts are bifunctional systems that promote both rearrangement and cracking of linear long-chain hydrocarbons at acid sites and dehydrogenation reactions to produce aromatic hydrocarbons at metal sites [1]. The acidic function is performed by a carrier based on alumina, which is modified with anionic (B, F, Cl) modifiers. The metallic function is carried out by elements of the platinum group, generally, a platinum itself and a cationic promoter (Re, Sn). Currently bi- and polymetallic reforming catalysts are used in petrochemical industry. Those contain platinum, rhenium, and a promoter metal (Sn, Ge, Ga, Zr, In) [1]. Adjusting the acidic and metallic functions of the catalyst to obtain the required reformate composition, as well as increasing the stability of the catalytic system, is remained topical engineering and scientific problem for the entire existence of the process [2, 3].

The aim of this work is to study metal promoters modified catalysts for the reforming of n-heptane.

Spherical industrial alumina (Sasol Germany GmbH) used as a support in this work. The catalysts were obtained by the active metal precursors impregnation to obtain 0.25-0.3% wt. Pt and 0.1-0.3% promoters (III, IV group metals). Mono- and polymetallic systems supported on chlorine-modified alumina were used as reference samples. The catalysts were calcined in an air flow at 500 ° C for 1 h, reduced in a hydrogen flow at 500 ° C for 1 h.

The n-heptane reforming process was carried out under the following conditions: 0.44 MPa pressure, 460, 480, 500, and 520 ° C temperature, LHSV = 3 h^{-1}, hydrogen / feed molar ratio = 3: 1.

The integral criterion of activity in the main reaction is the specific productivity value (SP, g of toluene / (gKat · h)) at a 490 ° C temperature (averaged over the temperature range of 460-520 ° C). The aromatization selectivity SA was determined as the ratio of the aromatization reaction rate constant to the total n-C7 conversion rate constant. Stability was assessed as the constant of deactivation C_D, calculated from SP value change during extended tests at 520 ° C. The efficiency coefficient was calculated as $K_{Eff} = SP \cdot SA \cdot C_D$.

The aromatics yield increases in Pt → Pt-Sn → Pt-Sn-In sequence. Thus, the aromatics yield at 520 ° C for the Pt-Sn system is 57.5% wt., and for the Pt-Sn-In system is up to 65% wt., wherein C_{5+} yields are similar - 77.8 and 78.2% wt. respectively. This may be due to an increase in the quantity of the active form of platinum [4], which is caused by the influence of In particles on the formation of Pt – Sn nanoclusters.

Acknowledgement. This work was carried out within the state task of the Boreskov Institute of Catalysis (Project AAAA-A17-117021450095-1).

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OP-V-14

Synthesis and Study of Nickel Catalysts Based on Ordered SBA-15 Modified with CeO_2-MnO_x Binary Oxides in the DRM Process

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Recently, mesoporous nanostructured materials have been used to develop heterogeneous catalysts for application in catalytic reforming due to their high specific surface and low density [1]. Ni-based catalysts supported on mesoporous supports, such as MCM-41, SBA-15 meso-Al_2O_3 and so on, are well known for their high activity and resistance to coke formation. Interaction with the support matrix favours the stabilization of Ni metal as dispersed nanoparticles and allows to lower the amount of introduced metal. However, at elevated temperatures, Ni nanoparticles (NPs) tend to diffuse from mesoporous channels onto the outer surface of the support due to the weakening interaction of the Ni-support [2]. A possible solution to this problem is the use of modifiers oxides that enhance the Ni-support interaction. High catalytic performance can be achieved by combining Ni/SBA-15 with binary oxides of La, Ce, Mn [3].

The present work is devoted to study the interaction of the nickel nitrate precursor with the support, SBA-15 and SBA-15 modified with binary oxides of CeO_2-MnO_x at different molar ratio of Ce/Mn, and to reveal the effect of the supports and their interaction with Ni on the catalytic performances in dry reforming of methane (DRM).

Mesoporous SBA-15 with a regular pore size (4-8 nm) was prepared by template synthesis using a surfactant of PEO20PPO70PEO2 (Pluronic P123 triblock copolymer). SBA-15 surface modification with CeO_2-MnOx/SBA-15 binary oxides was carried out by the incipient wetness impregnation using aqueous solutions of $Ce(NO_3)_3*6H_2O$ and $Mn(NO_3)_2*6H_2O$ with the addition of citric acid solution.

After calcination of the supports at 500 °C, Ni (10wt. %) was deposited by wetness impregnation and the resulting catalysts were calcined at 800 °C.

The physical chemical properties, the catalytic activity and the long-run stability of prepared catalysts have been evaluated in DRM reaction. The characterization of both fresh and spent catalysts was carried out using low-temperature N_2 adsorption/desorption, XRD, SAXS, TGA, H_2-TPR, Raman and TEM analyses.

After loading nickel over unmodified SBA-15 (Ni/SBA-15) a monomodal pore size distribution, with an average diameter of 5.3 nm, was found.

Based on the results of small-angle X-ray diffraction (SAXS), it was confirmed that the original structure of SBA-15 was preserved for this sample, however, the wall thickened due to the incorporation of Ni^{2+} into the SBA-15 structure. According to XRD data, the average crystal size was estimated, NiO particles of 18 nm and Ni^0 particles of 15 nm were detected. H_2-TPR experiments showed that the formation of Ni NPs in an H_2/Ar flow occurs in the temperature range of 400-725°C with a reduction extent of 82%.

In the SBA-15 modified by CeO_2-MnO_x binary oxides MnO_x was well dispersed in the CeO_2 lattice with the formation of a $Ce_{1-x}Mn_xO_{2-\delta}$ solid solution, according to XRD characterization. With an increase in the molar ratio of Ce to Mn (from 0.25 to 9) and the deposition of NiO on the corresponding supports, the defects of the CeO_2 crystal lattice increased due to the incorporation of MnO_x and/or NiO into the structure (a change in the lattice parameter of d_{111} (CeO_2). Moreover, the addition of MnO_x to CeO_2 has a strong effect on the NiO particles size that varies from 7.5 to 11.4 nm for the Ni/CeO_2-MnO_x/SBA-15 catalysts. TPR experiments revealed that reduction of NiO NPs interacting with CeO_2-free SBA-15 occurs between 300-400 ^oC, whereas NiO stabilized by $Ce_{1-x}Mn_xO_{2-\delta}$ solid solution is reduced at higher temperature, above 400 ^oC.

The DRM catalytic tests at gradient temperature performed between 400°C to 800 °C showed high catalytic conversion of CH_4 and CO_2 for the Ni/CeO_2-MnO_x/SBA-15 sample with a molar ratio of Ce/Mn = 9 (Fig.1 b). This catalyst also exhibits stable conversion of CH_4 and CO_2 (long run stability tests at 650 ° C during 24 and 80 h, Fig.1 c). The incorporation of Mn^{n+} cations into CeO_2 structure led to enhanced Ni-support interaction and increased concentration of oxygen vacancies in the support structure, thus, diminishing the content of carbonaceous deposits. According to TGA data, the sample weight loss after long run tests at 650 °C, for 24 h and 80 h, were 0 and 19 wt. %, respectively.

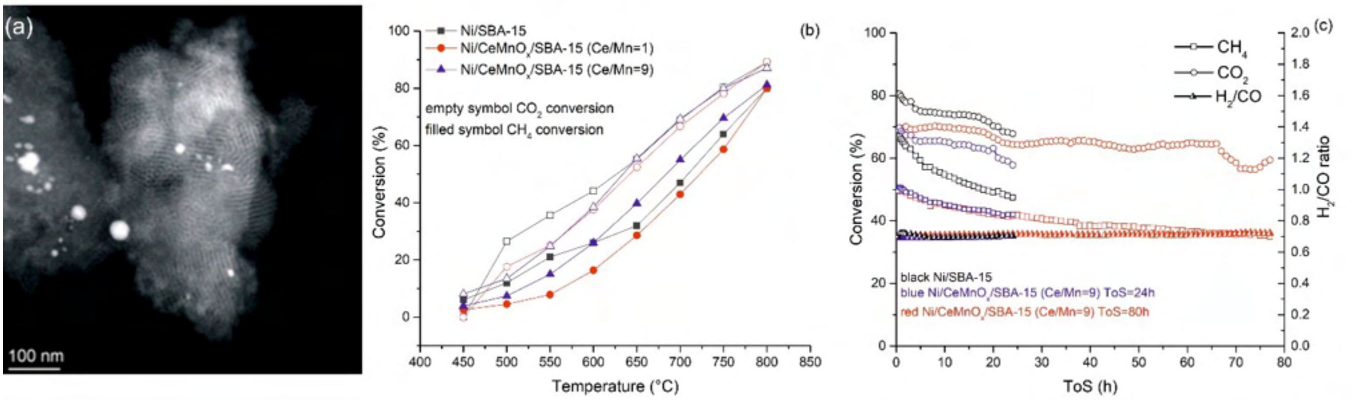

Fig. 1. TEM HR image of Ni/SBA-15 (a); temperature dependences of CH_4/CO_2 conversions (b); long run stability tests at 650 ° C for Ni/SBA-15 during 24 h and for Ni/CeMnOx/SBA-15 (Ce/Mn=9) during 24 h and 80 h (c)

Acknowledgement. This work was supported by the Russian Science Foundation, grant № 19-73-30026.

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OP-VI-1

The Influence of Composition of Electrodeposited NiCu Catalysts on Their Activity in the Borohydride Oxidation Reaction

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A rapid growth of electric power consumption [1] stimulates the necessity of the development of efficient and environmentally friendly sources for the generation of electricity close to the consumer. Low-temperature fuel cells are considered as one of the most promising systems. Among them, direct liquid fuel cells and, in particular, direct borohydride fuel cells have a number of advantages, such as high mobility due to using liquid fuel instead of fuel in gaseous form, that must be hold in heavy gas cylinders, simplicity of construction for the same reason and larger theoretical cell voltage (1.64 V) than that of oxygen-hydrogen fuel cell (1.23 V). To date materials based on platinum-group metals (PGM) remain the most popular and thoroughly investigated catalysts for the borohydride oxidation reaction (BOR) [2]. However, their efficiency is severely limited by the competition of the desired BOR with the unwanted hydrogen evolution reaction (HER) at potentials below 0 V *vs* RHE, not saying that PGMs are too expensive. Among PGM-free catalysts Ni is currently considered as one of the most promising candidates due to its high stability in alkaline media, low cost, and, most importantly, relatively high activity in the BOR even at potentials below 0 V *vs* RHE. The highest activity is achieved for the metallic Ni surface, while the performance decreases in the presence of surface oxides [3]. An addition of a second, specifically, more electropositive metal should help to stabilize the metallic Ni phase and might also affect its electronic properties. In particular, there are pieces of evidence that Ni is oxidized up to a less extent under contact with air in the presence of Cu [4]. However, the questions about the preparation of homogeneous metallic NiCu catalysts and their optimal composition for the BOR remain open.

In this work we have developed a protocol for fabrication of NiCu electrodes by using electrodeposition technique. Glassy carbon electrodes were used as a support for potentiostatic deposition of NiCu from the 0.1 mol L^{-1} $(NH_4)_2SO_4$ + 0.01 mol L^{-1} $NiSO_4$ + 0.001 mol L^{-1} $CuSO_4$ solution. A monometallic Ni electrode was also obtained for comparison with NiCu ones by electrodeposition from a similar solution but without adding copper sulphate. To obtain samples with different Ni:Cu ratio, the deposition potential was varied from -1.45 V to -1.25 V *vs* MSE. The surface concentration of both metals was derived from *in situ* cyclic voltammetry measurements (by evaluating electrochemically active surface area of each metal in 1 mol L^{-1} NaOH electrolyte) and *ex situ* X-ray photoelectron spectroscopy measurements. The bulk composition of NiCu electrodes was obtained by dissolving them in 30% HNO_3 and analysing the solutions by inductively coupled plasma atomic emission spectroscopy. Various regimes of electrodeposition (with controlling time or total charge of the deposition, with/without rotation of the electrode) were tested and optimized for preparing highly reproducible NiCu electrodes. It was defined that Ni content increases with applying more negative electrodeposition potential. The activity of the NiCu electrodes in the BOR was obtained under well-controlled mass transport conditions (through utilization of a rotating disk electrode) in the presence of 5 mmol L^{-1} $NaBH_4$ in 1 mol L^{-1} NaOH at room temperature. A volcano-type dependence between the composition of NiCu electrodes and their electrocatalytic activity in the BOR was observed with the highest activity measured at approximately 0.56:0.44 Ni:Cu surface ratio. In addition, it was found that NiCu electrodes remain to be active until more positive potentials compared to monometallic Ni sample supporting the idea about stabilization of the metallic Ni phase in the presence of Cu.

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OP-VI-2

Influence of the Evolution of the Composition and Structure of Bimetallic Nanoparticles in PtM/C Catalysts on Their Activity and Stability

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Platinum-containing nanostructured catalysts exhibit the highest catalytic activity in electrochemical reactions occurring in low-temperature fuel cells with a polymer membrane. The alloying of platinum with some d-metals makes it possible to further increase the activity of the catalyst, however, selective dissolution of the alloying component results in membrane poisoning and a decrease in the characteristics of the fuel cell. The attempt to use bimetallic nanoparticles with the M-core-Pt-shell architecture as an active component of the catalyst is very attractive if it is possible (i) to maintain the positive effect of the core-metal on the activity of the platinum shell and (ii) to make the shell defect-free and stable during operation of the catalyst. Unfortunately, obtaining a "core-shell" catalyst with such characteristics is a very difficult task. As a rule, PtM nanoparticles of different architecture undergo a change in composition and structure at the initial stage of the catalyst functioning, especially if the initial concentration of the alloying component is sufficiently high [1]. Thus, the formed secondary de-alloyed structures should have high activity and stability and should not undergo further composition changes due to selective dissolution of the alloying component.

The aim of this work was to study an evolution of structure and electrochemical performance of PtCu/C catalysts with different composition before and after acid and thermal treatment at different temperatures. Synthesis of PtCu/C catalysts with different composition and architecture of nanoparticles (from uniform solid solutions to nanoparticles with core-shell and "gradient" structures) by methods of joint and sequential reduction developed earlier in our laboratory [1-2] was carried out. Post-treatment of obtained PtCu/C catalysts with different nanoparticle architecture was held in order to remove the alloying component from "defective" nanoparticles with an imperfect platinum shell. Optimization of acid treatment conditions allows to obtain supported nanostructured de-alloyed PtCu(x-y)/C catalysts with higher stability and activity in electrochemical reactions of oxygen reduction.

The characterization of prepared PtCu/C materials was performed by HRTEM, XRD, CV, LSV and Pt L3- and Cu K-edge extended X-ray absorption fine structure (EXAFS).

The electrochemical behaviour of PtCu/C catalysts is compared for samples in the “as obtained” state and after their treatment in nitric acid which decreases the copper content in their composition. It is found that the partial selective dissolution of the alloying component renders no negative effect on the behaviour of bimetallic catalysts. The prepared materials exhibit the high tolerance toward intermediates of methanol oxidation and their specific activity exceeds by a factor of 5–7 the activity of the commercial Pt/C catalysts [3].

The obtained PtCu/C electrocatalysts shown high activity in oxygen redaction reaction (ORR), corrosion durability and satisfactory resistance to the selective dissolution of copper. Pretreatment of the platinum-copper catalysts in acids does not practically reduce their activity in ORR and MOR, but when the "excess" of copper is removed, resistance to its selective dissolution significantly increases [4].

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OP-VI-3

Effect of Mo on Catalytic Activity of $Ni_{1-x}Mo_x$ System in the Decomposition of Trichloroethylene

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Chlorinated hydrocarbons (CHCs) are widely used in many industries, agriculture, and pharmaceuticals. They are used as solvents in the synthesis of polymers, transformer oils, pesticides, and also as intermediates in the production of stable dyes, pigments, antibacterial drugs, medicinal substances, etc. [1]. In particular, trichloroethylene (TCE) is used for degreasing and cold cleaning of metal products; as a solvent for active ingredients of insecticides and fungicides, waxes, fats, resins, and oils; as an inhalation agent for anesthesia in medicine; as an extractant for essential oils from spices and caffeine from coffee, etc.

Unfortunately, industrial production of chlorine-substituted hydrocarbons often leads to the formation and accumulation of a large amount of wastes that pose a threat to the environment and humans due to their high chemical resistance and toxicity. Such wastes are multicomponent mixtures of aliphatic and aromatic chlorine-containing compounds, which disposal is still very difficult in practice.

One of the most promising methods for CHCs processing is their catalytic decomposition accompanied with the formation of carbon nanofibers (CNF) [2].

Nickel catalysts are usually used for the processing of organochlorine compounds, since in terms of resistance to chlorination, Ni is the most stable among the metals of the iron subgroup (Fe, Co, Ni) active in the process under consideration [3]. It is also well known that the catalytic activity and stability of catalysts based on Ni can be significantly affected by introducing various promoters (Mo, W, Pd, etc.). It was found that the addition of Mo (8 wt.%) increases the yield of the carbon product by almost 2 times compared to pure Ni in the decomposition of dichloroethane [4]. The proposed processing method is based on the process of metal dusting (MD) of massive nickel alloys, which leads to their rapid disintegration. Earlier it was shown that as a result of the fragmentation of alloys, active particles are spontaneously formed, on which the processes of catalytic decomposition of CHCs and growth of CNF are further carried out [4]. These particles as well as the formed fibers are shown in Fig. 1.

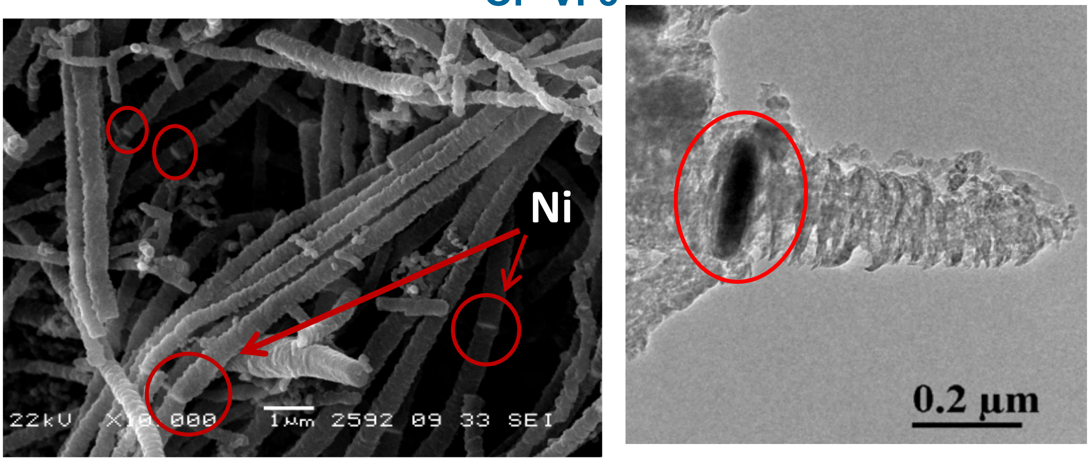

Fig. 1. SEM and TEM images of CNF grown on active Ni particles

The report will present the results of a comparative study of the activity of pure Ni and Ni$_{1-x}$Mo$_x$ catalysts in the TCE decomposition to obtain a nanostructured carbon material. The features of the metal dusting of Ni$_{1-x}$Mo$_x$ alloys in the atmosphere of TCE and the process of the formation of active particles that act as centers of the carbon filaments growth at the early stages of MD will be discussed. Also, the kinetic patterns of the catalytic decomposition of TCE on self-organizing bimetallic catalysts will be revealed, and the effect of additives on the kinetic characteristics of the process will be demonstrated. Optimal conditions such as temperature range, Ni-M alloy composition, hydrogen concentration, etc., will be established for the process of TCE decomposition with the carbon nanomaterial formation. The textural parameters of the obtained carbon product will also be presented and discussed in the report.

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OP-VI-4

Noble Metal Catalysts for Low-Temperature Water Gas Shift Reaction

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Hydrogen energy is one of the most perspective branches of alternative energy which follows a decarbonization strategy. The reaction of hydrogen electrochemical oxidation is used to produce electricity by means of proton exchange membrane fuel cells (PEMFC) which operate at relatively low temperatures (60-80 °C). Nowadays, the main process of hydrogen production is steam reforming of methane to yield syngas followed by its purification to remove CO. The second step is necessary since PEMFCs require highly pure hydrogen (CO <10 ppm) [1]. This study will focus on water gas shift reaction which allows converting CO and H_2O into CO_2 and H_2.

Since the water gas shift reaction is thermodynamically favorable at low temperatures, and kinetically at high temperatures, its industrial implementation consists of two successive stages. At the first high-temperature stage, traditional industrial catalysts are iron-chromium oxide systems, which are most active at temperatures of 300-500 °C. For the second low-temperature stage copper-zinc oxide systems are used, for which the operating range is 150-300 °C. It is possible to reduce CO concentration from 10 to ~0.5 vol.% by carrying out the reaction in this way. However, such a system is not lightweight and compact enough to be used on the board of portable devices [2]. In addition, the catalysts used are pyrophoric and require long-term activation. Therefore, at the moment, research is aimed at finding and optimizing catalysts based on noble metals (including bimetallic ones), which would make it possible to carry out the water gas shift reaction at low temperatures and in one stage, while ensuring high efficiency and small dimensions of the catalytic system.

A study was made of noble metal catalysts for low-temperature water gas shift reaction. It was shown that catalysts supported on SiO_2 and Sibunit (carbon material) are not active in this reaction, while Pt- and Au-containing ones supported on $Ce_{0.75}Zr_{0.25}$ proved to be highly active at 300-350 °C and atmospheric pressure in mixture simulating reformate. The influence of the method of preparation of $Pt_{0.5}M_{0.5}/Ce_{0.75}Zr_{0.25}$ catalysts (M = Cu, Fe, Co, Ni) on their activity in the same conditions was also studied. For all the catalysts under study the correlation between the composition, structure and catalytic properties was defined.

Acknowledgement. The work was supported by the Russian Science Foundation under the Project № 19-73-00157.

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OP-VI-5

Influence of the Parameters Modified by the Driving Mode on DeNOxing Activity of NSR-SCR Hybrid System

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The wide regulations to control, reduce and limit nitrogen oxides (NO_x) emissions from light Diesel engines exhaust gases have led to the development of high performance deNO_x technologies and strategies [1], being NO_x Storage and Reduction (NSR) and Selective Catalytic Reduction (SCR) the most widely used. NSR operates in two cycled fed conditions (lean and fuel rich phases) in which NO_x are stored as nitrates and nitrites and reduced to N_2 using a catalytic conformation of a noble metal as Pt, Pd and Rh and an alkaline or alkaline-earth such as K and Ba over a high surface area support as Al_2O_3. SCR utilizes NH_3 (from an aqueous urea tank, *AdBlue®Technology*) as NO_x reductant leading to N_2 and H_2O over Cu or Fe exchanged zeolite catalyst. The coupling of both technologies NSR-SCR leads to an improvement in N_2-selectivity, since the undesired NH_3 produced in the NSR catalyst is stored and reacts in the consecutive SCR catalytic bed [2]. Based on an approximation to real driving conditions where different parameters such as temperature, torque, cold-start emissions, exhaust gas humidity, longer stop lengths and lower maximum speeds, etc., are key factors, the study of the ability of this coupled system to cushion the emissions depending on driving parameters is decisive in order to achieve zero emissions at the outlet of diesel engine vehicles.

For this purpose, Pt-Ba-K/Al_2O_3 and 2Cu-SAPO-34, as NSR and SCR catalyst, respectively, were incorporated into Al_2O_3-coated cordierite monoliths using an impregnation method in consecutive steps [3]. Catalytic tests were performed in a vertical down stainless-steel reactor in which NSR-SCR catalysts conformed in monolithic form were placed using identical bed volume. The outlet gas composition (NO, NO_2, N_2O, NH_3, and H_2O) was measured *online* via MKS Multigas 2030 FTIR followed by a MKS Cirrus quadrupole mass spectrometer (N_2, H_2, and O_2). In order to represent different driving modes, different conditions were carried out as cyclic lean and reach phases such as NO-concentration [300-1000] ppm, operation temperature [150-400] ºC, GHSV $[2.5\text{-}9.1]\cdot 10^4\ h^{-1}$ and concentration of different reductant agents (H_2 or C_3H_6) in rich phase.

Several cycles were performed for each condition and selectivity and conversion values were calculated from the profile of a stable cycle in order to compare the activity and delve into the understanding of this coupled technology. As can be observed in Figure 1, nitrogen yield depended on the NO inlet concentration, which is modified depending on the gear, speed and temperature of the engine.

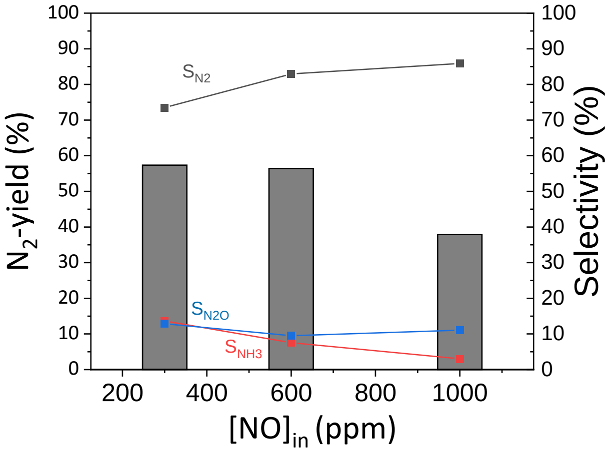

Fig. 1. N_2-yield and N-product selectivity at 200 °C for NSR-SCR catalytic system.

At higher NO concentration, nitrogen yield decreased due to the NO_x conversion was lower, because the regeneration of the catalyst was not complete, although N_2 selectivity values were between 70 and 90% in the whole operation range. In the same line, the influence of the temperature or the reductant agent and its concentration modified the composition detected at the outlet. Nevertheless, it is remarkable the high performance and N_2-selectivity in NO_x abatement under conditions similar to real driving modes obtained with this tandem NSR-SCR catalytic configuration.

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OP-VI-6

Hydrogen Evolution from Biomass Constituent Solutions Under Visible Light Irradiation

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Nowadays there is a great necessity to develop alternative energy sources to overcome the problem of increasing green-house gas emissions [1]. Hydrogen is considered to be the most perspective energy source. One of the environmentally-friendly technology for hydrogen production is photocatalytic water splitting [2]. However, in such case, the process does not show a high efficiency due to the recombination of electron and hole. The problem could be solved by the irreversibly reaction of holes with organic or inorganic electron donors [3]. Numerous compounds are used as electron donors, for instance, Na_2S/Na_2SO_3 system, alcohols, aldehydes, and saccharides [4]. From a practical point of view, it could be economically effective to use abundant and affordable compound, for example, plant biomass. If this, photocatalytic hydrogen evolution combines the following benefits: using only renewable/abundant sources (water, biomass, and sunlight) to produce H_2; obtaining pure H_2; proceeding the reaction at ambient conditions [5].

One of the common semiconductor materials for photocatalysis under visible light irradiation is cadmium sulfide (CdS) which possesses quite narrow bandgap and has an ability to absorb visible light irradiation. To improve the photocatalytic properties, the addition of ZnS is employed to form the solid solution $Cd_{1-x}Zn_xS$.

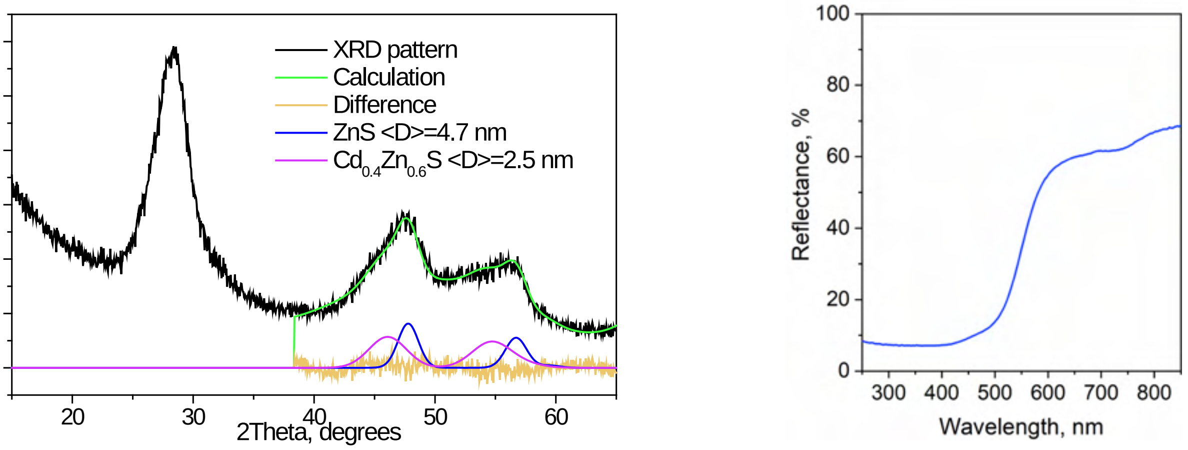
Based on the above, the aim of present work was to synthesize active photocatalyst based on solid sulfide solution $Cd_{1-x}Zn_xS$, to study the features of hydrogen evolution from plant biomass and to understand the influence of structural properties of photocatalyst on its activity. In this study, we used cellulose and starch as a model compounds.

A $Cd_{0.3}Zn_{0.7}S$ photocatalyst was prepared by the coprecipitation method from mixture of $Cd(NO_3)_2$ and $Zn(NO_3)_2$ solutions by adding Na_2S solution. The obtained sample was washed by multiple centrifugations and dried at 60 °C for 6 h.

The obtained photocatalyst was characterized by XRD technique (Fig. 1a). XRD pattern showed that the sample consisted of two phases: solid solution of cadmium and zinc sulfides, $Cd_{0.4}Zn_{0.6}S$, and ZnS. The average particle size of $Cd_{0.4}Zn_{0.6}S$ was 2.5 nm, and that of ZnS was 4.7 nm. As the synthesized sample had the multiphase structure, the transfer of charge carriers could appear which resulted in enhanced charge separation and therefore the hydrogen evolution rate. To study the optical properties of photocatalyst, UV-vis spectrum of the photocatalyst was obtained (Fig. 1b). It has been shown that the sample is able to absorb visible light irradiation, the width of band gap in the obtained photocatalyst is equal to ca. 2.6 eV

The synthesized sample was tested in the hydrogen evolution from aqueous solution of cellulose and starch under visible light (λ = 450 nm). The results of the kinetic measurements are presented in fig. 2. In could be seen the synthesized photocatalyst shows high activity in hydrogen production during biomass photoreforming.

Mass content of substrates has different effects on the reaction rate. The hydrogen evolution rate slightly increases with the increase of cellulose content, while rate dependence on starch content has a maximum at 0.1 g. In the absence of substrate, no hydrogen was detected. The difference could be explained by the process of forming a gel at high starch loading, which prevents mass transfer in the reaction suspension.



a) *b)*

Fig. 1. a) XRD-pattern; b) Diffuse reflectance spectrum of the synthesized photocatalyst

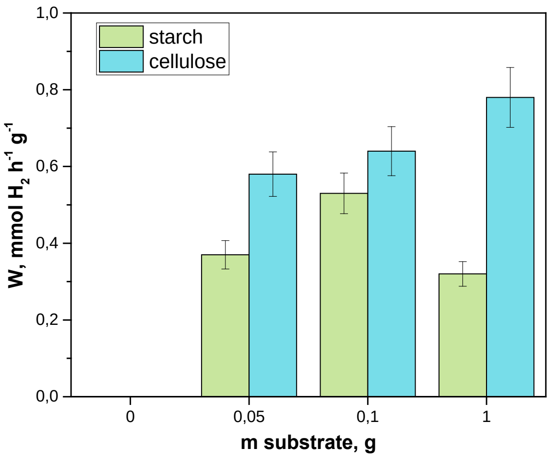


Fig. 2. Photocatalytic activities of $Cd_{0.3}Zn_{0.7}S$ sample in different substrates. Conditions: C_0(NaOH) = 5M, C(cat) = 2,5 g/L, T = 20 °C

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OP-VI-7

MOx (M = Mn, Ce) Doped WO_3-TiO_2 Catalysts for NO SCR by NH_3

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Nowadays researchers in the field of the selective catalytic reduction (SCR) of NOx by NH_3 continue to attract interest because land sources and naval emissions have to comply increasingly stringent regulations. Similarly to Euro 6 standard limits for vehicles, new standards, such as Tier II (valid outside Emission Control Areas, ECAs) and Tier III (applied only in ECAs) have been issued by the IMO (international maritime organization) of the United Nations in order to regulate NOx emissions for ships. Therefore, new formulations of NO SCR catalysts with high activity and N_2 selectivity in the entire range of temperature of exhaust gases are required and the catalytic performances are quite demanding when the aftertreatment of naval diesel engines fuelled by HFO (heavy fuel oil) is required, due to the high sulphur content [1].

In the present work, starting from the conventional WO_3-V_2O_5/TiO_2 system, that represents the main component of commercial DeNOx catalytic devices for stationary sources and trucks [2], new formulations have been investigated aiming to improve the catalytic performances at low-temperature (< 200 °C) by substituting the toxic V_2O_5 with other transition metal oxides, such as MnO_x or CeO_2.

The morphological, structural and redox properties of the prepared catalysts have been investigated and NO SCR by NH_3 tests have been performed over cordierite honeycomb structured catalysts and the corresponding bare powder oxides.

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OP-VI-8

Transition from Effective Photocatalysts to Photoelectrodes: Influence of Semiconductor Composition, co-Catalyst Nature and Amount

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Solar energy is known to be a promising energy source [1]. Its utilization may be realized in the photocatalytic processes (solar energy conversion to energy of chemical bonds) and direct conversion to electricity. Semiconductor materials were used in both processes, different photocatalysts were studied. It will be useful to get a strategy for developing effective photoelectrodes for electrochemical cells based on the photocatalytic experience. The present work is aimed at the studying of correlations between the photocatalytic activity and photoelectrochemical parameters obtained by different materials such solid solutions of CdS and ZnS, co-catalyst/$Cd_{1-x}Zn_xS$.

The $Cd_{1-x}Zn_xS$ photocatalysts were prepared via two-stage deposition method including metal hydroxide formation and their sulfurization. Nickel hydroxide, nickel sulphide, zinc hydroxide, zinc sulphide, cobalt hydroxide, and cobalt sulphide were use as co-catalysts. Photocatalytic activities of the prepared samples were measured in the reaction of hydrogen production from 0.1 M Na_2S/0.1 M Na_2SO_3 solutions under visible light irradiation (λ = 450 nm). All photoelectrodes were synthesized by the SILAR method. The photoelectrochemical cell has been fabricated by sandwiching the counter electrode (Cu_2S/brass) and the tested photoanode using a parafilm spacer. The electrolyte consisted of 1M Na_2S_n and 0.1M NaCl [2].

At first, the influence of the composition of solid solution on the target processes was investigated. The most effective photoelectrode was $Cd_{0.8}Zn_{0.2}S$/FTO, while the most active photocatalyst was $Cd_{0.3}Zn_{0.7}S$. The observed phenomenon was assisted with different factors defining high photocatalytic activity and photocurrent generation. Impedance spectroscopy results demonstrated that great values of J_{sc} were observed in case of high electron lifetime and electron concentration. Effective photocatalyst should possess high conduction band potential and electron lifetime.

Secondly, the co-catalyst deposition on the photocatalyst and photoelectrode surface was studied. The deposition of co-catalyst to $Cd_{0.3}Zn_{0.7}S$ and $Cd_{0.3}Zn_{0.7}S$/FTO leaded to increase in both photocatalytic activity and photoelectrocatalytic properties. In this case the charge separation was improved after the co-catalyst deposition. Moreover, the photocatalytic activity, short-circuit current density, electron lifetime, power conversion efficiency was changed at the same consequence. Some correlations between mentioned values were established.

Thirdly, the influence of co-catalyst amount on the target properties was studied over $Cd_{0.3}Zn_{0.7}S$ modified with zinc hydroxide. Fig. 1 showed that the deposition of zinc hydroxide leaded to the increase in the photocatalytic hydrogen production and photocurrent generation. The highest values of the target properties was observed for 20% $Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$. The following growth of the co-catalyst content was accompanied with the falling of reaction rate and photocurrent generation. It may be due to the decrease in the amount of photogenerated electrons. This hypothesis was confirmed by the impendance spectroscopy.

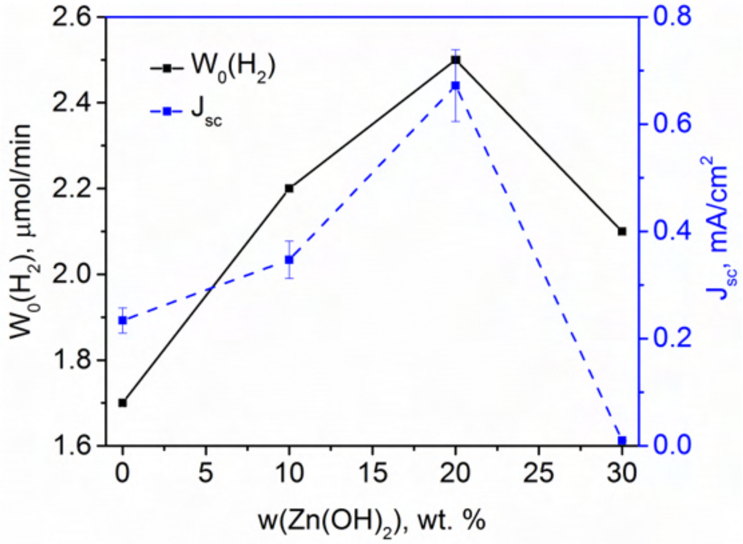

Fig. 1. Influence of the $Zn(OH)_2$ weight content on the photocatalytic reaction and photocurrent generation

Finally, the influence of composition of $Cd_{1-x}Zn_xS$, nature of co-catalyst and its amount on the photocatalytic hydrogen production and photoelectrochemical properties was studied. Some correlations between photocatalytic activity, short-circuit current density, electron lifetime, amount of the photogenerated electrons and conduction band position were found.

Acknowledgement. This work was supported by President of Russian Federation Scholarship SP-1029.2019.1.

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OP-VI-9

Bismuth Silicate Composite Materials Prepared via Gel Process: Phases Formation, Electrochemistry and Photocatalytic Performance

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The dependence on fossil fuels has raised concerns regarding the sustainability and environmental impact of modern energy production. The renewable energy sources are the best alternative that can address these issues. Photocatalysis is the chemical process of harvesting solar energy, which is considered renewable, safe, economically feasible and clean technology. Many new photocatalytic materials were developed, since publication of the remarkable paper about the photoelectrochemical water oxidation on a titanium oxide single crystal photoanode [1]. Among them, the Bi-based materials have attracted attention [2] due to their special electronic structure. The family of bismuth silicates (Bi_2SiO_5, $Bi_4Si_3O_{12}$, and $Bi_{12}SiO_{20}$) have been studied in a lesser extent, though they possessed photocatalytic activity. The bismuth metasilicate phase Bi_2SiO_5 is more interesting due to the perovskite-like structure and higher catalytic performance [3,4].

The report is focused on the preparation of composite materials based on bismuth silicate phase via simple gelation process that was not applied to $Bi_xSi_yO_z$ compounds yet. The prepared gel was calcined under different thermal modes. The synthesized samples were investigated by X-ray diffraction (XRD) analysis, IR spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, nitrogen adsorption-desorption measurements. The features of the processes at the semiconductor/liquid interface were studied by electrochemical methods. Photocatalytic activity was tested in model reaction of rhodamine B (RhB) photodegradation under Xe lamp irradiation (250 W).

Synthesis via gelation leads to the formation of composite materials regardless of the Bi/Si atomic ratio used and the thermal treatment mode. Simultaneously, the calcination mode affects the phase content and their distribution. At low temperature (300–400 °C), the bismuth beta-oxide was formed as the main phase, while at higher temperature (≤600 °C) the bismuth metasilicate was obtained as a primary phase in the composition. The increase of the Si content in the system facilitates the formation of larger amount of Bi_2SiO_5 phase in samples calcined at 600 °C for 2 h. Moreover, it was shown that both the amount of Si precursor along with thermal treatment conditions (temperature, duration) allows controlling the specific surface area (10–100 m^2/g) of the composites investigated. Conversion of the prepared photocatalysts in rhodamine B photodegradation varied in the range of 41–65 % (for 4 h). In addition, the RhB absorbance spectra point out the selective substrate deethylation. The highest performance was demonstrated by the samples containing 4 phases: Bi_2SiO_5, $Bi_{12}SiO_{20}$, β-Bi_2O_3, and α-Bi_2O_3. The difference in the optical properties as well as S_{BET} values for the most active samples (65 % conversion for 3 samples) may be associated with different phase distribution. Electrochemical data, including EIS measurements, will be also discussed along with the photocatalytic and electrophotocatalytic properties.

Acknowledgement. This work was supported by the Russian Science Foundation, grant No. 19-73-30026.

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SP-1

NAP-XPS Instrumentation and Applications: New Developments

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Modern devices are often only functional in environments far away from ultrahigh vacuum, which is still the standard operation condition for all surface science techniques. Additionally, the importance of surfaces for the correct device operation is continuously increasing due to miniaturization down to the nanoscale. In order to contribute to advanced materials analysis, it is necessary to use photoelectron spectroscopy combined with scanning probe microscopy and related techniques in the generic or near generic device environments. This means high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields applied. Extremely low or high temperatures might be necessary as well.

Over the last years it has been possible to develop XPS systems that can work far beyond the standard conditions of high or ultrahigh vacuum. Thus, Near Ambient Pressure (NAP) - XPS has become a rapidly growing field in research inspiring many scientists to transfer the method to completely new fields of application. Nowadays, this analysis technique is developing as a standard analysis tools in laboratory systems as well as at synchrotrons.

This work summarizes and presents existing solutions and future development routes to new instruments and material analysis methods being functional under generic or near generic device working conditions. Finally, applications, examples and results from existing operando investigation methods (NAP-XPS or NAP-SPM), liquid and electrochemical cells, as well as concepts and status of equipment working in these environments will be presented.

6th International School-Conference on Catalysis for Young Scientists

Catalyst Design

From Molecular to Industrial Level

POSTER PRESENTATIONS

Section 1. Preparation of catalysts and adsorbents
PP-I-1 ÷ PP-I-24

Section 2. Characterization and *in situ* studies of catalysts
PP-II-1 ÷ PP-II-9

Section 3. Mechanism and kinetics of catalytic reactions
PP-III-1 ÷ PP-III-4

Section 4. Catalysis for renewable sources
PP-IV-1 ÷ PP-IV-8

Section 5. Catalysis for fine organic synthesis, natural gas and petroleum chemistry
PP-V-1 ÷ PP-V-21

Section 6. Catalysis for environmental protection, photocatalysis and electrocatalysis
PP-VI-1 ÷ PP-VI-12

PP-I-1

Influence of the Hydrodynamic Growth Conditions on the Nanoporous Anodic WO_x Morphology and Its Photocatalytic Properties

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Tungsten trioxide (WO_3) is an n-type semiconductor oxide with impressive optical, electrical and photocatalytic properties. In particular, WO_3 is an attractive photoanode material owing to its high electron mobility, moderate hole diffusion length (≈150 nm) and non-toxicity. Tungsten trioxide has been employed in technologically advanced fields, such as photoelectrochemistry and photodegradation of organic pollutants, dye-sensitized solar cells, gas sensors or electrochromic devices.

Changing the morphology of the nanostructure determines its properties, photocatalytic properties in particular. Nanostructured WOx has a much higher effective surface area than non-porous oxides. Several previous reports have already found that photoresponse of the self-assembled nanoporous WO_3 has much higher photoconversion efficiency than WO_3 non-porous films [1]. More recently, self-assembled nanoporous WO_3 with preferential orientation of (002) planes showed better photocatalytic activity for the decomposition of pentachlorophenol than TiO_2 nanotube arrays. This study shows how photocatalitic properties depend directly on its oxide morphology.

A lot of regimes of nanostructured WOx synthesis have been discussed, and anodic WOx with different morphology (nanoholes, nanobowls, nanowires) has been shown. The resulting nanostructures are often inhomogeneous. Nanoporous films have a small diameter, which leads to the fact that photocatalytic treatment blocks access to the surface and the photocatalyst degrades rapidly. The films have low porosity and are deformed upon annealing, which is also bad for their properties as photocatalysts. Nevertheless approaches to the creation of tungsten with a suitable morphology needs additional studies. Most of the papers evaluate the influence of electrolyte composition or anodization current or potential under not well defined hydrodynamic conditions such as stirring. However, for other oxides, it was shown that hydrodynamic conditions play a crucial role in the kinetics of nanostructured oxide formation and can determine its morphology.

In the present study, we investigated the influence of hydrodynamic conditions on the growth kinetics and morphology of nanostructured anodic WOx via the Rotating Disk Electrode (RDE) system. The effect of the obtained morphological features on the photocatalytic properties has been investigated.

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PP-I-2

Effect of CeO_2 Reductive Pretreatment on the Formation of Bimetallic Particles in Ag-Doped Pt/CeO_2 Catalysts for 4-Nitrophenol Reduction

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It is known that bimetallic nanoparticles feature unique properties different from those of the corresponding single-metal materials. These properties are assumed to result from the interaction of the metals and also depends on the preparation conditions and support used. The Pt-based catalysts are used in a wide range of oxidative and reductive reactions such as hydrogenation of aromatic compounds, NO_x conversion, VOCs abatement, etc. [1-3]. The addition of the second metal (in particular, Ag) to the supported Pt catalysts results in an increase of the selectivity towards the target products in the hydrogenation reactions and a decrease of the loading of expensive platinum [4,5]. High catalytic activity of these catalysts can be achieved due to the synergistic effect of the metals.

One of the approaches towards the formation of the bimetallic particles is the preparation of catalyst based on the prereduced CeO_2. The use of the support reductive pretreatment leads to the formation of a large number of surface Ce (III) sites in the CeO_2 structure that react with the precursor of the active components during the impregnation step. The metal–support interaction in the catalyst obtained is high due to the formation of the metal/CeO_2 interface, while the formation of the $PtCe_xO_y$ solid solution does not practically occur.

Thus, the present work is focused on the metal–support interaction and interaction of Pt and Ag in the ceria-supported Pt–Ag bimetallic catalysts and their catalytic activity in p-nitrophenol reduction with $NaBH_4$.

Ceria was prepared by thermal decomposition of cerium nitrate at 500 °C. The catalysts were prepared by incipient wetness impregnation of the prereduced CeO_2 support. In monometallic nM(M=Pt or Ag)/CeO_2 samples, the metal content was n = 0.5-2 wt. %. Bimetallic samples were prepared by sequential impregnation. The prereduced CeO_2 was impregnated with the H_2PtCl_6 solution. Prior to the addition of the second component, the catalyst was dried at 120 °C and reduced again. Then the catalysts were impregnated with the $AgNO_3$ solution. The total content of the metals in the (n-x)PtxAg/CeO_2, (n), was 2 wt%, and x was 0.5, 1.0 or 1.5 wt%. Then all samples were dried in air at 120 °C and reduced in 10%H_2/Ar flow at 300 °C. The catalysts were characterized by the low-temperature N_2 sorption, XRD, Raman and UV-vis DR spectroscopies, pulse CO adsorption, temperature-programmed reduction and oxidation. The catalytic activity was tested in the 4-nitrophenol hydrogenation with $NaBH_4$ to aminophenol.

According to the H_2-TPR results, in the temperature range from 25 to 300 °C the increase of the metal content in the monometallic samples leads to the shift of the reduction peak maximum towards higher temperatures. However, the TPR profiles of the bimetallic catalysts contain single peak in the temperature range from 50 to 180 °C. The effect of the Pt-Ag interaction on the formation of the active sites and activity of the Pt-Ag/CeO_2 catalysts in 4-nitrophenol hydrogenation to aminophenol will be discussed.

Acknowledgement. This work was supported by the RFBR grant No. 20-33-70122.

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PP-I-3

Synthesis and Investigation of a Pt-Containing Micro-Mesoporous Catalyst for Xylene Isomerization

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Due to the growing demand of the chemical industry for aromatic hydrocarbons, there is a strong tendency to develop heterogeneous catalysts exhibiting high activity in aromatics processing. Isomerization of the C-8 aromatic fraction obtained from pyrolysis or catalytic reforming is one of traditional hydro-processing of aromatic hydrocarbons. It is usually carried out at 260–440 ^oC on bi-functional metal-containing catalysts based on zeolites at atmospheric or hydrogen pressure.

Zeolites are widely used as heterogeneous catalysts in the oil industry due to their high activity in the reactions occurring on acid sites. Catalytic activity and selectivity are significantly influenced by size and shape of zeolite pores, as well as the nature and stability of acid sites. In particular, H-ZSM-5 type zeolite constituting of channel structures formed by 10-membered rings contains many homogeneous microporous structures and possesses high acidity, which enables application of the material in acid catalysis. However, microporous structure of H-ZSM-5 prevents large molecules from efficient diffusion during catalytic process, which leads to blocking of the inlets in the active sites and, as a result, to a decrease in catalytic activity. To solve this problem, catalysts based on micro-mesoporous materials can be used. Such materials formed by micro-mesoporous nanostructures, can allow not only to facilitate diffusion of large molecules into pores, but also to increase significantly mechanical and thermal stability of the catalysts [1-3]. To reduce the cost of such materials, we suggest using a natural mesoporous clay mineral – halloysite nanotubes.

The structure and chemical composition of halloysite are close to those of kaolinite, the main difference is that aluminosilicate layers in halloysite are rolled and separated by water molecules. Alumina and silica in the rolled structure of halloysite are correspondingly located on inner/outer surfaces of the nanotube. Due to their different ionization and dielectric properties, the outer surface is negatively charged, and the inner surface has a positive charge [4,5].

Within this work we have synthesized a new functional micro-mesoporous material based on halloysite nanotubes (HNT) and zeolite of ZSM-5 type. The catalyst support was prepared by adding boehmite to the as-synthesized functional micro-mesoporous material in 60/40 wt. % ratio and further extrusion of the resulting substance. After platinum addition (0.5 wt. %) we obtained a catalyst of the following composition: Pt/H-ZSM-5 + HNT/Al_2O_3.

The composition and structure of the synthesized catalyst were studied by X-ray fluorescent analysis (XRF), low-temperature nitrogen adsorption/desorption, transmission electron microscopy (TEM), and temperature-programmed ammonia desorption (TPD-NH_3).

H-ZSM-5+HNT micro-mesoporous material has a high specific surface area (188 $m^2\,g^{-1}$). Though, it appreciably decreased after platinum deposition, with could be explained by blocking of zeolite pores by metal particles. Nitrogen adsorption-desorption curves for all the samples are of the IV type with a hysteresis loop which indicates that the micro-mesoporous structure was saved at all the steps of the synthesis.

The activity and selectivity of the obtained catalyst in isomerization of xylene fraction was investigated in a flow-type laboratory unit with a fixed catalyst bed in the temperature range of 240–460 °C under hydrogen pressure of 1 MPa. At 400°C in the presence of Pt/H-ZSM-5 + HNT/Al_2O_3, the conversions of m-xylene and ethylbenzene were 40 and 81 %. The highest selectivity to p-xylene (81 %) was obtained over Pt/H-ZSM-5 + HNT/Al_2O_3 catalyst at 380 °C. With increasing temperature, the selectivity to o- and p-xylenes decreased. It may be connected with xylene dealkylation reactions with formation of benzene and toluene. The amount of benzene and toluene also correlated with the concentration of methane and ethane in gaseous reaction products, which reaffirms the occurrence of dealkylation.

Acknowledgement. The reported study was funded by RFBR according to the research project № 20-38-90267\20.

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PP-I-4

Titanium Dioxide Nanotubes Modification in Hot Hydrogen Steam

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Nanoscale structures of titanium dioxide (TiO_2) are widely studied for their use in photocatalysis, both for the oxidation of harmful organic substances and for the synthesis of new organic molecules at the visible range of light. At present time, the fabrication of ordered TiO_2 nanotubular structures lays under a great focus of researchers due to their superior performance over TiO2 nanoparticles. So, this study is aimed at the synthesis and modification of TiO2 nanotubes for organic synthesis in dehydrogenative cross-coupling of (hetero) arenes.

Nanotubes of TiO_2 were synthesized by anodic oxidation of 100 µm thick titanium foil using "Digma" setup with an electrochemical cell, thermostat and power supply. It is carried out at ambient temperature and a 60 V voltage for 60 min in electrolyte of ethylene glycol with fluorine (0.5 wt.% NH_4F). Corrosion-resistant steel was chosen as the cathode material. Subsequent mechanical separation from the titanium foil and annealing was performed to obtain crystalline non-stoichiometric titanium dioxide. The annealing of TiO_2 nanotubes was carried out in a stream of hydrogen (from device of the generator of pure hydrogen GPH-12A) within 1 h (in furnace MTF-2MP) at temperatures of 350 °C.

The X-ray diffraction patterns of the synthesized TiO_2 nanotubes before and after annealing in a hydrogen stream were obtained on a STADI (STOE) diffractometer in Cu$K\alpha_1$ radiation with PSD in Bragg-Brentano geometry in stepwise scanning mode with $\Delta(2\theta) = 0.015^\circ$ in the 2ϑ (10°-80°) angular range. High-resolution scanning electron microscopy Sigma VP (Carl Zeiss) was used to study the morphology of the TiO_2. The band gap (E_g) was calculated using the Kubelka-Munk function from the spectra of diffuse optical reflection recorded on an Edinburgh Instruments FS-5 spectrophotometer. The measurement of the specific surface was carried out by the BET method using Gemini VII 2390 analyzer.

It was established that synthesized TiO_2 have an amorphous structure. The annealing at 350 °C phase transforms from amorphous structure to anatase. The specific surface area and the band gap increases when going from amorphous to anatase phase from 14 to 54 m^2/g and from 3.8 to 3.2 eV, respectively.

The modified TiO_2 samples will be tested in the oxidative S_N^H cross-coupling of acridine with indole under the same experimental conditions like it was done in [1].

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PP-I-5

Kinetic Regularities of Methane Dry Reforming Reaction over Bimetallic Catalysts Based on Ceria-Zirconia Prepared by Supercritical Synthesis

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It is known that the methane dry reforming process is very promising way to produce synthesis gas using carbon dioxide and methane, which are co-called greenhouse gases [1].

In recent years, Ni-containing catalysts are attractive due to low cost. Nevertheless, there are some disadvantages as high coke formation and Ni sintering. The solution of these problems is Ni deposition on the support with high oxygen mobility such as $Ce_{1-x}Zr_xO_2$.

It is worth noting that the method of support preparation has important role. Thus, in our work [2], it was shown that the technique in supercritical medium allows to obtain mixed oxide with high Ni distribution.

This work is devoted to obtain bimetallic catalysts based on Ni-containing ceria-zirconia. Cobalt and copper were also deposited on the support surface. All samples have been prepared in supercritical medium (isopropanol) using flow-type installation followed by impregnation with nickel, cobalt and copper nitrates. The reference Ni-containing sample (without Co and Cu) was prepared by the polymeric precursor method (Pechini).

Catalysts and supports were investigated by a complex of physicochemical methods (XRD, BET, SEM). It was shown that all supports have a fluorite structure of ceria-zirconia solid solution without impurity phases. The oxide crystallites are 10-20 nm in size.

All catalysts have been studied in methane dry reforming reaction in flow-type installation. Samples were pretreated before process in 10 vol.% O_2/N_2 at 600 °C during 30 minutes and reduced in 5 vol.H_2/He at 600 °C during 1 hour. The reaction was carried out at contact time of 7.5 and 10 ms, temperature range 600-750 °C, initial mixture: 15 vol.% CH_4 + 15 vol.% CO_2 + N_2 balance.

Reagents conversions, product yields, H_2/CO ratio have been evaluated. It was shown that metal doping influences on catalytic activity and stability. It was revealed that Ni-containing catalyst prepared in supercritical isopropanol showed higher activity than sample prepared by conventional Pechini method.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 18-73-10167.

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PP-I-6

Hydrothermal Synthesis of Samarium-Containing Layered Double Hydroxide

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Layered double hydroxides (LDH), also called hydrotalcite-like compounds or anionic clays, consist of positive charged brucite-like layers, in which part of divalent cations are isomorphically substituted by trivalent ones. Positive charge of layers is balanced by anions located in interlamellar space. LDHs can be described by the general formula $[M(II)_{1-x} M(III)_x (OH)_2]^{x+} [A^{n-}_{x/n}\cdot yH_2O]^{x-}$, where M(II) and M(III) are divalent and trivalent metal cations respectively, and A^{n-} is n-valent anion. Layered double hydroxides have notable ability to vary widely cationic and anionic composition, which allows synthesizing materials with predetermined properties [1]. Thereby, the application area of LDHs is highly extensive.

In recent years significant attention is paid to the incorporation of rare earth elements into hydrotalcite-like structure to obtain novel materials with specific properties, such as catalytic, optical or electrical ones [2]. Among lanthanide containing LDHs samarium-doped materials are rarest. There are only few publications dedicated to these compounds, e.g. [3]. Meanwhile, samarium loaded compounds were reported to demonstrate photocatalytic properties [4].

In the present study Ni/AlSm layered double hydroxide was obtained via coprecipitation method followed by hydrothermal treatment. The technique and synthesis conditions were chosen based on our previous work [5], in which Ni/AlCe LDH was synthesized. Predetermined M(II)/M(III) molar ratio and trivalent cation molar ratio were equal to 3 and 0,05 respectively. The obtained sample was investigated by powder X-ray diffraction, energy-dispersive X-ray spectroscopy and scanning electron microscopy.

X-ray diffraction (Fig.1) shows that the synthesized material has hydrotalcite-like structure and the presence of impurity phases is not observed. However its crystallinity is low. Crystal lattice parameters were determined using PDXL program: *a* = 3,065 Å, *c* = 23,864 Å. According to EDX data, the sample contains samarium and its amount corresponds to that which was set before synthesis. Thus, there is valid reason to affirm that incorporation of samarium into LDH structure was successful.

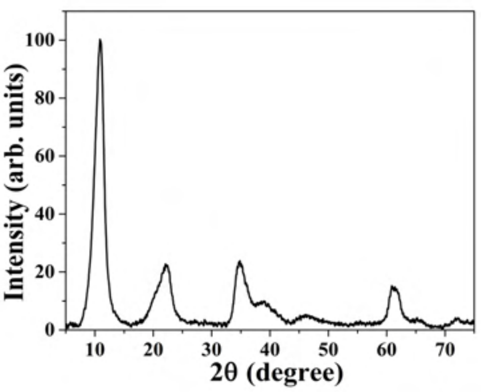

Fig.1. PXRD pattern of Ni/AlSm layered double hydroxide

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PP-I-7

Integrated Extraction-Catalytic Processing of Mechanically Activated Pine Bark

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Bark wood wastes are a major problem of wood processing enterprises, where they accumulating on large scale. A number of studies conducted aiming to develop methods of valorization products from the bark [1, 2]. The aim of this research is to develop the fundamental scientific foundations of a new environmentally friendly integrated extraction-catalytic technology of pine bark-wood waste processing into a range of chemical products with high added value [3, 4].

The effect on the yield and properties of obtained resinous, pectin substances and β-sitosterol with mechanical activation of pine bark by explosive autohydrolysis and mechanical pretreatment in a drum mill studied by IRS, 1H-NMR and GC-MS methods. Analysis of the pine bark samples after activation with IRS, XPS and CHNSO provided an insight to physicochemical properties. Experimental modeling and optimization helped to determine the conditions of processing activated pine bark samples leading to the greatest increase in the yield of extractives. That occurs during extraction of explosive autohydrolysed samples with hexane for 10 hours with following usage of 0.5 N alkali solution saponification to obtain the maximum yield of β-sitosterol; for extraction of pectin substances, the most advantageous is the use of 1% hydrochloric acid solution, which provide the highest yield of target products.

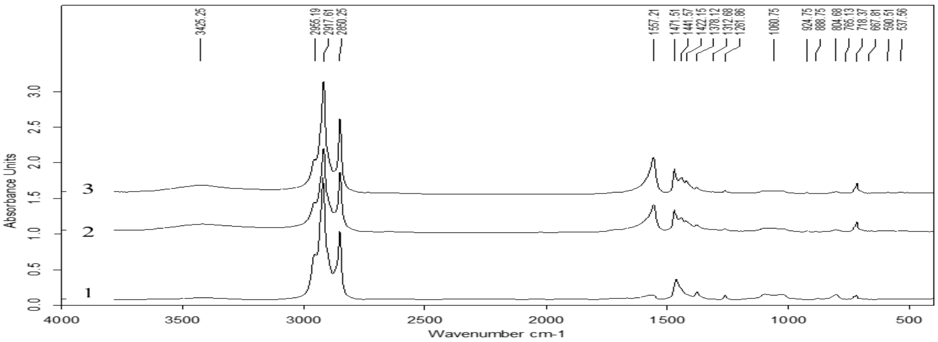

Fig. 1. IR spectrum of β-sitosterol isolated from the original pine bark (1) and its activation products (2, 3): 2 - activation by explosive autohydrolysis under the following conditions: 120 ºC, time 30 s, water vapor pressure 1.0 MPa; 3 - activation in a drum mill for 1 hour.

Additionly, series of Ru-containing catalysts on a carbon support also produced, differing in the acidity of the support and the content of ruthenium, followed by their physicochemical studies and testing in the lignocellulose reductive catalytic fractionation processing of the used pine bark samples for phenols from lignin and holocellulose in an ethanol / water medium. As a result, the presence of a catalyst in the reaction medium revealed to intensify the hydrodeoxygenation process, especially with high amount ruthenium containment in the catalyst. The analysis of the molecular weight distribution showed that in the course of hydrogenation on a catalyst of 1% Ru / C, compounds with an average molecular weight (Mw) of 1001 g / mol and a polydisperity of 2.82

formation. Finally, presence of a 3% Ru / C catalyst leads to decrease in the average molecular weight of liquid products to 855 g / mol, but the polydispersity rises to 3.75.

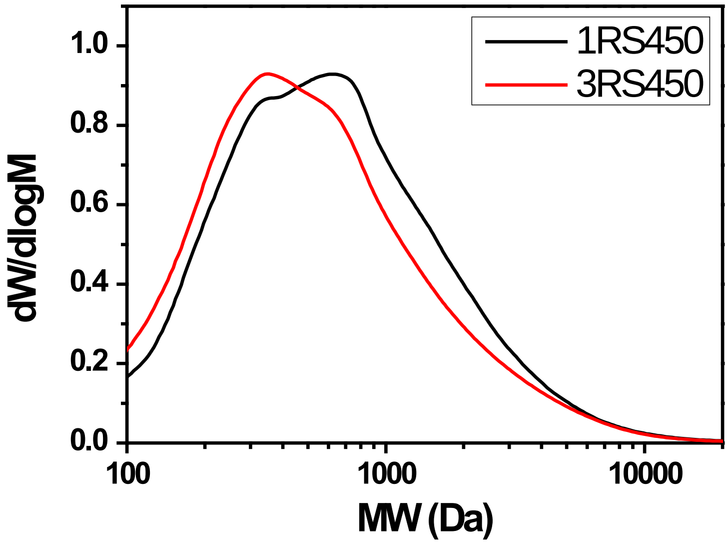

Fig. 2. Curves of the molecular weight liquid products distribution obtained by pine bark hydrogenation with presence of 1% and 3% Ru / C.

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PP-I-8

Synthesis of $Pt^{20}/SnO_2^x/C$ – Electrocatalysts by Magnetron Sputtering of Tin in an Oxygen Environment

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The reduction of carbon-support degradation during operating time is a major task of polymer electrolyte membrane fuel cells (PEMFCs) lifetime prolongation. The promising strategy aimed to mitigate carbon supports limitations is using of carbon-based hybrid supports. One of the most attractive materials is a tin oxide (SnO_2) owing to its availability, cost-effectiveness, and non-toxicity [1-3]. High durability of the $Pt-SnO_2$-based catalysts is attributed to the strong metal-support interaction (SMSI) that inhibits migration and agglomeration of the nanoparticles at the electrode surface [3]. The tin oxide-carbon composites are attractive due to their high oxidation resistance properties, as well as an improved electrochemical activity for the oxygen reduction reaction (ORR) as compared to Pt/C [4].

The uniformly distributed coating of tin dioxide on the carbon support surface can significantly improve the durability of the catalytic layers and reduce the degree of degradation of the catalyst. However, if the carbon surface is totally covered by the oxide phase, the semi-conductive behaviour of tin oxide sharply decreases the support of electrical conductivity [5]. For formation the uniformly distributed coating of tin dioxide on the carbon support magnetron sputtering (MS) method can be used. Magnetron sputtering is recognized as a convenient method for Pt deposition in PEM fuel cell applications. During the process, the deposited platinum particles form a thin nanostructured metallic film at the surface [6]. There are strong mechanical and electronic interactions between platinum particles and the carbon support and this is beneficial to reduce the catalyst degradation during accelerated stress-test [7].

The use of the MS method for the synthesis of $Pt^{20}/SnO_2^x/C$-electrocatalyst hybrid support resulted in a uniform coating of carbon support by tin dioxide with a strong interaction of which increased the resistance of catalysts to degradation. The obtained samples were also compared with electrocatalysts of a similar composition obtained by chemical reduction methods (CR) [8].

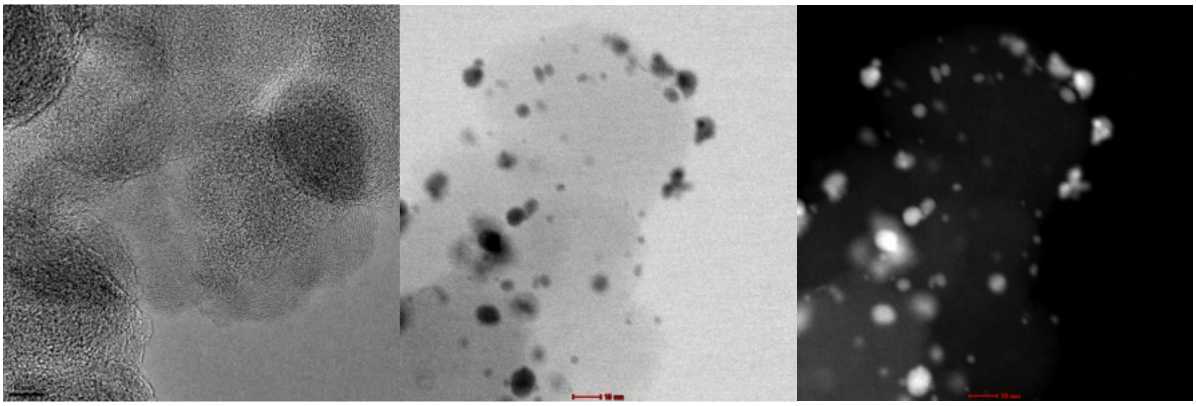
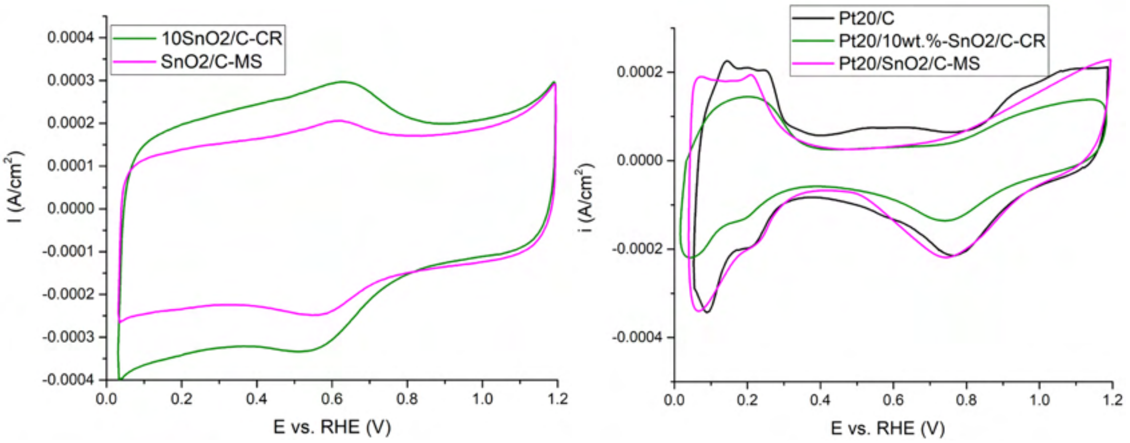

A B C

Fig. 1. TEM-images of SnO_2^x/C-MS (A) and $Pt^{20}/SnO_2^x/C$-MS (B, C) (scale bar 10 nm).



A B

Fig. 2. CVs of SnO_2^x/C-MS (A) and Pt^{20}/SnO_2^x/C-MS (B) vs SnO_2^{10}/C-CR (A) and Pt^{20}/SnO_2^{10}/C-CR (B). CVs of SnO_2^{10}/C-CR and Pt^{20}/SnO_2^{10}/C-CR

Hybrid support SnO_2^x/C-MS was synthesized according to the sputtering methods described earlier [7, 8]. A pulsed sputtering with a frequency of 100 kHz was used. Magnetron current was 0.19-0.22 A, voltage - 450 V, working gases = argon +oxygen, gases pressure – 7 x10^{-3} mbar. We chose bipolar pulsed direct current magnetron sputtering with pulsed frequency 100 kHz as the mode for hybrid support SnO_2^x/C-MS synthesis as in our previous reports [7]. Pt^{20}/SnO_2^x/C-MS was made using the chemical reduction method as in Ref. [8]. Sputtered time was 15 min.

The uniformly distributed coating of tin dioxide particles with an average size of 1 nm (fig. 1B, 1C) was made by MS. The average size of Pt-particles was 3.2 nm. However, the low concentration of tin dioxide (1 wt. % by EDX) and the small size of the SnO_2-particles did not allow the formation of stable hetero clusters Pt- SnO_2 on the surface vs Pt^{20}/SnO_2^{10}/C from Ref. [8]. Small peaks at around 0.59 and 0.71 V vs NHE (Fig. 2A) on the cyclic voltammograms (CVs) are assigned to the adsorption and desorption of oxygen-containing species resulting from the dissociation of water on SnO_2. The presence of clear peaks in a hydrogen desorption region of CVs (Fig. 2B) and high values of the electrochemically active surface area of platinum for Pt^{20}/SnO_2^x/C-MS (67 m^2/g) vs Pt^{20}/SnO_2^{10}/C CR (53 m^2/g from Ref. [8]) evidence about the no attraction between platinum and tin dioxide particles on the carbon-support. The obtained results are in good agreement with TEM-study.

To update these results, we need to extend the duration of deposition.

Acknowledgement. This study was supported by National Research Centre "Kurchatov Institute" (directive No 1919 from 25.09.2020, subprogram 6) and Russian Foundation for Basic Research according to the research project No 18-29-23030.

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PP-I-9

Synthesis of Core – Shell Zeolite Composites

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Zeolite-based catalysts are widely used in the petrochemical and refinery processes due to a high surface area and acidity. However, too strong catalyst acidity often leads to rapid catalyst deactivation because of coke formation resulted from side reactions [1]. For example, alkylation of isobutane with olefins requires strong acidity of zeolite to obtain the desired product, but the catalyst lifetime is extremely short [2]. To slow down surface coking and to prolong catalyst lifetime for this type of reactions, the authors propose to apply the zeolite core-shell composites which can be used to control the zeolite external surface acidity and diffusion of substances to active sites [3]. The composite obtaining includes the following main stages: synthesis of the micron-sized "core" crystals with high acidity, synthesis of the "shell" seeds (nano-sized crystals) with low acidity, covering the "core" micron-sized crystals with "shell" nano-sized crystals with subsequent growth of the homogeneous shell [4].

Thus, we have been developing a method for the preparation of a core-shell zeolite composite based on BEA ("core") and MFI ("shell") structure types. For this purpose, we determine the optimal synthesis conditions to produce both nano-sized Silicalite-1 and micron-sized zeolite Beta crystals, as well as searching the conditions for covering the "core" crystals with "shell" particles and subsequent "shell" growth.

We have carried out the number of syntheses of nanosized Silicalite-1 crystals and micron-sized zeolite Beta crystals by varying a temperature and time of hydrothermal synthesis (HTS) as well as precursor mixture compositions. Silicalite-1 crystals of 100 nm in size are determined to be synthesized at the following conditions: molar composition is $1SiO_2$: 0,244 TPAOH: 0,045 Na_2O: 11,4 H_2O, HTS was carried out at 95°C for 48 hours. Zeolite Beta crystals with a size of about 4-5 μm were synthesized at the following conditions: molar composition is 1 SiO_2 : $8,3*10^{-3}$ Al_2O_3 : 0,65 TEAOH : 0,65 HF : 10,8 H_2O, HTS was carried out at 140°C for 168 hours. XRD patterns and scanning electron microscope image of Silicalite-1 and Beta zeolite are presented in Fig. 1.

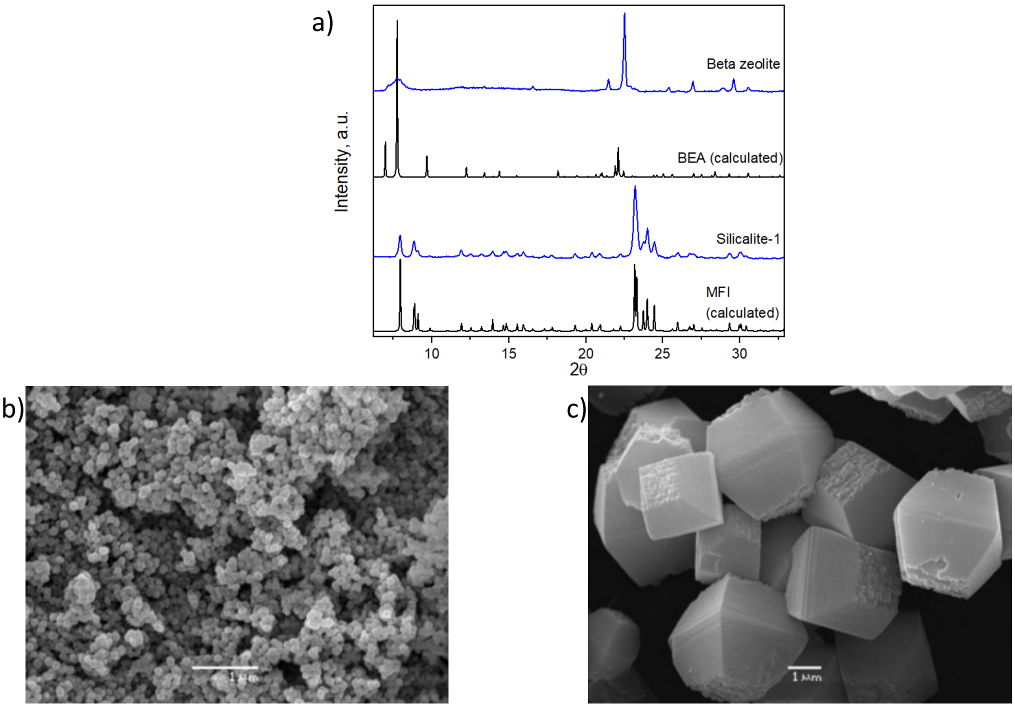

Fig. 1. a) XRD pattern of the obtained Silicalite-1 and zeolite Beta samples and calculated XRD pattern of the MFI and BEA structure types; b) SEM image of Silicalite-1 particles, c) SEM image of zeolite Beta particles

Zeolite Beta surface modification was performed using poly(diallyldimethylammonium chloride) (polyDADMAC), HTS of covered with Silicalite-1 nanocrystals "core" was carried out under varying conditions (T = 170-200 ° C, t = 60-90 min) to obtain a layer of Silicalite-1 on the Beta core. The final product of core-shell zeolite composites is shown in Fig. 2.

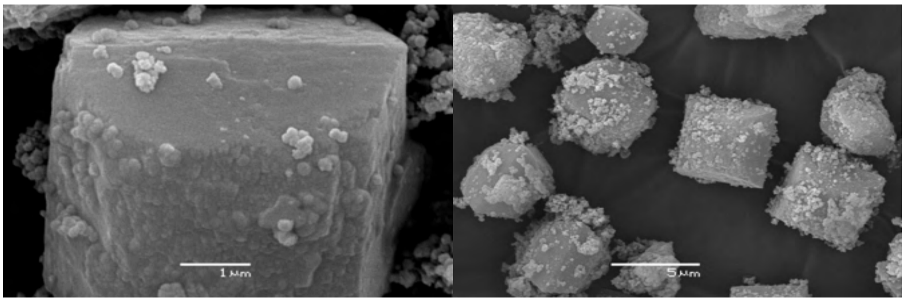

Fig. 2. SEM images of core-shell zeolite composites

In summary, core-shell composites based on zeolites BEA and MFI have been obtained. We are going to seek the optimal conditions for obtaining micron-sized Beta zeolite without using hydrofluoric acid, and test the obtained composites in the alkylation of isobutane with olefins.

Acknowledgement. The research was funded by RFBR and Novosibirsk region, project number 20-43-543036.

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PP-I-10

Synthesis of Bridging NHC Complexes of Palladium and Assessment of Their Catalytic Activity in the Buchwald-Hartwig Reaction

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One of the most common cross-coupling reaction with the formation of a C-N bond is the Buchwald-Hartwig arylamination. This commonly palladium-catalyzed reaction is often used to prepare *N*- and *N, N*-substituted arylamines – compounds, exhibiting biological activity, which therefore can be found as drug fragments. In addition to complexes with Buchwald ligands and phosphorus-containing precatalysts, NHC-based catalysts can also be used in the Buchwald-Hartwig reaction. Moreover, they show high resistance to oxygen and moisture, as well as ease of synthesis.

In this work, we have synthesized six bridging Pd-NHC complexes using published methods [1], [2], [3]; four of them (**2b, 2c, 3b, 3c**) are novel:

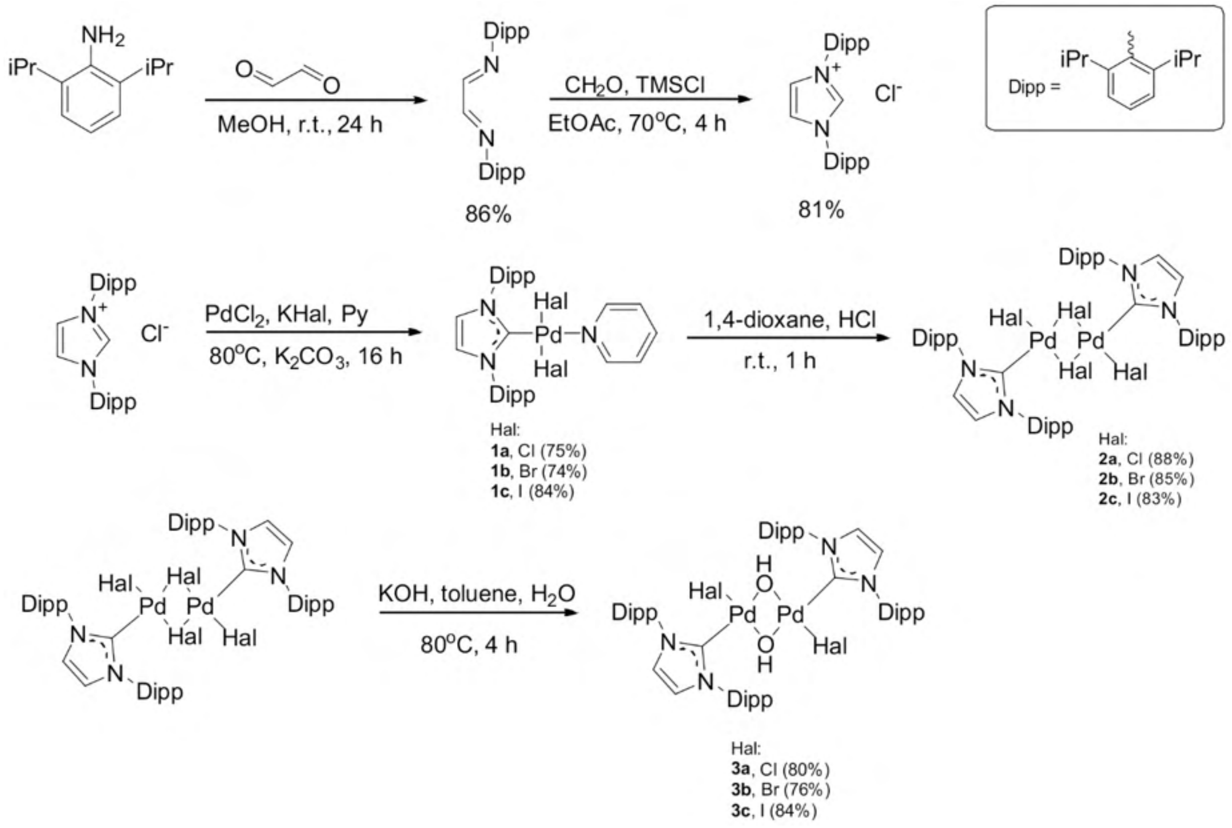
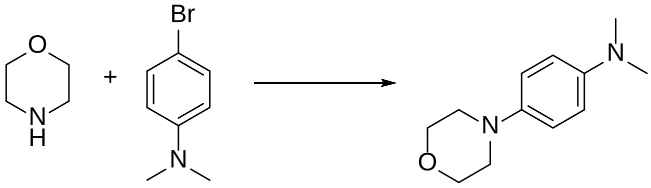


Fig. 1. Scheme of catalyst synthesis

The novel compounds structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy and mass-spectrometry. Also, single-crystal X-ray diffraction data were obtained for complexes **2a** and **2c**.

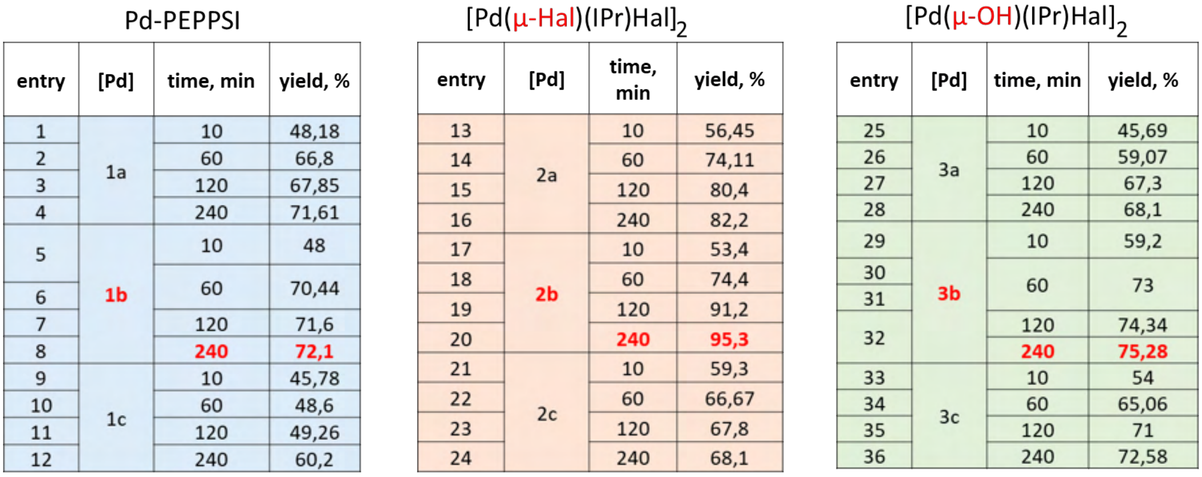
It is known from the literature that the catalytic activity of different complexes depends on the composition (PEPPSI – **p**yridine-**e**nhanced **p**recatalyst **p**reparation **s**tabilization and **i**nitiation or bridging) and the halogen in their structure. To the test the catalytic activity of the obtained complexes we needed the model reaction with specific requirements: simple substrates, high conversion (> 90%), and moderate reaction rate (around 1h untill full conversion). Reaction between morpholine and *p*-brom-*N*,*N*-dimethylaniline fully satisfies these requirements (requirements, conditions).



Conditions: morpholine 1.2 mmol, *p*-Brom-*N*,*N*-dimethylaniline 1 mmol, [Pd] 1 mol%, *t*BuOK, toluene 1 ml

Fig. 2. Model reaction for evaluating the catalytic activity of complexes

Reaction yield was measured at four time points (10, 60, 120, 240 minutes) to estimate kinetics.



Pd-PEPPSI

entry	[Pd]	time, min	yield, %
1	1a	10	48,18
2		60	66,8
3		120	67,85
4		240	71,61
5	**1b**	10	48
6		60	70,44
7		120	71,6
8		**240**	**72,1**
9	1c	10	45,78
10		60	48,6
11		120	49,26
12		240	60,2

[Pd(μ-Hal)(IPr)Hal]$_2$

entry	[Pd]	time, min	yield, %
13	2a	10	56,45
14		60	74,11
15		120	80,4
16		240	82,2
17	**2b**	10	53,4
18		60	74,4
19		120	91,2
20		**240**	**95,3**
21	2c	10	59,3
22		60	66,67
23		120	67,8
24		240	68,1

[Pd(μ-OH)(IPr)Hal]$_2$

entry	[Pd]	time, min	yield, %
25	3a	10	45,69
26		60	59,07
27		120	67,3
28		240	68,1
29	**3b**	10	59,2
30		60	73
31			
32		120	74,34
		240	**75,28**
33	3c	10	54
34		60	65,06
35		120	71
36		240	72,58

Fig. 3. Kinetic control results (Hal: a-Cl, b-Br, c-I)

The product yields were determined using the ^{1}H NMR spectroscopy. In agreement with literature [4], bromide complexes showed the highest efficiency.

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PP-I-11

Rhodium (I) Complexes of Type Rh(CO)(CN-Ad)(Bident): Synthesis, Reactivity, Electrochemistry and Catalytic Application

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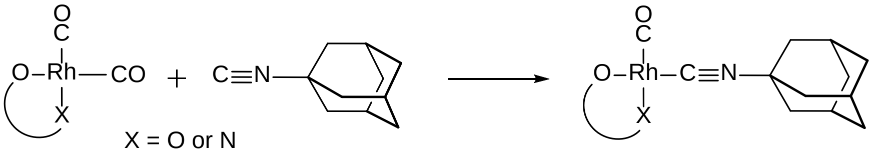
Rhodium complexes are widely used in various catalytic processes, for example, polymerization, activation/functionalization of sp^2 and sp^3 C-H bonds, heterocycles synthesis, hydrofunctionalization of alkynes, and others [1-4]. Rhodium (I) dicarbonyl $Rh(CO)_2$(bident) complexes containing various donor O,O- and N,O- bidentate ligands are promising compounds for the preparation of new rhodium catalysts. The lability of one of the carbonyl groups in these compounds allows the introduction of various donor ligands into the coordination environment of the rhodium atom, for example, isocyanide C≡N-R molecules.

Isocyanides are extremely popular synthetic reagents for many organic preparations and polymeric materials. Their organometallic complexes are catalysts and intermediates of catalytic processes. Moreover, isocyanides coordinated by a metal atom are capable of selectively attaching nitrogen- and oxygen-containing nucleophile molecules at the carbon atom of the CN-R group, forming various acyclic diamino carbene ligands, promising catalysts in organic chemistry [5]. However, the number of systematic studies on synthesis, characterization, and reactivity of isocyanide complexes containing the [Rh(bident)(CO)] fragment are limited to a few examples, there is no information on the electrochemical as well as catalytic properties of such compounds. Therefore, the study of the ability of rhodium (I) dicarbonyl complexes with O,O- and N,O- donor ligands to coordinate and activate further transformations of isocyanide molecules, study of their properties, the determination of their structure and relationship between their structures and properties are actual and promising research area.

Here we studied the possibility of rhodium (I) dicarbonyl complexes with anionic O-O and N-O bidentate ligands $Rh(bident)(CO)_2$ (bident = acetylacetone, hexafluoroacetylacetonate, thenoyltrifluoroacetone, 8-hydroxyquinolate, 1-phenyl-3-(phenylimino)butene-1-olate) to coordinate the 1-adamantyl isocyanide. The reactions performed in CH2Cl2 at room temperature showed that interactions of C≡N-Ad and $Rh(bident)(CO)_2$ results in substitution of carbonyl ligands by isocyanide molecule to give complexes of type Rh(bident)(CO)(C≡N-Ad) (Scheme 1).

PP-I-11



Scheme 1

The structural, spectroscopic (IR, NMR) characteristics of the synthesized rhodium complexes were determined. The redox properties (number of redox stages, number of electrons involved in each stage, reversibility) of complexes have been studied by dc polarography at a dropping mercury electrode, cyclic voltammetry at platinum or glassy carbon electrodes. The mechanisms of their redox reactions were established. The ability of the rhodium coordinated 1-adamantyl isocyanide ligand in Rh(bident)(CO)(C≡N-Ad) to selectively attach nitrogen-containing nucleophiles at the carbon atom of the CN-Ad group was also explored.

The influence of the nature of the bidentate ligands at the rhodium atom in the obtained complexes Rh(CO)(CN-Ad)(bident) (bident = acetylacetone, hexafluoroacetylacetonate, thenoyltrifluoroacetone, 8-hydroxyquinolate, 1-phenyl-3-(phenylimino)butene-1-olate) on their physicochemical properties, reactivity and catalytic activity in the hydrofunctionalization of phenylacetylene are discussed

Acknowledgement. This work was conducted within the framework of the budget project # 121031500209-6 for Institute of Chemistry and Chemical Technology SB RAS using the equipment of Krasnoyarsk Regional Research Equipment Centre of SB RAS.

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PP-I-12

N-Substituted α-Diphenylphosphinoglycines: Electrochemical Properties and Reactivity in the Presence of Organonickel Complexes

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Nickel complexes based on α-diphenylphosphinoglycines exhibit high catalytic activity and by varying the substituents at the nitrogen atom in these ligand, it is possible to fine-tune the molecular weight distribution of linear α-olefins, formed as a result of catalyzed homogeneous oligomerization of ethylene [1]. However, the classical method for obtaining a catalytically active form involves the use of an expensive and low stable [Ni(COD)$_2$], where COD is cycloocta-1,5-diene [2]. Guided by the principles of "green chemistry", we are developing an alternative way to obtain organonickel catalysts, based on α-diphenylphosphinoglycines - electrochemical generation.

N-(pyrazin-2-yl)- (**1**), *N*-(2,5-dimethoxycarbonylphenyl)- (**2**), *N*-(2-methoxycarbonylphenyl)- (**3**), *N*-(2-carboxylphenyl)- (**4**), *N*-(2-methoxybenzyl)- (**5**), *N*-(1-adamantyl)- (**6**) diphenylphosphinoglycines had been synthesized by reaction of three-component condensation [1]. The study of the electrochemical properties of the obtained compounds were studied by cyclic voltammetry on a glassy carbon electrode. The values of peak potentials registered in CV curves of α-diphenylphosphinoglycines are presented in Table 1.

*Table 1. Potentials of peaks on the CV curves of the obtained compounds **1**-**6** in DMF from -2.5 V to 1.5 V (substrate concentration 5 × 10^{-3} M, GC working electrode, the reference electrode is Ag/AgNO$_3$ 0.01 M in CH$_3$CN, ^{n}Bu$_4$NBF$_4$ (0.1 M), v = 50 mV/s).*

Compound	E_p^{red}, V	E_p^{ox}, V	Compound	E_p^{red}, V	E_p^{ox}, V
1	-1.90	+0.76 / +1.23 / -0.19	**4**	-	+0.72 / +0.97
2	-2.04 / -2.26	+0.77 / +1.18 /-2.11	**5**	-	+0.52 / +0.87
3	-2.21	+0.82 / +1.12 / -2.14	**6**	-	+0.70

Diphenylphosphinoglycines **1–6** exhibited electrochemical activity in the anodic region of potentials due to the presence of an oxidizable diphenylphosphine fragment in the molecule. Compounds **1-3** can also be electrochemically reduced at the cathodic potentials of the working electrode due to the pyrazine (**1**) and the ester groups (**2**, **3**) in the aromatic fragment [3, 4]. However, all compounds **1-6** are inactive in the region of electrochemical generation potentials complexes of Ni(0), which makes them promising objects or the electrochemical production of active forms of organonickel catalysts for ethylene oligomerization.

The addition of α-diphenylphosphinoglycines (1st, 2nd and 3rd equivalents) to solutions of stable nickel complexes changes the morphology of the CV curve (Table 2).

Table 2. Potentials of peaks on the CV curves some complexes of Ni(II) in the presence of the obtained compounds in DMF from 0 V to -2.5 V (substrate concentration 5×10^{-3} M, GC working electrode, the reference electrode is $Ag/AgNO_3$ 0.01 M in CH_3CN, $^nBu_4NBF_4$ (0.1 M), v = 50 mV/s, potential of new peak in bold).

Compound	**Amount of ligand**	**E_p^{red}, V**	**E_p^{ox}, V**
$NiBr_2$ +	1st equivalent **1**	-1.41 / **-1.97**	-
	2nd equivalent **1**	-1.40 / **-2.02**	-
	3rd equivalent **1**	-1.37 / **-2.06**	-
[$NiBr_2$bpy] +	1st equivalent **4**	-1.41 / **-1.82** / -2.19	-2.10
	2nd equivalent **4**	-1.41 / **-1.90** / -2.17	-2.09
	3rd equivalent **4**	-1.44 / **-2.07** / -2.23	-2.12
[$NiBr_2(bpy)_2$] +	1st equivalent **3**	-1.46 / **-1.74** / -2.21	-2.14
	2nd equivalent **3**	-1.52 / **-1.81** / -2.25	-2.13
	3rd equivalent **3**	-1.55 / **-1.86** / -2.27	-2.14

The table shows three examples where a new reduction peak (in bold) can be observed in the cathodic region. When increasing amounts of compound **1** are added to a solution of $NiBr_2$, **3** to a solution of [$NiBr_2(bpy)_2$] and **4** to a solution of [$NiBr_2$bpy], a new reduction peak corresponds to the formation of a nickel complex, according to the literature [5].

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 19-29-08051.

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PP-I-13

Porous Anodic Alumina as a Catalyst Carrier with Hierarchical Porosity

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Aluminum anodization in acidic media leads to the formation of porous anodic aluminum oxide (AAO) on the metal surface. AAO can be represented as a solid film containing an array of cylindrical pores aligned parallel to the film normal. As-prepared AAO is unstable in acidic and alkaline solutions. The AAO chemical resistance can be significantly improved by annealing of the porous films in the temperature range of 800–1000 °C, owing to the crystallization of initially amorphous AAO into the low-temperature alumina polymorphs. After annealing, the specific surface area of AAO increases significantly owing to the formation of mesopores in the cell walls at moderate annealing temperatures. It is believed that the presence of mesopores can enhance AAO efficiency when it is used as a catalyst carrier.

Here, we present a comprehensive investigation of the annealing behavior of AAO, obtained by Al anodization in different electrolytes. Porous structure, phase composition, and surface morphology of thermally treated AAO are studied in detail.

AAO films were prepared by aluminum anodization at the temperature of 1 °C in 0.3 M sulfuric acid at 25 V, in 0.3 M oxalic acid at 40 and 120 V, and in 0.1 M phosphoric acid at 185 V. After selective aluminum dissolution, 50-µm-thick porous alumina films with pore diameter from 25 to 250 nm and the through porosity of about 20% were obtained.

X-ray diffraction (XRD) analysis was performed at the beamline ID22 (ESRF). The full-profile refinement was carried out by the derivative difference method implemented in the DDM software. Selective anisotropic peak broadening correction due to structural imperfections was performed. As a result, the temperature dependence of the phase composition of AAO (oxalic acid, 120 V) was determined quantitatively [1]. Amorphous AAO crystallizes to γ-Al_2O_3 with a small part of θ-Al_2O_3 at 750 °C. Above 800 °C, a gradual transformation of γ-Al_2O_3 to δ-Al_2O_3 takes place. Finally, all low-temperature alumina polymorphs transform to α-Al_2O_3 at 1000–1100 °C. Proper choice of an annealing protocol for AAO crystallization into the corundum phase allows one to preserve its starting morphology. As a result, polycrystalline alumina films consisting of nanoporous corundum single crystals with an average size of ca. 5÷10 µm were obtained [2].

The first phase transition of AAO into the mixture of low-temperature alumina polymorphs induces the main stage of electrolyte impurities decomposition, followed by their elimination in the form of CO_2 in the case of oxalic acid anodization. The impurities removal leads to a rapid increase in the specific surface area (S_a). The initially smooth surface of the cell walls becomes rough (Fig. 1a). The AAO films annealed at 750–950 °C consist of crystalline particles of low-temperature alumina polymorphs with an average size of about 15 nm. Mesopores with complex geometry are observed between the particles. According to nitrogen adsorption-desorption isotherms recalculated using the BJH approach, the mean diameter of mesopores after AAO thermal treatment is about 4 nm with a slight increase with an increase in annealing temperature. The highest S_a values reach 70 m^2/g for AAO (oxalic acid, 40 V) after thermal treatment at 750 °C (Fig. 1b). We stress that the specific surface area may be tuned up to 100 m^2/g by varying both time and temperature of annealing.

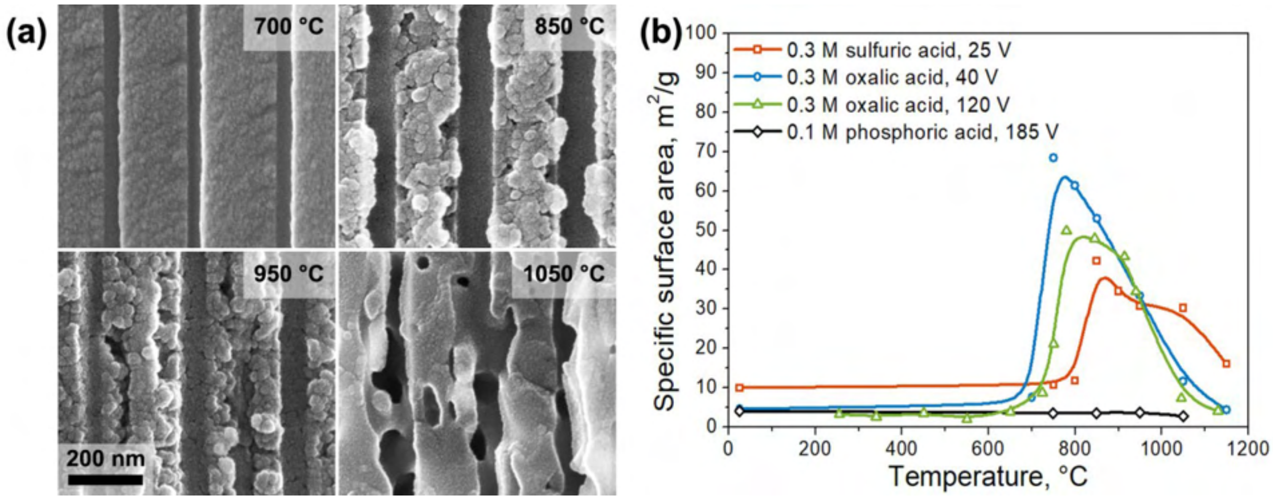

Fig. 1. Cross-section SEM images of the mesoporous structure of AAO cell walls (a). The specific surface area of AAO subjected to annealing at the temperature range up to 1200 °C for 24 h (b).

Based on the AAO films with a hierarchical porous structure (electrochemically formed 100-nm-size channels with mesopores in their walls), the microhotplate catalytic sensors were designed [3]. Bimetallic Pd-Pt catalytic nanoparticles were successfully embedded into AAO channels, and their uniform distribution through the thickness of the porous film is achieved. The response of the sensor nodes in methane detection approached the value of 15 mV/vol. % CH_4 at a bridge supply voltage of 3.9 V, corresponding to the temperature of the active area of about 400 °C. An untypical wide hysteresis in the sensor response for methane detection was observed. According to *operando* analysis using XRD and thermogravimetry in an air-methane atmosphere, the hysteresis is arisen from the different PdO_x/Pd ratio during the forward and reverse sweep.

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PP-I-14

Methods for Obtaining Cross-Linked Polymer Particles and Their Prospects for Application in Pseudo-Homogeneous Catalysis

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The interest toward homogeneous catalysts immobilized on the particles of colloidal dimensions has motivated numerous investigations in the field of preparation of various potentially perspective materials[1]. Polymeric particle are considered as one of such potential carrier for the catalyst due to their ease of functionalization, wide variety of possible sizes and chemical composition, ease of separation by centrifugation or filtration[2]. Moreover, the particles can be modified by magnetic nanoparticles to allow magnetic separation. However often for the catalytic applications the polymeric particles must withstand "hard" solvents and to be stable at elevated temperatures. Polymeric particles with such properties are usually polymerized in the presence of high amount of cross-linking agent. However, a significant drawback of such method, especially in dispersion polymerization, is the uncontrolled aggregation of particles and a high value of the polydispersity coefficient of the resulting particles.

In this work we have prepared the highly cross-linked particles by the following methods: dispersion polymerization, dynamic swelling, seeded polymerization, precipitation polymerization. Further, the particles were modified by magnetic nanoparticles to make them susceptible to the permanent magnetic field.

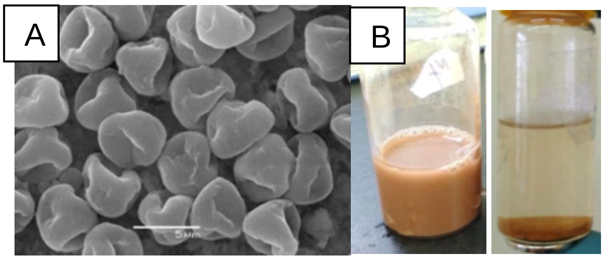

Fig. 1. A – SEM image of hollow polymeric particles prepared by two-stage swelling method; B – polymeric magnetic particles water suspension in the absence and the presence of the permanent magnet

Prepared highly-cross-linked particles withstand "hard" solvents, such as toluene, acetone at the elevated temperature, at least up to 60°C. Magnetic polymeric particles can be separated from their water suspension by Nd-Fe-B magnet with a holding strength 20.65 kg within two-three minutes.

Acknowledgement. This work was supported by Ministry of Science and Higher Education of the Russian Federation

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PP-I-15

Bimetallic Pt-Ag/MCM-41 Catalysts for 4-Nitrophenol Reduction to 4-Aminophenol

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Supported Pt catalysts are widely used in various types of reduction reactions, including selective reduction of aromatic nitrocompounds into corresponding amines. The introduction of the second component (e.g., less expensive Ag) to Pt that can improve the catalytic properties of the supported metal catalysts due to the appearance of the synergistic effects between the metals is widely discussed in the literature [1, 2]. The using of mesoporous structured materials, such as MCM-41, as a support may be one of the approaches to form small-sized bimetallic Pt-Ag particles. Their structure comprises ordered hexagonal packing of open cylindrical pores with a diameter of 3-4 nm that can act as "nanoreactors" for the formation of bimetallic Pt-Ag particles.

The aim of this work was to synthesize the MCM-41-supported bimetallic Pt-Ag catalysts with different metal ratios and to establish the effect of the interaction of the supported components on the physical-chemical characteristics, catalyst reactivity in TPR-H_2, and catalytic properties in the 4-nitrophenol reduction to 4-aminophenol.

The MCM-41 support was synthesized by the hydrothermal method from industrial sodium silicate ($SiO_2/Na_2O \approx 3$) with the CTAB addition as a template [3]. The prepared MCM-41 was characterized by high specific surface area (1134 m^2/g) and a narrow pore size distribution (3.6 nm). Bimetallic catalysts were prepared by sequential incipient impregnation with aqueous solutions of H_2PtCl_6 and $AgNO_3$ of appropriate concentrations. During the synthesis, the MCM-41 support was impregnated with H_2PtCl_6 solution, dried and calcined at 500 °C to remove chlorine in order to avoid the formation of insoluble AgCl.

The synthesized Pt catalysts (Pt/MCM-41 sample and reference samples 0.5Pt/MCM-41 and 0.2Pt/MCM-41) were reduced in a 10% H_2/Ar mixture at 500 °C. The obtained 0.5Pt/MCM-41 and 0.2Pt/MCM-41 catalysts were impregnated with $AgNO_3$ solution dried and calcined at 600 °C (0.5 Pt-0.5Ag/MCM-41 and 0.2Pt-0.8Ag/MCM-41). Thus, a series of mono- and bimetallic catalysts (Ag/MCM-41, Pt/MCM-41, and Pt-Ag/MCM-41) with a mass content of metals of 4.71 wt% was obtained.

Table 1. Metal content and textural characteristics of the prepared support and catalysts on the basis thereof.

Sample	w (Pt), wt.%	w (Ag), wt.%	S_{sp}(BET), m^2/g	V_{pore}, cm^3/g
MCM-41	-	-	1134	1.14
Ag/MCM-41	-	4.71	906	0.85
Pt/MCM-41	4.71	-	855	0.61
0.2Pt-0.8Ag/MCM-41	1.48	3.23	824	0.60
0.5Pt-0.5Ag/MCM-41	3.06	1.65	820	0.60

The textural characteristics of the Pt-Ag/MCM-41 catalysts were investigated by low-temperature N_2 adsorption. It was shown that with an increase in the Pt content, the specific surface area (S_{sp}) of the samples decreased to up to 855 m^2/g for Pt/MCM-41 sample. For Ag/MCM-41 catalyst, S_{sp} was 906 m^2/g. The Pt-Ag/MCM-41 catalysts were characterized by close S_{sp} values of 820-824 m^2/g and the average pore diameter d_{pore} of 3.4 nm calculated using the BJH-desorption method.

The reactivity of the samples was investigated by the TPR-H_2 method. The preoxidized samples of mono- and bimetallic catalysts were reduced in 10% H_2/Ar mixture to up to 600 °C at a rate of 10 rpm. The reduction of the Pt/MCM-41 catalysts occurred in the range of 25-200 °C with a maximal H_2 consumption at 88-90 °C (reduction of dispersed Pt oxides) and in the range of 200-500 °C with maxima at 320 and 410-420 °C (reduction of oxidized states of platinum bonded to the substrate surface). The reduction of Ag/MCM-41 catalyst was observed in the temperature range of 0-150 °C. The reduction of bimetallic Pt-Ag/MCM-41 catalysts occurred up to 200 °C with a maximum at 130 °C. No hydrogen absorption was observed in the high-temperature region. A change in the profile and a shift in the H_2 consumption maximum indicate the presence of contact between the metals and the formation of bimetallic particles.

The bimetallic Pt-Ag/MCM-41 catalysts as well as monometallic Pt/MCM-41 and Ag/MCM-41 samples were investigated in the 4-nitrophenol reduction to 4-aminophenol at room temperature and atmospheric pressure using $NaBH_4$ as a reducing agent. The increased activity for bimetallic Ag-Pt catalysts was observed in comparison with the monometallic Ag/MCM-41 and Pt/MCM-41 catalysts.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (project No. 20-33-70122).

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PP-I-16

Effect of Copper Modification and Ce:Si Ratio on the Catalytic Properties of Mesoporous Ceria-Silica Catalysts in CO-PROX

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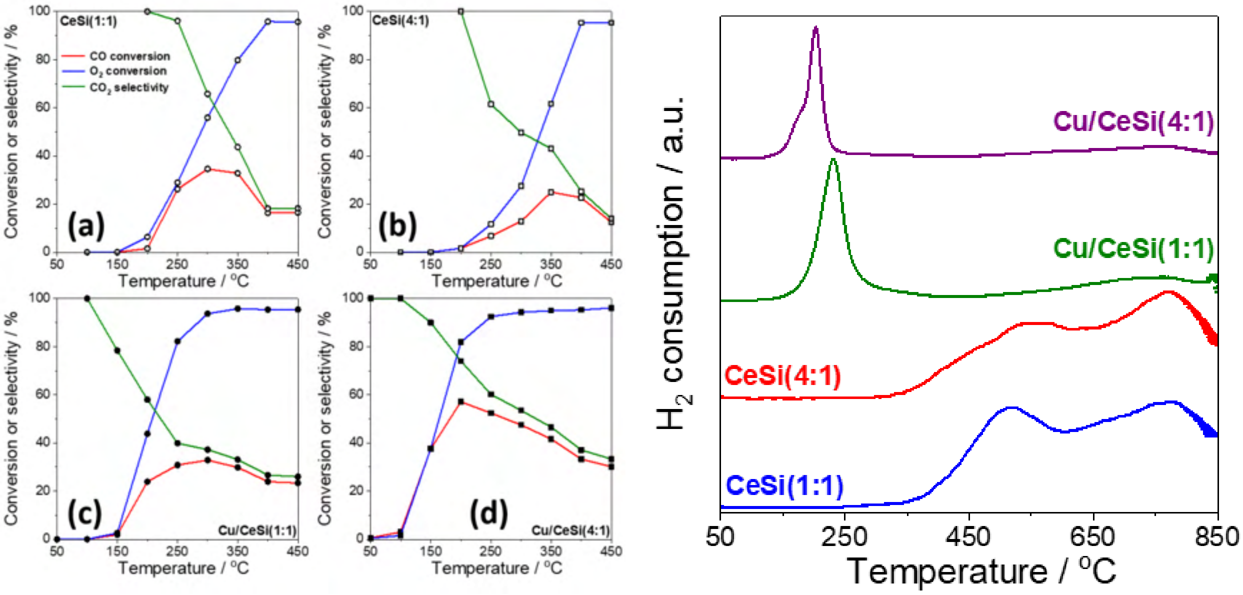
One of the most effective ways to purify gas mixtures from CO is catalytic oxidation by ceria-based systems. This process is important, for example, for the production of high-purity hydrogen used in fuel cells (the preferred CO oxidation in the presence of hydrogen excess, CO-PROX). The catalytic properties of CeO_2 in this reaction can be improved by different ways. Very efficient method is an improvement of textural properties of the oxide catalysts, which can be performed by the addition of SiO_2 to ceria. Currently, silicon dioxide has widespread application as a catalytic support and surface stabilizer with a high specific surface area [1]. Another method is the use of oxide modifiers that can positively affect the catalytic properties of ceria-based systems. Oxides of transition metals such as copper, manganese and tin are widely used in this way [2].

CeO_2-SiO_2 oxides with Ce:Si ratios of 4:1 and 1:1 were prepared in this work using CTAB as a template, tetraethoxysilane (TEOS) as a surface stabilizer and $Ce(NO_3)_3{\cdot}6H_2O$ as a cerium precursor. They were designated further as CeSi (4:1) and CeSi (1:1). Also two copper-modified samples Cu/CeSi (4:1) and Cu/CeSi (4:1) comprising 5 wt.% Cu were prepared by impregnation method using $Cu(NO_3)_2{\cdot}3H_2O$ as a copper oxide precursor. The catalytic performance of the samples in CO-PROX was studied using ULCat-1 setup equipped with fixed-bed continuous-flow stainless steel reactor (4 vol.% CO, 3 vol.% O_2, 13 vol.% N_2 and 80 vol.% H_2, 95 ml/min). The experiments were carried out in the temperature range from 50 to 450°C using 150 mg of catalyst. The reaction products and unconverted reagents were quantified by GC using Chromatec-Crystal 5000.2 ("Chromatec", Russia) with Carboxen-1010 PLOT column ("Supelco", USA).

The results of catalytic tests are presented in Fig.1 (a). It is seen that the CO and O_2 conversions were low (< 10%) on both CSi catalysts at relatively low temperatures (50-200°C). However, when the reaction temperature was raised to 250°C the CO and O_2 conversion values increased in much higher extent (to about 30%) for CeSi (1:1) while for CeSi (4:1) catalyst X(CO) and X(O_2) increased to 6% and 12% respectively. Thus, in spite of the high cerium content, the sample CeSi (4:1) provide lower CO and O_2 conversion and CO_2 selectivity values at increased temperatures. The reasons of such behaviour were studied by TPR-H_2, the results are presented in Fig.2 (b).

For non-modified CeSi systems, the first peak in the TPR-H_2 profile of CeSi (4:1) (in the range of 450 – 550°C) attributed to the surface reduction of CeO_2 is shifted to a lower temperature region in comparison with that in the profile of CeSi (1:1). It can be due to an increase in the mobility of lattice oxygen, which is important for CO oxidation proceeding through the Mars-van Krevelen mechanism.

Comparing TPR-H_2 profiles for the copper-modified catalysts, it is evident, that in the profile of Cu/CeSi (4:1) the temperature of the maximum of the first reduction peak (attributed to copper reduction) is shifted to the lower temperature region in comparison with that for Cu/CeSi (1:1), possibly due to stronger synergetic interaction between copper and a support. Moreover, the presence of the shoulder at low temperature which was found for Cu/CeSi (4:1) confirms the presence of copper both as an individual oxide, and incorporated into the crystal lattice of CeSi, providing a positive effect on catalytic activity in the CO oxidation.



(a) *(b)*

Fig. 1. (a) CO conversion (%), O_2 conversion (%), CO_2 selectivity (%) vs reaction temperature for CeSi (1:1) – (a), CeSi (4:1) – (b), Cu/CeSi (1:1) – (c), Cu/CeSi (4:1) – (d); (b) results of TPR-H_2.

At the same time, the TPR-H_2 profile for Cu/CeSi (1:1) system has only one low-temperature peak, indicating the presence of copper only as a separate oxide phase.

Thus, it can be concluded, that In the case of non-modified CeSi systems, the most effective Ce:Si ratio to perform CO-PROX is 1:1 due to the higher mobility of lattice oxygen. In contrary, the most effective copper-modified system in CO-PROX was Cu/CeSi (4:1) due to the presence of Cu both incorporated into crystal lattice of the support, and as a separate oxide phase, which has a stronger interaction with the supporting CeSi oxide.

Further the investigation of the catalysts using XRD, XPS, microscopic methods etc. will be performed to corroborate the findings of the TPR-H_2 study.

Acknowledgement. This work was funded by the Russian Foundation for Basic Research, project number 20-33-90065. The authors acknowledge support from M.V. Lomonosov Moscow State University Program of Development.

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PP-I-17

Optimization of Synthesis Conditions of Biocatalytic Systems on the Base of Alginate Microspheres and Glucose Oxidase

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Glucose oxidase (EC 1.1.3.4; β-D-glucose: oxygen oxidoreductase) is a dimeric flavoprotein consisting of 2 identical polypetide chains covalently linked by disulfide bonds [1]. The enzyme contains 2 flavinadenindinucleotide (FAD) molecules as a coenzyme (one for each subunit of the protein molecule) and catalyzes the oxidation of β-D-glucose to D-glucono-δ-lactone (δ-glucono-1,5-lactone) and H_2O_2 using molecular oxygen as an electron acceptor [2]. In many processes, it is more appropriate to use immobilized forms of glucose oxidase, which can significantly increase its resistance to inhibitory effects, as well as provide the possibility of repeated use of the biocatalyst [3]. A number of papers describing the successful experience of immobilization of glucose oxidase on various solid carriers have been published [4].

In this work, the conditions of glucose oxidase immobilization on biodegradable and environmentally safe natural biopolymers were optimized. To immobilize glucose oxidase, two types of carriers based on sodium alginate were synthesized: macrospheres with a diameter of 2-2.5 mm obtained by the drop method; microspheres obtained by emulsification and internal gelation [5]. The resulting macrospheres were kept for 12 hours in 50 ml of a solution containing 0.394 g of carbodiimide and 0.144 g of N-hydroxysuccinimide, washed with distilled water, kept for 6 hours in a glucose oxidase solution (25 mg in 50 ml of a phosphate buffer solution with pH = 6.0), washed again with distilled water, and stored in a refrigerator at a temperature of 3±1°C.

To determine the activity, microspheres with deposited glucose oxidase were mixed with 40 ml of glucose solution (2.2 mmol/L) and the oxidation reaction was carried out under constant stirring at a temperature of 25 °C for 60 minutes with periodic sampling from the reaction mixture with a micropipette. An indicator of glucose oxidase activity was the concentration of hydrogen peroxide in the reaction mixture, which was determined by the interaction of hydrogen peroxide formed in the reaction with potassium iodide in an acidic medium and photometry of the resulting blue complex "iodine-starch".

It was found that immobilized glucose oxidase preparations have a slightly lower activity compared to its free form (by 20-30%). This is primarily due to the heterogenization of the process, as well as to the loss of the enzyme during immobilization. However, immobilization makes it easy to separate the enzyme from the reaction medium and reuse it, which compensates for the loss of activity with a single use. In addition, experiments have shown that immobilization on alginate micro- and macrospheres slightly expanded the optimal temperature and pH ranges in comparison with the soluble form of the enzyme, which indicates a higher resistance of the synthesized biocatalysts to inhibitory effects.

PP-I-17

One of the most important parameters affecting the success of enzyme immobilization on alginate spheres is the particle size. The optimal diameter for use of macrospheres is no more than 2 mm, microspheres – no more than 100 mm. As the diameter increases, the "dead volume" of the system significantly increases, in which the reaction is not carried out due to the absence of enzyme molecules in it, which significantly reduces the efficiency of the process.

The developed biocatalysts can be used in the food industry as baking improvers, in the chemical industry for producing gluconic acid, and in analytical chemistry for determining the concentration of glucose. To increase the resistance of biocatalysts to inhibitory effects, micro-and macrospheres made of sodium alginate (polyanion) can be coated with natural polycations (for example, chitosan). Such systems can be used, in particular, as drug delivery systems to certain parts of the gastrointestinal tract.

Studies have proved the effectiveness of glucose oxidase immobilization on micro- and macrospheres made of sodium alginate, the carboxyl groups of which are activated by carbodiimide and N-hydroxysuccinimide.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 18-08-00424.

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PP-I-18

Synthesis of Vanadium-Substituted Phosphorus-Molybdenum Keggin Type Heteropolyacids - Precursors for Hydroisomerization Catalysts

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Hydrotreating is one of the most important processes in the oil industry. This process removes sulfur from oil fractions and improves their quality. Since the environmental requirements for commercial fuels are becoming more stringent, it is necessary to improve the refinery process. The most perspective way to increase the efficiency of refinery hydro-processes is to apply new high active catalysts.

Commonly used hydrotreating (HDT) catalysts include Co(Ni) and Mo(W) sulfides supported on γ-Al_2O_3 and prepared by impregnation with aqueous solutions of precursors. The heteropoly compounds (HPCs) application in HDT catalysts preparation has significant positive effect [1]. The HPCs of Mo and W can include atoms of various elements and provide a synergetic effect in catalytic properties. It was proven that the addition of small amounts of vanadium to the HDT catalysts increases their activity [2]. Taking into account the available results of vanadium-containing catalysts application in refinery processes, further studies of such catalytic systems is a topic of considerable relevance. Therefore, the purpose of this study is to synthesize the active phase precursors for vanadium-containing catalysts. Heteropolyacids (HPA) of the Keggin structure based on Mo and containing from 1 to 3 atoms of vanadium in their composition $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 0,1,2,3) were chosen as perspective precursors.

A series of vanadium-containing heteropolyacids (HPAs) was prepared according to the method [3]. Stoichiometric amounts of Na_2HPO_4 and $NaVO_3$ were dissolved in water at an elevated temperature. Then the solution was cooled and H_2SO_4 was added until the color of the solution changed to the red. Then the $Na_2MoO_3 \cdot 2H_2O$ solution was added with vigorous stirring. After cooling, the strongly acidic HPA solution was extracted by the ethereal method.

The structure of the synthesized HPAs was confirmed by IR spectroscopy. Samples of crystalline HPA were tabletted with KBr powder and their spectra were recorded in the range 400–4000 cm^{-1} on an IRTracer-100 spectrometer (Shimadzu).

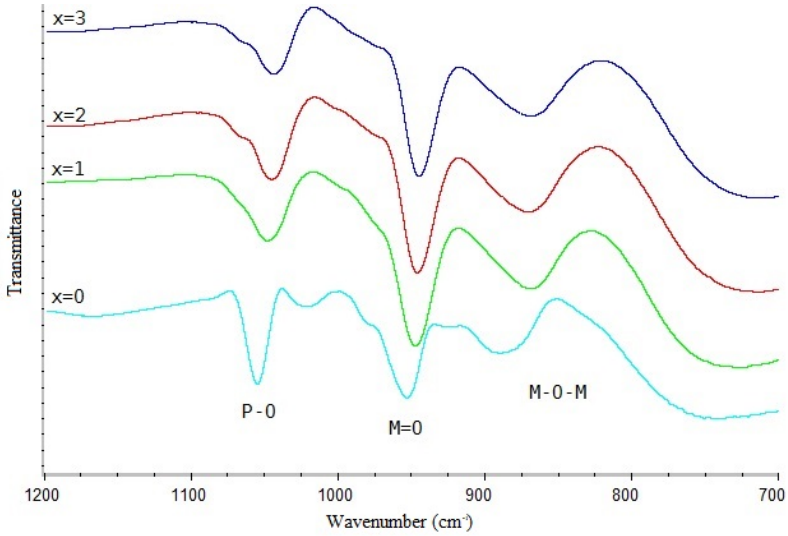

Fig. 1 IR spectra of the synthesized $H_{3+x}PMo_{12-x}V_xO_{40}$ *HPAs of the Keggin structure*

Fig. 1 shows the IR spectra of the synthesized phosphoric-vanadium-molybdenum HPAs with the Keggin structure. In a series of vanadium-containing HPA, characteristic IR bands were observed in the range of 700 - 1200 cm^{-1}, which can be used to identify the required heteropolyanions [4]. The absorption bands located in the range 1043 - 1055 cm^{-1} correspond to P - O bonds, and the bands in the range 945 - 953 cm^{-1} - to M (Mo, V) = O bonds. Also in the range 868 - 889 cm^{-1} there are M – O – M bonds. As the number of vanadium atoms in the $H_{3+x}PMo_{12-x}V_xO_{40}$ molecule increased, each IR band in the series of the obtained HPA shifted towards lower wavenumbers. The results obtained are consistent with the literature data [4].

Supported catalysts were prepared using synthesized vanadium-containing HPAs. Then they were tested in the isomerization reaction.

Acknowledgement. This work was supported by the Government of the Russian Federation (resolution no. 220 of April 9, 2010; grant no. 14.Z50.31.0038 of February 20, 2017).

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PP-I-19
Synthesis and Properties of MIL-100(Fe)/Diatomite Composites

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Today, the materials with the hierarchical porous structure find practical applications in sorption, catalysis and environmental safety [1]. The composites based on silica and MOFs feature the enhanced properties due to the high utilization efficiency of the porous structure of materials [2]. In this work diatomite was used as a primary matrix with opened wide pores to create the composites by the assembly of MIL-100(Fe) inside these pores. The dependence of the features of the composite structure on the synthesis conditions was studied.

The reference sample MIL-100(Fe) was synthesized according to the reported procedure using the hydrothermal synthesis [3]. The MIL-100(Fe)/diatomite composites were prepared by the assembly of the microporous MIL-100(Fe) in the meso-macroporous diatomite structure by hydrothermal synthesis in the presence of diatomite under the same conditions.

The porous structures of the diatomite, MIL-100(Fe) and composites were studied by low-temperature N_2 adsorption-desorption. The MIL-100(Fe) has high surface area (1864 m^2/g) and pore volume (1.02 cm^3/g). The initial diatomite is characterized by the surface area and pore volume of 29 m^2/g and 0.08 cm^3/g, respectively. The surface area of the MIL-100(Fe)/diatomite composite is 336 m^2/g and the pore volume is 0.26 cm^3/g. The micropore size distributions of the composites are characterized by the maxima corresponding to the MIL-100(Fe) structure. A hysteresis loop for the composite is identical to the one for diatomite. This indicates the presence of wide diatomite mesopores in the composite. The presence of both micropores of MOF and macropores of diatomite is observed for the synthesized composites confirming that the hierarchical materials are formed. The crystal structures of the samples were examined by the XRD method. The XRD pattern for MIL-100(Fe) indicates the structure of bare MIL-100(Fe). The diatomite structure is composed of the amorphous silica and α-quartz phases. In the case of the MIL-100(Fe)/diatomite, the MIL-100(Fe) and diatomite phases are observed. These results indicate the formation of MIL-100(Fe) particles on the diatomite surface. The formation of the MIL-100(Fe) structure for the MIL-100(Fe)/diatomite composite is also confirmed by the thermal analysis data.

Thus, the opportunity to synthesize the diatomite-based composite with the hierarchical porous structure has been demonstrated. The MIL-100(Fe) can be easily prepared by the hydrothermal synthesis from the diatomite surface (the Fe impurities in diatomite) or from the iron salt $Fe(NO_3)_3$ previously introduced into the diatomite pores.

Acknowledgement. This work was supported by the state assignment of the Ministry of Science and Higher Education of the Russian Federation (project No. 0721-2020-0037).

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PP-I-20
Design of Micro-, Meso- and Macroporous Silica Particles

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Homogeneous catalysis by metal complexes is widely used in fine organic synthesis and takes a leading position in pharmaceutical production. However, the process of restoring the catalyst after the reaction is currently quite tedious and energy-consuming. The realization of the process in pseudo-homogeneous catalysis conditions makes it possible to extract the catalyst without loss and without reducing the process efficiency. A method could be based on the use of microspherical particles with controlled characteristics[1]. For this reason, the search for the cheapest, affordable and non-high-temperature approach to obtaining particles with the necessary properties is currently relevant.

The main method for obtaining monodisperse spherical silica particles is the hydrolysis of tetraethoxysilane (TEOS). Hydrolysis of TEOS with further polycondensation, known as the Stober process, is usually carried out in an alcohol-ammonia solution [2]. However, the particles obtained by this method have a low specific surface area. Preliminary addition of surfactants, surface-inactive substances and polymer microspheres with further removal of the template makes it possible to create a hierarchical porous structure of particles.

We develop methods for the micro -, meso- and macroporous monodisperse spherical silica particles synthesis with required size and morphology by searching for molar ratios of components and optimal preparation conditions. It was shown that the use of a continuous supply of TEOS, as well as the introduction of surfactants such as hexadecyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) at concentrations lower than the critical micelle formation concentrations (CMC), lead to the formation of particles with the narrowest size distribution due to an increase in the electrokinetic potential (Fig. 1).

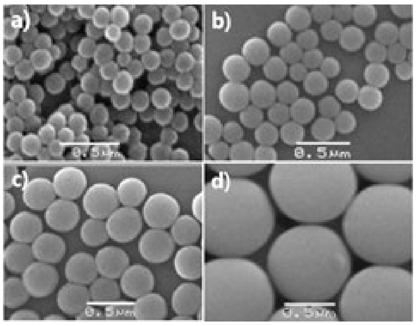

Fig. 1. SEM image of spherical SiO_2 particles obtained a) by the addition of glycerin, b) without additives c) by the addition of CTAB, d) by the addition of SDS

It was found that the following conditions increase the particle size: the use of continuous TEOS supply and its supply rate decrease, the increase in the amount of SDS, synthesis temperature decrease. The results illustrated in the diagram below were obtained in syntheses using identical molar ratios of the precursor and the solvent (Fig. 2). Based on the growth mechanism, this dependence can be explained by the fact that less amount of seeds is formed during continuous supply, after which the growth of existing seeds becomes thermodynamically more profitable than the formation of new ones [3]. Addition of CTAB close to CMC lead to the formation of particles with high surface area.

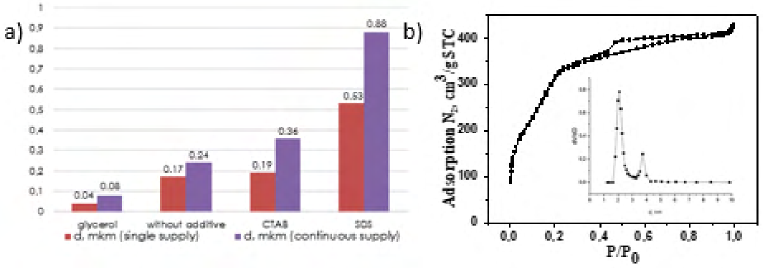

Fig. 2. Dependence of the size of the obtained SiO_2 particles on the method of supplying the reagent and the choice of the added surfactant / surface-inactive substances (a); adsorption isotherm of SiO_2 particles prepared by the addition of CTAB (A = 1328 m^2/g, V_{sum} = 0,7 cm^3/g) (b)

The introduction of polystyrene (PS) and polymethylmethacrylate (PMMA) microspheres into the reaction mixture, followed by the removal of the template, makes it possible to obtain hollow SiO_2 microspheres. However, the excess of TEOS, instead of "microspheres-frameworks", results in the formation of macroporous silica (Fig. 3a). A lower TEOS/PS ratio results in a layered material with a hierarchical porous structure was obtained (Fig. 3b). By adding polyelectrolyte to achieve a positively charged surface, it is possible to provide easier interaction with the precursor, and, consequently, a more uniform distribution of TEOS on polymer microspheres (Fig. 4).

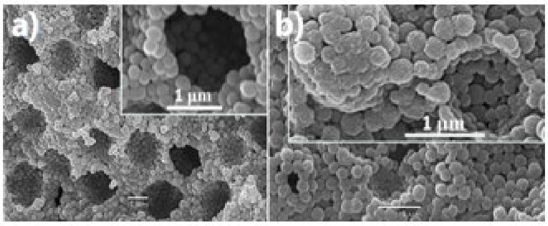

Fig. 3. SEM image of macroporous SiO_2 obtained with the addition of PS as a template with the molar ratio TEOS:PS a) 10^8, b) 10^9

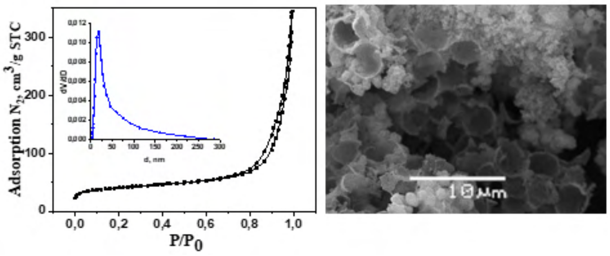

Fig. 4. Adsorption isotherm and SEM image of spherical hollow SiO_2 particles

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PP-I-21

Co-Based Hybrid Catalyst System in Fischer-Tropsch Synthesis Combined with Hydroprocessing

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Natural gas is an ideal fossil fuel, which has recently become favored over coal and oil in power production due to its fairly large reserves, new advanced technologies for gas extraction, as well as the stringent environmental regulations associated with flaring, pollutants and greenhouse gases. Production of syngas (a mixture of CO and H_2 gases) is the first stage of conversion of natural gas to liquid fuels. Syngas conversion via the Fischer-Tropsch synthesis (FTS) protocol provides a promising alternative to flaring or re-injection of associated petroleum gas to monetize it. The most attractive way for this is direct conversion of syngas into transportation fuels over hybrid catalyst systems comprising both a catalyst for FTS and a zeolite component that catalyzes hydroprocessing (HP) of primary hydrocarbons. This report will describe a hybrid catalyst system in which a pre-formed silica-supported cobalt catalyst for FTS and ZSM-5 zeolite component as an HP catalyst reside within a single extruded particle, in nanoscale vicinity to each other, while the sizes of the extrudates are suitable for their commercial application. The prepared hybrid catalysts were tested for their performance in a bench-scale fixed bed reactor operating at T = 240-250 °C, P = 1.0-2.0 MPa, GHSV = 1000 h^{-1} and H2/CO = 1-3 and showed higher activities in both FTS and HP as compared with some recently reported catalysts. The prepared catalysts were characterized by temperature-programmed desorption of hydrogen (H2-TPD) and ammonia (NH3-TPD), X-Ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), as well as energy-dispersive X-ray spectroscopy (EDX). As has been shown by TEM, the procedure applied to prepare the hybrid catalyst system does not change the size distribution of cobalt nanoparticles in the resulting hybrid catalyst as compared with the parent FTS catalyst.

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PP-I-22

A New Approach to the Formation of Highly Dispersed LSX Zeolite

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High usage of zeolites can be defined by their specific physical and chemical properties. Due to zeolites' microporous structure, they are used in both adsorption and catalytic processes. LSX-type zeolites are presently widely applied in different industries since they combine zeolite X's features of micropores and zeolite A's cation-exchange capacity. The most important characteristics of the studied alumosilicates, such as dispersion and crystallinity, are their technological application factors. The unique structure of zeolites provides controlled crystalline structure parameters during synthesis. However, there isn't sufficient information on the critical early stages of crystallization, so our objective was to develop a new approach to discover the formation of highly dispersed particles of LSX zeolite based on low-temperature hydrogel ageing before crystallization.

A source for the synthesis of LSX zeolite crystals amorphous alkaline alumo silica gel was used: $5{,}5Na_2O{:}1{,}65K_2O{:}Al_2O_3{:}2{,}2SiO_2{:}122H_2O$. The hydrogel was prepared from solutions of sodium and potassium alkalis, silicate and sodium aluminate. Before crystallization, the gels were kept between 15C to 500C for 24 hours. Then, the zeolite was crystallized according to the method described in [1]. The chemical composition of the obtained alumo silica gels was analyzed using a flame photometer CL-378 and an energy dispersive X-ray fluorescence (EDXRF) spectrometer EDX-800HS (Shimadzu) with an X-Ray tube with a rhodium anode (voltage range 15-50kV, current range 20-1000 mkA, vacuum, collimator 3-5 mm). Diffractograms were recorded on an Ultima IV "Rigaku" diffractometer in monochromated CuKα radiation in the area of angles from 3 to 50 2θ with a step of 0.5 deg/min and an accumulation time at each point of 20 s. The relative degree of crystallinity was estimated by summing the areas of the five most intense peaks. X-Ray phase analysis was performed by comparing the obtained diffractograms with the pdf 2 database (Rigaku). Crystal morphology was studied using an electron microscope JEOL JSM-6490 LV, accelerating voltage-20-30kV.

In this research, we investigated the relationship between the hydrogel's ageing temperature and the size of the formed particles. There was a decrease in the average size of zeolite crystals from 5.0 to 2.9 microns, with a decrease in the hydrogel's holding temperature from 50 to 15˚C, respectively. In addition to studying the effect of the gel ageing temperature on the size of crystals, we also looked at the effect on the range of their size distribution.

In summary, a new method of highly-dispersed LSX zeolite formation has been shown. Experimental data confirmed that there is the possibility of reducing both the size of zeolite crystals and their size distribution range by reducing the hydrogel holding temperature before crystallization.

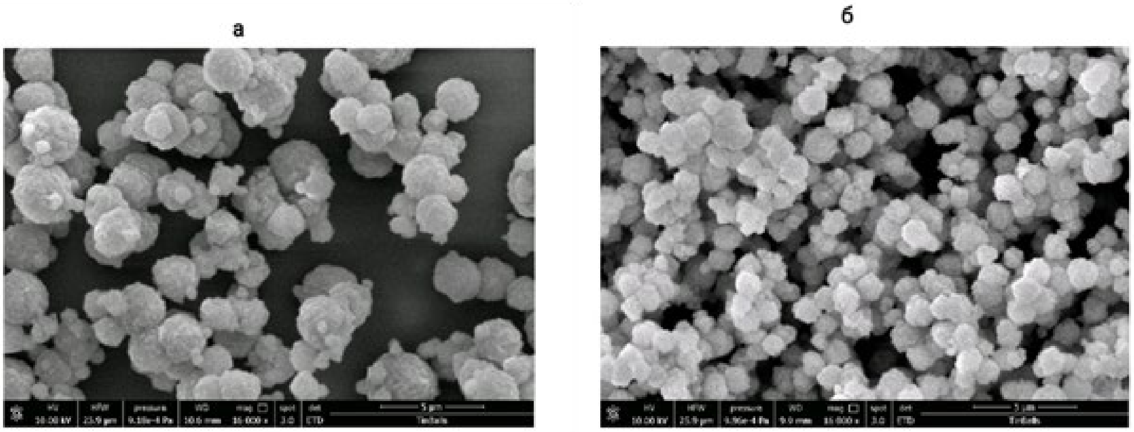

Fig. 1. 16 000 times magnified images of NaKLSX zeolite (with the usage of electron microscope) (a-Large Zeolite Crystals, b-Small Zeolite Crystals).

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PP-I-23

The Study of the Catalytic Properties of Copper and Gold Nanoparticles in the Reaction of Deuterium-Hydrogen Exchange

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A study of the catalytic properties of copper and gold nanoparticles, as well as the binary gold-copper nanosystem (50:50 ratio) in the reaction of homomolecular isotope exchange of hydrogen has been carried out. It is shown that copper nanoparticles do not exhibit catalytic activity, while gold nanoparticles of the same size are active. Synergism of catalytic activity is observed in a binary system.

Methods

The samples were prepared by impregnation of a support followed by thermal decomposition of salts. To prepare solutions, the following reagents were used: crystalline hydrate $CuCl_2 \cdot 2H2O$ and an aqueous solution of $AuCl_3$. Three solutions were prepared for the metal ratios: 100% Au, 100% Cu, 50% Au: 50% Cu. The solutions were prepared in such way that the ratio of the mass of the metal to the mass of the carrier was 1%. Al_2O_3 "Trilistnik" was used as a carrier. For samples containing copper, additional reduction was carried out in a stream of hydrogen for 2 hours.

Sizing of nanoparticles

To determine the size and shape of nanoparticles, the method of transmission electron microscopy (TEM) was used. The samples were examined on a JEOLJEM-1011 device. The TEM studies were carried out before thermal decomposition and after, after reduction of copper nanoparticles in a stream of hydrogen and after unloading the catalyst from the reactor. TEM photographs were processed using the Nano Measurer 1.2 software.

Experimental part

The studies were carried out in a glass high-vacuum installation, which consists of four main parts: an vacuum system, a reaction volume, a pressure measurement system, and a gas purification system (H_2, D_2). The reaction of homomolecular isotopic exchange of hydrogen was carried out in a wide temperature range from 77 K to 500 K at a pressure of the reaction medium of 0.5 Torr.

Results

Table 1 shows the results of studies of gold, copper and binary gold-copper nanoparticles in the H_2-D_2 exchange reaction.

Sample	D, nm	S_{act}, cm^2/g	H_2-D_2 exchange			
			K^{77K}_{sp}, molecules$\cdot s^{-1} \cdot cm^{-2}$	$E^{77\text{-}130\ K}$, kJ/mole	lgB	K^{300K}_{sp}, molucules$\cdot s^{-1} \cdot cm^{-2}$
Au	7-11	900	$(2,4 \pm 0,8) \cdot 10^{12}$	0,12	12,61	$2,0 \cdot 10^{12}$
Cu	4-11	467	-			
Au-Cu	6-13	660	$6,9 \cdot 10^{13}$	1,35	14,56	$1,6 \cdot 10^{15}$

No hydrogen isotope exchange reaction was recorded on copper nanoparticles. This may be due to both the absence of chemisorbed hydrogen on the surface of nanoparticles and the gradual oxidation of the most active centers. Gold nanoparticles showed a fairly high catalytic activity, which is consistent with our previous studies [1,2].

The highest catalytic activity was shown by the binary system Au-Cu, which indicates the synergistic effect of these two metals. It should also be noted that the segregation of gold on the surface of nanoparticles, which was found by us when studying the surface of the samples. This is consistent with the data from [3,4]. The binary system was stable during the entire study period, which indicates the promoting effect of gold nanoparticles.

Conclusions

1. Copper nanoparticles did not show catalytic activity in the deuterium-hydrogen exchange reaction in the temperature range from 77 to 470 K.

2. The binary Au-Cu nanosystem has a high catalytic activity in comparison with monometallic systems in the reaction of H2-D2 exchange. A synergistic effect is shown when these metals are combined in a catalytic system.

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PP-I-24

Electrochemically Promoted Synthesis of Triazoles in the Presence of Ionic Liquids

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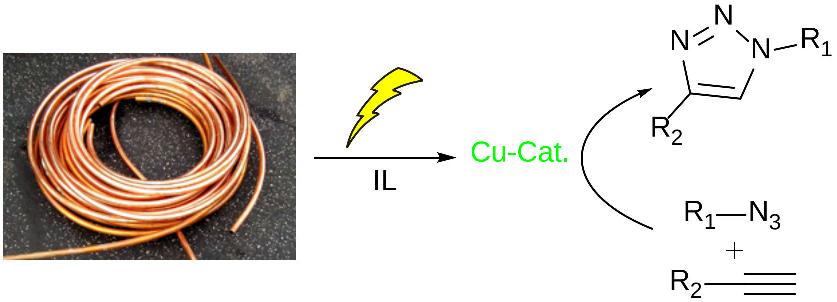
A major variety of well-known reactions require the use of catalysts [1]. Different salts [2], metal particles of various sizes [3] are widely used as catalysts. These catalysts are used not only in laboratory practice, but also in industry. Addition a catalyst leads to dissolution or dispersion, and at the end of the reaction we need to return the catalyst to in initial conditions. Potentially, an electrode can be used as a catalyst. In this case, the electrode may continuously supply catalytic amounts of ions at a constant concentration for continuous industrial processes, facilitating a process of uniform distribution of the catalyst in the reaction mixture. Tuning the current allows not only to change the amount of the dissolved catalyst, but also to restore its operable state by changing the polarity of the current. We tested the mentioned possibility for the selected reactions using the copper-promoted cycloaddition of alkynes to azides (Scheme 1).



Scheme 1. Synthesis of triazoles using an electrochemical approach to catalyst synthesis

The selected "click" reaction is widely used in the synthesis of substances that have applications in medicine [4], biology [5], and materials science [6]. Both copper compounds and metal compounds are used as a catalyst for this reaction [7]. Electrochemical approaches to the preparation of these compounds are based on the use of special compounds containing functional groups [8].

In our work, we developed an electrochemical approach to the preparation of a catalyst in an ionic liquid medium, which was used for further synthesis of 1,2,3-triazoles. A cheap and readily available material is used as a catalyst source, which is a copper electrode. And the efficiency of the spent catalyst can also be restored using electric current.

We tested various conditions for obtaining a copper catalyst in an ionic liquid, thereby showing the possibility of changing the amount of catalyst in the reaction mixture. After optimization, we have successfully tested the efficiency of the tool for preparing a catalyst in the synthesis of 1,2,3-triazoles from azides and alkynes (Fig. 1).

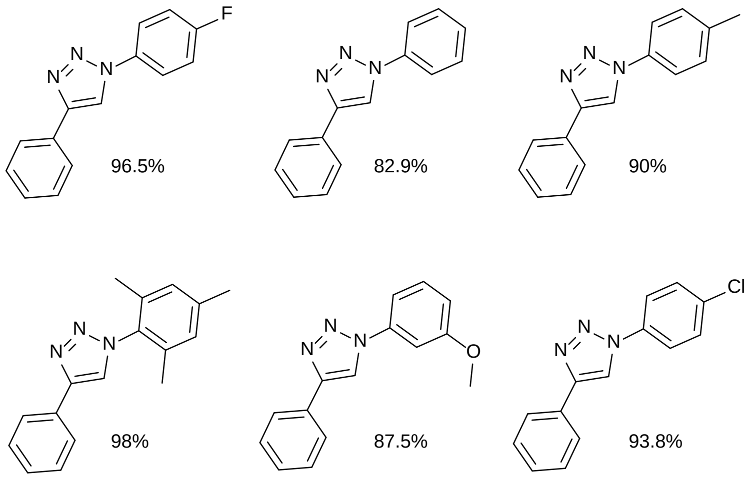


Figure 1. 1,2,3-triazoles obtained using an electrochemically prepared catalyst

After the synthesis, the reaction mass was green, since the Cu^+ were oxidized to Cu^{2+}. This phenomenon leads to a significant decrease in the yield of the target product (30%), however, it is found that that the oxidized catalyst can also be easily reduced using an electric current. Using the current, we were able to restore the catalytic activity of the catalyst and successfully reuse it in the reaction with a high product yield (98.1%).

Thus, we have electrochemically obtained a catalytic system that can be effectively used in the synthesis of organic compounds, and also has a simple method for restoring catalytic properties using an electric current without additional procedures for separating the catalyst from the system.

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PP-II-1

Features of Phase Transformations of K-Ce Iron Oxide Systems in the Process of Dehydrogenation of Isoamylenes

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Nowadays iron oxide catalytic systems are mainly used in the production of isoprene by catalytic dehydrogenation of isoamylenes.

The activity and selectivity of iron-oxide systems are significantly influenced by both the preparation method and the conditions of its activation. It was shown in [1-3] that the catalytic properties of catalysts promoted by potassium and cerium are largely affected by the structural and textural properties of precursors, as well as by the promotion and thermal activation methods. The promotion of cerium-iron oxide catalysts with alkali metals and the subsequent thermal activation lead to the formation of mono and polyferrites. In general, the promoted iron oxide systems are so unique that in [4] they were characterized as materials possessing self-development and self-regulation properties.

The effect of the phase composition and structure of iron oxides promoted by cerium and potassium on their catalytic properties is highly relevant and this is the purpose of our study.

The objects of our research were iron hydroxides and iron oxides promoted by cerium and potassium. Iron hydroxides and oxides were obtained by chemical deposition. Iron hydroxide was activated by heat treatment at 600 ^{0}C in various medium: air, nitrogen, hydrogen. Iron oxide promoted by cerium and potassium was activated at 600 ^{0}C and 800 ^{0}C in air.

Comparative catalytic experiments were carried out in a fixed-bed isothermal displacement reactor at 600 ^{0}C. The reaction products were analysed on a gas chromatograph using thermal conductivity detector and capillary non-polar column. Phase and structural analysis of the catalysts was carried out by the powder diffraction method.

The results of phase identification show that iron hydroxide dried at 25 ^{0}C is a mixture of oxyhydroxides with an admixture of α-Fe_2O_3, where γ-FeOOH is the main one. Thermal activation in air and nitrogen results in the formation of the α-Fe_2O_3 phase. Thermal activation in a hydrogen atmosphere leads to the reduction of oxyhydroxides to Fe_3O_4 with an impurity of metallic iron (3 %).

The highest activity and selectivity degrees are shown by iron hydroxide samples, which were thermal activated at 600 ^{0}C in a pure nitrogen and air medium before catalytic tests. Therefore the optimal conditions for the preparation of the catalyst from precursors are the thermal activation at 600 ^{0}C in air. The same conditions were used for the thermal activation of iron oxide catalysts promoted with cerium and potassium.

According to X-ray diffraction data, iron oxide promoted by cerium and potassium after its thermal activation at 650 ^{0}C in air consists of α-Fe_2O_3 (50 %), CeO_2 (15 %), and potassium monoferrites

(20 %). Thermal activation at 800 ^{0}C leads to the formation of the predominant phase of potassium polyferrite (50 %), phases of α-Fe_2O_3 (4 %), CeO_2 (14 %) and potassium monoferrites (31 %).

A study of the catalytic activity of cerium and potassium-promoted iron oxides showed that their thermal activation at 650 ^{0}C results in activity and selectivity values equal to 40 % and 72 % respectively. Thermal activation at 800 ^{0}C leads to an increase in selectivity up to 77 % and activity up to 44 %.

For the unpromoted iron oxides, according to XRD data the only identified phase is the Fe_3O_4 phase of magnetite. For the spent iron oxides, promoted with potassium and cerium, the main phase is also Fe_3O_4 (62 %) and, in addition, the FeO phase (14%) is also present.

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PP-II-2

Catalytic Properties of ZrO_2 Support for CrO_x Catalyst in the Isopentane Dehydrogenation Reaction

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Catalytic dehydrogenation is an on-purpose method for the production of unsaturated hydrocarbons from alkanes and olefins, which makes it possible to obtain important compounds of the chemical industry of polymer-quality purity. Dehydrogenation of light alkanes is a highly endothermic process that requires a large amount of heat to be supplied to achieve high conversions [1]. The high process temperature and the reactivity of olefins favor the occurrence of side reactions and coke production, which is important to consider in catalyst design [2].

Since side reactions such as cracking and coking mainly occur at acid sites, zirconium oxide, which has limited surface acidity compared to the most common carrier – alumina, is considered a promising material as a support for a chromium oxide catalyst. Furthermore, Cr_2O_3/ZrO_2 catalyst possess the higher activity in the dehydrogenation reaction in comparison to Al_2O_3 or SiO_2-supported chromium catalysts and relatively high resistance to sintering [3]. This is explained by the formation of a larger amount of Cr^{6+} species on a freshly prepared catalyst which are reduced to the catalytically active Cr^{3+} sites under reaction conditions, their stabilization, and high dispersion [4]. In turn, it is related to the strong interaction between chromia and the basic support and also presence of such surface defects as oxygen anion vacancies, produced by partial removal of lattice oxygen upon reductive treatment [5, 6]. These oxygen vacancies and coordinatively unsaturated Zr cations in the lattice of ZrO_2 are believed to form the active sites for the dehydrogenation reaction providing thus the catalytic activity of the bare support itself [7, 8].

In this work the intrinsic catalytic activity of ZrO_2 support was tested in isopentane dehydrogenation. ZrO_2 was prepared by precipitation method using aqueous solutions of zirconium(IV) oxynitrate and ammonia. The obtained samples were calcined at different temperatures in static air to investigate the effect of ZrO_2 crystallite size, phase composition and specific surface area on the support catalytic activity. In addition, a nanocrystalline zirconia with the largest surface area and the smallest crystallite size was prepared for comparison by calcination of zirconium oxyhydroxide at 300 °C. In order to evaluate the effect of ZrO_2 surface defects on the activity, samples calcined in static air were additionally treated at corresponding temperatures in H_2 or O_2 gas flow. The properties of the studied samples are shown in Table 1.

Table 1. Physico-chemical characteristics of the catalysts.

Sample name	Phase composition	Crystallite size, nm	Specific surface area (BET), m^2/g
ZrO_2_300	$ZrO_{2\ \mathrm{Tetragonal}}$ (?), 100 %	1	265
ZrO_2_550	$ZrO_{2\ \mathrm{Tetragonal}}$, 55 %	12	88
	$ZrO_{2\ \mathrm{Monoclinic}}$, 45 %	10	
ZrO_2_800	$ZrO_{2\ \mathrm{Tetragonal}}$, 22 %	17	10
	$ZrO_{2\ \mathrm{Monoclinic}}$, 78 %	19	

Catalytic properties of the obtained catalysts were evaluated using an in-house developed microcatalytic setup with fixed-bed reactor at 550 °C, gas hourly space velocity 315 h^{-1}, total feed flow rate 315 cm^3·h^{-1} (30 vol.% i-C_5H_{12} in He). The reaction products were analyzed by gas chromatograph equipped with capillary non-polar column and flame ionization detector.

For the entire investigated sample series (calcined at different temperatures) slightly higher methylbutenes yield is observed for the samples reduced in hydrogen atmosphere compared to the samples treated with oxygen (Table 2). Thus, the reduced samples are characterized by higher selectivity at the same isopentane conversion. In addition, hydrogen treated samples deactivate faster with time-on-stream, what can be related to the more defective surface structure.

Table 2. Catalytic activity properties of the catalysts.

Sample name	Yield, %	Selectivity, %	Conversion, %
ZrO_2_300_O_2	10,7	51,3	20,8
ZrO_2_300_H_2	11,4	53,9	21,1
ZrO_2_550_O_2	13,9	50,8	27,4
ZrO_2_550_H_2	14,3	53,4	26,8
ZrO_2_800_O_2	5,1	45,3	11,3
ZrO_2_800_H_2	5,6	47,9	11,7

Regarding heat treatment temperature, in terms of catalytic activity, 550 ^{0}C is a more optimal temperature than other selected ones. On the one hand, it can be explained by the smallest specific surface area and the largest crystallite size for the ZrO_2_800 sample. On the other hand, the ZrO_2_300 sample, which is characterized by the biggest surface area and the minimal crystallite size possess similar, but still the lower activity compared to the ZrO_2_550 sample. Obviously, initially nanocrystalline zirconia undergoes phase transformations under reaction conditions and in terms of surface area, phase composition and crystallite size parameters becomes closer to the ZrO_2_550 sample. But such catalyst activation *in situ* negatively reflects on the catalytic performance.

The results obtained in this study show that zirconia reduction to some extent affects its catalytic performance, but the more prominent effect is expected after the impregnation of the support by the chromia since it was found that CrO_x are able to activate H_2, that reacts with lattice oxygen [9]. Dispersing of the Cr_2O_3 on the surface of zirconia also should improve its thermal stability and prevent such drastic surface area decrease as well as stabilize phase composition.

Acknowledgement. This work was supported by the state assignment No. 075-00315-20-01.

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PP-II-3

CO Oxidation Reaction over Pd-Au/Ir Film: NAP XPS and MS Study

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Bimetallic systems attract the great interest of many scientific groups due to its ability to improve significantly catalytic properties in comparison with monometallic catalysts [1-2]. Good example proving this statement is the bimetallic Pd-Au catalysts, which exhibit extremely high activity in a number of industrially important reactions. This motivated researchers on numerous investigations of Pd-Au systems, which have shown that not only the ratio of the introduced metals, but also temperature of calcination will affect the surface composition causing the essential difference between Au/Pd atomic ratios in the bulk and surface [1-2]. Furthermore, surface composition can be varied under the influence of reaction mixture due to enrichment of the surface with one of the metals. It is evident that to clarify the influence of the above-mentioned effects on catalytic properties, the detailed in situ study of surface structure and composition of bimetallic Pd-Au catalysts is necessary to understand the nature of active sites and help to optimize the catalyst composition for the best activity, selectivity and stability.

A thin Pd-Au film (~4-5 nm) was prepared using thermal vacuum deposition on the surface of Ir (111) single crystal. The surface of the single crystal was preliminarily cleaned of possible impurities by etching with argon ions and heated to a temperature of 1100 °C in vacuum. The resulting film was heated in vacuum to a temperature of 450 °C to form Pd-Au alloy. The formation of the alloy is confirmed by the shifts of the Pd3d and Au4f lines towards lower binding energies from 335.0 and 83.9 eV to 334.8 and 83.6 eV, respectively [1]. All NAP XPS experiments were carried out on HIPPIE beamline at MAX IV synchrotron facility (Lund, Sweden). The experiments were carried out at UHV conditions and at 0.5 mbar of reaction mixture ($CO+O_2$) at different temperatures. First, the sample was heated stepwise from room temperature to 300°C, and then cooled in the reaction mixture back to room temperature. The XPS spectra of Pd3d, Au4f, C1s, O1s and Ir4f regions were measured for different kinetic energies of electrons (300, 450 and 600 KE) to investigate the distribution of elements, as well as their individual states, in depth of the sample.

The redistribution of Au and Pd atomic concentration on the surface in the course of the reaction was investigated using NAP XPS. The influence of different reaction conditions on the formation and evolution of different Pd and Au states, as well as the different carbon and oxidative states, were analyzed. It also should be noted that, according to mass spectrometry data, the bimetallic Pd-Au film demonstrates catalytic activity in the CO oxidation reaction at temperatures above 200 °C.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 19-13-00285.

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PP-II-4

The *N*- and *P*-Substituents in α-Phosphinoglycine Ligands in the Question of the Selectivity in Ni-Catalyzed Ethylene Oligomerization

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In the West, the leading position is occupied by the technology for the production of linear α-olefins based on organophosphorus ligands and nickel complexes, patented back in 1972, namely the Shell Higher Olefin Process [1]. This work reveals the possibilities of using new catalysts for catalytic oligomerization and polymerization of ethylene based on natural amino acids, which can be synthesed by phosphorylation to the α-position. As a result, a ligand with a PCCO-chelate center is formed, which is a modified form of Shell catalysts. The main advantage of α-phosphinoglycines is the tuning of the molecular weight distribution of oligomers in the catalytic oligomerization of ethylene by varying the substituent at the nitrogen and phosphorus atoms [2].

Within the framework of this work, *N*-(phenyl)-, *N*-(pyrazin-2-yl)-, *N*-(pyridin-3-yl)-, *N*-(pyridin-4-yl)-, *N*-(2, 5-dimethoxycarbonylphenyl)- and new *N*-(2-methoxycarbonylphenyl)-, *N*-(2-carboxylphenyl)- α-diphenylphosphinoglycines, as well as *N*-(pyrazin-2-yl)- and *N*-(2-methoxycarbonylphenyl)- α-mesityl(phenyl)phosphinoglycines were synthesized by a three-component condensation reaction [2].

In combination with a complex of $Ni(COD)_2$, where COD is cycloocta-1,5-diene, α-diphenylphosphinoglycines showed different selectivity to low molecular weight fractions, which is consistent with the literature data [3]. Therefore, to establish the influence of the electronic effects of the substituent at the nitrogen and phosphorus atoms, quantum-chemical calculations of the charges of nitrogen, phosphorus, and nickel atoms in catalytically active complexes were carried out. The results showed that replacing a substituent with more electron-donating or electron-withdrawing ones does not lead to a significant change in charges and, accordingly, to a redistribution of the electron density. Thus, the various *I*- and *M*- effects of substituents are insignificant, and the effect is exerted by steric loading both at the phosphorus atom and at the nitrogen atom.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 19-29-08051.

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PP-II-5

Study of the Electrochemical Properties of 2,2′-Bibenzimidazoles and Nickel Complexes Based on Them

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Compounds of the 2,2′-bibenzimidazole type are relatively poorly studied in the literature, despite the great promise of their application in medicine, biology and homogeneous catalysis [1]. The study of the electrochemical properties of 2,2′-bibenzimidazoles in terms of coordination chemistry is also of paramount importance. Along with bidentate diimine ligands, they are promising components of metal complex systems for homogeneous catalysis [2].

In this work, the electrochemical properties of 2,2'-bibenzimidazoles 1H,1'H-2,2'-bibenzimidazole (**L₁**), 5,6-dimethyl-1H,1'H-2,2'-bibenzimidazole (**L₂**), 5,5',6,6'-tetramethyl-1H,1'H-2,2'-bibenzimidazole (**L₃**), 1,2-dimethyl-2,2'-bibenzimidazole (**L₄**) and their nickel complexes have been studied utilizing the electrochemical methods of analysis, such as cyclic voltammetry and square-wave voltammetry (Fig. 1).

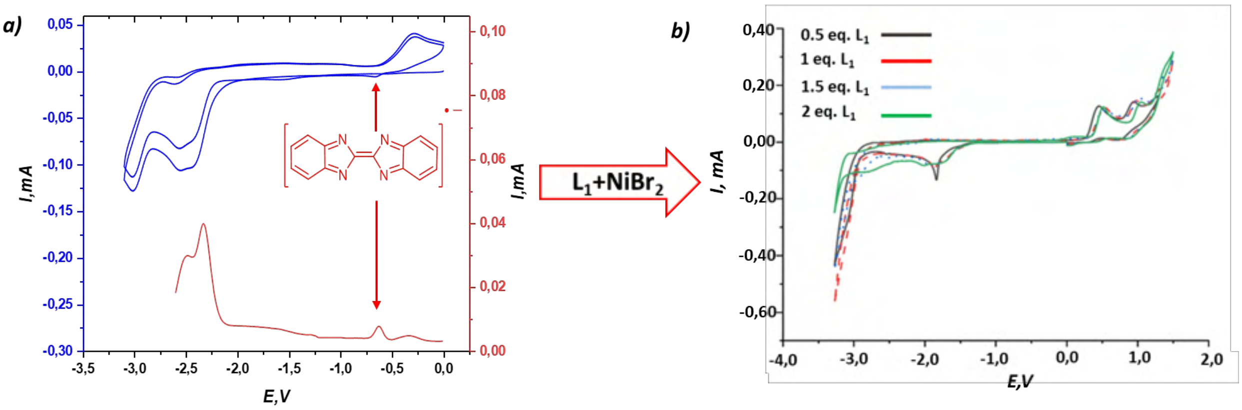

*Fig. 1. CV-curves of 2,2'-bibenzimidazole (**L₁**) by cyclic voltammetry in the absence (a) and in the presence (b) of a nickel precursor.*

The electrochemical reduction of 2,2'-bibenzimidazoles allows obtaining their deprotonated form, suitable for complexation with nickel precursor, which open up new possibilities in coordination chemistry.

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PP-II-6

The Comparative Study of Different Type Catalyst in the Dry Reforming of Methane

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Dry reforming of methane is one of the promising processes for the production of synthesis gas suitable for further synthesis of acetic acid, oxo-alcohols, ethyl acetate and other valuable products [1]. One of the areas of research required for its industrial implementation is the creation of a highly efficient catalyst and the choice of the type of reactor.

Among the proposed catalysts carbides of transition metals, in particular molybdenum carbide, are of great interest due to the high catalytic activity, resistance to the action of catalytic poisons and coking [2]. The choice of the sol-gel method using dispersions of molybdenum blue as a molybdenum carbide precursor allows to vary the properties of the resulting molybdenum carbide, as well as to synthesize catalysts of various structures [3].

The aim of this work was a comparative analysis of the activity of catalysts of various types, including bulk, supported and membrane, in the reaction of dry reforming of methane.

Catalyst samples were synthesized using molybdenum blue dispersions obtained by reducing a molybdate solution with ascorbic acid. A microfiltration membrane made of α-Al_2O_3 was used as a support. For the synthesis of the supported catalyst, a crushed membrane was used; in the case of a membrane, the precursor was deposited on the support by the dip-coating method.

Catalytic tests of the samples were carried out in a fixed bed reactor and in a membrane catalytic reactor in the contactor mode. The following conditions were chosen: t = 830 – 900^0C; molar ratio CH_4 / CO_2 = 1; flow rate of the gas mixture from 30 to 150 ml/min. To compare the catalytic activity, the specific rate constants of methane dissociation were calculated, referred to 1 g of Mo_2C and 1 m^2 of catalyst surface, and the ratio of H_2/CO products was determined.

The synthesized catalyst samples were studied by DTG, XRD, SEM, and low-temperature nitrogen sorption analysis. Comparison of the values of the specific rate constants showed that the highest values are observed in the case of a membrane catalyst, then supported and the minimum values are characteristic for bulk catalyst. It was suggested, that for an identical catalyst composition the acceleration of dry methane reforming occurs due to the change of mass transfer mechanism in the porous structure of the membrane catalyst.

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PP-II-7

Prediction of the Catalytic Activity of Nickel in Hydrogenation Reactions Using IR Spectrometry

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In the reactions of liquid-phase hydrogenation, transition metals are used as catalysts, most of them nickel, copper, cobalt, and molybdenum. It is known that the activity and selectivity of catalysts depends on the adsorption capacity of the surface of the active metal with respect to the reactants, in hydrogenation reactions mainly of hydrogen. The main goal of catalysis science is to anticipate catalytic action. The search for correlations between the regularity of adsorption and the activity of the catalytic system is highlighted by the European Association of Catalytic Societies as one of the priority tasks.

It is known that hydrogen is adsorbed on the surface of transition metals in various states that differ from each other in energy and type of bond [1]. Ideas about the different reactivity of the adsorption states of reactants are often used to explain the observed kinetic regularities; however, the reactivity has been little studied in the literature, conclusions are often made speculatively, there is no numerical expression for the reactivity of adsorbed compounds, and there are also no descriptions of direct experimental methods for its measurement.

IR spectrometry is a method capable of identifying hydrogen on the surface of transition metals and catalysts based on them. The review [2] provides data on the vibration frequencies of hydrogen particles (adsorbed and occluded), the vibration frequencies in the IR spectra were obtained mainly by calculation methods. For example, for a catalyst based on cobalt, the calculated vibration frequency corresponding to adsorbed hydrogen molecules was 1092 cm^{-1}, and for occluded hydrogen, it was about 1447 cm^{-1}.

We have obtained infrared spectrometry data for the reduced catalysts for liquid-phase hydrogenation reactions obtained by the methods [3]. All of the above allows us to draw a conclusion about the efficiency of the proposed theory and the possibility of its improvement in other reactions.

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The theoretical part was implemented with financial support from the Presidential grant for young PhD scientists (project MK-771.2020.3).
The study was carried out by using the resources of the Centre for collective use of scientific equipment FSBEI of HE "ISUCT".

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PP-II-8

Investigation of Aluminosilicate Halloysite Nanotubes as a Component of a Zeolite-Containing Catalyst for the Conversion of Methanol to Olefins

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Production of hydrocarbons from alternative sources of raw materials, in particular, from methanol, has been of great interest during the recent years. The composition of the products obtained - lower olefins C_2-C_4, liquid hydrocarbons C_5-C_{11}, aromatic compounds – are determined by the reaction conditions, such as pressure, temperature, catalyst [1]. Traditionally, catalysts based on zeolite of ZSM-5 type and SAPO-34 aluminosilicate are applied for this process.

In this work, catalysts based on zeolite type ZSM-5 were investigated in the methanol to olefins (MTO) reaction. To obtain good strength and mechanical characteristics the catalysts were synthesized using binding components — synthetic γ-Al_2O_3 and mesoporous aluminosilicate halloysite nanotubes [2].

Halloysite is a promising natural mesoporous aluminosilicate, which is a mineral, consisting of multilayer kaolin plates ($Al_2Si_2O_5(OH)_4{*}nH_2O$, n = 0, 2) rolled into tubes with the length of 0.5 to 1.5 µm and the internal diameter of about 10-30 nm. Composite materials based on halloysite are characterized by high thermal and mechanical stability [3]. Halloysite exploitation as a binder component can also lead to significant changes in the catalytic properties of zeolite catalyst, reduce the rate of catalyst deactivation and positively affect its operation life. Due to its mesoporous structure, halloysite allows to obtain more aromatic compounds.

The results of the catalyst samples physico-chemical studies by the XRD method showed that the peak distribution in the diagrams for all the samples corresponds to the standard distribution characteristics of H-ZSM-5 zeolite, halloysite and γ-Al_2O_3. The relative crystallinity values of the samples are close to each other and make up about 92-95%. It was also found that the synthesized H-ZSM-5/Al_2O_3 and H-ZSM-5/Halloysite samples correspond to micro-mesoporous materials. With an equal micropore volume of 0.07 cm^3/g, the halloysite-based catalyst has a lower specific surface area (277m^2/g) compared to the sample based on γ-Al_2O_3 (336 m^2/g).

Catalytic studies were carried out in a flow-type laboratory unit with a fixed catalyst bed at atmospheric pressure in the temperature range of 380-460°C at WHSV of 1 h^{-1}. Methanol was used as a substrate.

According to the catalytic tests results, H-ZSM-5/Halloysite catalyst showed the best results at temperature 420°C. The methanol conversion was 85 %, the selectivity of C_2-C_4 olefins was 45 %, the formation of higher C_5-C_8 hydrocarbons was 42%. The parameters obtained on H-ZSM-5/Al_2O_3 catalyst were significantly worse. The set out catalytic properties of halloysite make it a promising component of zeolite catalysts for the MTO synthesis.

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№ 20-38-90269.

PP-II-8

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PP-II-9

Investigation of CO-Induced Segregation on the Surface of Bimetallic Pd-Ag Catalyst by CO-DRIFTS and XPS

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The phase composition and the element ratio at the surface and in the bulk are often differing from each other in case of bimetallic Pd-based catalytic systems, which is caused by surface segregation. The driving force of this process is the tendency to decrease the surface energy in bimetallic system. Surface rearrangement can be controlled by the adsorption of different adsorbate molecules (CO, O_2, C_2H_2, etc), leading to enrichment of the catalyst surface with a component whose binding energy with the adsorbate molecule is higher. Since the structure of surface layers of bimetallic catalytic system depends on sample treatment conditions (temperature, exposure time), the surface segregation can be used as a simple and convenient method of controlling the surface structure of catalyst.

It was shown earlier that configuration of active Pd sites at the surface of Pd-Ag system can be tuned by exposing the catalyst to CO-containing atmosphere [1]. Nevertheless, the existing experimental data dedicated to investigation of temperature and CO exposure time on the dynamics of surface changes of bimetallic Pd-Ag catalyst are incomplete. This work provides a thorough study of segregation process in Pd-Ag_2/Al_2O_3 catalyst induced by CO at different temperatures and treatment durations. DRIFT spectroscopy of adsorbed CO and XPS were chosen as most appropriate methods for observation of surface changes during segregation.

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PP-III-1

IR Manifestation of Organic Fluid Formation in the Near-Surface Area at Ambient Conditions

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Usually the term “fluid” means the state of substances, exhibiting the properties of both liquid and gas arrangements. Currently this phenomenon was observed only for systems at high pressure and temperature. However, thin layers with similar behaviour at room temperature and atmospheric pressure, playing a crucial role for modelling of heterogenic catalysis processes, in the near-surface area can form [1,2].

In this work the IR manifestation of state formation with both gas and liquid IR absorption for organic solvents: benzene, methane dichloride, chloroform, carbon tetrachloride and methyl iodide, in near-surface area at ambient conditions is presented. These systems were elected, because their spectral features demonstrate different molecular interaction in liquid and gas phase [3].

For the state generation, forming in near-solid surface area, the organic liquids were evaporated at equilibrium pressure of their vapours and ambient temperature during 2, 20 and 70 hours in the volume of KBr cell with the following expansion-compression of the thickness between KBr windows (fig. 1). The spectra were recorded by a Fourier-spectrometer FSM 1202 (InfraSpec Ltd.).

In fig.2 the spectrum fragment of benzene (band of C-H out of plane vibration) is given: spectrum at 6 mm thickness cell (sp.1), spectrum at 1 mm (sp.2) and spectrum of liquid benzene thin layer, recorded between KBr windows (sp.3). The absorbance manifests the transformation of sp.1 (with P-, Q-, R-branches), corresponding to the gas phase spectral picture, into the sp.2, in which along with the disappearance of P-, R-branches, the band contour of Q-branch remains. Thus, sp.1 loses the gas features, but the specie of the liquid state band does not appear. At thickness expansion to 6 mm with open filling ports (without plugs) the spectrum turns into a specie and relative intensity of sp. 1 again.

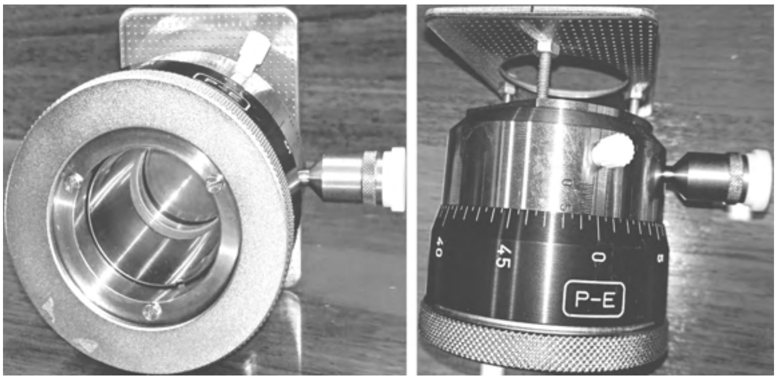

Fig. 1. Variable thickness KBr cell (Perkin-Elmer Inc.)

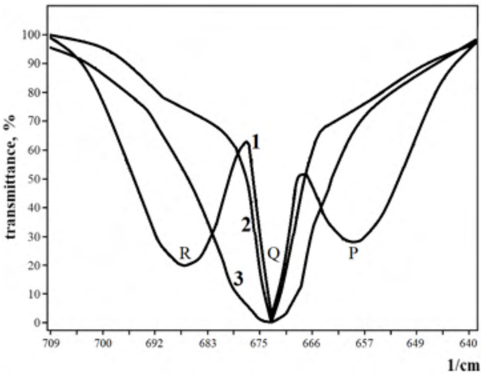

Fig. 2. Fragment of benzene spectrum.

In the spectrum of methyl iodide (region of H-C-H bending vibration), recorded at cell thickness 6 mm, a band with the rotational structure (band A, sp. 1) and two components (bands B and C, sp.1) were revealed. At thickness of cell 1 mm (sp.2), the rotational structure of band A remains, but instead of two bands B and C one band like in the spectrum of the liquid thin layer (sp. 3) is shown (fig.3). These data allow to exclude the idea that the observed state is the superposition of liquid phase and gas layer over it, because the recorded spectra do not manifest the transfer of all gas phase bands into liquid state absorption. Besides, the gas phase spectra cannot be observed at this cell thickness.

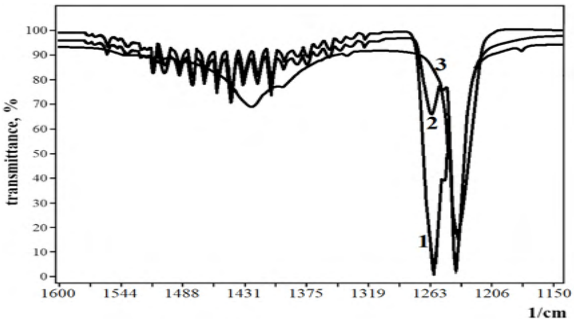

Fig. 3. Fragment of methyl iodide spectrum.

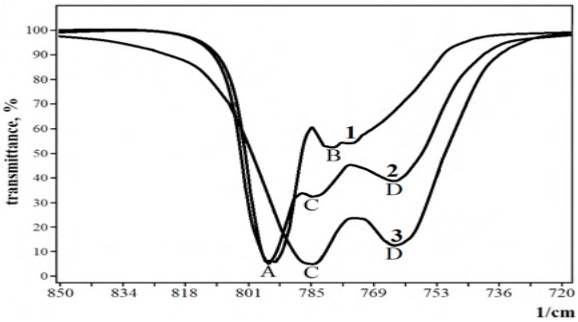

Fig. 4. Fragment of carbon tetrachloride spectrum

The spectra of carbon tetrachloride (fig. 4) show the similar changas in the presented thickness variation procedure. The gas phase bands (A, B) in the sp.1 (the cell thickness is 6 mm) are observed. The multicomponent band B resembles the gas band with overlapping rotational components. In sp.2 the gas band A and liquid bands C, D (like as in spectrum of liquid thin layer, sp.3) appear, but the multicomponent band B is absent in sp. 2.

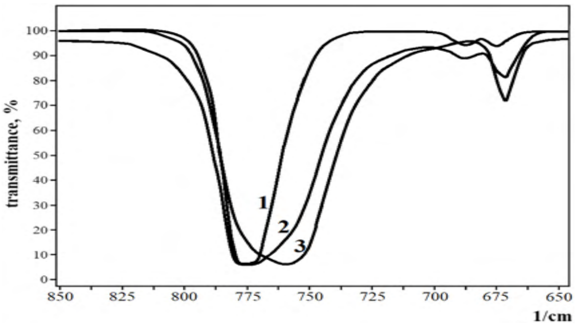

Fig. 5. Fragment of chloroform spectrum.

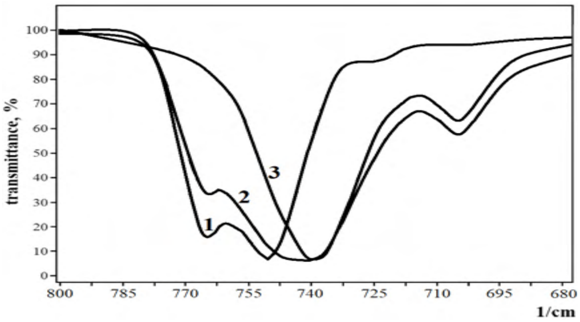

Fig. 6. Fragment of methane dichloride spectrum.

The spectra of chloroform (fig. 5) and methane dichloride (fig. 6) demonstrate the transfer of phase state with gas properties (sp.1) in the gas-liquid state (sp.3) at cell thickness compression from 6 to 1 mm, as well as in the previous cases.

Thus, the obtained data indicate that at ambient conditions in near-solid surface area the dynamic layers with gas and liquid phase IR spectral properties, transforming into each other at volume expansion-compression can form. Therefore, we can conclude that this state can be reasonably defined as "non-critical fluid".

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PP-III-2

Data Science Tools for Heterogeneous Catalysis: Unravelling Exemplarily Trends in Syngas to Ethanol Catalysis

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Modern catalysis research and data-driven methods are building a rapidly-growing and strong connection [1]. Data science is becoming an essential element in each step of catalysis research, from synthesis to test, characterization and respective performance analysis [2]. Of equal importance are methods for generating reliable, reproducible, relevant and diverse experimental data [3]. Measuring, storing and assessing the data in a systematic way would enable fundamental understanding and models with predictive power [4]. We report new tools for data cleaning, visualization, exploration, statistical investigation as well as correlation analysis. The methods are illustrated exemplarily for the hydrogenation of CO to ethanol [5].

In order to process the data generated by different experiments, a global pipeline is developed for each reaction, which is used to import, sort and clean each dataset. Other sources for the reaction at hand are combined with textbook knowledge to compute new descriptors and extend the cleaned dataset. The so-called extended global data-frame is then fed into different layers of data analysis toolbox. (Fig. 1)

The data are visualized by semi-automatic plotting of performance descriptors. The visualization toolbox provides methods to create a comprehensive view for selected performance descriptors. In addition to the obtained qualitative understanding from visualization toolbox, *meta analysis* and *twin-pairing* techniques are designed to provide detailed quantitative analysis of catalysts' performance. *Meta analysis* is used for hypothesis testing and in turn, to identify statistically significant correlations between physico-chemical properties assigned to a catalyst material and its performance in a given reaction. Twin-pairing toolbox highlights the effect of a certain treatment to the catalyst and reflects the effect size for any given performance descriptors throughout the test time of the catalyst. Combing analysis toolboxes with statistical methods on one hand and characterization techniques on the other, facilitates in-depth understanding of reaction network which leads to clear links between properties and treatments of a catalyst to its performance and structure.

In our work we illustrate exemplarily for the case of syngas-to-ethanol how these methods are exploited to translate observations from data analysis into a complex reaction network and to improve the mechanistic understanding thereof.

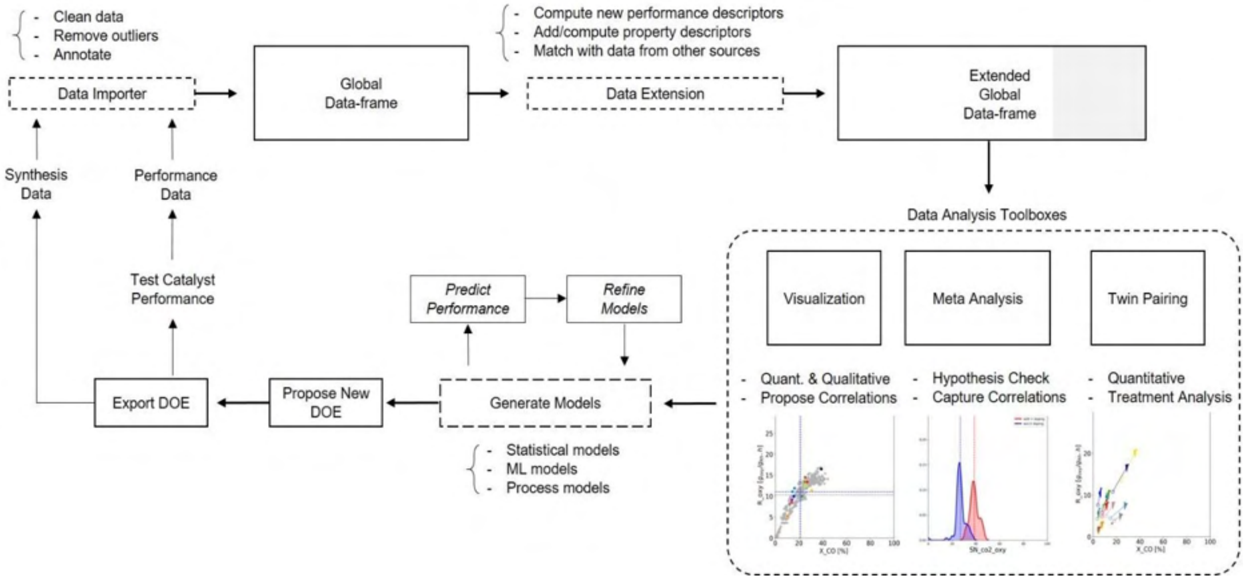

Fig. 1. Schematic depiction of the proposed data-driven approach for catalysis research

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PP-III-3

The Nature of Active Palladium Species in the Suzuki-Miyaura Reaction with Aryl Chlorides Using "Ligandless" Catalytic Systems

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The Suzuki–Miyaura cross-coupling represents one of the most powerful and widely used methods for the constructing new C-C bond between organohalide and organoboron reagents using Pd catalytic systems in both academia and industry [1]. In spite of progress in the development of effective catalytic systems for Suzuki–Miyaura coupling, some common problems exist for the reaction with aryl chlorides. Aryl chlorides are less expensive substrates than aryl bromides and iodides. However, aryl bromides and iodides in the Suzuki-Miyaura coupling reaction work better, while their chloride analogues are less reactive, require harsher conditions and longer reaction times and give the coupling products in lower yields. It is known that salts, dissolved in solutions, as additives can accelerate some organic reactions. The results of a kinetic study of the influence of halide salt on the differential selectivity of the Suzuki – Miyaura reaction with aryl chlorides are presented here.

To establish the effect of halide salts on the nature of active complexes we used a competing reaction method. Under this way the main evaluated parameter was the differential selectivity of a catalyst on competing substrates. In comparison with catalytic activity measurements, the differential selectivity study allows unambiguously revealing possible changes of the nature of active species due to its independence on their concentration [2]. Experiments with two pairs of competing aryl chlorides were carried out: activated (4-chloroacetophenone) and non-activated (chlorobenzene) aryl chlorides were used as substrates in competition with a substrate possessing moderate reactivity (1,4-dichlorobenzene) for investigation the nature of the active Pd(0) species (being active in the aryl chlorides oxidative addition step). Comparative study of the catalytic systems with and without various halide salt (LiCl, NaCl, NBu_4Cl, KBr, NaBr, LiBr, NBu_4Br, KI, NaI, NBu_4I) demonstrated that differential selectivity of the reaction with less reactive aryl chlorides (chlorobenzene - 1,4-dichlorobenzene) was sensitive to the added ammonium salt. Differential selectivity using another pair of aryl chlorides (4-chloroacetophenone - 1,4-dichlorobenzene) was found to be more sensitive to the nature of inorganic salts, than to the nature of ammonium salts. Furthermore, differential selectivity in the series of competitive experiments with both pairs of competing aryl chlorides has been found to depend on the nature of anion of a salt used as an additive in catalytic system. This fact indicates that such anions presenting in the system are involved in active anionic Pd(0)species reacting with aryl chlorides in oxidative addition step.

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PP-III-4

The Effect of CeO_2 Support on the Mechanism of CO Oxidation on Thiolate-Protected Gold Clusters

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The development of a catalyst for CO oxidation into CO_2 is an important task. Also, CO oxidation reaction is considered to be a model for studying the mechanism of heterogeneous-catalytic processes. Oxidation of CO on gold nanoparticles can proceed at low temperatures. The compounds with precise atomic composition and well-defined structure, thiolate-protected gold clusters are active in the oxidation of CO. However, some questions remain open: 1) the role of ligands; 2) influence of support; 3) reaction mechanism. We have earlier investigated interaction oxygen with $Au_{20}(SCH_3)_{16}$ cluster and its fragments and $Au_{20}(SCH_3)_{16}/CeO_2$. The presence of CeO_2 slightly increases the interaction energy of oxygen with the gold cluster [1]. The aim of this work is to establish how CeO_2 support affect the reaction mechanism of CO oxidation. The DFT/PBE method were used in PRIRODA and VASP program on center Complex for Simulation and Data Processing for Mega-science Facilities at NRC "Kurchatov Institute".

According to results, $Au_{20}(SCH_3)_{16}$ thiolate-protected gold cluster is inert with respect to O_2 and CO due to the strong bond of Au-S. To activate the gold cluster, heating was used with partial removal of the ligands. The highest O_2 and CO activation was observed in the cluster lacking three SCH_3 groups. According to results, adsorption energies decreases in the order monomeric > trimeric > octomeric. This indicates that gold cluster protected by monomeric motifs is more energetically favorable in O_2 and CO activation.

Then we investigated $Au_{20}(SCH_3)_{16}$ on CeO_2. The interaction of thiolate-full protected gold cluster with CeO_2-support is very weak. The ligand removal is also required for cluster interaction with support.

Acknowledgement. This work has been carried out using computing resources of the federal collective usage center Complex for Simulation and Data Processing for Mega-science Facilities at NRC "Kurchatov Institute", http://ckp.nrcki.ru/.

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PP-IV-1

Hydrodeoxygenation of Bio-Oil Model Compounds over Unsupported Ni–Mo-Sulfide Catalysts

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The depletion of fossil fuels and the increasing demand for energy resulted in unconventional feedstocks need to be refining. Hydrodeoxygenation (HDO) is one of the most promising pathways for removing the oxygen from biomass-derived streams and production of bio-based fuel. Nevertheless, due to its high viscosity, abundance of acid, heteroatomic contaminants and water, the bio-oil ought to be upgraded and hydrotreated in order to be applied as an alternative fuel [1]. In this case, the catalyst must provide selective conversion of oxygen-containing compounds, aromatics, and also must be stable in water. The lack of active and effective catalysts limits the possibilities of developing and scaling up technologies in the field of components related to biofuel, as well as the search for new catalytic systems and improvements. Thereby, new approaches for refining of bio-oil should be developed.

Mo sulfides promoted by Ni or Co are major components of hydrocracking and hydrotreatment catalysts. Thereby, catalysts based on transition metal sulfides could be explored as potential catalysts for HDO [1, 2]. For this process the unsupported metal sulfides are the most suitable: while for supported catalysts reactant blocks the pores because of high molecular compounds deposits on the active sites, unsupported catalysts provide contact of substrate molecules with active component excluding diffusion limitations and mass transfer [3]. Also, unsupported catalysts are less affected by deactivation and more resistant to coking.

Furthermore, transition metal sulfides also active in water-gas shift reaction (WGSR) [4, 5]. Thus, the hydroconversion of water-containing raw materials under CO pressure on sulfide catalysts excludes water removal and provides both *in situ* hydrogen generation through a WGSR and hydrogenation of aromatics and other heteroatomic compounds [6]. So, bio-oil hydrodeoxygenation under CO pressure could allow excluding water separation step from the process of bio-mass refining.

The present work is devoted to testing of dispersed unsupported Ni-Mo sulfide catalysts in HDO of bio-oil model compounds (guaiacol, phenol, etc) in aqueous medium under CO pressure. These unsupported catalysts were formed in situ during HDO through high temperature decomposition-sulfidation of oil-soluble metal precursors (molybdenum carbonyl and naphthenate nickel) using elemental sulfur as a sulfiding agent. The structure of Ni-Mo-sulfide catalysts were revealed by XRF, TEM and XPS. The catalytic testing was performed over the temperature range of 320-380°C, CO pressure of 3 - 5 MPa and CO/H2O molar ratio of 1.8 (20wt.% of water). The influence of reaction conditions (temperature, reaction time) on the activity and selectivity of the catalysts were established.

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PP-IV-2

Modern Catalysts Used for the Conversion of Cellulose to Glycols

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The procedures and processes for the conversion of cellulose have been studied in detail over the past several decades. The efforts of many research teams are focused on the development of new, efficient and environmentally friendly methods for producing polyalcohols from plant biomass, primarily from cellulose. Direct hydrogenolysis of cellulose makes it possible to obtain low molecular weight (C2 – C3) polyols such as ethylene glycol (EG), 1,2-propylene glycol (1,2-PG) and glycol (GL), which are the basis of chemicals and precursors in fuel synthesis, complex polyesters and other additives [1].

One-stage hydrogenolysis of cellulose to polyalcohols (one-pot process) in the presence of heterogeneous metal-containing catalysts has been known for a long time; however, this process using traditional metal catalysts does not allow obtaining high yields of target products [2–3]. In the literature, there is also a large number of works aimed at studying catalysts based on alkali oxides ZnO, CaO, MgO and bases (Ca $(OH)_2$, Ba $(OH)_2$) [4-6]. In works [7-9] it is shown that the presence of even a small amount of Ni in W_2C or in a W catalyst based on activated carbon (AC) can significantly increase the conversion of cellulosic biomass into 1,2-propylene glycol. The authors of [9], on the basis of their studies, argue that it is necessary to search for a polymer substrate for bimetallic catalysts. It was shown in [4] that bimetallic catalysts synthesized by wet impregnation allow obtaining higher conversion and selectivity than monometallic catalysts.

The study [10] showed the effect of the atomic ratio in the range of 0–0.2 Sn / Ni in catalysts based on aluminum oxide or zirconium oxide on the conversion and selectivity of the reaction. The catalysts were tested at 210 ° C in a hydrogen atmosphere at a partial pressure of 6 MPa [10]. Guanfeng Liang et al. [26] note that Ni is rapidly deactivated during the reaction at high temperatures, which makes its use unprofitable. In their work [6], the authors propose to use bimetallic Pt / Ni catalysts for the hydrolytic hydrogenation of cellulose. During the synthesis, Pt / Ni nanoparticles are formed on the surface of a platinum alloy with zeolite [11]. The synthesis of new bimetallic catalysts for the cellulose conversion process, as well as the search for an optimal carrier for bimetallic catalysts, is currently attracting much attention of researchers.

In the present work, we investigated the conversion of cellulose to glycols in the presence of ruthenium catalysts on various polymer substrates. experiments were carried out using various types of hypercrosslinked polystyrene: MN 270 (not functionalized), MN 100 (functionalized with amino groups) and MN 500 (functionalized with sulfo groups). Ru-containing catalysts based on HPS of different types in the process of hydrolytic hydrogenation of cellulose showed different efficiency, which was estimated by the total yield of the target conversion products - glycols (Table 1). During the study, it was shown that this difference is due to the structural and morphological properties of the catalysts.

Table 1 - Results of the cellulose conversion process, with different types polymeric carrier ruthenium catalyst

Catalyst	Cellulose conversion,%	Glycol selectivity,%
3 % Ru/СПС MN 270	**64.0**	**20.5**
3 % Ru/СПС MN 100	64.6	54.4
3 % Ru/СПС MN 500	60.7	59.4
205 0 C, 60 атм H_2, 30 мл water, 0.042 mmol Ru per 1 g of cellulose, 60 min, 600 min^{-1}		

This difference in results is explained by the morphological and structural properties of the catalysts, as well as different specific pore surface areas. It was found that the 3% Ru / HPS MN 500 catalyst based on sulfonated HPS is unsuitable for use in this process. The process on this catalyst is characterized by a brown color of the solutions obtained at the end of the reaction, which is due to the presence of glucose degradation products in them. However, the use of catalysts based on MN 500 and MN 100 is characterized by relatively high glycol selectivities. Thus, the use of Ru-containing catalysts based on hypercrosslinked polystyrene in the process of hydrolytic hydrogenation of cellulose is expedient only if the inert MN 270 HPS is used as a substrate.

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PP-IV-3

Liquid-Phase Oxidation of Betulin to Its Oxo-Derivatives over Silver Supported Catalysts

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Betulin is a pentacyclic triterpenoid of the lupane series with a broad pharmacological activity. The outer part of the birch bark is especially rich in extractives, being the main source of betulin. The active growth of research of betulin derivatives began after a publication [1], which positioned betulinic acid as a potential selective inhibitor of human melanoma cells. Later, other reports came on the activity of oxo-derivatives of betulin against several tumors and their anti-inflammatory, antimicrobial, antifibrotic, antiviral and other properties [2]. The main way to obtain oxo-derivatives of betulin is by oxidation using systems containing toxic chromium compounds. This approach is characterized by a large number of disadvantages and does not correspond to the principles of green chemistry. As shown in our previous works [3-5], an alternative way to obtain biologically active oxo-derivatives of betulin can be its heterogeneous catalytic oxidation using catalysts based on gold and silver nanoparticles and air, as a cheap and accessible oxidizing agent. Although it is known that nanosilver catalysts are inferior in activity to nanogold analogues in liquid-phase oxidation of alcohols, our previous studies showed the promise of using silver-containing systems as catalysts for such kind of processes [3]. In this study, we aim to show that through optimization of the composition and selection of the optimal method for the preparation and pretreatment of nanosilver catalysts, it is possible to achieve catalytic performance comparable to Au catalysts, as well as to reveal the effect of these factors (support nature, method of preparation and pretreatment) on the catalytic behavior of supported silver catalysts in liquid-phase betulin oxidation.

Betulin oxidation was carried out using synthetic air as an oxidant at 140 °C for 6 hours. Mesitylene was used as a solvent. Aliquots were analyzed on a gas chromatograph. Silver catalysts with a nominal loading 3 wt.% were prepared by deposition–precipitation with NaOH and incipient wetness impregnation methods. Different type of alumina was used as supports. The catalysts were characterized by XRD, BET, ICP, HRTEM, XPS.

Kinetic experiments were carried out in the temperature range of 80–140 °C using 0.05 – 0.4 g catalyst Ag/AlOOH_cal_dp_pH$_2$ and the initial concentration of betulin varied from 1.13 mmol/l to 9.04 mmol/l. In addition, the oxygen content in the gas atmosphere was changed from 0 % to 100 % by adjusting the oxygen level with nitrogen.

The best results in terms of conversion were obtained using Ag/γ-Al$_2$O$_3$_dp_pH$_2$ with betulin conversion of 83%, giving mainly betulonic aldehyde (tab. 1). Results obtained earlier for silver- and gold-containing systems showed that betulin conversion after 6 h was 27% on Ag/CeO$_2$/TiO$_2$ [3], 69% and 97% on Au/La$_2$O$_3$/TiO$_2$_pH$_2$ [5] and Au/γ-Al$_2$O$_3$_pH$_2$ [4], respectively. For Ag/CeO$_2$/TiO$_2$ and Au/La$_2$O$_3$/TiO$_2$_pH$_2$, betulone was the main reaction product, while for Au/γ-Al$_2$O$_3$_pH$_2$ it was betulonic aldehyde. Thus, it is obvious that the optimization of the composition and preparation procedure for nanosilver catalysts allowed to approach the catalytic performance of nanogold ones.

The influence of the preparation method and the pretreatment atmosphere on the catalytic behavior of Ag supported systems in betulin oxidation was also studied in this work. The best results were obtained using the deposition–precipitation with NaOH method followed by reduction treatment (if simultaneously take into account the conversion, GCPLA and total product yield). Silver catalytic systems were found to be more selective with respect to betulonic aldehyde than gold supported ones. The conditions favorable for obtaining a specific oxo-derivative of betulin with higher selectivity were determined. The final work will present a detailed study dealing with a correlation of physical chemical properties of catalysts with their performance in betulin oxidation, as well as the conditions for obtaining specific oxo-derivatives of betulin.

Table 1. Catalytic results for betulin oxidation using Ag catalysts.

Catalyst	Pretreatment	X (%)	GCLPA (%)	Selectivity (%)					$\sum Y_{product}$ (%)
				S_1	S_2	S_3	S_4	S_5	
Ag/γ-Al_2O_3_dp	H_2	83	77	36	49	0	15	0	64
	O_2	19	88	3	70	3	24	0	16
Ag/γ-Al_2O_3_iw	H_2	75	60	31	48	1	20	0	62
	O_2	73	70	25	57	0	18	0	60
Ag/AlOOH_dp	H_2	31	91	7	71	2	20	0	30
	O_2	33	86	6	72	2	20	0	31
Ag/AlOOH_iw	H_2	30	89	6	74	2	18	0	30
	O_2	24	85	5	73	3	19	0	21
Ag/AlOOH_cal_dp	H_2	51	90	12	70	1	17	0	47
	O_2	42	96	9	68	1	21	1	41
Ag/AlOOH_cal_iw	H_2	58	78	12	74	1	13	0	52
	O_2	44	78	9	75	1	15	0	38

X - conversion of betulin after 6h (%); GCLPA - the mass balance closure(%); Selectivity after 6 h (%): S_1 - to betulone; S_2 - to betulonic aldehyde; S_3 - to betulonic acid; S_4 - to betulinic aldehyde; S_5 - to betulinic acid; cal – support was calcined at 600 °C for 3h before the synthesis of catalyst; dp - deposition–precipitation with NaOH; iw - incipient wetness impregnation; $\sum Y_{product}$ - total product yield after 6 h (%).

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PP-IV-4

Hydrodeoxygenation of Lignin-Derived Compounds Using Ru Catalysts

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Lignin is one of the most widespread biopolymers and a promising renewable natural source of phenols and cycloalkanes. Lignin is usually converted into various substituted phenols that are refined into fuel components and products valuable for the petrochemical industry. This process, called hydrodeoxygenation (HDO), could be performed on both industrial sulfide catalysts and noble-metal catalysts. Among the latter, Ru catalysts showed the highest activity in hydrogenation and hydrodeoxygenation and the best results could be obtained using Ru nanoparticles. However, these nanoparticles should be stabilized to prevent agglomeration and loss of activity.

One of the approaches to prevent aggregation of nanoparticles is the use of porous carriers. An example of such material is porous aromatic frameworks (PAFs) - high-stable porous polymers with rigid structure of aromatic units. The aromatic structure not only stabilize metal nanoparticles, but also facilitates faster diffusion of aromatic substrates to the active sites of catalysts. This makes PAFs a good candidate for development of hydrodeoxygenation catalysts on their basis.

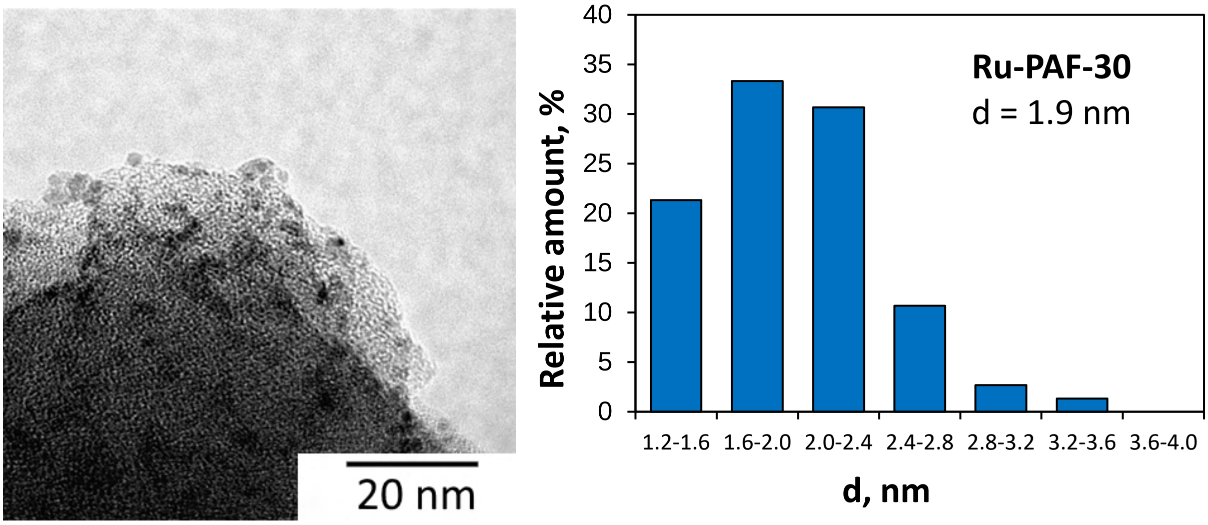

Fig. 1. TEM microphotographs and particle size distribution for Ru-PAF-30.

The aim of current work is to study the activity of Ru catalysts based on PAFs, which were prepared by impregnation of PAFs with ruthenium chloride and subsequent reduction by sodium borohydride. In order to study the effect of the support and its acidity, different materials were studied: non-modified porous aromatic framework - PAF-30 and one modified with sulfo-groups - PAF-30-SO_3H. The properties of the obtained catalysts were studied in the hydrogenation of guaiacol, catechol and veratrole at temperature of 250 °C and hydrogen pressure of 3.0 MPa in the presence of isopropyl alcohol. It was found that the presence of acid sites leds to a significant increase of yield deoxygenation products - cyclohexane and cyclohexanol.

Based on the results a possible reaction mechanism was proposed.

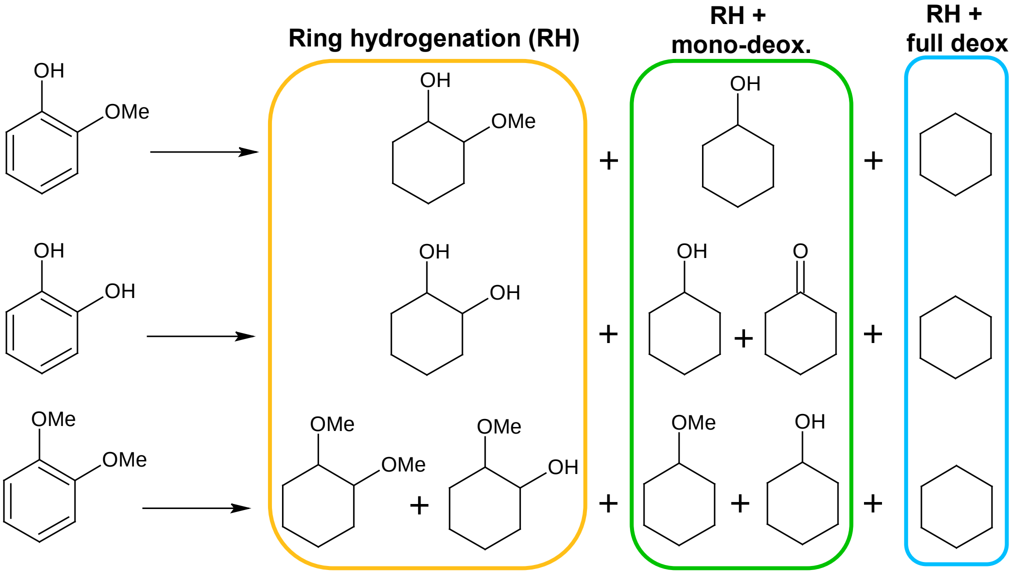

Fig. 2. Scheme of the hydrodeoxygenation reaction of guaiacol, catechol and veratrole.

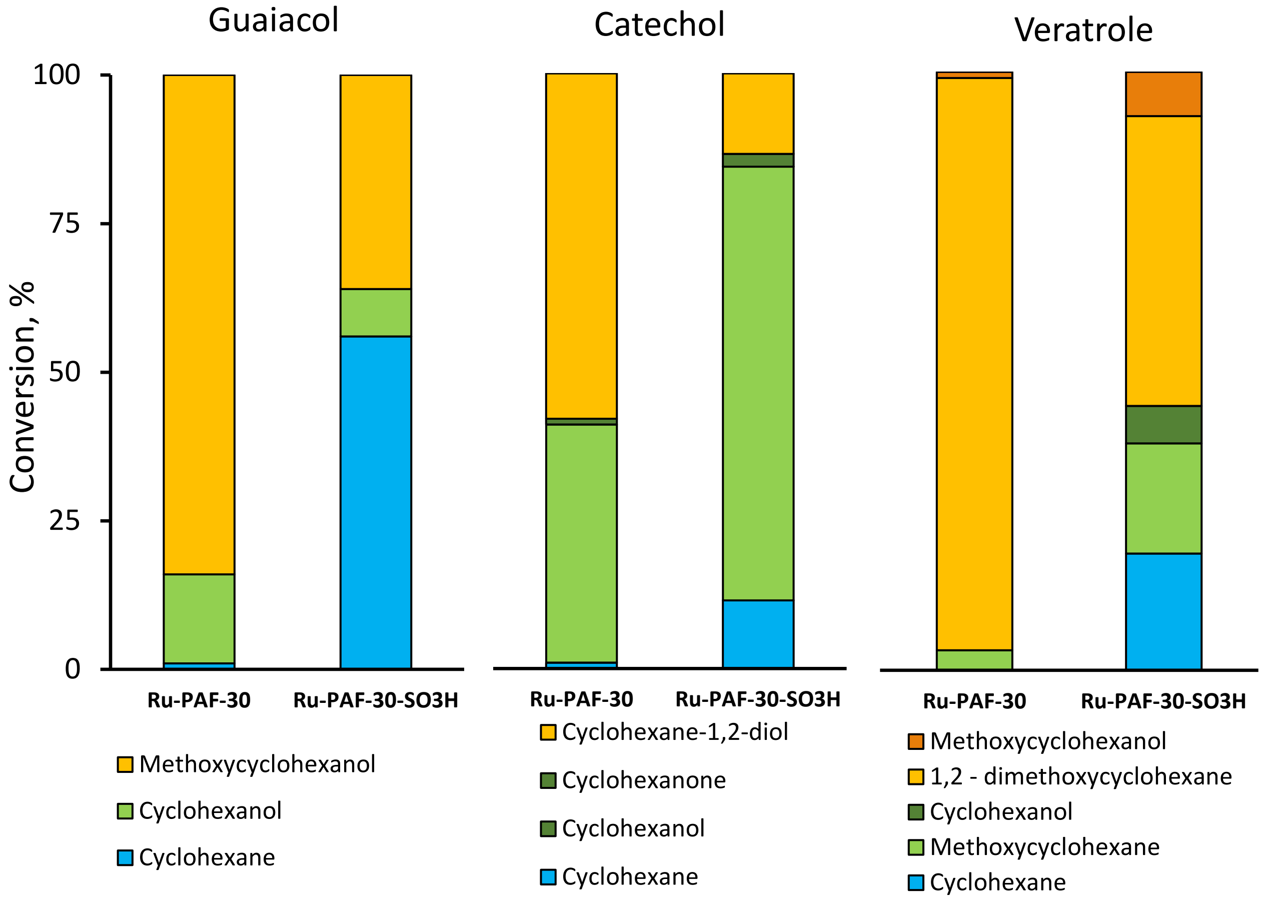

Fig. 3. The effect of different Ru-based catalysts on HDO. Reaction conditions: 6 mg of the catalyst; 600 μL of i-PrOH, substrate : metal = 742:1, 250°C, 3.0 MPa H_2, 2 hours.

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PP-IV-5

Hybrid AgAu@UiO-66 Catalysts for Propylene Glycol Oxidation into Lactic Acid

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Valorisation of biorenewable feedstocks is a roadmap for the modern chemistry. Bioglycerol is a by-product of biodiesel production. It can be converted into propylene glycol (PG) by catalytic hydrogenolysis. There are many valuable chemical products that can be produced from PG, including lactic acid (LA). Cosmetics, biodegradable plastics, biocompatible materials production and other industries that use lactic acid as a basic component grow rapidly. Thus, the development of green and cost effective LA synthesis is a topical challenge. The supported gold nanoparticles (NPs) demonstrate great activity in PG oxidation to LA in alkaline media [1]. In neutral media, the Au NPs posses low catalytic activity in polyol oxidation in neutral media [1]. The improvement of the activity of gold NPs in neutral media is challenging task.

Liquid phase PG conversion into lactic acid includes two possible parallel pathways. At first, the primary hydroxyl group of PG is oxidized to form lactaldehyde (LAl), which can be further oxidized into LA. According to the second pathway, the secondary hydroxyl group of PG may be dehydrogenated to yield hydroxyacetone (HA) with further oxidation of the -CH_2OH group into pyruvaldehyde (PA). Then the PA can easily convert into LA by Cannizzaro rearrangement. All steps of each pathway can be catalysed by redox species except for the last case. The Cannizzaro rearrangement can be catalysed by alkali agent or solid Lewis acid [2]. The main goal of the present work is to develop the active catalyst for PG conversion into LA in neutral media. In the order to enhance the activity of Au NPs in neutral media we added silver to the metal NPs. We used porous zirconium terephthalate UiO-66 as an active support for AgAu NPs. The UiO-66 featured large amount of accessible Lewis acid sites, large specific surface area and pore volume.

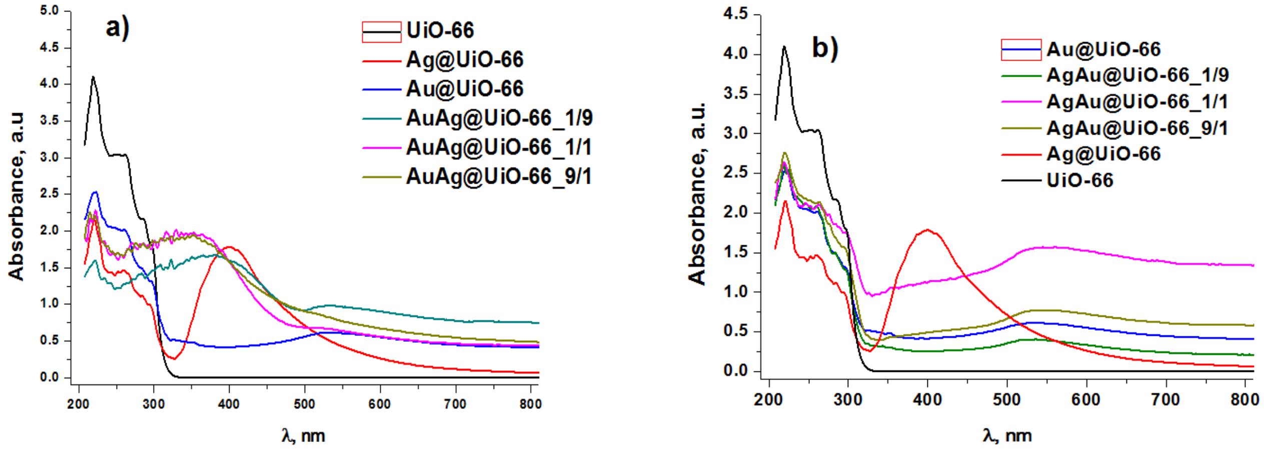

Figure 1 UV-vis DRS spectra for AgAu@UiO-66 hybrid materials with different metal immobilization sequence

The AgAu@UiO-66 hybrid materials were synthesized by double solvent technique [2] with a consecutive metal immobilization. The sequence of metal immobilization affected the distribution of the metals within the structure of the NPs. The Au immobilization for the first step led to the

$Au_{core}Ag_{shell}$@UiO-66 structure (fig.1 a). The SPR peak wavelength for the $Au_{core}Ag_{shell}$@UiO-66 sample was located near the band characteristic of Au NPs (fig. 1 b). The Ag immobilization for the first step led to the predominant formation of $Ag_{core}Au_{shell}$ in the UiO-66 structure. The presence of both metals in the samples was confirmed by the XRD (fig. 2). Close inspection of the XRD patterns showed that the reflection of the metal NPs were located between the main reflections of Au (111) and Ag (111) that was connected with the Ag–Au interaction in the NPs.

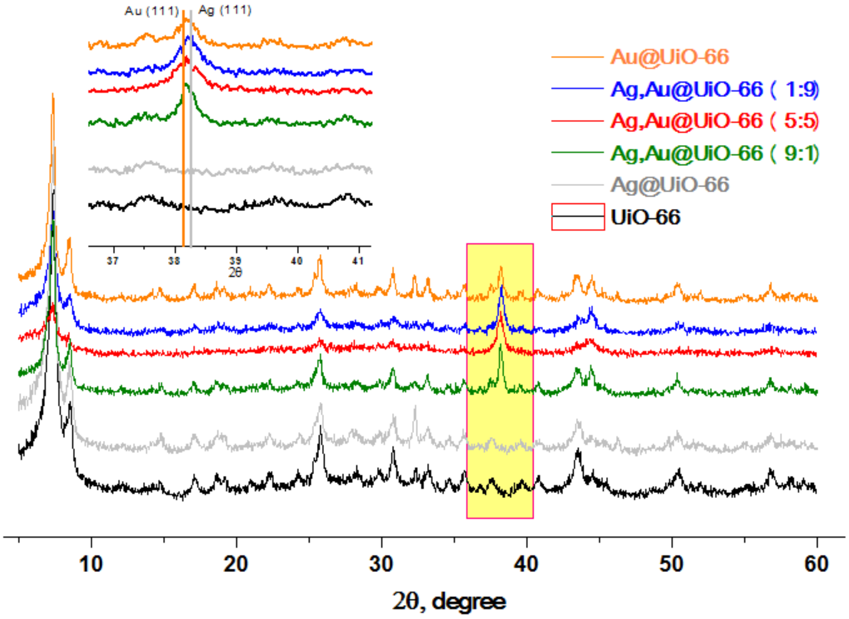

Figure 2 XRD patterns for obtained Me@UiO-66 materials

The $Ag_{core}Au_{shell}$@UiO-66 materials demonstrated good selectivity towards LA (80 %) at 100 ^{o}C without the alkali addition into the reaction mixture, while the $Au_{core}Ag_{shell}$@UiO-66 material was completely inactive in PG oxidation in neutral media. Probably, these results were connected with relative inactivity of the silver shell (Ag@UiO-66 was also inactive in this process [2]). The catalytic activity of the hybrid $Au_{core}Ag_{shell}$@UiO-66 materials was compared with the one of bimetallic AgAu NPs prepared by PLA in liquid. The influence of the reaction temperature, O_2 pressure, Ag/Au ratio, and total metal loading will be discussed.

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PP-IV-6

Reductive Amination of Ethyl Levulinate to Pyrrolidones Using Ni_2P Catalysts in a Flow Reactor

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Over the past decades, conversion of biomass and its derivatives to valuable chemicals has become a significant research area. Levulinic acid (LA), which can be produced by acid hydrolysis of lignocellulosic biomass, has been determined as one of the most promising chemicals from biomass feedstock. LA can be converted to a wide range of interesting derivatives such as γ-valerolactone, 1,4-pentanediol, valerate esters, and N-alkyl-5-methyl-2-pyrrolidinones. N-alkyl-5-methyl-2-pyrrolidones can be applied as an alternative to common solvent N-methyl-2-pyrrolidone, surfactants, and building block for the synthesis of biologically active compounds [1].

Reductive amination of levulinic acid or its esters (e.g., ethyl levulinate) with primary amines over heterogeneous catalysts using H_2 as hydrogen source is the attractive approach for production of N-alkyl-5-methyl-2-pyrrolidones [1–3]. This reaction has been successfully realized in the presence of noble metal-based catalysts; however, the high price and limited availability of precious metals are stimulated interest in catalysts based on earth-abundant elements [3]. In the most cases, reductive amination of LA (or levulinic esters) has been investigated in batch reactors [1, 2]. Meanwhile, organic reactions under flow conditions have attracted increasing attention. Potential advantages of continuous flow synthesis over traditional batch protocols include higher efficiency, environmental compatibility, simplified scaling, and enhanced safety profile [3, 4]. However, the obtained yields of N-substituted 5-methyl-2-pyrrolidones in flow reactors are much lower than that in the batch reactors [2, 3] that can be explained by a low rate of imine formation during the condensation of LA (or its ester) with primary amine due to the weak electrophilic properties of the ketone group [4]. In addition, the reaction should be carried out using a large excess of one of the reagents at a high hydrogen pressure [3] or an extremely low flow rate of the reaction mixture [2].

Recently, various secondary amines were obtained through a two-step one-pot reductive amination of aromatic aldehydes with primary amines [4]. The non-catalytic condensation of benzaldehyde derivatives or furanic aldehydes with amines during the first stage gives imines, which are then hydrogenated in a flow reactor over heterogeneous catalyst at the second stage. Herein, we investigated the efficiency of two-step procedure for reductive amination of ethyl levulinate (EL) with *n*-hexylamine (HA) via hydrogenation of the intermediate imines over Ni_2P catalysts in a flow reactor. Bulk and SiO_2-supported nickel phosphides were investigated.

The condensation of EL with HA was carried out at room temperature in the absence of a solvent. The mixture obtained by reaction of EL with HA for 16 h was dissolved in isopropanol to total concentration of levulinate of 0.05 M and then hydrogenated in a flow reactor at temperature of 150–190 °C and hydrogen pressure of 20 bar over Ni_2P catalysts. The silica-supported catalysts were prepared by the incipient wetness impregnation of SiO_2 with aqueous solutions of Ni and P precursors with the subsequent temperature-programmed reduction [5]. Bulk Ni_2P catalyst was obtained similarly to the method described in [6].

It was shown that 2.5% Ni_2P/SiO_2 catalyst provide the high yield of N-hexyl-5-methyl-2-pyrrolidone **4** which reached 83%. In addition to target product, unsaturated ring compounds **3** and N,N-diisopropyl acetamide **5** was observed among the reaction products. Therefore, the conversion of EL can proceed via two routes: through catalytic hydrogenation of imine **2** to secondary amine, followed by cyclization with formation of **4** [2] or via cyclization of imine to intermediate compounds **3**, which can then be hydrogenated to **4** (Fig 1). The undesired product **5** is probably obtained due to the hydrogenolysis of the C–C bond in **4** and the subsequent interaction of the formed amide with isopropanol.

The influence of the Ni loading and the nature of the phosphorus-containing precursor (H_3PO_3 or $(NH_4)_2HPO_4$) on the catalyst performance was studied. An increase in nickel content to 7.5% leads to a decrease in the selectivity for the target product. Bulk Ni_2P phosphide showed a much lower hydrogenation activity than the SiO_2-supported samples. As a result, the product yield over bulk catalyst did not exceed 63%.

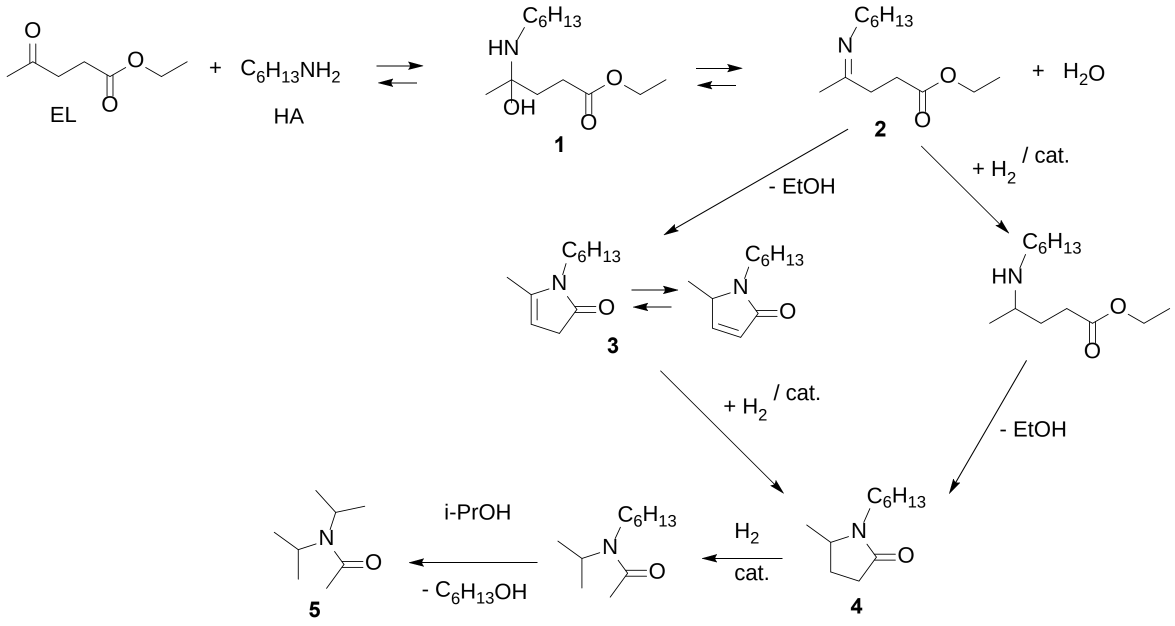

Fig. 1. Proposed reaction network for reductive amination of EL over Ni_2P catalysts

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PP-IV-7

Hydrogenation of Phenol and Benzene on Nanostructured Ru-and Pt-Containing Catalysts

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Today, in many countries, there is growing interest in the production of liquid fuels and petrochemicals from bio-oil, obtained by pyrolysis of plant biomass. However, bio-oil is characterized by a high amount of oxygen-containing compounds, which limits its use as a fuel due to its high corrosivity (TAN - 100 mg KOH kg^{-1}), low mass calorific value (16-19 MJ/kg) and tendency to polymerization [1]. Catalytic hydrotreating can solve these problems, which makes this process especially relevant.

The use of catalysts based on noble metals (Ru, Pt) deposited on natural aluminosilicate micro-mesoporous halloysite nanotubes (HNT) is promising due to their unique structure, availability and low cost [2].

The features of catalytic hydrogenation of model mixtures of phenol and benzene on the catalysts Ru/HNT and Pt/HNT with an active component content of 2% by weight were studied. The activity of the synthesized catalysts in the deep hydrogenation of phenol was investigated at 140 °C and benzene at 80 °C in autoclaves at a H_2 pressure of 3.0 MPa. The experimental results are presented in Fig. 1.

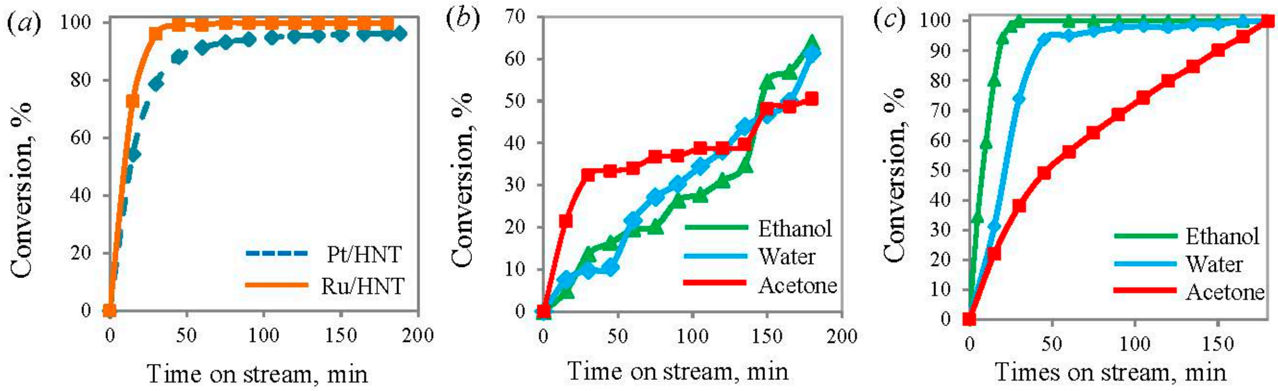

Fig. 1. Catalytic hydrogenation of benzene (a) and phenol in different solvents on Pt/HNT (b) and Ru/HNT (c) catalysts

It was found that the Pt/HNT and Ru/HNT samples exhibit high catalytic activity in the hydrogenation reaction of model phenol mixtures in polar solvents, directing the process along the route of direct hydrogenation of the aromatic ring to form a single product – cyclohexanol. In the benzene hydrogenation reaction, a complete conversion of the substrate is achieved with 100 % selectivity for the target product – cyclohexane.

Acknwledgement. The work was carried out with the financial support of the Russian Science Foundation (project No. 19-19-00711).

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PP-IV-8

High-Loaded NiCu Sol-Gel Catalysts for Dehydrogenation of Liquid Organic Hydrogen Carriers

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Nowadays there is growing interest in the use of alternative energy sources and energy carriers, which encourages the development of sustainable technologies for accumulation and storage of hydrogen. Various approaches based on chemical binding have been proposed for hydrogen storage, including the use of sorbents and chemical hydrides; however, their efficiency and applicability are limited [1,2]. Among the promising approaches, the reversible accumulation of hydrogen in the form of saturated hydrocarbons or so-called liquid organic hydrogen carriers (LOHC) is being elaborated. The reliability of this technology is to a large extent determined by high activity, selectivity, and stability of the catalyst for the endothermic dehydrogenation process.

Many studies have been focused on dehydrogenation of methylcyclohexane (MCH), as an example of the LOCHs concept. The catalysts for MCH dehydrogenation were based primarily on Pt or other precious metals supported on alumina [3]. Nevertheless, the high cost and not always sufficient selectivity prompted researchers to lower their use and search for non-noble alternatives. In this respect, Ni-based systems have proven to be one of the most active and cost effective catalysts. It should be noted that monometallic nickel catalysts possess high activity in the hydrogenolysis of C–C bond and therefore low selectivity in the target reaction [4]. The activity of nickel in hydrogenolysis transformations can be significantly reduced by the introduction of a second metal, particularly copper [5].

Here we propose a new type of Ni-based catalysts being synthesized via heterophase sol-gel technique and additionally modified by copper. To ensure high activity and selectivity of catalysts in the target dehydrogenation reaction, the structure-reactivity relationship was extensively investigated. A special focus was made on the effect of nickel-to-copper ratio and the way of copper introduction on the catalyst performance in MCH dehydrogenation into toluene. Herewith, two approaches with different ways of copper introduction were applied: i) simultaneous mixing of solid copper and nickel precursors at the sol-gel stage (NiCu-SiO_2), and ii) wetness impregnation of the nickel sol-gel catalyst with copper precursor (Cu/Ni-SiO_2). The MCH dehydrogenation was performed in a fixed-bed reactor at temperatures in the range of 250-350 °C. The structure features of the catalysts were studied by a number of advanced techniques, including TPR, XRD in situ, HRTEM along with EDX mapping, CO chemisorption, XAS, etc.

The heterophase sol-gel preparation approach allows one to obtain the nickel-based catalyst with a high specific surface area despite high metal loading. This ensures high activity of the catalyst in MCH dehydrogenation. Regardless of approach to catalyst preparation, copper introduction (up to 30 wt% of total metal content) was shown to cause only a slight reduction of MCH conversion. At the same time, it significantly suppressed hydrogenolysis and therefore resulted in increasing selectivity to toluene (fig. 1). Based on TPR, XRD, and XAS data, the consecutive introduction of copper to the nickel sol-gel catalyst ensures effective interaction between two metals due to the formation of solid nickel-copper solutions. This in turn is expected to be a reason for higher selectivity and yield of toluene. The selectivity values as high as observed for the Cu/Ni-SiO_2 catalyst (with Ni:Cu ratio of 80:20) at high MCH conversions, have not been achieved for the nickel-based catalysts so far. In general, these data point out the prospectiveness of the heterophase sol-gel approach, in combination with the second metal deposition by impregnation, to the synthesis of dehydrogenation catalysts.

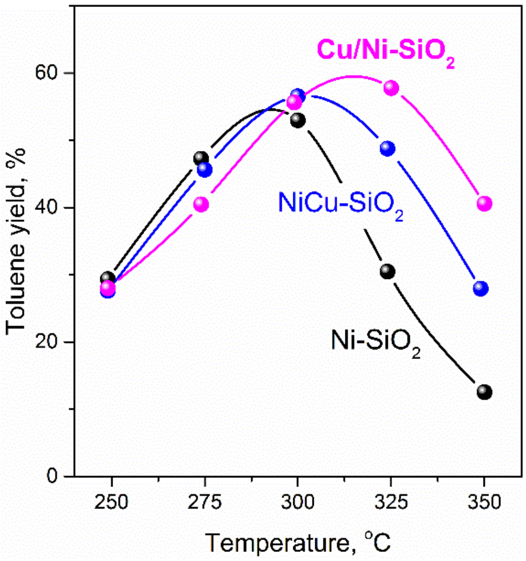

Fig. 1. Performance of Cu/Ni-SiO_2, NiCu-SiO_2 (Ni:Cu = 80:20 wt%) and Ni-SiO_2 catalysts in the dehydrogenation of MCH

Acknowledgement. This work was supported by the Russian Science Foundation, grant 19-73-20020. The characterization was performed using facilities of the shared research center “National center for investigation of catalysts” at Boreskov Institute of Catalysis.

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PP-V-1

Immobilized Multifunctional Ionic Liquids for Highly Efficient Oxidative Desulfurization of Model Fuel

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Oxidative desulfurization is a promising mild conditions method to produce clean fuels with ultra-low sulfur content [1]. Herein, we present for the first time multifunctional ionic liquid catalysts immobilized on mesoporous SBA-15 for highly efficient oxidation of dibenzothiophene. A combination of two catalytic active sites (phosphomolybdic acid fragment and carboxylic group) allows us to achieve complete oxidation of the most intractable dibenzothiophene to the corresponding sulfone in 5 min at 80°C and H2O2:S = 6:1 (molar). The structure of both support and catalysts was investigated by low-temperature nitrogen adsorption/desorption, Fourier-transform infrared spectroscopy, X-ray fluorescence analysis, CHN analysis, and transmission electron microscopy techniques. A comparison of catalysts activity under equal conditions is shown in Fig. 1.

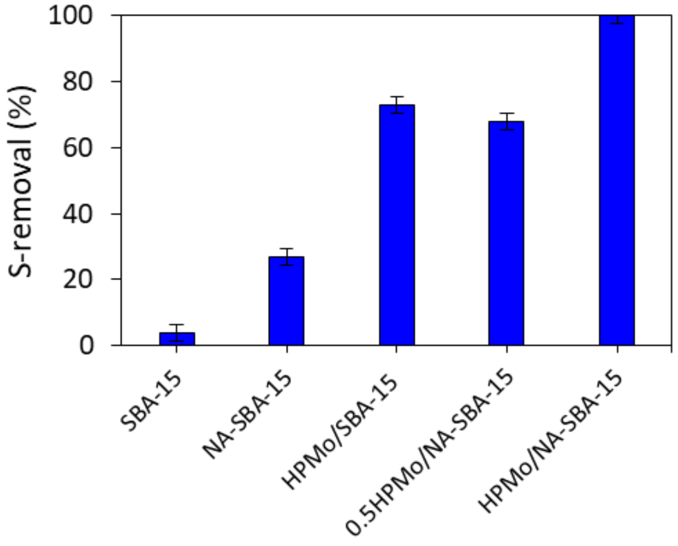

Fig. 1. Oxidation conditions: 5 min, 6:1, 80℃, catalyst dosage = 0.018 g/5 mL, the concentration of the DBT solution = 500 mg/kg

The support SBA-15 shows DBT conversion less than 10% which is connected with DBT adsorption. Immobilization of nicotinic acid (NA-SBA-15) leads to an increase of DBT conversion up to 30%, which is due to carboxylic acid fragment, acting as a catalytic center. The catalyst HPMo/SBA-15 shows high catalytic activity and allows to archive conversion of DBT up to 75%. A combination of carboxylic acid active sites with phosphomolybdic active sites in synthesized catalyst HPMo/NA-SBA-15 significantly increases its activity and allows the achievement of complete DBT oxidation in 5 minutes.

Nicotinic acid fragments, connected with support via a covalent bond, are also connected with phosphomolybdic acid anion with ion bond, which prevents active sites from leaching and allows to retain catalysts activity at least 10 reaction runs with preliminary regeneration, making them promising systems for clean fuel production.

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PP-V-2

Embryonic Zeolite Carriers Decorated with Metal Oxides and Metal Sulfides Nanoparticles

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Catalytic conversion of one-carbon (C1) molecules, such as CH_4, CO, CO_2, into value-added chemicals is a highly important process in the modern chemical industry [1]. The application of porous zeolite-based systems decorated with metal oxide nanoparticles has proved their effectiveness for C1-chemistry processes [2], especially for methane conversion to aromatic compounds [3, 4]. On the other side, the metal sulfide-decorated carriers have found an application for CO_2 hydrogenation or conversion to chemicals [5].

Embryonic zeolites (EZ) are an alternative to zeolite materials. Their usage allows decreasing the diffusion limitation for molecular transportation through the zeolite pores leading to blocking pores and catalyst deactivation. The embryo is a precursor of zeolite structure, which exhibits only a short-range order [6]. The embryonic zeolite is characterized by a very small particle size (3-5 nm) and an open-porous structure with micropore volume and specific surface area much higher than the fully crystalline counterpart.

We report on the use of the silica and silica-alumina embryonic counterpart of ZSM-5 as a carrier of MoO_3 and MoS_2 nanoparticles. The basic characteristics of embryonic zeolite carriers and MoO_3-, MoS_2-containing composites were studied by complementary physicochemical methods such as ^{29}Si, ^{27}Al MAS NMR, RAMAN and IR spectroscopy, powder X-ray diffraction, and N_2 physisorption. The impact of the preparation methodology on the metal oxide and metal sulfide species characteristics was studied. Special attention was paid to controlling the micro- and mesoporosity of the material. Thus a procedure to maintain the high specific surface area and porosity even after sulfiding (450-630 m^2/g and 0.2-0.67 cm^3/g) was developed. The systematic study of EZ – metal composites allowed us to improve their thermal stability and to be used in high-temperature processes (700 °C).

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PP-V-3

Silica-Supported Tungsten Oxide as Oxo/Imido Heterometathesis Catalyst

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Since its discovery in sixties, olefin metathesis has found very broad application both in industry and fine organic synthesis. At the same time, heterometathesis reactions, i.e. metathesis of multiple bonds containing heteroatom(s), are less studied. In previous works of our group oxo- and imido-complexes of early transition metals (Mo, V, Nb, Ta, Ti), homogeneous or silica-grafted, were reported to catalyze oxo/imido heterometathesis reactions, in particular, imidation of aldehydes and ketones with N-sulfinylamines leading to the formation of imines. This reaction is complementary to classical methods and allows obtaining imines based on sterically hindered ketones and/or electron-deficient anilines. However, routine application of this approach in organic synthesis is limited by the air- and moisture-sensitive nature and sophisticated techniques of preparation of the catalysts.

In the present work we are searching for more cheap, robust and easy-to-handle oxo/imido heterometathesis catalysts. Simple and widely used as industrial catalysts silica-supported early transition metal oxides (V_2O_5/SiO_2, MoO_3/SiO_2 and WO_3/SiO_2) prepared via wet impregnation, are the candidates due to the presence of terminal M=O bond. It is shown that MoO_3/SiO_2 and WO_3/SiO_2 mediate imidation of ketones with activities comparable with some of the previously reported systems prepared via Surface Organometallic Chemistry. W-based catalyst showed the highest activity, and thus, practical application and scope of WO_3/SiO_2-catalyzed reactions was further investigated. We also study for comparison some silica-supported tungsten imido complexes prepared via SOMC.

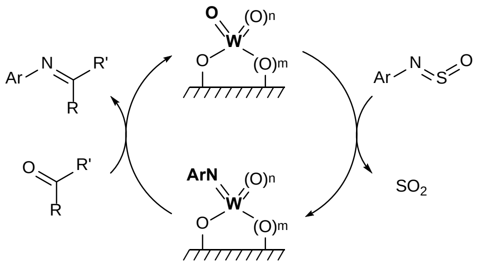

Fig. 1. Heterometathetical imidation of ketones with N-sulfinylamines catalyzed by silica-supported tungsten oxide

Acknowledgement. This work was supported by the Russian Science Foundation, grant 19-73-10163.

PP-V-4

A Mesoporous Carbon-Supported Copper-Based Catalysts for the Hydrogenation of CO_2 to Form Methanol and Dimethyl Ether

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The production of methanol and dimethyl ether is one of the potential routes for carbon dioxide utilization [1]. The main direction of upgrading these processes is to create new catalysts. The catalysts supported on carbon (graphene, graphene oxide, graphite and carbon nanotubes), have high specific surface area, have increased dispersion and reduced sintering of active components [2].

The aim of this study is to create catalysts for methanol and dimethyl ether synthesis from CO_2 and syngas. Mesoporous carbon-based material was obtained by the template method and was used as a carrier [3]. Based on this material, a series of Cu/ZnO/C catalysts with a different ratio of components was obtained by co-precipitation and impregnation methods from aqueous solutions of proper salts.

In this study, synthetic route and physicochemical properties of the synthesized catalysts has been investigated. The factors which impact on the phase composition and crystallite size of active metals have been estimated as well.

The activity of catalysts was evaluated in the methanol and dimethyl ether synthesis from CO_2 and syngas at a flow catalytic installation. A mesoporous carbon-supported catalysts exhibit higher activity in comparison with the well-known alumina-supported catalysts.

Experimental data shows that the developed approach may be promising to synthesize efficient catalysts for the methanol and dimethyl ether synthesis from CO_2 and syngas.

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PP-V-5

Determination of the Optimal Ratio of the Initial Reagents of the MTBE Synthesis Process

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The influence of the feedstock on the quality of high-octane additives (methyl tert-butyl ether) and process parameters when it is received is studied. A mathematical model describing the synthesis of methyl tert-butyl ether is proposed for comparison with empirical data.

Methyl tert-butyl ether (MTBE) is an effective non-toxic high-octane component, the octane mixing number of which reaches 135 points according to the research method, depending on the hydrocarbon composition of gasoline. The use of MTBE makes it possible to produce highoctane gasoline based on a wide range of base gasoline [1].

The main goal of modern research is to solve the problem of determination of the optimal ratio of the initial reagents of the MTBE synthesis process. To determine the parameters that have the greatest impact on the quality and yield of the target product, it is necessary to create a mathematical model of the process and evaluate its compliance with empirical data.

The production technology of MTBE consists in the addition of methyl alcohol CH_3OH to isobutylene C_4H_8. MTBE is obtained in one stage, under "soft" conditions of the process (low temperatures and pressures). The reaction is carried out on a special catalyst (most often ion exchange resins) with high selectivity and almost complete conversion per pass [1].

The flow chart contains two nodes. In the first node, the ether is directly synthesized and isolated, in the second node, the unreacted hydrocarbons are purified from alcohol and the alcohol is returned back to the process.

Experimental studies were conducted to verify the adequacy of the description. For this purpose, the indicators of isobutylene content in the feedstock (BBF), methanol content in commercial MTBE, as well as technological parameters of the process were recorded for 2 days: the temperature of the control plate of the reaction-rectification unit, the consumption of methanol in the mixing unit and synthesis reactor, the consumption of BBF in the mixing unit [2].

Let's make an equation of the material balance according to the model of the reactor of ideal displacement for reagent A [3]. Reagent A enters the elementary volume of dVp with the input flow, and the flow rate - with the output flow and as a result of chemical transformation in this volume.

According to this:

$n_A|_l = n_A|_{l+dl} + W_A(C)dV_p$,

where $dn_A/dV_p = -W_A(C)$, or taking into account, that $dV_p = Sdl\ dn_A/dl = -W_A(C)S$,

where n_A is molar flow rate of the reagent *A, mol/sec*.

If the volume of the reaction mixture does not change during the reaction (V = const), then the volume flow rate v = const. Given that nA = vCA and Vp = vτ, under these conditions we obtain dCA/dτ = - WA(C).

PP-V-5

A further stage of the study was the need to compile a system of ordinary differential equations.

$$\begin{cases} x_0 - isobutylene \\ x_1 - methanol \\ x_2 - MTBE \\ x_3 - H2O \\ x_4 - \ isobutanol \\ x_5 - \ isooctyl \\ x_6 - \ dimethyl\ either \end{cases} \begin{cases} x_0 + x_1 = x_2 \\ x_0 + x_3 = x_4 \\ 2x_0 = x_5 \\ 2x_1 = x_6 + x_3 \end{cases} \begin{cases} w_0 = k_0 x_0 x_1 \\ w_1 = k_1 x_0 x_3 \\ w_2 = k_0 (x_0)^2 \\ w_3 = k_3 (x_1)^2 \end{cases}$$

A program was developed for performing calculations. It is developed in the Python programming language. Implicit Runge-Kutta method of the Radau IIA family of order 5 was utilized to solve a system of ordinary differential equations (SciPy-package).

The model obtained from the calculation results is shown in figure 1. The X axis is the length of the catalyst layer. Figure 1 shows the dependence of the molar fractions of the reaction components along the length of the catalyst layer (L, length).

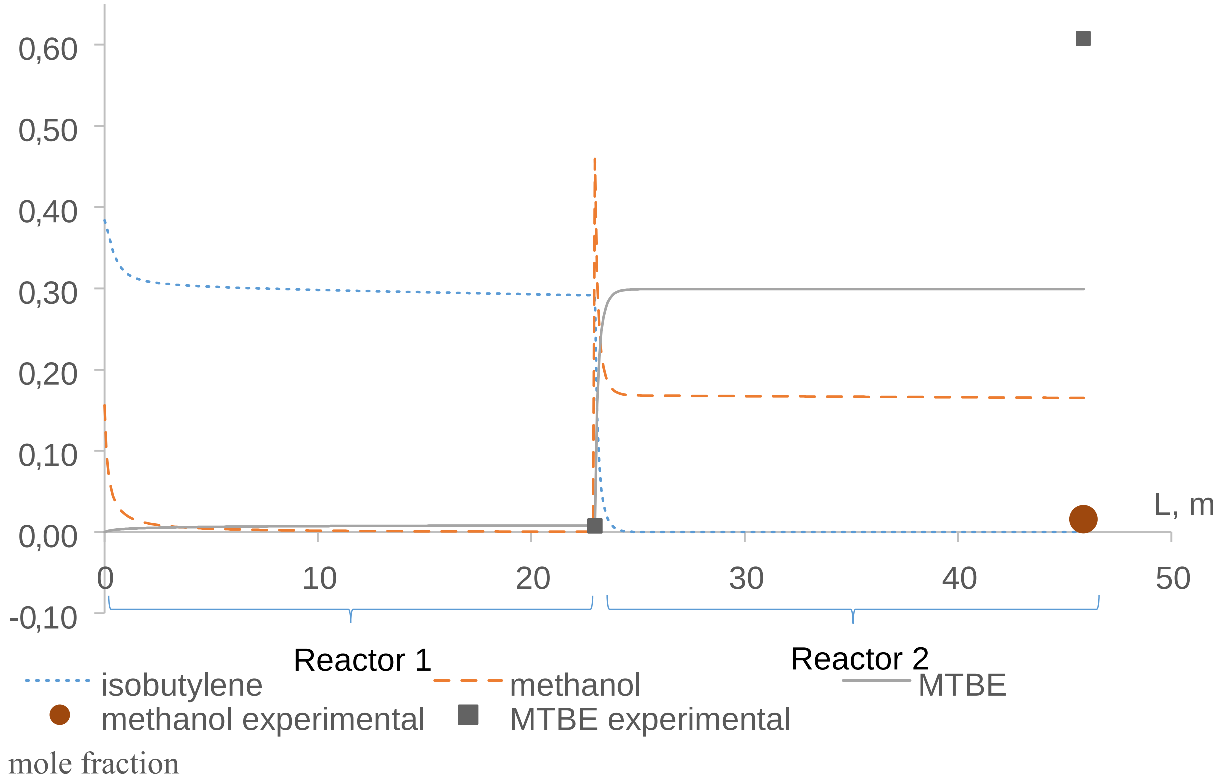

Fig. 1. Model of the MTBE synthesis process

The resulting model does not fully describe the MTBE synthesis process. Solution of the inverse problem of chemical kinetics for determining the kinetic parameters of the process is the goal of further research.

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PP-V-6

Heterogeneous Catalysts Based on Anderson-Type Polyoxometales for Aerobic Oxidation of Sulfur-Containing Compounds

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The problem of sulfur removal in oil fractions is still urgent [1]. The annual increase in the sulfur content of produced oil has a negative impact on the environment around the world [2]. Sulfur-containing compounds in the petroleum crude oil are toxic and corrosive substances, as well as poisons for catalysts for secondary oil processing [3]. In many countries, the permissible values of sulfur content in commercial fuels are strictly regulated, but there is a tendency to tighten standards.

Traditional methods of desulfurization (hydrodesulfurization) include the use of expensive hydrogen-containing mixtures, the use of high pressure and temperature [4]. Mercaptans, sulfides, and disulfides are removed during hydrodesulfurization, but hydrogenation of the main class of sulfur-containing compounds, namely condensed thiophene derivatives, is difficult due to their low reactivity. In the last decade, alternative methods for removing sulfur with a high degree of purification and based on the use of adsorbents, extractants, oxidizers, and various biologically living organisms have been proposed. The most widely known alternative method is the oxidative desulfurization (ODS), which includes the removal of sulfur-containing compounds under the action of oxidants, followed by the removal of oxidized products by extraction and adsorption methods. The use of various oxidizers is known from the literature, but the most interesting of them is air oxygen [5]. An important advantage of using air oxygen is its availability and safety, and in the case of O_2 contained in air as an oxidizer, it is also cheap.

Polyoxometalates (POMs) are universal oxidation catalysts that have received wide interest as a result of high activity in the presence of oxygen or air [1, 6]. The advantage of polyoxometalates as aerobic oxidation catalysts over other systems is their multifunctional active center, containing protons, atoms of oxygen, and metals. Anderson-type polyoxometalates with a mixed valence of a transition metal atom, which exhibit high catalytic activity under rather mild conditions (150 °C) in oxidative desulfurization reactions with atmospheric oxygen, attract great attention. Anderson-type polyoxometalates are a planar structure containing a central metal-oxygen octahedron surrounded by six edge MO_6 octahedra (where M = W or Mo). Each skeleton of a metal atom is bonded to two terminal oxygen atoms, which provide high catalytic activity in oxidation reactions of sulfur-containing substrates.

In this work, new highly active heterogeneous catalytic systems based on immobilized polyoxometalates of the Anderson type has been developed. In this work, catalysts with an Anderson type polyoxometalate anion ($[X^{n+}Mo_6O_{24}]^{m-}$, where $X = Co^{3+}$) were synthesized for the first time as an active phase by chemical grafting onto the functionalized surface of mesoporous silicate of SBA-15 types with highly developed surface and pore diameter satisfying the requirements for diffusion of condensed thiophene derivatives. The obtained catalysts were effectively used for the oxidation of organosulfur substrates with air oxygen as an oxidizing agent. The optimal conditions for the oxidation of model mixtures and the regularities of the oxidation of sulfur substrates were determined depending on the pore volume of the support structure, the nature of the support material, the nature of the functionalized group, and the amount of polyoxometalate as an active center on the support surface. The effect of temperature, oxidant feed rate, catalyst dosage, initial sulfur content and nature of the sulfur substrate in the process of aerobic oxidation on the conversion of the sulfur-containing compound is shown. The possibility of the catalyst reuse was investigated, and the conditions for deactivation of the catalyst and the conditions for regeneration of catalytic activity were determined. Complete oxidation of dibenzothiophene was achieved in the presence of chemically grafted polyoxometalate of the Anderson type on the imidazole-functionalized SBA-15 surface at 120℃ for 4 hours with an air flow of 6 l / h.

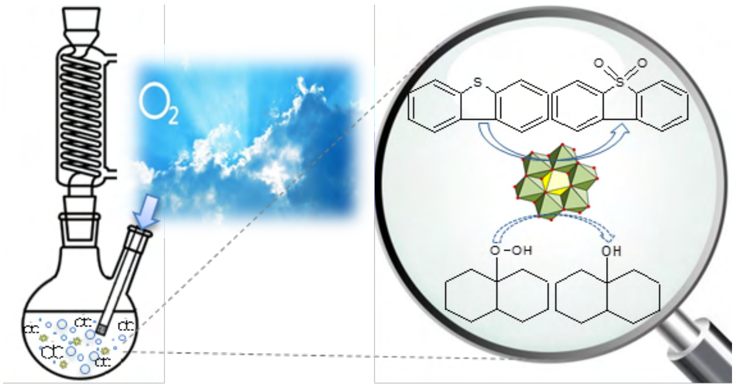

Fig. 1. Graphical abstract of aerobic oxidation of sulfur-containing compounds in the presence of a heterogeneous catalyst.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant № 20-33-90330\20.

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PP-V-7

Kinetic Characteristics of Catalysts Based on Mesoporous Silicagels Doped with Disprosium, Lanthanum and Modified with Ni, in the Hydrogenation Reactions of Aromatic Hydrocarbons

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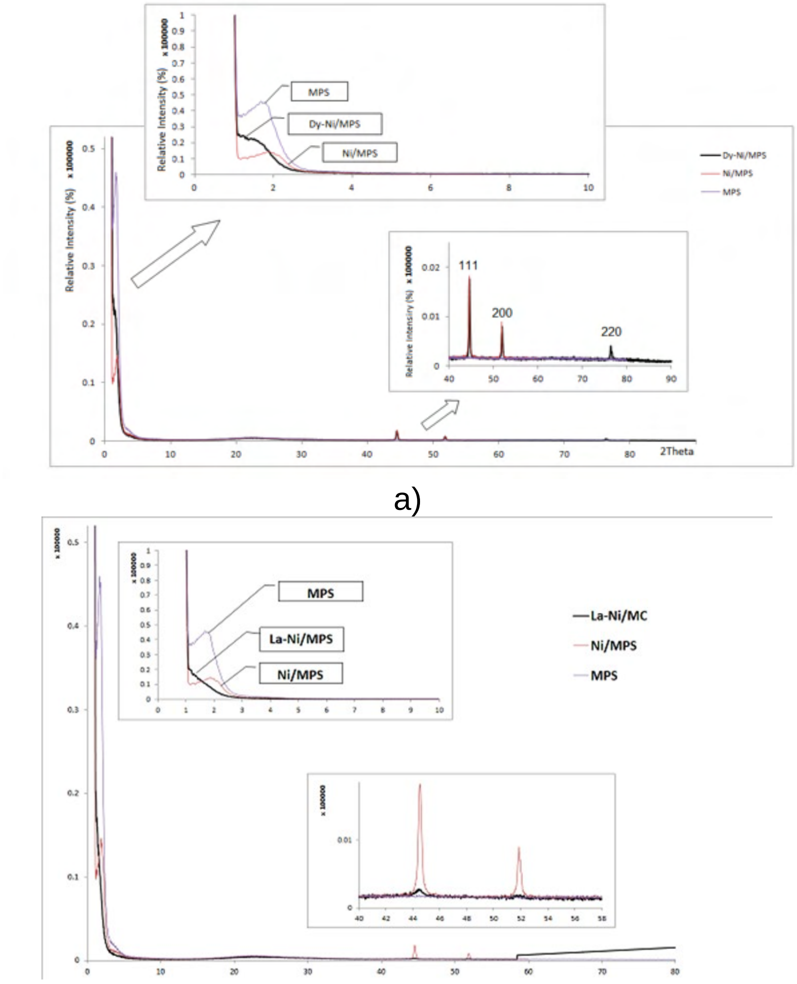
Samples of mesoporous silica gel doped with dysprosium and lanthanum and modified with nickel (Dy-Ni/MC, La-Ni/MC) were synthesized by the template method. To confirm the presence of metals in mesoporous silica gels, X-ray fluorescence analysis (XRF) and inductively coupled plasma (ICP) spectrometry were used. The ICP method was used for quantitative determination of metals by the method of absolute calibration. The metal concentrations for Dy-Ni/MC were: Ni - 7% by mass, Dy - 1.3% by mass, for La-Ni/MC: Ni - 7% by mass, La - 1.8% by mass. For a more detailed study and confirmation of the phase composition of samples of mesoporous silicagels, X-ray phase analysis (XRD) was used (Fig. 1).



a)

b)

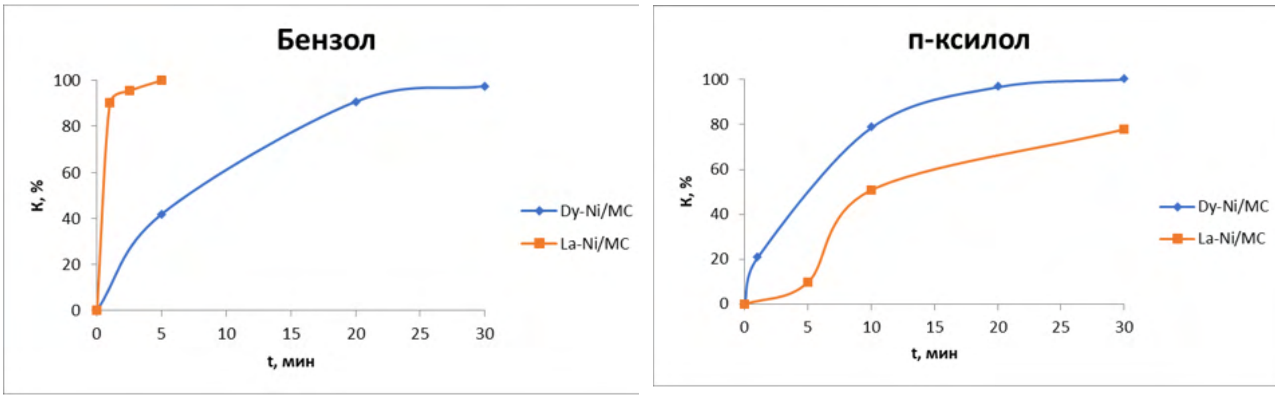
Fig. 1. Diffractograms for samples a) MC, Ni/MC u Dy-Ni/MC, b) MC, Ni/MC u La-Ni/MC.

The characteristic peak in the low-angle region indicates the presence in the structures for all synthesized mesoporous silicagels of an ordered mesoporous system corresponding to the MCM-41 type phase. Nickel in the form of a metallic phase is confirmed by the corresponding reflections

(2Θ = 44.5, 51.9, 76.4) in the diffractograms corresponding to a cubic face-centered cell of metallic nickel with Bravais indices (111), (200) and (220), respectively.

The textural characteristics of the samples were determined by the nitrogen adsorption-desorption method on a Quantochrome Autosorb-1. The specific surface area was calculated by the BET method. The obtained Dy-Ni/MC and La-Ni/MC samples are characterized by the following surface areas of 215 and 467 m^2 g^{-1}, respectively.

The hydrogenation of benzene and o-, m- and p-xylenes was carried out in a static mode, in the temperature range 80 - 170 ° C and a hydrogen pressure of 3 atm, on an original installation that allows the analysis of the reaction mixture in on-line mode.



a) b)

Fig. 2. Dependence of the conversion of benzene and p-xylene on the reaction time on the Dy-Ni/MC and La-Ni/MC catalysts (temperature 150 ° C, pressure 3 atm).

In the hydrogenation of benzene on La-Ni/MC,the maximum conversion is achieved within 5 min from the beginning of the reaction, and on the Dy-Ni/MC catalyst it is achieved in 30 minutes (Fig. 2a). The conversion of p-xylene after 30 minutes from the start of the reaction on Dy-Ni/MC is higher and reaches a maximum, and on La-Ni/MC it is reaches only 80% (Fig. 2b).

Acknowledgement. This work was supported by the RFBR grant No. 19-33-90207 and the government grant No. FSSS-2020-0016.

PP-V-8

Polymerization of Ethylene Catalyzed by Fluorinated Phenoxyimine Catalysts

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Post-metallocene transition metal complexes are promising catalyst systems for olefin polymerization allowing the production of polymers with valuable properties. Among the various organometallic complexes phenoxyimine catalysts (also known as FI catalysts) discovered by T. Fujita in the late 1990s are of particular interest. Bis(phenoxymine) titanium (IV) complexes have a number of important properties, such as high catalytic activity, stereo selectivity, thermal stability. Polymerization catalyzed by fluorinated FI complexes, in some cases proceeds according to the “living” mechanism. It allows to produce polyethylene with ultra-high molecular weight (>10^6 g/mol) and high crystallinity [1]. This type of polymer has many distinctive properties such as increased shock and wear resistance, low coefficients of friction and water absorption, high resistance to radiation and aggressive chemical environments. Combination of these properties allow to use UHMWPE for substituting high stress materials like a steel or polyamide.

In the present work the fluorine-containing phenoxyimine chelate ligands are synthesized in high yields by the Schiff base condensation of the corresponding fluorine containing aniline with 2-hydroxy-3-[1-[4-(tert-butyl)phenyl]ethyl]-benzaldehyde using p-toluenesulfonic acid as a catalyst. The titanium complexes **1**-**7** are prepared in good yields by the reaction of $Ti(O^iPr)_2Cl_2$ with 2 equiv of the fluorine-containing phenoxyimine ligand in dried dichloromethane. The catalytic properties of a series of titanium complexes containing polyfluorinated phenyl or naphthyl fragments have been studied in the suspension ethylene polymerization. It was found that these complexes activated with modified polymethylaluminoxane MMAO-12 (ratio Al_{MMAO}/Ti = 1000, 30 °C, 1 h, ethylene pressure 0.25 MPa, solvent - toluene), showed activity in the range 100-310 kg_{PE}/g_{Ti} · MPa · h (Fig. 1).

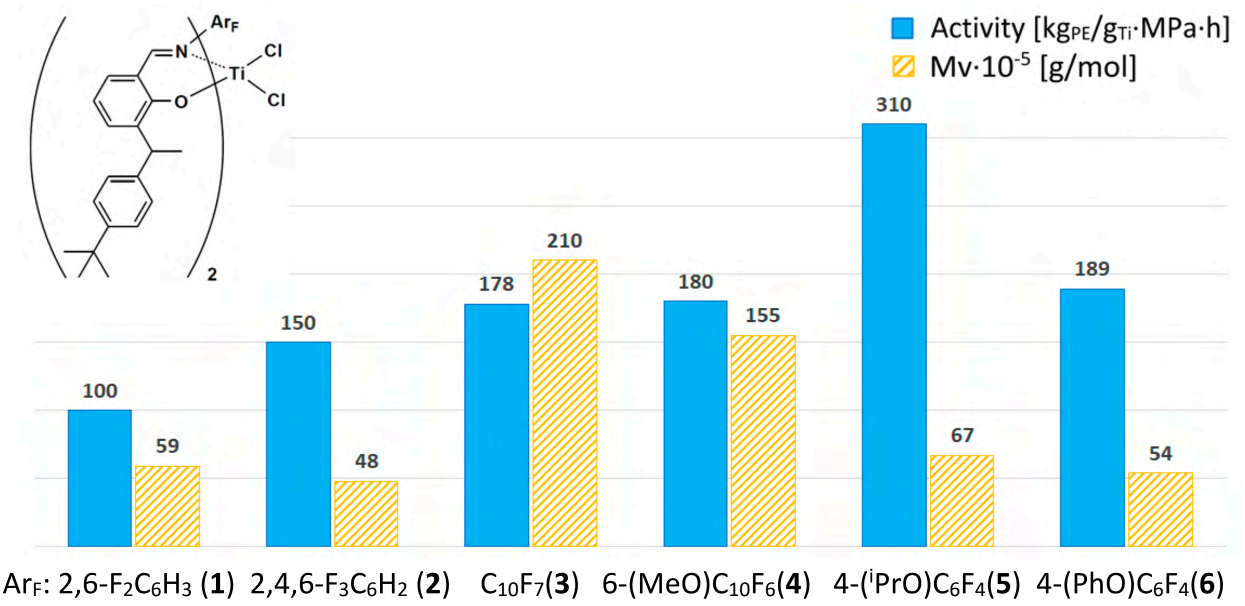

Fig. 1. Ethylene polymerization results with FI catalysts.

Properties of polyethylene nascent powders were investigated by differential scanning calorimetry and capillary viscosimetry. All PE's obtained possess high degree of crystallinity (>64%) and melting temperature 135 - 143°C.

Table 1. Properties of the nascent polyethylene powders

PE	Ar_F	T_m, °C		Crystallinity, %		M_v, g/mol
		T_1 [a]	T_2 [b]	X_1 [a]	X_2 [b]	
PE-**1**	$2,6\text{-}F_2C_6H_3$	143,0	134,8	68,2	34,7	$5{,}9\times10^6$
PE-**2**	$2,4,6\text{-}F_3C_6H_2$	142,9	134,0	64,4	31,7	$4{,}8\times10^6$
PE-**3**	$C_{10}F_7$	142,6	136,2	70,3	36,6	$>21{,}3\times10^6$
PE-**4**	$6\text{-}MeO\text{-}C_{10}F_6$	141,1	135,4	70,5	35,9	$15{,}5\times10^6$
PE-**5**	$4\text{-}{}^iPrO\text{-}C_6F_4$	143,5	135,3	66,3	33,2	$6{,}7\times10^6$
PE-**6**	$4\text{-}PhO\text{-}C_6F_4$	142,7	136,4	65,1	33,4	$5{,}4\times10^6$
PE-**7**	$3,4,5\text{-}F_3C_6H_2$	135,3	136,3	67,6	55,8	$3{,}3\times10^5$

[a] – first melting, [b] – second melting

The effect of polymerization conditions on catalyst activity and molecular weight of the resulting polymer was investigated using complex containing 3,4,5-trifluorophenyl fragments (**7**) (Fig. 2).

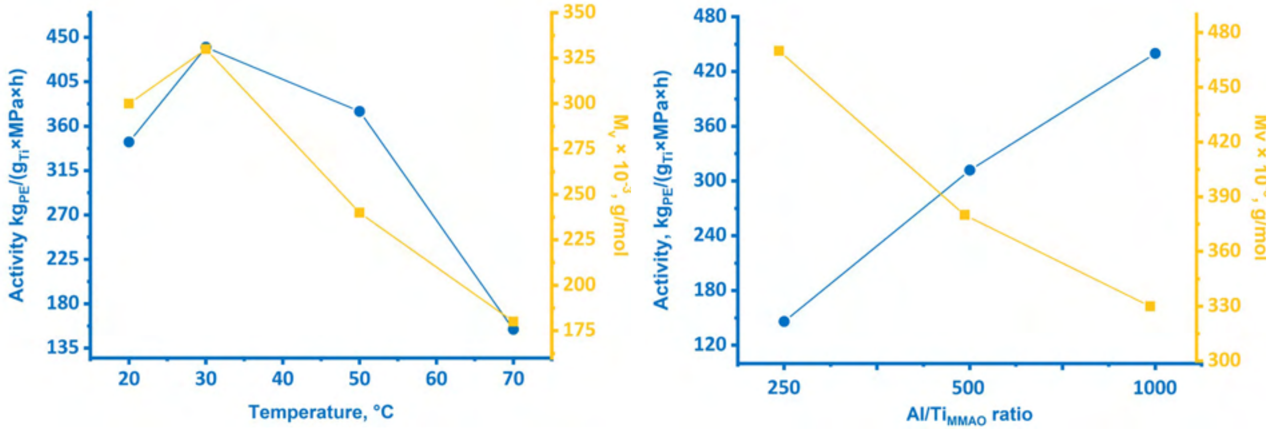

Fig. 2. Temperature and co-catalyst concentration dependency of catalytic activity (catalyst with 3,4,5- trifluorophenyl fragments)

As the temperature increases, the catalytic activity and molecular weight of the PE behave in a similar manner - first they increase and then decrease when the temperature reaches about 30-40°C. An increase in the concentration of organoaluminum activator leads to an almost linear growth in activity with a simultaneous drop in the molecular weight of the resulting PE.

In conclusion it has been shown that the structure of fluorinated aryl fragments in imine moieties of the ligands has a significant effect on the activity titanium phenoxyimine complexes and properties of the obtained polymers.

Acknowledgement. The work was conducted within the framework of budget project for Boreskov Institute of Catalysis.

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PP-V-9

Study of the Effect o-Phenanthroline on Cumene Oxidation and Composition of Products in the Presence of an Organic Catalyst N-Hydroxyphthalimide and Fe(III)/o-Phenanthroline Promoter

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Liquid-phase aerobic oxidation of hydrocarbons affords industrially important chemicals such as terephthalic acid, cyclohexanon, tert-butyl and alkylbenzene hydroperoxides. Recently, cyclic imides, especially N-hydroxyphthalimide (NHPI), have attracted much attention as promising catalysts [1,2]. The initiators and cocatalysts can be transition metals or non-metal compounds, such as hydroperoxides, azo-compounds, quinones and etc. [4]. Hydroperoxide is obtained with high selectivity in the presence of non-metallic cocatalysts, while it decomposes in the presence of transition metal compounds to form stable products such as alcohols and ketones.

However, we have previously observed the oxidation of cyclohexene and ethylbenzene to the corresponding hydroperoxides in the presence of NHPI and Fe(III) salt as initiator [5]. Since NHPI seems to be a very promising catalyst for the preparation of cumene hydroperoxide (CHP) [6], we tried to use NHPI together with an iron (III)/Phen cocatalyst in the oxidation of cumene. Indeed, *o*-phenanthroline (Phen) is known to be an effective additive for regulating autooxidation processes, for example, the well-known studies of Emmanuel et al. [7] and more recent study of the combined action of NHPI, Br_2 and Phen [8]. Thus, the aim of our study is to investigate in detail the effect of the Fe(III)/ Phen cocatalyst on efficiency and products of the NHPI catalyzed oxidation of cumene.

The oxidation of cumene was studied at a temperature of 40-60 °C. As the temperature decreased, the reaction rate decreased, although even at 40 °C the reaction proceeded faster in the presence of Phen than at 50 °C without Phen (Fig.1).

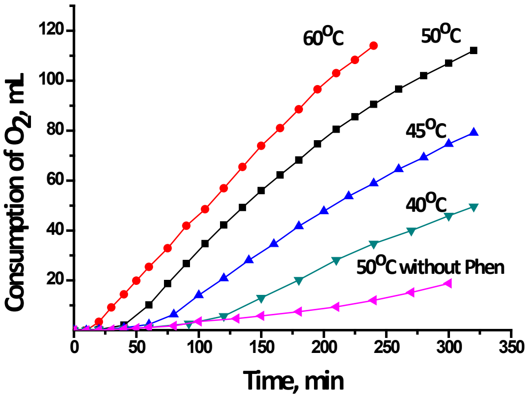

Fig. 1. Oxygen consumption during cumene oxidation at different temperatures Conditions: 14.4 mmol (2.0 mL) cumene, 141 µmol NHPI, 0.36 µmol Fe(acac)$_3$, 0.108 µmol Phen, acetonitrile, volume of solution 2.5 mL, O_2 atmosphere.

In a series of tests, the reaction continued until conversion of cumene was close to 20%. It was found that with an increase in the amount of Fe (III) salt from 1.6 10^{-6} to 7.2 10^{-6} M, a significant increase in the reaction rate was observed with a slight change in the selectivity for hydroperoxide. A further increase in the amount of salt to 5.8 · 10^{-4} M didn't affect on the rate and selectivity of the reaction. An increase of NHPI from 7.2·10^{-3} M to 5.6·10^{-2} M resulted in reduction of the reaction time to reach the appointed conversion of cumene and in increase of selectivity to hydroperoxide (Fig.2A). In this case, a weak dependence of products on the amount of NHPI was observed. The promoting effect of Phen was noticeable even with a tenfold excess of Fe(III) in relation to Phen and further intensified under increase of Phen to Fe(III) ratio (Fig.2B).

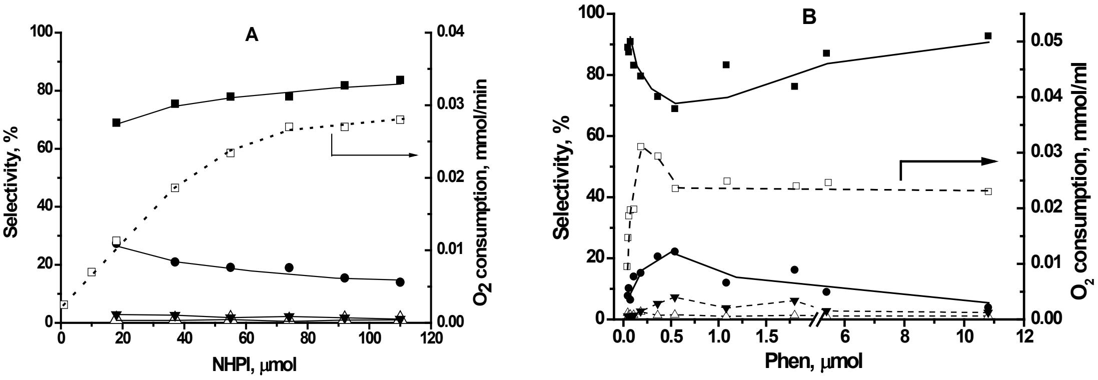

Fig. 2. Oxidation products and stationary rate of O_2 consumption ***A*** *– depending on NHPI quantities with 0.108 µmol Phen;* ***B*** *– depending on Phen with 141 µmol NHPI. Conditions: 0.36 µmol Fe(acac)$_3$, NHPI, 14.4 mmol cumene, CH_3CN, solution volume 2.5 mL, O_2 atmosphere, 50 °C. ■ – CHP, ● –2-phenyl-2-propanol, Δ – α-methylstyrene, ▼ – acetophenone*

Phen causes a shorter initial period and an increase in the stationary rate of O_2 consumption (Fig.1). Composition of the products also changed significantly: with addition more than one and a half excess of Phen as compared to Fe(acac)$_3$ the selectivity for CHP increased from 68 to 96%.

As a result of our study, it was possible to understand the action of the complex initiator Fe(III)/Phen and to select the optimal composition of the catalytic system, which made it possible to obtain CHP under mild conditions and without loss in selectivity as compared to the reaction catalyzed by NHPI only carried at 110-130 °C.

Acknowledgements. This work was performed as part of a State Task for the Boreskov Institute of Catalysis, project No AAAA-A17-117041710083-5, and was supported by the Russian Foundation for Basic Research and Novosibirsk Region Government, project No 19-43-540008.

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PP-V-10

Hydrogenation of Eutectic Mixture of Biphenyl and Diphenylmethane over Supported Platinum Catalysts

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Hydrogen energy has become increasingly important in recent times because of the increasing emission requirements for air pollutants. The application of new technologies is impossible without the development of safe hydrogen storage and transport methods.

Liquid Organic Hydrogen Carriers (LOHC) represents a potential solution to this problem using the existing fossil fuel infrastructure. There are several requirements for LOHC systems: high hydrogen capacity, thermal stability, suitable boiling and melting temperatures, favorable thermodynamic conditions for hydrogenation-dehydrogenation, accessibility, low toxicity, and acceptable cost [1].

A potential hydrogen storage carrier was studied and was obtained by mixing biphenyl ($C_{12}H_{10}$, solid) and diphenylmethane ($C_{13}H_{12}$, liquid) with a mass ratio (mass%) of 35:65. The eutectic mixture is liquid at ambient temperature, potentially meeting the requirements for an effective hydrogen storage system [2]. The hydrogenation scheme of the eutectic mixture is shown in figure 1.

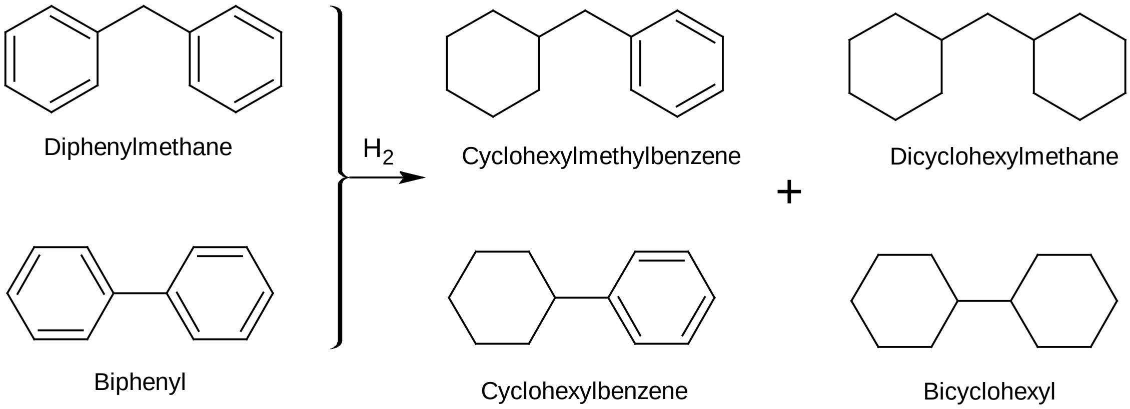

Fig. 1. Hydrogenation scheme of the eutectic mixture of the biphenyl and diphenylmethane

Platinum catalysts on Al_2O_3, MCM-48, and SiO_2 carriers have been tested in the hydrogenation of the eutectic mixture. The active ingredient was applied to the prepared carrier fraction by a single impregnation method based on the moisture content. 2 wt.% of platinum was loaded from the aqueous chloroplatinic acid solution H_2PtCl_6. Synthesized catalysts were studied by low-temperature nitrogen adsorption, temperature-programmed reduction, high-resolution transmission electron microscopy.

The activity of the synthesized catalysts in the hydrogenation reaction of a mixture of biphenyl and diphenylmethane was carried out under the following conditions: temperature range 150-170°C, pressure 1-4 MPa, liquid hourly space velocity (LHSV) of 5-15 h^{-1} and hydrogen to feedstock ratio 500 nl/l. A model mixture of 2 wt.% solutions of the eutectic mixture in heptane was used as a raw material.

Table 1

Textural and structural characteristics of prepared catalysts

Sample	S_{BET}, m^2/g	V_{pore}, sm^3/g	D_{pore}, nm	Particles size Pt, nm	Conversion, %mass	
					biphenyl	diphenylmethane
2 Pt/MCM-48	1348	0,56	3,8	2.0	86,0	98,0
2 Pt/SiO_2	320	0,93	8,4	3.1	83,0	80,0
2 Pt/Al_2O_3	229	0,81	11,2	5.6	61,6	44,0

Based on experimental data on the study of Pt/Sup catalysts' activity in the hydrogenation reaction of a eutectic mixture of biphenyl and diphenylmethane, it was found that the activity of catalysts decreases in the order $2Pt/MCM\text{-}48 > 2Pt/SiO_2 > 2Pt/Al_2O_3$. The conversion of biphenyl and diphenylmethane was close to maximum (80-90 %mass), which confirms the high hydrogen storage capacity.

Catalyst support nature has a significant influence on the morphology of the formed active phase of Pt/sup catalysts. Alumina and silica-supported catalysts have bigger platinum nanoclusters on the surface than structured silicate MCM-48. The use of mesostructured silicate as catalyst carriers allows to increase the active phase dispersion.

Catalyst Pt/MCM-48 can be considered a promising catalyst for implementing the catalytic LOHC hydrogenation-dehydrogenation cycle based on a eutectic mixture of biphenyl and diphenylmethane.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14Z50.31.0038.

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PP-V-11

Directed Synthesis of Porous Aromatic Frameworks as Supports for Transition Metal Nanoparticles in Various Hydrogenation Processes

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Porous aromatic frameworks (PAFs) are polymer materials constructed of aromatic rings, connected to each other by covalent C–C bonds. Their distinctive features are high specific surface areas, chemical and physical stability and rigid structure. Due to aromatic nature of PAFs, a wide range of well-known and relatively simple techniques of functionalization is available. Thorough selection of reagents and synthesis conditions allows to obtain materials with already implemented functionalities and structural characteristics tuned for specific purposes.

All aforementioned advantages make PAFs promising materials for heterogeneous catalysis, because they allow them to effectively stabilize transition metal nanoparticles – one of the most effective type of catalysts in fine organic synthesis and petrochemistry. The use of PAFs as supports for metal nanoparticles solves the problem of aggregation and deactivation of the latter and improves selectivity, activity and stability of the catalysts. It is possible therefore to tune characteristics of the catalyst for any specific process.

In our current study we developed transition metal catalysts based on different PAFs for hydrogenation of unsaturated hydrocarbons and levulinic acid. In all cases catalysts were synthesized by wetness impregnation of the material with the salt of corresponding metal followed by its reduction with sodium borohydride.

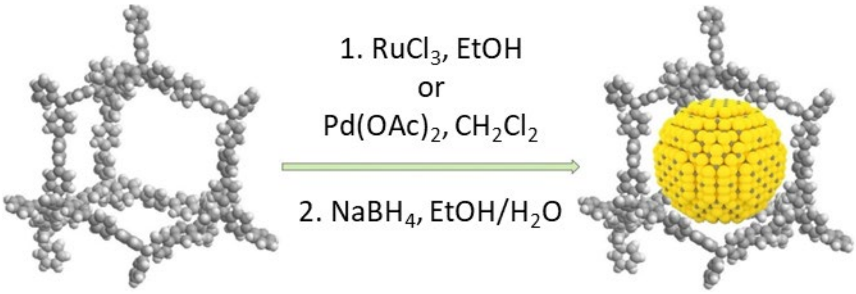

Fig. 1. Schematic synthesis of the catalyst.

It is well-known, that palladium catalysts are one of the most effective in the hydrogenation of alkenes and dienes and that nitrogen-containing additives significantly improve their performance. Firstly, we synthesized PAFs with amino groups using two approaches: post-modification, which involves functionalization of previously obtained polymer [1]; and pre-modification, when monomers, modified with functional groups, are used in the synthesis of PAF. It was demonstrated, that post-modification method leads to the decrease of PAFs surface area, whereas pre-modification allows to retain it. All Pd-catalysts prepared from this series exhibited high activity and stability in the hydrogenation of 1-octyne, phenylacetylene and 2,5-dimethyl-2,4-hexadiene.

However, for catalysts based on pre-modified materials selectivity towards needed olefin improved significantly.

We also applied post-modification approach to synthesize PAFs with dendritic functionalities using diethanolamine and acrylonitrile. It was shown, that the structure of the catalyst influence drastically the morphology of an active phase and therefore the activity of the catalyst. For the material PAF-20 with the pore size about 3 nm, modification with diethanolamine blocked the pores of the framework for the substrate, and synthesized catalysts were almost unactive. However, for material PAF-30 with slightly bigger pores (~5 nm) the first modification with diethanolamine (PAF-30-G0) improved distribution of the Pd nanoparticles in the pores of the material and stability of the catalysts. However, the second one (PAF-30-G1) blocked the pores of the framework for both active phase and substrate, which led to the dramatic loss of activity (Fig. 2, A) [2].

Post-functionalization technique was also used to obtain materials PAF-20-SO_3H and PAF-30-SO_3H, that were further used as supports for ruthenium nanoparticles. Synthesized catalysts were examined in the hydrogenation of levulinic acid. It was demonstrated, that pore size plays critical role in the process. While for Ru–PAF-20-SO_3H with smaller pores conversion of levulinic acid only reached 40% after 4 hours of the reaction (1 MPa H_2, 80°C), for Ru–PAF-30-SO_3H full conversion into γ-valerolactone was observed at the same conditions (Fig. 2, B).

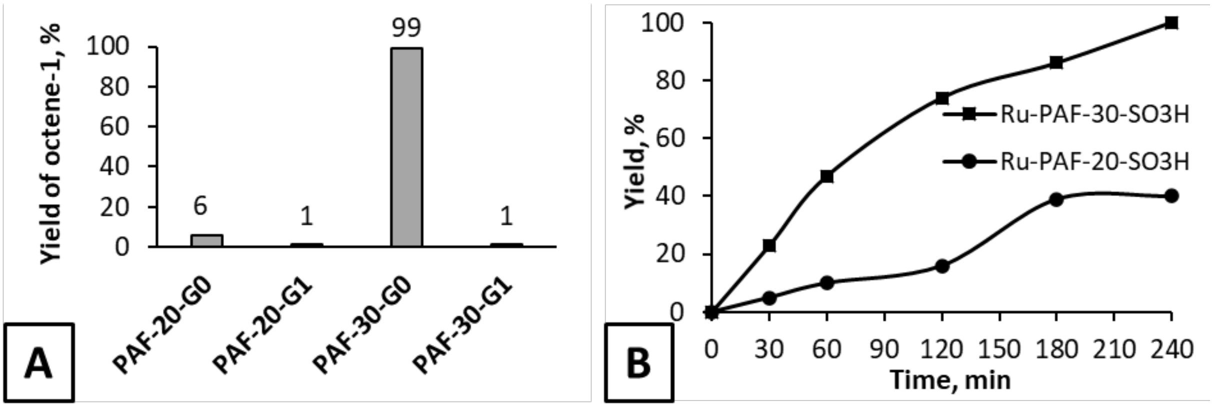

Fig. 2. Catalytic results. A) Conversion of octyne-1 to octene-1 over Pd-catalysts based on PAFs, modified with diethanolamine groups. Reaction conditions: 80 ℃, 1 MPa H_2, 30 min. B) Conversion of levulinic acid to γ-valerolactone over sulfo-modified Ru-catalysts. Reaction conditions: 80 ℃, 1 MPa H_2, substrate:metal = 420.

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PP-V-12

Synthesis of Mannitol from Inulin Using a Magnetic Catalyst

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Mannitol, $C_6H_{14}O_6$, is employed in pharmaceutical, chemical, and food industry as well as in biotechnology. It is used to treat brain diseases, as a food supplement (E421) and a sweetener in diabetic foods, in the production of resins, linseed oil, coatings, surfactants, explosives, and cosmetics.

There are several methods for mannitol syntheses. It can be obtained by hydrolytic hydrogenation of inulin [1], a polysaccharide which is not digested by humans and which is present in significant amounts in such plants as *Heliánthus tuberósus* (16 - 18%) and *Cichorium intybus* (up to 20 %). The polysaccharide hydrolytic hydrogenation can be carried out as a one-pot procedure in the presence of heterogeneous catalysts containing various precious metals. Ru-containing catalysts are considered most active in hydrolytic hydrogenation and hydrogenolysis [2].

Magnetically separable catalysts received considerable attention due to easy magnetic separation from reaction mixtures, facilitating the catalyst repeated use and allowing one to save energy and materials, thus decreasing the target product costs [3]. It is noteworthy that when the biomass conversion is incomplete, the magnetic separation is especially valuable for the catalyst recovery and the process optimization.

Here, we report utilization of a magnetically separable Ru-containing catalyst based on magnetic silica (Fe_3O_4-SiO_2) in the inulin hydrolytic hydrogenation to mannitol. We studied the behavior of the Ru-containing magnetically separable catalyst in the conversion of inulin to mannitol, exploring different reaction conditions. In the hydrolytic hydrogenation of inulin the maximum selectivity to mannitol of 44.3% was obtained at 150°C, $P(H_2)$ 60 bar, 0.1167 mmol of Ru per 1 g of inulin for 45 min with the catalytic activity of 2.53 h^{-1}. Under these conditions, the inulin conversion reached 100%. It is noteworthy that the selectivity reported here exceeds that of commercially available Ru/C. Moreover, the 5% Ru-Fe_3O_4-SiO_2 catalyst is more efficient than other catalysts reported in literature, judging by the activation energy. These factors and the excellent catalyst stability under hydrothermal conditions as well as easy magnetic separation make 5% Ru-Fe_3O_4-SiO_2 the catalyst of choice for practical applications in biomass conversion.

Acknowledgement. This work was supported by the Russian Science Foundation (grant 19-19-00490), and by the Russian Foundation for Basic Research (20-08-00079, 19-08-00414, 18-29-06004_мк).

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PP-V-13

Surface Modified Bimetallic Catalysts for Selective Hydrogenation of Acetylene

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Ethylene cuts produced by steam cracking of hydrocarbon feedstocks typically contain 0.5-2% of acetylene, which is a strong poison for polymerization catalysts[1]. The common method for acetylene removal is its selective hydrogenation to acetylene. The main issue is the achievement of high selectivity to ethylene.

A new method for preparation of selective hydrogenation catalysts by decomposition of metal-organic compounds such as ferrocene and cymantrene has been developed. The method allows to cover palladium surface atoms by a promoter atoms layer, i.e. to prepare bimetallic Pd-M/Al_2O_3 catalysts (where M = Fe, Mn).

The decompositions of ferrocene and cymantrene in a H_2 flow over reduced Pd/Al_2O_3 were studied by mass spectrometry of the reactor effluent. The decomposition of ferrocene proceeds in two steps. At the first one, at 100-210 ºC, a part of the ligands is eliminated in the form of cyclopentane. At the second stage, at 300-500 ºC, the rest of ligands are eliminated in the form of ethane and ethylene. In the case of cymantrene, the decomposition also proceeds in two steps. At the first stage, at temperatures of 80-150 ºC, some of the carbonyl groups are separated from the cymantrene, as well as the cyclopentadienyl rings, which are immediately hydrogenated to cyclopentene or cyclopentane. At the second stage, at temperatures of 270-400 ºC, mainly CO is removed, accompanied by its conversion to CH_4.

It was found that promotion with iron or manganese significantly suppresses both weakly and strongly hydrogen adsorption. For the most selective catalysts, hydrogen adsorption is almost completely suppressed. The hydrogen temperature-programmed desorption spectra of the catalysts provided additional data about the hydrogen adsorption. The monometallic Pd catalyst desorbs H_2 in the range 70-250C, which indicates the presence of both weakly and strongly chemisorbed H_2. The surface-modified catalysts desorb significantly less strongly and weakly chemisorbed hydrogen. This is a crucial point as it is commonly accepted that strongly chemisorbed hydrogen is responsible for the total hydrogenation of acetylene. The most selective to ethylene were the Pd-Mn/Al_2O_3 catalysts treated at 300 ºC (up to 88% at 87% acetylene conversion) and Pd-Fe/Al_2O_3 catalysts treated at 500 ºC (up to 81% at 87% conversion).

So, new Pd-Fe and Pd-Mn catalysts for selective hydrogenation of acetylene have been developed. It was established that the addition of Fe and Mn changes hydrogen chemisorption properties of Pd – strongly chemisorbed hydrogen is significantly reduced. The catalysts show both high activity and high selectivity.

PP-V-13

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PP-V-14

New Heterogeneous Rh/Tertiary Amine Catalysts for Tandem Hydroformylation/Hydrogenation of Olefins

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Hydroformylation, the industrial way of aldehyde production, is often followed by hydrogenation of aldehydes obtained, which is usually conducted as a separate stage. The one-stage process for direct conversion of olefins to alcohols (with one carbon longer chain) also exists, it uses Co/phosphines as homogeneous catalytic complexes [1] and shares some common limitations of homogeneous industrial processes. So, the development of new heterogeneous catalysts for tandem hydroformylation/hydrogenation can be regarded as an important and challenging issue. Complexes of rhodium with tertiary amines are known to catalyze this reaction sequence both under homogeneous [2] and heterogeneous [3] conditions. In this work, we developed new Rh/tertiary amine heterogeneous catalysts, based on hybrid materials BP-1 and WP-1, which are mesoporous silica with anchored nitrogen-containing polymers (fig. 1). The initial materials were modified with methyl groups to increase the number of tertiary nitrogen atoms and then treated with the solution of $Rh(acac)(CO)_2$ in dichloromethane to obtain catalysts K_N (from BP-1) and K_w (from WP-1). After washing with dichloromethane (2×10 ml), 1.93 and 2.14 wt % of rhodium were found by ICP-AES analysis in K_N and K_w, respectively.

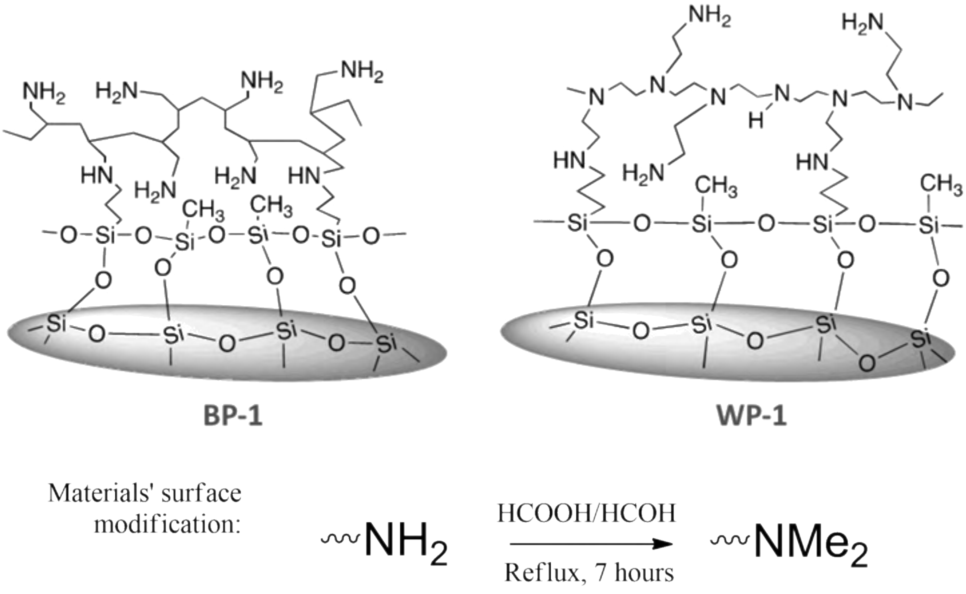

Fig. 1. The support synthesis

The results of catalytic experiments (tandem hydroformylation/hydrogenation of octene-1) are shown in Table 1.

Table 1. Homogeneous and heterogeneous catalysts in tandem hydroformylation/hydrogenation of octene-1.

Catalyst	Conv., %	Selectivities					
		Int. octenes, %	Octane, %	Aldehydes, %	n:iso $_{ald+alc}$	Alcohols, %	n:iso $_{alc}$
$Rh(acac)(CO)_2$ [a]	100	<1	2	97	0.9	-	-
$Rh(acac)(CO)_2$/ TMPDA[b]	97	25	3	56	2.0	16	3.0
K_N[c]	97	29	10	27	2.1	34	3.1
K_N*[c]	98	22	11	32	2.0	34	3.1
K_W[c]	94	21	18	7	2.1	52	2.4
K_W*[c]	98	23	10	24	2.0	41	3.0

*Conditions: octene-1 0.6 mL (4 mmol), solvent 2 mL, 80°C, syngas ($CO:H_2$=1:3) 6.0 MPa, 5 h; [a] $Rh(acac)(CO)_2$ 2 mg (0.008 mmol; [b] $Rh(acac)(CO)_2$ 2 mg (0.008 mmol), N,N,N′,N′-Tetramethyl-1,3-propanediamine 0.005 mL (0.03 mmol); [c] heterogeneous catalyst 30 mg, * – recycle.*

Both K_N and K_W catalysts demonstrated higher selectivity to alcohols than homogeneous Rh/amine catalytic system. They were active in the second reaction cycles, however, K_N performed better stability than Kw. K_N catalyst was studied with ICP-AES, XPS, IR spectroscopy, and high-resolution TEM – in its "fresh" state and after nine reaction cycles. After these nine reactions, the rhodium content decreased to 1.13 wt %. In both cases, no nanoparticles were found, and rhodium is the most probable to be in +1 oxidation state in complexes with amines.

Acknowledgement. The reported study was financially supported by the Russian Science Foundation (RSF) grant (project № 20-79-00143).

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PP-V-15

Well-Defined Silica-Supported Titanium Imido Complex as a Catalyst for Direct Imidation of Lactones

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Application of the surface organometallic chemistry (SOMC) approach in heterogeneous catalysis allows for better understanding of the active sites of classical catalysts and provides the opportunities for the design of new catalytic reactions. Thus, using SOMC approach our group has recently discovered a very active catalyst for oxo/imido heterometathesis reactions (fig. 1, a) — a well-defined silica-supported titanium imido complex prepared by grafting of the corresponding molecular precursor onto the surface of silica partially dehydroxylated at 700°C (fig 1, b). Immobilization on the support allowed avoiding the dimerization of highly active Ti=O intermediates, which precluded the catalytic application of such complexes as homogeneous catalysts. The resulting material was fully characterized by physicochemical methods (solid-state NMR, IR, elemental and mass balance analysis).

While previously the scope of oxo/imido heterometathesis was mainly limited to the imidation of carbonyl derivatives, aldehydes and ketones, to produce imines, in this study we extend this methodology to carboxyl compounds. We report here the first examples of direct imidation of lactones (the reaction that does not have a classic analogue in organic chemistry) giving the corresponding cyclic imidates (fig. 1, c). It was shown that the reaction proceeds readily and quantitatively for the substrates containing no α-CH_2 groups prone to enolization. The mechanism of the catalytic process is also investigated by stoichiometric reactivity studies.

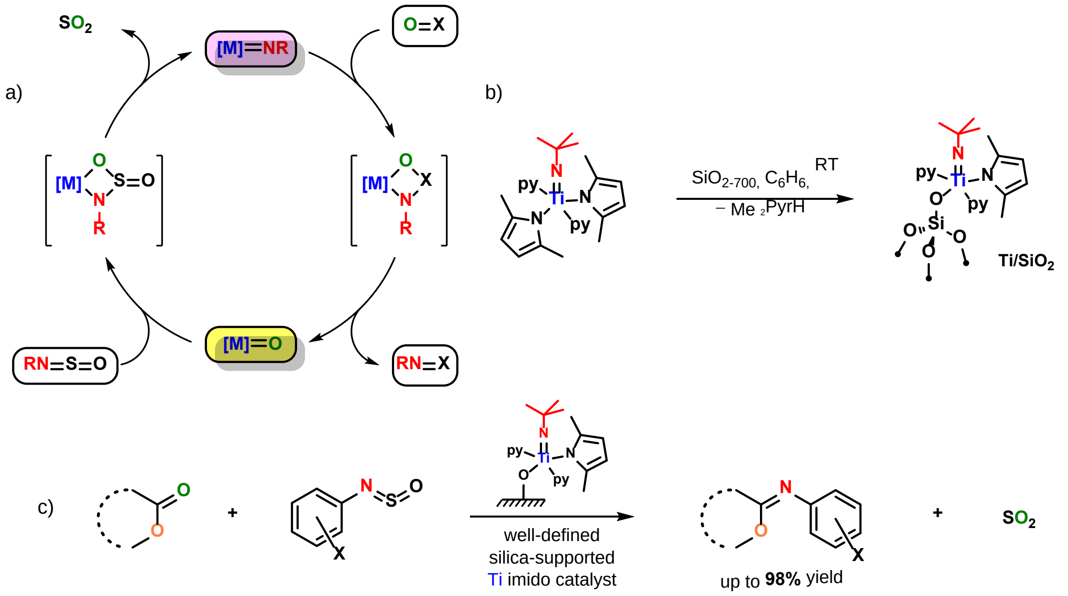

Fig. 1.

Acknowledgement. This work was supported by the Russian Science Foundation (grant 19-73-10163).

PP-V-16

Aluminosilicate Modified Supports for CoMo Catalysts for Hydroisomerization of n-Hexadecane

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The hydroisomerization process of n-alkanes is widely used in the oil refining and petrochemical industries for improving the octane number of gasolines and the low-temperature properties of diesel fuels and base oils [1].

Commonly used catalysts are bifunctional ones. Catalysts have both (de-)hydrogenation and acidic sites.

The hydrogenation/dehydrogenation sites are usually presented by noble metals (platinum, palladium). Their main disadvantage of noble metals is low resistance to catalytic poisons. Therefore, devoid of this drawback, transition metal sulfides are becoming more and more in demand [2, 3].

The presence of acid sites is ensured by modifying the support with zeolites and aluminosilicates. In this case, it is important to keep high accessibility of active sites despite the microporous structure of zeolites.

This paper presents the results of a study of CoMo- supported catalysts on aluminosilicate modified supports. Supports were prepared by co-extrusion of aluminum hydroxide and modifiers: MCM-41 and Halloysite (HNT) as a perspective additive [4].

The catalysts were prepared by incipient wetness impregnation with aqueous solutions of precursors: phosphomolybdic heteropoly acid, cobalt carbonate, and citric acid as an chelating agent. The Co Mo ratio was kept equal to 1/2 mol. The impregnated catalysts were dried at 40, 60 and 120 °C.

The isomerization reaction of n-hexadecane was studied in a lab scale flow reactor under the following conditions: temperature range 300–340 °C; pressure 1.5 MPa, hydrogen flow rate 1 nL/h, volumetric feed rate (SPF) 1–3 h^{-1}. The reaction products were studied by GC-MS chromatography. The results are summarized in Table 1.

Table 1

Catalytic tests results

Catalyst	Reaction rate constants, ×10^5 mol g^{-1} h^{-1}					
	320°C		340°C		360°	
	k_{iso}	k_{cr}	k_{iso}	k_{cr}	k_{iso}	k_{cr}
CoMo/Hal-Al_2O_3	2.3	0.6	4.2	3.7	7.6	5.9
CoMo/MCM-41/HNT-Al_2O_3	2.2	1.6	4.2	3.6	5.5	7.3
CoMo/MCM-41-Al_2O_3	3.3	2.8	2.4	5.9	6.7	14.7
CoMo/Al_2O_3	0.6	-	1.2	-	1.7	0.7

* LHSV = 1 h^{-1}

The obtained results indicate that the aluminosilicate modifiers addition to the catalysts support affects the catalytic properties in both hydroisomerization and cracking reactions due to the formation of new Al-O-Si bonds and further acidic properties modification.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 19-79-00293.

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PP-V-17

The Effect of Mesoporous Zeolite Additive Application in Supported Sulfide Catalysts for 4,6-DMDBT Conversion

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The deep removal of sulfur compounds from petroleum feedstock and especially from diesel is challenging and actual issue of modern oil refinery and petrochemical industry. It is becoming more difficult to produce clean fuels meeting strict specifications from increasingly lower quality raws using conventional catalysts. One of the approaches to improve catalytic activity is the support modification . The addition of zeolites into support allows to increase HDS activity of sterically hindered molecules such as 4,6-DMDBT due to the addition of an isomerization reaction pathway. However zeolites application as support leads to an undesirable cracking reaction, and the microporous structure leads to diffusion restrictions.

The composite materials on the base of Al_2O_3 modified with conventional zeolite Y as well as mesostructured zeolite Y [1] with modified mesoporous structure were synthesized and characterized by X-ray powder diffraction, NH_3-TPD, TEM. Supported CoMo catalysts on the base of composite support were prepared by wetness impregnation and studied in hydrodesulfurization reaction of 4,6-DMDBT.

The addition of a small amount of zeolite (10% wt.) has a significant increase in HDS activity of the synthesized catalytic systems. The catalyst with the additive of mesostructured material exhibited higher activity and lower cracking selectivity in comparison with a catalyst with conventional zeolite additive. This may be due to the fact that the mesostructured material combine advantages of the ordered mesoporous materials and the modulated acidic properties of zeolite Y.

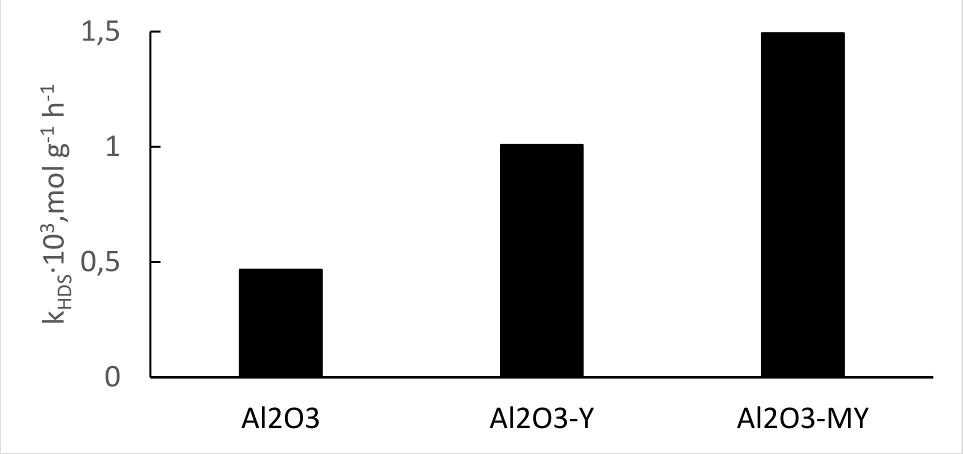

Fig. 1. Reaction rate constants of 4,6-DMDBT HDS over prepared catalysts

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PP-V-18

Hydrodenitrogenation of Heavy Oil Feedstock on Composite Catalysts: SAPO-5 and SAPO-11 as a Part of Conventional Hydrotreatment Catalysts

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Because of the rapid exhaustion of light oils reserves, the development of hydrotreating and hydroprocessing of heavy oil feedstock is an important problem. Such feedstocks contain highly reactive complex polyaromatic compounds having sulfur, nitrogen and metals. Traditional catalysts for such oils hydrotreating are sulfidated NiMoCo/Al_2O_3. Upgrading the conventional catalysts can improve the degree of hydrodenitrogenation of heavy oil feedstock.

The hydrodenitrogenation includes several stages: coordination of the heterocycle, its hydrogenation, cracking of the C-N bond with breaking the heterocycle, and cracking of the C-N bond to form NH_3 [1]. Moreover, the proper heterocycle coordination on the active cite makes it more likely to nitrogen remove from the feed [2]. Thus, the catalyst should combine the functions of selective coordination of heterocycles and cracking. Taking into account the complexity of the refined feedstock, the catalyst must also have optimal acidity and improved texture to reduce the possibility of coking and, as a consequence, catalyst deactivation.

It is possible to create an improved texture by using the template method of synthesis. Using a template means using a compound that is able to build an inorganic framework around itself, and when it is removed, a connected pore network with a characteristic arrangement and shape remains. Various compounds, such as polystyrene microspheres or acrylic copolymers, are used as templates to obtain Al_2O_3 with improved texture (Fig.1).

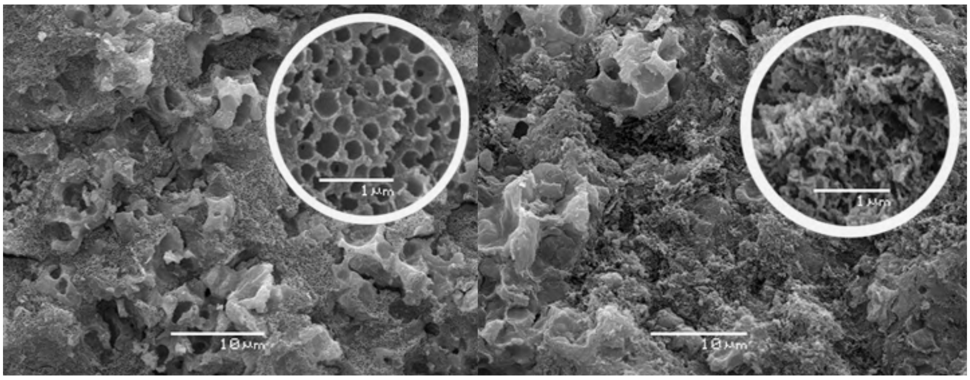

Figure 1 Al_2O_3 synthesized with polystyrene microspheres (left) and acrylic copolymer (right)

It is important to note that the supported conventional NiMoCo catalyst and its variations fully satisfy the condition of selective coordination. In turn, the cracking function is proposed to be assigned to SAPO-5 and SAPO-11. Molecular sieve materials silicoaluminophosphates SAPO – n are considered as promising ones for using as catalysts and adsorbents in petrochemical processes [3]. SAPO-11 and SAPO-5 are members of SAPO family having a one-dimensional system of non-intersecting tubular elliptical pores with an average size of 0.44 x 0.65 nm and 0,73 x 0,73 nm for SAPO-11 and SAPO-5 respectively [4]. These materials are microcrystals. It can lead to differences in the fraction of the available reactive surface if different polymer compositions are used as template.

Thus, as an experiment, the authors used 15% SAPO-11 as a part of a conventional sulfidized NiMoCo/Al_2O_3 catalyst in hydrodenitrogenation of heavy oil. An acrylic copolymer with a particle size of 20 and 100 nm was used as a template. The 56-hour test resulted in a significant reduction in residual nitrogen and sulfur content from 0.56 to 0.33 wt.% and from 1.46 to 0.13 wt.%, respectively. Thus, the authors suggest that using SAPO-n has potential in hydrodenitrogenation of heavy oil denitrogenation. Thus, a comparative study of the effect of the used template composition on the availability of zeolite-like material SAPO-5 and SAPO-11 in the composite, as well as the effect of these acid additives on the quality of the obtained feedstock, including hydrodenitrogenation, will be shown.

Acknowledgement. This work was supported by Ministry of Science and Higher Education of the Russian Federation.

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PP-V-19

Aromatization of Propane over Zn-Aluminosilicates with a Hierarchical Pore System

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Today, one of the main challenges that the oil and gas industry is facing is the need to utilize associated petroleum gas (APG). However, due to the lack of cost-effective processing technologies, a significant part of this very valuable hydrocarbon raw material is burned in flares of oil fields. Typically at least 95 vol% of associated petroleum gas extracted together with the produced crude oil is utilized in oil fields remote from the regions of its consumption. Hence, it is necessary to develop technologies for in-situ processing of associated petroleum gas into valuable petrochemical products.

One of the promising directions of APG processing may be the process of aromatization of lower alkanes in the presence of zeolite-containing catalysts. However, narrow channels formed by micropores of zeolites hinder mass transfer processes, which results in a rapid deactivation of catalysts during the reaction. The creation of secondary mesoporosity is one of the possible ways to increase the time of stable operation of zeolite systems. The presence of mesopores having a diameter of more than 2 nm facilitates diffusion processes in catalysts and enhances their stable activity in hydrocarbon conversion processes.

The aim of this work was to study the physicochemical and catalytic properties of Zn-aluminosilicates with a micro-mesoporous structure during the conversion of propane to aromatic hydrocarbons.

A zinc-containing MFI structure type zeolite (SiO_2/Al_2O_3 + ZnO = 40) was prepared via hydrothermal crystallization by partial substitution of aluminum for zinc. The content of ZnO in the reaction mixture was 0.82 wt% and that of Al_2O_3 3.09 wt%). Liquid glass (19% of SiO_2) was used as a silicon source, Al^{3+} and Zn^{2+} ions were introduced into the reaction mixture as their nitric acid water-soluble salts. Ammonium bicarbonate was chosen as the structure-forming component and carbon black N660 rubber grade served as the second template. The amount of added carbon black varied from 1 to 3 wt%, depending on the SiO_2 content.

The conversion of propane to aromatic hydrocarbons (ArHC) and the investigation of the properties of catalysts were carried out using a bench flow plant. The catalytic conversion of propane (purity 99.95 vol%) was studied at atmospheric pressure, a reaction temperature of 550 °C, and a feed space velocity of 250 h^{-1}.

Based on the results of X-ray phase analysis, it was established that all synthesized samples were MFI zeolites. The IR spectroscopy data showed that the addition of the second template to the composition did not lead to any significant changes in the structure of zinc aluminosilicate and all samples were characterized by a high degree of crystallinity.

The results of studies of the acidic properties of the synthesized samples showed that for the initial zinc aluminosilicate obtained with ammonium bicarbonate (ABC), the concentration of weak acid sites was 982 µmol/g and that of strong ones 356 µmol/g. The introduction of 1.0% of carbon black N660 into the zinc aluminosilicate at the stage of hydrothermal synthesis led to an increase in the concentration of acid sites of both types. With a further increase in the content of carbon black, a decrease in the strength of weak and strong acid sites was observed, as evidenced by the shift of the maximums of the peaks to the region of lower temperatures, while their concentration has increased. The highest number of acid sites was contained in zinc aluminosilicate synthesized with 3.0% of C_{N660}. The total concentration of acid sites for this catalyst was 1782 µmol/g, which was 444 µmol/g more than that for the initial zinc aluminosilicate.

The highest activity in the process of propane aromatization was exhibited by the initial zinc aluminosilicate. The yield in aromatic hydrocarbons over it was 55.5% with a propane conversion of 96%. Zeolites obtained using carbon black exhibited a slightly lower aromatization activity, while the total activity of the catalysts remained practically unchanged. In comparison with liquid products obtained over the initial zinc aluminosilicate, the content of BTX fraction increased in the composition of aromatic hydrocarbons formed over these samples, while the concentration of naphthalene hydrocarbons decreased.

Studies of the stability of the synthesized samples after one reaction cycle showed that they were characterized by almost the same initial activity, but with an increase in the operating time for the initial catalyst a sharper decrease in activity was observed. Hence, after 6 h of operation the yield in aromatic hydrocarbons has decreased from 55 to 18%, while the propane conversion has decreased from 96 to 41%. For samples synthesized with carbon black, a smoother decrease in these parameters was observed. The highest stability of operation was exhibited by zinc aluminosilicate synthesized with 1.0% C_{N660}; hence, after 6 hours of operation, the yield in aromatic hydrocarbons obtained over it was 33.7% with propane conversion of 74%.

According to the data of differential thermal analysis, the highest amount of coke was formed over the initial zinc aluminosilicate, which exhibited the maximum aromatization activity in the course of propane conversion. The total mass of coke deposits for this sample was 8.86%, the onset temperature and maximum burnout temperature of coke were shifted to the region of higher temperatures compared to other samples. This suggests the formation of denser (condensed) carbon deposits on it. The amount of coke contained on the zinc aluminosilicates obtained with carbon black was decreased. The lowest amount of coke (6.78%) was observed on the sample obtained with 1.0% of carbon black.

Thus, zinc aluminosilicates with a hierarchical pore system have been obtained by the method of hydrothermal synthesis with the addition of carbon black to the reaction mixture. The most effective catalyst in the course of propane aromatization was a zinc aluminosilicate synthesized with 1.0% of carbon black C_{N660}.

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PP-V-20

Study of Catalyst Activity and Selectivity in Oxidative Coupling of Methane in Presence of Water

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The oxidative coupling of methane (OCM) is an attractive method for production of ethylene from methane. In comparison with the current oil-based processes yielding this important building block of the chemical industry, the OCM reaction enables the involvement of longer available and more environmentally friendly natural gas as raw material. Although this reaction has been intensively studied since 1982, no catalyst with industrially accepted C_2-selectivity and CH_4 conversion has been developed up to now [1-2]. A promising approach for improving the selectivity is to perform the OCM reaction in water presence as reported for $NaMnWO_x/SiO_2$ [3-5]. However, it remains unclear how water improves both the selectivity and the activity as required for tailored catalyst design. Thus, the purpose of the present contribution is to elucidate the fundamentals of the enhancing water effect. To this end, a series of monometallic (W, Na, K, Rb, Cs) SiO_2-supported catalysts and $NaMnWO_x$/support (SiO_2, $AlSiO_x$, TiO_2, $TiSiO_x$, ZrO_2, $SiZrO_x$, $CeZrO_x$ $TiZrO_x$) have been prepared and tested for their activity and selectivity in the OCM reaction under different conditions. The loading of alkali metals and tungsten was adjusted as in the $NaMnWO_x/SiO_2$ catalyst.

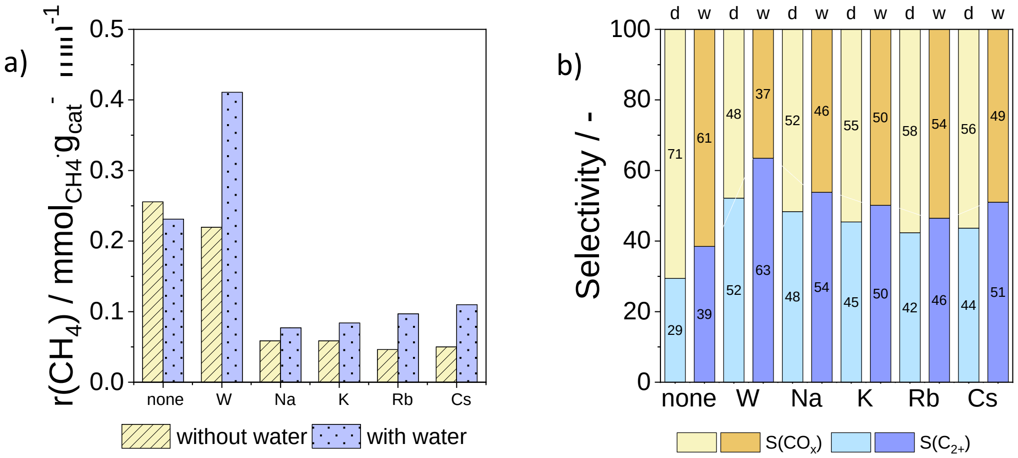

Fig. 1 (a) The rate of methane conversion and (b) product selectivity over bare SiO_2 and SiO_2-supported catalysts at 800°C using $CH_4/O_2/N_2$=8/1/11 (dry) or $CH_4/O_2/N_2/H_2O$=8/1/6/5 (wet) feeds.

Fig. 1 exemplarily shows the rate of methane conversion and product selectivity over the monometallic catalysts and bare SiO_2 in the absence and the presence of co-fed water. This catalyst performance was determined under differential conditions (CH_4 conversion<10%) after 50 hours on stream. In comparison with SiO_2, the rate in the absence of co-fed water was improved after addition of WO_x but decreased after addition of alkali metals. The dopants were established to positively affect the rate and the selectivity to C_2-hydrocarbons when performing OCM with co-fed water, while a slight negative effect on the rate was determined for SiO_2 (Fig.1). The catalysts can be ordered regarding the strength of the positive water effect on the rate as follows: Cs>Rb>W>K≥Na. The 3%wtWO_x/SiO_2 catalyst improved its activity and C_2-selectivity with rising time on stream. The improvement is probably related to water-induced dispersion of WO_x species as concluded from the results of XRD analysis of fresh and spent samples. The former material contains hexagonal and monoclinic WO_3 whereas these phases could not be seen in the spent catalyst. It is also important to mention that no activation was observed when using a catalyst with 10wt% of W. This catalyst also shows same selectivity level as its lower-loaded counterparts but directly after starting the OCM reaction. Thus, the positive effect of promoters for SiO_2 on C_2-selectivity (Fig. 1(b)) should be related to blocking of non-selective sites on the surface of bare SiO_2.

When analysing the positive water effect on C_2-selectivity in Fig.1 (b), it becomes obvious that the strongest effect was obtained for bare SiO_2. The selectivity over this material was improved by a factor of 1.5. Although there are no significant differences between the supported metal oxides in terms of the enhancing water, one can conclude that the presence of WO_x is more essential for this effect. Thus, the water-induced selectivity improvement can be explained as follows. Water enhances the rate of methane conversion into C_2-hydrocarbons over supported MO_x (M=Na, K, Rb, Cs or W) and inhibits the non-selective reactions over bare SiO_2. It is also worth mentioning that the C_2-selectivity over SiO_2-supported alkali metal oxides and the strength of the enhancing water effect are lower in comparison with $NaMnWO_x/SiO_2$. These results suggest that the individual catalyst components can additively contribute to this effect.

In addition to the above-discussed factors related to the enhancing water effect, the kind of support for $NaMnWO_x$ also determines the strength of activity and selectivity improvements. Regarding the activity improvement, the supports can be ordered as follows $SiO_2 > TiO_2 \geq TiSiO_x > TiZrO_x > SiZrO_x > CeZrO_x > ZrO_2$. No positive but negative effect was established for $AlSiO_x$-based catalysts. The strongest positive effect on the selectivity to C_2-hydrocarbons was determined for the catalysts based on TiO_2 and $TiSiO_x$. Taking our recent studies with $NaMnWO_x/SiO_2$ into account [5], water should affect the activation of gas-phase oxygen and accordingly the kind of adsorbed oxygen species participating in selective and non-selective pathways. Further deeper mechanistic analysis is in progress with the purpose to establish selectivity-conversion relationships, clarify reaction-induced catalyst restructuring and elucidate the kind of adsorbed oxygen species using isotopic tracers.

To sum up, for the first time, the positive water effect both on the rate of methane conversion and C_2-selectivity was established for SiO_2-supported catalysts with oxides of W, Na, K, Rb or Cs. It was related to inhibiting unselective conversion of methane and C_2-hydrocarbons probably through converting non-selective oxygen species into selective ones. Furthermore, the water effect is sensitive to the kind of supports. The obtained results may be used for designing and preparation of OCM catalysts with improved C_2-selectivity.

Acknowledgement. This work was supported by the German Research Foundation within joint Sino-German project.

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PP-V-21

$Ru/Ce_{0.75}Zr_{0.25}O_{2-\delta}$-η-$Al_2O_3$/FeCrAl Structured Catalyst for CO_2 Methanation and Steam Reforming of Natural Gas

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Carbon dioxide produced by human civilization has a significant influence on climate action. In 2019 at the Climat Action Summit announced that 77 countries will achieve zero carbon emissions by 2050. On the other hand, it is expected that fossil fuels will be a major energy source longer than 2050. The goal of zero-carbon emission and energy forecasts create a request for new effective technologies of carbon dioxide capture, utilization, and storage.

One of the perspective ways of CO_2 utilization is catalytic methanation. This approach makes possible utilization of carbon dioxide and production of renewable fuel – synthetic natural gas. One of the important parts of optimization this process is the development of a highly efficient catalyst.

The reaction between CO_2 and H_2 is accompanied by heat production. Heat effect can lead to local overheating of the catalyst. The catalysts supported on structured carriers (FeCrAlloy blocks) provide controlled reaction conditions, for example, temperature profile [1], throughout the reactor volume.

The present work is a study of catalytic activity of 7wt.%$Ru/Ce_{0.75}Zr_{0.25}O_2$ supported on FeCrAl metal meshes in two processes – CO_2 methanation and steam reforming of natural gas. Catalysts were obtained from a new type of Ru source – $RuNO(NH_3)_2(NO_3)_3$. This compound was attractive because of composition (only Ru, O, N and H atoms, there are no “catalytic poisons”), water-solubility, composition stability, and easy synthetic scheme [2]. The obtained catalysts were tested in the methanation of CO_2 in diluted (80% N_2, 16% H_2, 4% CO_2) and stoichiometric (80% H_2, 20% CO_2) mixtures at different temperatures. It was shown that 0.5wt.%Ru/(12wt.%$Zr_{0.25}Ce_{0.75}O_{2-\delta}$-η-$Al_2O_3$)/FeCrAl catalyst provided high efficiency of CO_2 methanation and rather good activity in process of steam reforming of natural gas.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 20-33-90162.

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PP-VI-1

Designing Ag/CeO_2 Sorbent-Catalysts for Toluene Removal

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Volatile organic compounds (VOCs) are harmful for both the environment and human health [1]. Toluene is one of the typical toxic VOCs. There are many methods for toluene removal: adsorption, condensation, thermal incineration, catalytic oxidation, biological decomposition, photocatalytic degradation, etc. In our work we combine the adsorption and catalytic oxidation that feature many advantages, e.g., low energy consumption, high selectivity, the formation of environmentally friendly products (H_2O and CO_2) [2]. The most promising catalysts for toluene removal comprise supported materials with noble metals as active components. The Ag/CeO_2 materials are promising for VOCs abatement. Silver is cheaper in comparison with Pt, Pd or Au. CeO_2 prevents the agglomeration of supported Ag NPs, features own catalytic activity and contributes to the changing of the properties of supported metal due to enhanced metal–support interaction [3]. The aim of this work is to synthesize the Ag/CeO_2 materials with different Ag loading and to study their adsorption and catalytic properties in toluene removal.

The CeO_2 support was prepared by thermal decomposition of $Ce(NO_3)_3{\cdot}6H_2O$ at 500°C for 4 h. Then the support was impregnated with an aqueous $AgNO_3$ solution. Catalysts were synthesized by varying the silver content from 1 to 10 wt. %. All catalysts were dried at 80 °C during 12 h. The prepared samples were characterized by a complex of physical-chemical methods: low-temperature N_2 adsorption (3Flex, Micromeritics, USA), XRD analysis (XRD-600 diffractometer Riguku, USA), TEM and TEM HR (JEM-2200 FS, JEOL, Japan), TPD-C_7H_8 and TPR methods (Chemisorb 2750, Micromeritics, USA). Catalytic activity of the samples was studied in the reaction of total oxidation of toluene.

The CeO_2 is characterized by the $S_{BET} = 76$ m^2/g and $V_{pore} = 0.236$ cm^3/g, while the corresponding parameters for 10Ag/CeO_2 catalyst are 46 m^2/g and 0.156 cm^3/g. The pore diameter for all samples remains comparable to the one of the support (~12 nm). The XRD data shows that the lattice parameter of CeO_2 is not changed for all samples, therefore, silver is not incorporated into the support structure, but is located on its surface. The XRD method does not allow detecting silver metal NPs for the samples with Ag content of 1, 3 and 5 wt. %, which is confirmed by the TEM and TEM HR results, where weakly crystallized Ag NPs up to 4 nm in size are detectable. For 10Ag/CeO_2 sample, the well crystallized Ag NPs with a size of 3-6 nm are observed (Fig. 1 a).

The TPD-C_7H_8 data show (Fig. 1 b) that the desorption of weakly adsorbed toluene at temperatures below 180 °C and strongly adsorbed toluene at temperatures above 180 °C is observed for all samples. The desorption of physically adsorbed molecular toluene is observed only up to 150 °C. The emission of CO_2 (detected by MS) during the TPD at temperature above 180 °C confirms the oxidation of chemically adsorbed toluene by the active oxygen of the catalyst. Chemically adsorbed toluene is completely oxidized into CO_2 and H_2O. Similar results are observed in the TPSR-C_7H_8, where adsorption and oxidation proceed in an oxygen-containing environment. The effectiveness of toluene conversion increases with the Ag loading.

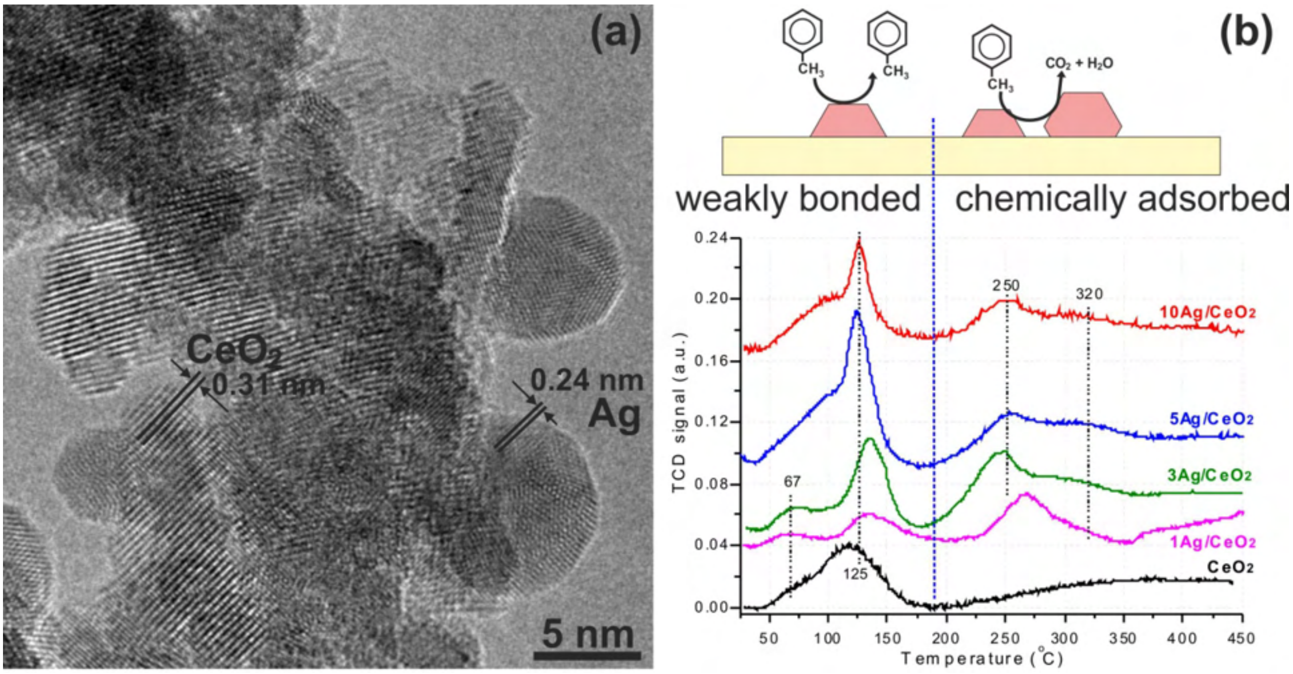

Fig. 1. (a) TEM image for 10Ag/CeO_2; (b) TPD-C_7H_8 profiles for the samples.

The catalytic properties were studied in the TPR mode using the gas mixture comprising 0.2% $C_6H_5CH_3$ and 4.6% O_2 in helium. The toluene adsorption is observed at room temperature. Both toluene desorption combined with its total oxidation into CO_2 occur in the temperature range of 50-150 °C. The oxidation of chemically adsorbed toluene is observed at 180-300 °C.

Thus, it was shown that with an increase in the silver content, the amounts of adsorbed toluene and the oxidized toluene converted to CO_2 and H_2O increase. The 5Ag/CeO_2 and 10Ag/CeO_2 catalysts were characterized by the highest sorption capacity and catalytic activity. Thus, the materials based on Ag-CeO_2 are promising for combined sorption-catalytic toluene removal.

Acknowledgement. This work was supported by the Russian Science Foundation, grant No. 18-73-10109.

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PP-VI-2
The Study of Surface Morphology of Conductive Biopolymer Matrices

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Currently, it is very important to develop bio-conducting materials for the further construction of biosensors and biofuel cells. In such electrochemical devices, chemical energy is converted to electrical energy using biocatalysts. Among the biocatalysts enzymes (enzyme fuel cells) or organelles and whole cells (microbial fuel cells), in which energy is transformed by the metabolic activity of microorganisms, can be used. The widespread introduction of such elements will significantly reduce the consumption of organic fuel without reducing the level of energy consumption [1-2].

Biopolymer samples were synthesized using sequential modification of solutions of the following polymers: polyvinylpyrrolidone (PVP), acetylcellulose (CA), polyaniline (PAN). The modifying agents - chitosan (at heating) and glutaraldehyde (Glu) - were added to a solution. The redox enzymes peroxidase (HRP) and glucose oxidase (GOx) in a ratio of 2:5 were used as an active part of the biopolymer matrices. Reactions catalyzed by the redox complex of enzymes are shown in scheme (1, 2).

$$O_2 + \beta\text{-D- glucose} \xrightarrow{GOD} \beta\text{-D- glucose -}\delta\text{- lactone} + H_2O_2 \qquad (1)$$

$$\text{ABTS} + 2H_2O_2 \xrightarrow{HRP} \text{ABTS} + H_2O \qquad (2)$$

In this work, the choice of polymer carriers is primarily due to its high mechanical strength and chemical stability, the presence of highly reactive ionogenic groups (OH^-), (NH_2^+), which makes it possible to modify the carrier by various functional groups. A large number of meso and macropores contribute to the stabilization of covalently bound enzymes.

The following samples of biopolymer materials were obtained: PVP/Chit/Glu/HRP:GOx, CA/Chit/Glu/ HRP:GOx, PAN/Hit/Glu/HRP:GOx. Based on the obtained data, adsorption-desorption isotherms were constructed (Fig. 1, 2). The analysis of the obtained samples was carried out using a surface area and pore size distribution analyzer BECKMAN COULTER™ SA 3100™ (COULTER CORPORATION, Miami, Florida).

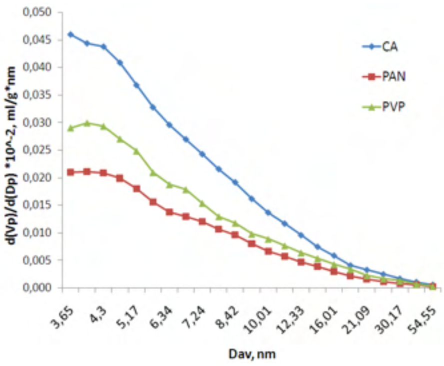

Fig.1. Diagram of pore distribution depending on their diameter for pure samples

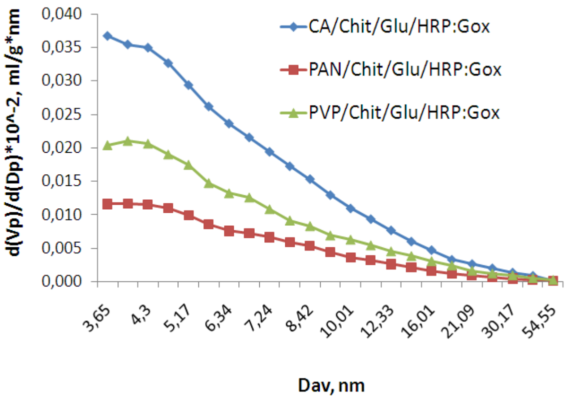

Fig. 2. Diagram of pore distribution depending on their diameter after modification and application of enzymes

Based on the obtained data on low=temperature nitrogen adsorption, it can be concluded that all the samples presented have a mesoporous structure. The pore average diameter was found to be 3.65-9 nm, which provides free access of enzyme molecules, having an average diameter of the native structure of 4-7 nm. During the modification of polymer carriers, the number of mesopores with a diameter of 8-16 nm decreases. This allows us to make an assumption about the localization of large molecules of covalently crosslinked enzymes in the macroporous surface of polymer carriers.

In this way, the biopolymer matrices presented in this paper can be recommended for applying to electrodes and increasing the performance of biofuel cells.

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PP-VI-3
CuO NPs Obtained by Laser Ablation for 4-Nitrophenol Hydrogenation and Dye Degradation

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Recently, Cu-based nanostructures have attracted particular attention due to their fundamental importance, photoconductive and photochemical properties. They have various potential applications in the field of heterogeneous catalysis and photocatalysis [1,2], including reduction of nitroaromatics in the presence of $NaBH_4$ as well as in dye degradation. A variety of methods have been developed to synthesize different morphologies and dimensions of Cu-based nanostructures [1], with pulsed laser ablation (PLA) in liquid being one of the most promising techniques. The CuO_x NPs with various phase composition (Cu, Cu_2O, $Cu@Cu_2O$, CuO), sizes, and morphology can be obtained by PLA [3].

In the present work, the features of formation of CuO_x NPs by PLA of copper in aqueous solutions of hydrogen peroxide and their catalytic properties towards reduction of nitroaromatics and dye degradation were studied.

The CuO_x NPs colloids were obtained by PLA of copper in aqueous solutions of hydrogen peroxide with different H_2O_2 concentrations (0.25, 0.1, 1%). The effect of H_2O_2 concentration on the composition, structure, and morphology of CuO_x NPs formed was studied by XRD, UV-vis spectroscopy, SEM, and TEM. The catalytic activity of CuO_x NP colloids was studied using the model reaction of 4-nitrophenol (4-NP) reduction to 4-aminophenol (4-AP) in the presence of $NaBH_4$ and oxidative degradation of methylene blue (MB) in the presence of H_2O_2. The photocatalytic activity of CuO NPs was additionally assessed towards the model dye degradation by visible light.

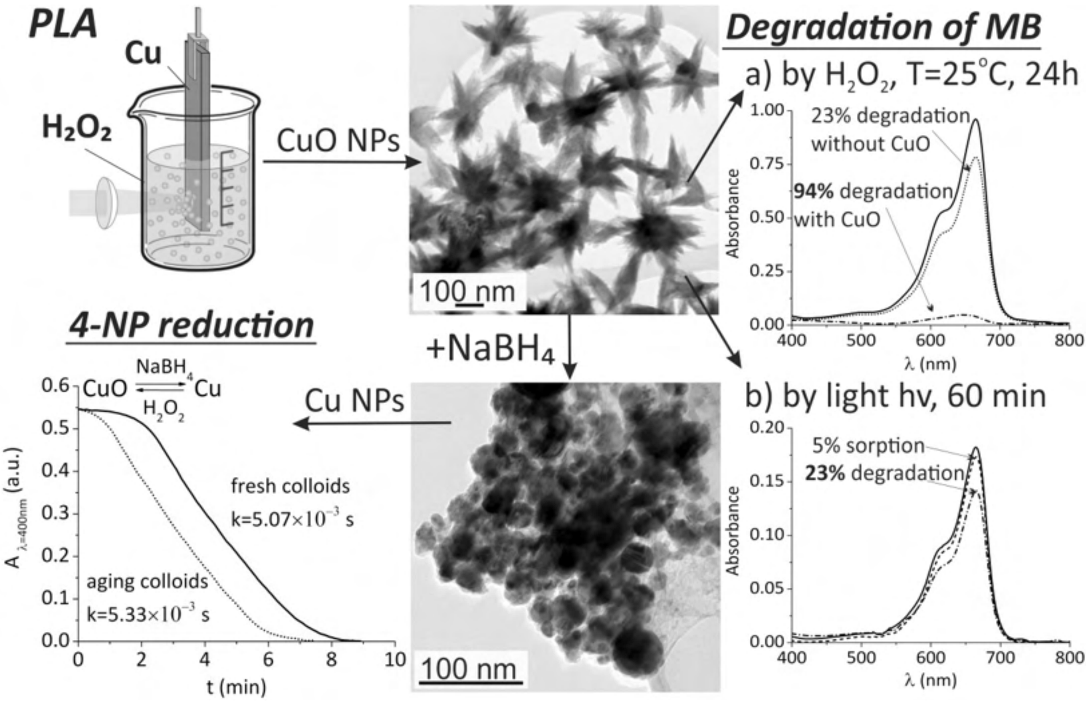

Fig. 1. A schematic representation of results

The stable CuO_x NP colloids were obtained, with sheet- and flower-like CuO NPs being primarily formed in the presence of H_2O_2 (Fig. 1). The H_2O_2 concentration did not affect the structure and morphology of CuO NPs, but after the H_2O_2 consumption, the formation of cubic Cu_2O particle began.

It was found that the sheet- and flower-like CuO NPs obtained by PLA in H_2O_2 had a polycrystalline structure that contributed to their rapid reduction to 10–50 nm spherical Cu nanoparticles in the presence of $NaBH_4$ (Fig. 1). The obtained Cu NPs showed high catalytic activity towards 4-NP reduction to 4-AP in the presence of $NaBH_4$. The presence of H_2O_2 residues in the as-prepared CuO NP colloids was shown to prevent the reduction of CuO NPs, but did not affect the 4-NP reduction by $NaBH_4$ over the Cu NPs formed.

The oxidative degradation of the MB in the presence of H_2O_2 was shown to be very slow without the catalyst, while in the presence of the CuO NPs obtained by PLA in hydrogen peroxide solution the degradation was more efficient even at room temperature. Besides, the photocatalytic potential of the CuO NPs obtained by PLA under visible light was proved (Fig. 1).

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PP-VI-4

Cr-Co Catalysts for Benzene Oxidation Based on Double Salt Oxidation Products

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Benzene (C_6H_6) is highly toxic and carcinogenic. A large amount of C_6H_6 gets into the air during incomplete combustion of fuel in internal combustion engines and in accidents at oil refineries. High performance catalysts exist for the oxidation of small amounts of C_6H_6. They are made on the basis of noble metals. However, they are expensive and prone to catalyst poisoning. Removing benzene from polluted air will help to reduce damage from its impact on the environment and human health.

Double complex salts (DCS) are promising precursors for catalysts, including catalysts for the oxidation of benzene.

DCS of composition $[CrX_6][CoY_6]$ (X = 0.5en, ur ($CO(NH_2)_2$); Y = NO_2^-, CN^-, $0.5C_2O_4^{2-}$) have been synthesized and characterized by a number of physic-chemical methods. The studies were carried out using elemental, X-ray phase, crystal-optical, thermal analyzes, IR spectroscopy.

Calcination temperatures were selected using thermal analysis in air. Large weight loss does not occur when these temperatures are reached. The catalytic compositions were obtained by isothermal oxidation of DCS at 450 and 600 °C. The carbon content does not exceed 10% in these samples. Catalyst compositions consist of mixtures of simple and complex oxides of Cr and Co.

We have oxidated benzene with atmospheric oxygen. Catalytic tests were carried out in a flow-through tubular reactor. The apparatus scheme is given in [1]. The gas-air flow rate was 15 l/h, the experiment temperature was 350 °C, and the catalyst sample weight was 0.1 g. Compositions were the most active when obtained by thermolysis of DCS with the $[Co(NO_2)_6]^-$ anion. The reaction rate constant reaches 4-4.2 sec^{-1}.

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PP-VI-5

Custom Build 3D-Printed Reactor for Photochemical Synthesis

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Visible light photoredox catalysis is perspective and rapidly developing branch of organic synthesis. Laboratories all over the world make new photocatalysts, which are able to oxidize and reduce the most unexpected substrates. Chemists make new compounds, which were unavailable with classical methods and without new photocatalytic reactions. However, research of photoredox-catalyzed reactions involves nontrivial problems, slowing down the process and even making desired result unattainable [1][2].

First problem is control of reaction temperature. Traditionally, heating or cooling can be easily implemented with liquid baths or metal blocks. But such approach makes irradiation complicated or even impossible. Second problem can be faced not only in photoredox research. Side reactions of intermediates and substrates always have been a headache for a chemist. Rates of these processes depends on concentrations. Thus, control of concentrations can provide the control of rates. Low concentration of any component can be maintained with syringe pump; however, commercial solutions are often too bulky and unprogrammable.

These problems were solved by design and construction of compact multi-layered photoreactor. First layer is a matrix of four 30W LEDs, cooling with water. Second layer is a jacket with glass bottom, where water of required temperature is circulating. The matrix of reaction vessels with flat bottom is installing into the water. Third layer consists of 4 independent syringe pumps, made of 3D-printed gears and controlling by servo motors and Arduino. Each next layer is installing on top of previous if it's required for an experiment.

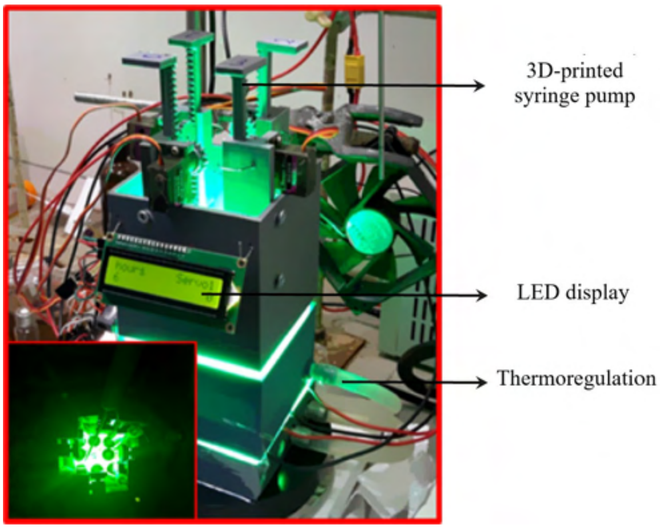

Fig 1. Custom build 3D-printed phortoreactor.

For investigation of influence of addition rate model reaction was chosen. In that case exponential mode of addition (the more component added, the less rate of addition) lead to 15%

increase of yield in comparison with constant rate. Function of the yield of model reaction of temperature had maximum at 40˚C.

Thus, in this work importance of investigation of temperature influence on yields of photoredox-catalyzed reactions is outlined. Gradual addition of component into reaction system and its dependence on time can also be essential in optimization process and requires attention.

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PP-VI-6

Partial Catalytic Oxidation of Dimethoxymethane to Synthesis Gas over Supported Noble Metal Catalysts

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Dimethoxymethane (DMM) is an environmentally friendly oxygenated compound of C1 chemistry with a wide scope of applications. At present, DMM is commonly synthesized from methanol. It is worth noting that bio-DMM synthesis using renewable feedstocks - namely, CO_2 produced from biomass and hydrogen generated by water electrolysis (using solar or wind energy) is currently under development. Since DMM is a relatively inert (non-corrosive and non-toxic) liquid compound, it can be easily handled, stored and transported.

In the past decades, DMM as well as methanol has been recognized as a promising synthetic fuel for hydrogen production for fuel cell feeding. Recently, we proposed efficient bifunctional catalysts for DMM steam reforming [1]. The best catalysts provide complete DMM conversion, hydrogen yield up to 90 %, and low CO content at temperatures ~ 300 °C. However, the steam reforming process has some shortcomings, especially with regard to portable/autonomous low-power applications, because it needs significant heat supply for water evaporation and implementation of the endothermic reaction. Favorably compared to DMM steam reforming, DMM partial oxidation by air demonstrates a higher energy-efficiency, water independence, and allows quick start-up of a solid oxide fuel cell (SOFC) based power unit even at temperatures below zero.

Herein, we report the catalytic properties of composite oxide $Ce_{0.75}Zr_{0.25}O_2$ supported Pt catalyst due to it is activity in the DMM decomposition [2], estimate the contribution of homogeneous oxidation of DMM in the gas phase, present the calculated data on thermodynamic equilibrium product distribution of DMM partial oxidation that are used as the reference data for interpreting experimental results, and consider the feasibility of DMM partial oxidation by air for producing synthesis gas for SOFC feeding applications.

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PP-VI-7

Photocatalytic and Photoelectrochemical Properties of Carbon Modified Anodic TiO_2 Nanotube Arrays

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Self-assembled anodic titania nanotube arrays (Fig. 1) are well known as photocorrosion stable photoanode material with a high surface area. However, like a non-nanostructured titanium dioxide, titania nanotube arrays aren't active in the visible light spectrum due to wide bandgap (3,2 eV). That fact is a most disadvantage of the material for photocatalytic applications. Using a particular composition of as-prepared anodic TiO_2 nanotube arrays in organic based electrolytes for modification of the material by thermal treatment in inert atmospheres can be a good solution to enhance photocatalytic properties [1].

In the presented work investigated photocatalytic properties of carbon modified anodic titania nanotube arrays in various irradiation light spectra by photoelectrochemical measurements and photocatalytic oxidation process of organic dye. Structure, composition, and morphology of the material were investigated by XRD, Raman spectroscopy, EDX and SEM.

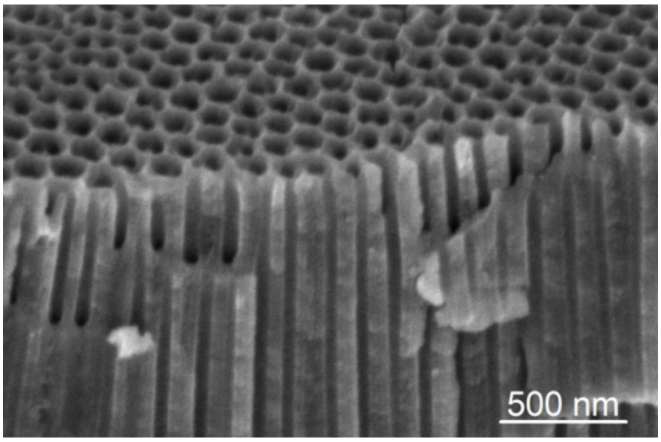

Fig. 1. SEM image of anodic titania nanotubes cross-section (top)

Acknowledgement. The reported study was funded by RFBR according to the research project, grant 20-33-90251.

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PP-VI-8

Hydrolysis of Element (White) Phosphorus in the Presence of Heterometallic Cubane-Type {Mo_3PdS_4} Cluster Complexes

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Organic and inorganic phosphorus-containing compounds are applied widely in various industrial areas. Classical approaches for the synthesis of phosphorus compounds imply oxidation and chlorination of element (white) phosphorus (P_4) and use the obtained substances as phosphorylating agents for the preparation of various P-containing substrates [1]. Such methods frequently demand hard conditions (temperature, pressure, pH) and negatively impact on the environment because of presence toxic chlorine-containing compounds (HCl, Cl_2, phosphorus chlorides).

Heterometallic cubane-type complexes with {M_3PdS_4} (M = Mo; W) cluster core have demonstrated catalytic activity in a range of chemical processes [2]. In the present work we report the synthesis of new heterometallic complexes $[Mo_3(Pd(dba))S_4(dbbpy)_3Cl_3]PF_6$, $[Mo_3(Pd(dba))S_4(py)_3(acac)_3]PF_6$ (Fig. 1) as well as their reactivity and reactivity of early described complex $[Mo_3(Pd(tu))S_4(dbbpy)_3Cl_3]Cl$ [3] towards white phosphorous (P_4). The hydrolysis process of P_4 to phosphoric acid (H_3PO_3) catalyzed by {Mo_3PdS_4} complexes has been studied.

It was established by $^{31}P\{^1H\}$ NMR spectroscopy that the presence of heterometallic complexes allows to obtain almost full conversion of P_4 and H_3PO_3 as product in yields up to 60%.

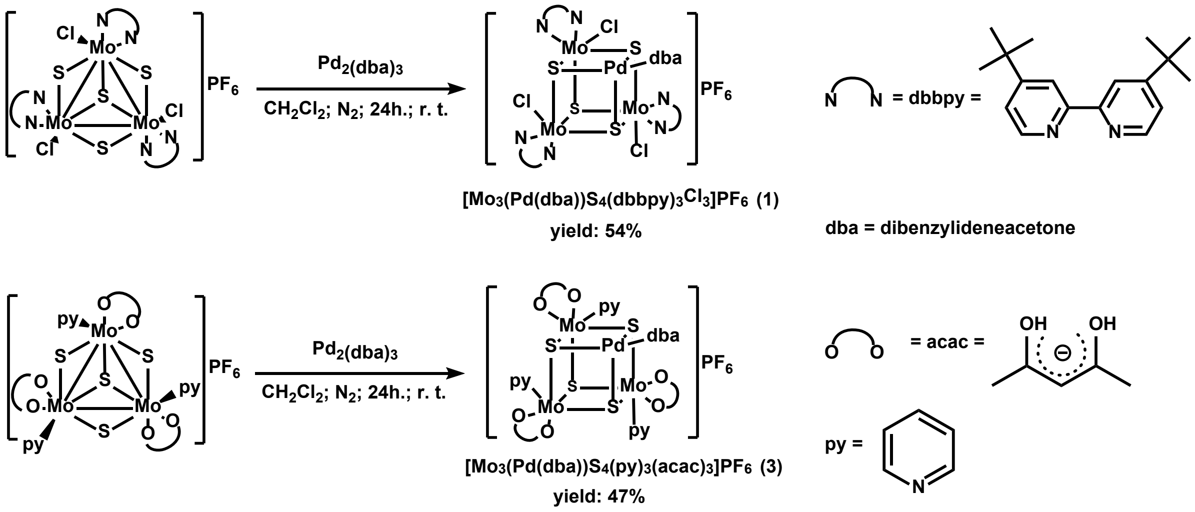

Fig. 1. Synthesis of new heterometallic cubane-type {Mo_3PdS_4} cluster complexes

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 19-33-90097.

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PP-VI-9

Ternary Mixed Oxide of Silver, Copper and Manganese - Novel Catalytic Material for Oxidation Reactions

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Copper- and silver-containing oxide systems are traditionally used as catalysts to perform various oxidation reactions. Great interest to such systems is caused by a need to search and develop cheap and highly efficient catalysts without noble metals. Note that the crystal structure of mixed metal oxides provides the stabilization of particular oxygen species with modified reactivity and catalytic properties in comparison with individual metal oxides. Particularly, mixed oxides based on copper and/or silver are characterized by the enhanced activity in the reaction of CO oxidation [1-3]. In this work, the synthesis and investigation of ternary mixed oxide of copper, silver and manganese as catalyst for reactions of CO, ethylene and ammonia oxidation were performed.

Ternary mixed oxide of copper, silver and manganese (Ag_2CuMnO_4) was synthesised under hydrothermal conditions using nitrates or corresponding metals in alkaline solution. Prepared sample was characterized by delafossite type crystal structure (Fig.1). Such a structure is built due to the alternation of brucite layers of BO_2 (B is the combination of Cu and Mn) connected by linear O–Ag–O bonds. The layered structure of delafossites also assumes a developed defect structure, including stacking faults and cation vacancies, which additionally contribute to the stabilization of reactive oxygen species.

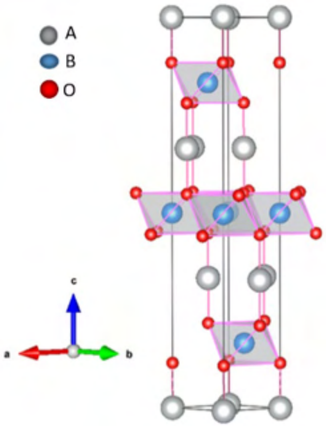

Figure 1. Delafossite crystal structure of ternary mixed oxide Ag_2CuMnO_4 (A=Ag, B=Cu/Mn)

Ternary oxide showed activity in the oxidation of CO, starting from a temperature of 0°C. The temperature of 50% conversion (T_{50}) during CO oxidation was close to 100°C. Note, that evident catalytic activity was demonstrated at room temperature in the presence of O_2 in reaction mixture. In the initial part of the CO conversion curve, the value of apparent activation energy during CO oxidation was estimated to be near 15-30 kJ/mol. During the reaction of ethylene oxidation, the ternary oxide preliminary treated in a flow of O_2/He (at 250°C) demonstrated noticeable activity only at temperature >150°C. At a low ethylene conversion (<20%), CO_2 and acetaldehyde (CH_3CHO) were found to be the main products with the predominant contribution from CO_2 (80-100%). It indicated a high oxidative activity of the ternary oxide, which demonstrated an ethylene conversion of above 80% already at 250°C.

A noticeable activity of ternary oxide Ag_2CuMnO_4 was observed in the reaction of ammonia oxidation above 100°C. In the range of 100-250°C, the predominant products of ammonia oxidation were molecular nitrogen (N_2) and nitrous oxide (N_2O). Above 250°C, the appearance of NO and NO_2 was observed, the contribution of which increased with increasing temperature, reaching 70% at 400°C.

The preservation of delafossite crystal structure was observed after all catalytic measurements, while the nanoparticles of metallic silver were additionally appeared in the case of high-temperature reaction treatment (above 300℃), especially, with ethylene-containing mixture.

Based on the obtained catalytic data it can be concluded that the ternary oxide of silver, copper, and manganese (Ag_2CuMnO_4) with delafossite structure is a promising system for catalytic reactions of oxidative type. First of all, attention should be paid to the significant potential of Ag_2CuMnO_4 in the implementation of catalytic activity at room temperature in the oxidation of CO,, as well as the ability to selectively oxidize ammonia depending on the reaction temperature.

Acknowledgement. This work was financially supported by the Ministry of Higher Education and Science of the Russian Federation, grant MK-503.2021.1.3.

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PP-VI-10

Reduced Graphene Oxide Decorated with Ag and CeO_2 Nanoparticles Composite for 4-Nitrophenol Reduction

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Green chemistry is a novel research area of chemical science that addresses the challenges in material and technology design for both energy-efficient manufacturing and environment protection. The Ag-based nanocatalysts are in the focus of “green” chemistry approach as advantageous systems due to relatively low cost, low-temperature activity, nontoxicity, and facile preparation and modification procedures [1]. The CeO_2 incorporation into Ag-containing systems provides the enhancement of the catalytic activity due to the metal-support interaction resulting in the interfacial charge transfer and synergistic action of the metal and oxide active sites [2, 3]. Graphene is a two-dimensional carbon nanomaterial with a uniform slit-like microporous structure and high surface area (up to 1500 m^2/g). Graphene and its derivatives (e.g., graphene oxide (GO), reduced graphene oxide (RGO)) are considered promising environmentally benign adsorbents and catalyst supports. Moreover, unique electroconductivity and synergy to metals and semiconductors allows utilizing this material as an active support in photocatalysis [4]. This work aims to prepare the Ag-CeO_2/RGO system and study its catalytic activity in the 4-nitrophenol (4-NP) reduction into 4-aminophenol (4-AP) at room temperature and ambient pressure.

Graphene oxide (GO) was prepared by the modified Hummers’ method [5]. Silver- and/or ceria-containing catalysts (Ag/RGO, CeO_2/RGO, Ag-CeO_2/RGO) were synthesized by the deposition-precipitation technique using $AgNO_3$ and/or $Ce(NO_3)_3{\cdot}6H_2O$ aqueous solutions. The nominal loadings of silver and CeO_2 in the catalysts were 5 and 10 wt.%, respectively. The synthesized samples were characterized by a set of physical-chemical methods: powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), low-temperature N_2 adsorption-desorption, etc. Catalytic activity of the samples was tested in 4-NP reduction into 4-AP by sodium borohydride ($NaBH_4$) as a reducing agent at room temperature and atmospheric pressure in water medium.

According to the TGA results, in the oxidizing medium the synthesized support decomposes through two characteristic steps at 200 ^oC (decarboxylation) and 600 ^oC (combustion) indicating the graphene oxide structure. The combustion temperature region is shifted towards lower temperatures for Ag/RGO, CeO_2/RGO, and Ag-CeO_2/RGO samples since the active components catalyse the support combustion.

Fig. 1 illustrates the XRD results. The GO sample possesses characteristic reflection at $2\theta \approx 11^o$ attributed to the graphene/graphite oxide (002) phase. There is a small amount of graphite phase (reflections at 26 and 42^o) occurring due to incomplete graphite oxidation during the Hummers’ process. The reflection corresponding to graphite oxide (002) is absent for the synthesized catalysts, and those typical for graphite remain. This indicates the GO reduction to RGO during the catalyst preparation. Silver species in the Ag/RGO sample exist as large crystalline metal particles. Their size decreases in the Ag-CeO_2/RGO catalyst that indicates the role of ceria in Ag stabilization in a more dispersed state. Unlike silver, CeO_2 exists both in CeO_2/RGO and Ag-CeO_2/RGO as small nanoparticles. This is attributed to the much stronger interaction between ceria precursor and graphene oxide during the deposition-precipitation.

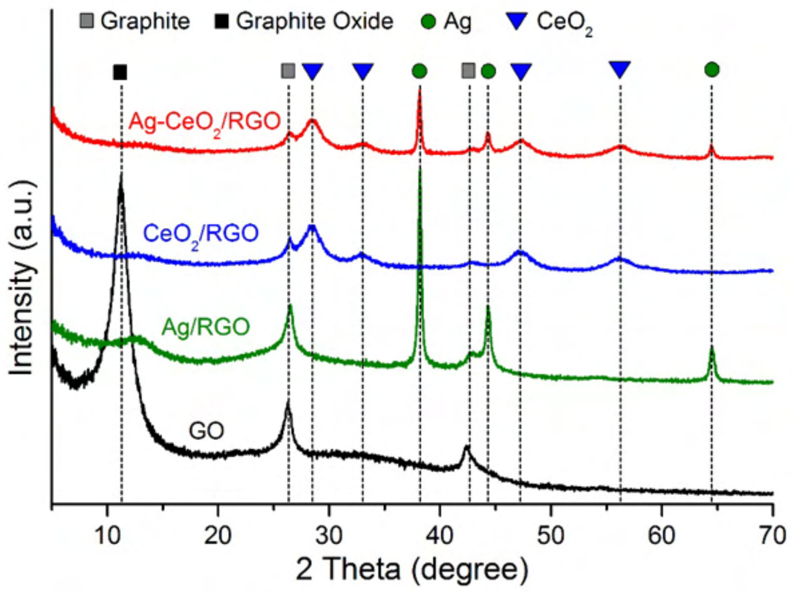

Fig. 1. XRD results for the synthesized catalysts and support

To sum up, the considered synthesis technique allows preparing the silver- and/or ceria-containing catalysts (Ag/RGO, CeO_2/RGO, Ag-CeO_2/RGO) that are advantageous and environmentally benign systems for catalytic processes such as nitroarenes reduction [6]. Joint loading of the active components results in the synergistic effect that enhances the catalytic activity. In addition, photosensitivity of Ag and CeO_2 and electroconductivity of GO support allows utilizing these systems as active photocatalysts [7].

Acknowledgement. This work was supported by the Russian Science Foundation, Grant № 18-73-10109.

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PP-VI-11

Aspects of the Synthesis of Catalytic Layers Based on Structured Carbon Materials by Impregnation

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The use of proton exchange membrane fuel cells (PEMFC) is one of the promising areas for the development of new environmentally friendly and resource-saving energy. The characteristics of fuel cells are largely determined by the structure of the catalyst (mainly platinum) and the carbon carrier that forms its basis [1]. The main disadvantage of the carbon carrier is its rapid corrosion during the operation of the fuel cell and in start/stop modes, which reduces the lifetime of the device as a whole [2].

To increase the efficiency and durability of catalytic layers (CL), structured carbon materials, such as carbon nanofibers (CNF) and nanotubes (CNT), graphene-like materials reduced graphene oxide (RGO), can be used as supports for electrocatalysts [3- 4].

The developed surface of the CNT array reduces the formation of surface oxides and corrosion current, promotes the deposition of nanosized platinum particles and prevents its agglomeration, which significantly reduces the cost of CL and increases their efficiency. Due to the CNT morphology, the gas permeability of the reagents also significantly improves, and the hydrophobic properties ensure the prevention of water condensation on the cathode, which provides the long-term stability of the PEMFC [5]. The electrical conductivity of such materials is much higher: the output power density of FC with CNT-based paper is 45% higher than that of FC with conventional carbon paper [6].

To increase the adhesion of nanotubes array of to an electrode, methods for growing CNTs directly on the surface of the GDL are proposed. However, in this case, the problem arises of an efficient method of depositing an active metal (platinum) on structured carbon materials. The method of impregnation of GDL with a platinum precursor followed by its reduction, which we studied earlier in [7] can be the solution to this problem.

In this work, we consider some aspects of the preparation of a platinum catalytic layer, namely, optimization of the composition and creation of an impregnation-reduction technique. Carbon papers and clothes presented in the table 1 were used as GDLs, which were impregnated with a solution of hexachloroplatinic acid in a water-alcohol solvent, subsequently reduced by chemical methods (using ethylene glycol and hydrogen gas). The loading of platinum for all samples was 0.3 mg/cm^2, the content of the ionomer (Nafion aqueous solution) by dry residue was 15 wt. %. To create an additional layer on the surface of some electrodes, Vulcan XC-72 carbon was used. Electrochemical studies to determine the electrochemically active surface area of platinum (EASA) were carried out according to the procedure described in [8].

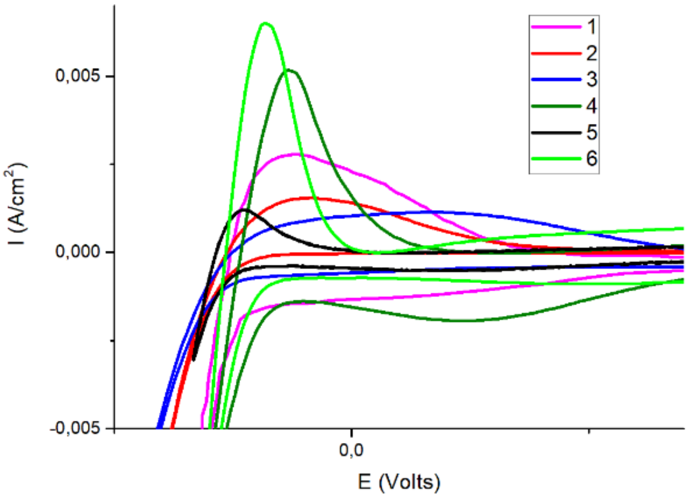

Figure: 1. Curves cyclic voltammograms (CVs) of the studied samples (numbers correspond to table 1)

According to the results, presented in table 1 and fig. 1, in the case of hydrogen using, a double increase in the reduction time did not improve the characteristics of the electrocatalyst. The optimal reduction mode was 4 hours at 160°C. This result was similar for different types of GDL (EASA 41.0 m^2/g for Sigracet 39 BB with Pt and 35.2 m^2/g for ELAT LT 1400 W with Pt). The method of chemical Pt-reduction in ethylene glycol is also effective (EASA for ELAT LT 1400 W with Pt was 33.4 m^2/g). These methods of electrocatalytic layer synthesis used to deposit Pt on carbon structures directly fixed as a microporous layer on the surface of FC electrodes.

Table 1. Main characteristics of the studied samples.

№	Type GDL	Loading Vulcan XC-72, mg/cm^2	Reduction aspects			EASA, m^2/g
			Time, hour	Temperature, °C	Reagent	
1	Sigracet 39 BB	-	4	160	H_2	41.0
2	ELAT LT 1400 W	-	4	140	H_2	24.3
3	ELAT LT 1400 W	1	8	140	H_2	29.5
4	ELAT LT 1400 W	1	4	160	H_2	35.2
5	ELAT LT 1400 W	-	4	180	H_2	5.9
6	ELAT LT 1400 W	1	4	180	EG	33.4

Acknowledgement. This study was supported by the Russian Foundation for Basic Research (projects № 20-08-00927, 18-29-23030).

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PP-VI-12

Composites Based on Solid Sulfides Solutions of Cd and Zn and Graphitic Carbon Nitride for the Photocatalytic Hydrogen Evolution under Visible Light Irradiation

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One of the most urgent areas of sustainable energy development is the development of solar energy. Photocatalytic water splitting under visible light irradiation is a promising way to convert solar energy into chemical bond energy [1]. The main factor constraining the development of this process is the absence of active photocatalysts activating in visible light. Graphitic carbon nitride (g-C_3N_4) is one of the most interesting materials for the photocatalytic water splitting, as it has many advantages over the already used photocatalysts but, despite a large number of advantages, g-C_3N_4 has one significant disadvantage — fast recombination of charges on the catalyst surface. To provide spatial separation of photogenerated charges, composite semiconductor materials are created [2]. The aim of this work was to create highly active complex photocatalysts based on composite materials $Cd_{1-x}Zn_xS$/g-C_3N_4, in which heterojunctions of the semiconductor/semiconductor type are implemented to obtain hydrogen in visible light.

As previously found, the most active g-C_3N_4 was obtained from melamine with a calcination time of 600 °C and a heating rate of 5 °C/min for 2 hours. Platinum (1 wt. %) was deposited on the prepared photocatalysts by impregnation with H_2PtCl_6 followed by reduction with a 2.5-fold excess of $NaBH_4$. Two schemes for the synthesis of photocatalysts based on $Cd_{1-x}Zn_xS$/g-C_3N_4 have been proposed. To prepare $Cd_{0.7}Zn_{0.3}S$/g-C_3N_4 and $Cd_{0.8}Zn_{0.2}S$/g-C_3N_4 samples with a certain percentage of $Cd_{1-x}Zn_xS$ (10, 20, and 50%), the required amount of according compounds was added to the g-C_3N_4 suspension (Scheme 1) or 1% Pt/g-C_3N_4 (Scheme 2). In the case of Scheme 1, 1 wt. % Pt was deposited on the prepared $Cd_{1-x}Zn_xS$/g-C_3N_4 samples by the impregnation method as described above.

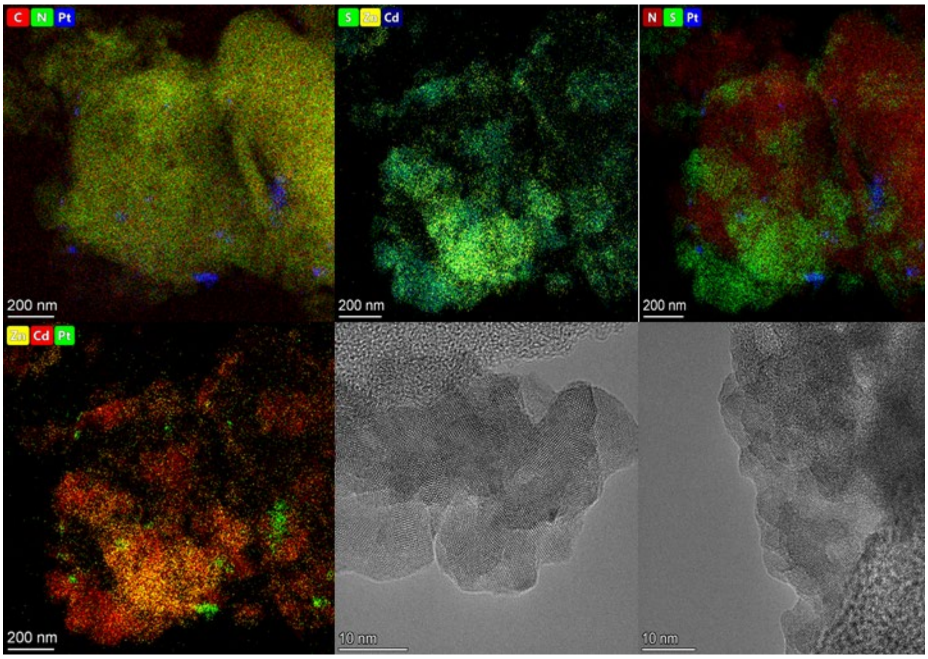

Fig. 1. SEM with sample mapping Cd20%$Cd_{0.8}Zn_{0.2}S$/1%Pt/g-C_3N_4

It was found by high resolution TEM with elemental mapping that the proposed synthesis according to the 1 and 2 schemes led to the formation of two fundamentally different types of photocatalysts (figure 1).

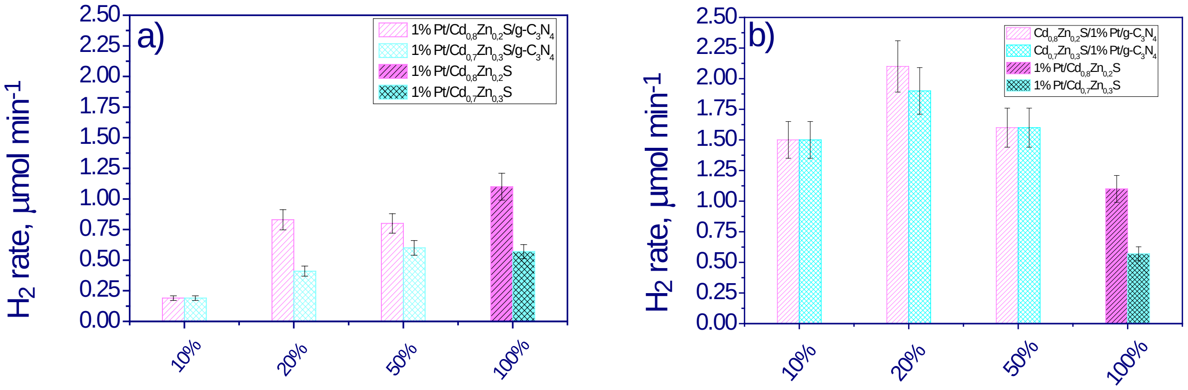

Fig. 2. Activity of photocatalysts 1% Pt/10-50%$Cd_{0.8(0.7)}Zn_{0.2(0.3)}S/g-C_3N_4$ (a) and 10-50% $Cd_{0.8(0.7)}Zn_{0.2(0.3)}S$/1% $Pt/g-C_3N_4$ (b) in hydrogen evolution from aqueous solutions (10 vol. % TEOA + 0.1 M NaOH) under visible light irradiation with wavelength 450 nm

The photocatalytic hydrogen evolution rate was measured from aqueous solutions of 0.1 M NaOH + 10 vol. % TEOA. In the case of composites without platinum, the hydrogen evolution rate does not exceed 0.13 µmol min^{-1}. Platinum deposition on composites results in a significant increase in activity. However, for photocatalysts synthesized according to Scheme 1, when platinum is deposited on $Cd_{1-x}Zn_xS$, the activity of composite samples does not exceed the activity of $Pt/Cd_{1-x}Zn_xS$, this is due to the low specific surface area of the obtained composites. The positive effect due to the formation of heterojunctions between $Cd_{0.8}Zn_{0.2}S$ and $g-C_3N_4$ does not compensate for the significant loss of specific surface area. A noticeable increase in activity, approximately twofold compared with $Pt/Cd_{0.8}Zn_{0.2}S$ and $Pt/Cd_{0.7}Zn_{0.3}S$, was observed for photocatalysts synthesized according to Scheme 2. The 20% $Cd_{0.8}Zn_{0.2}S/1\%Pt/g-C_3N_4$ sample showed the maximum hydrogen evolution rate equal 2.1 µmol min^{-1} (activity equal ≈ 2500 µmol g_{cat}^{-1} h^{-1}) with apparent quantum efficiency at a wavelength of 450 nm equal to 6.0%. Photocatalysts synthesized according to Scheme 2, in which platinum was located between two semiconductors and serves as a "bridge" for transferring photogenerated electrons from the conduction band (CB) of $g-C_3N_4$ to the CB of $Cd_{1-x}Zn_xS$, showed higher activity. The formation of heterojunctions according to Scheme 2 is more efficient than in the case of Scheme 1.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 20-30-70086.

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VIRTUAL PRESENTATIONS

Section 1. Preparation of catalysts and adsorbents
VP-I-1 ÷ VP-I-4

Section 2. Characterization and *in situ* studies of catalysts
VP-II-1 ÷ VP-II-5

Section 3. Mechanism and kinetics of catalytic reactions
VP-III-1 ÷ VP-III-3

Section 4. Catalysis for renewable sources
VP-IV-1 ÷ VP-IV-3

Section 5. Catalysis for fine organic synthesis, natural gas and petroleum chemistry
VP-V-1 ÷ VP-V-9

Section 6. Catalysis for environmental protection, photocatalysis and electrocatalysis
VP-VI-1 ÷ VP-VI-3

VP-I-1

Potential Catalysts for ATRP: Copper(I) and Copper(II) Complexes with the 4-(Pyridinyl)-1,2,3-Thiadiazole Ligand Series

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Widely used in the modern chemistry of macromolecular compounds, a polymerization method – atom transfer radical polymerization (ATRP) [1] allows to get: a wide range of polymers with narrow molecular-mass distribution, copolymers with unusual properties, and other macromolecular materials. The most used catalysts in this method are metal complexes, especially copper(I) complexes. They interact with organic compounds, which have a mobile atom of halogen, and bind with it. This reaction is accompanied by the formation of an active radical that initiates the chain growth process

The problem of ATRP, as a laboratory and/or semi-industrial method, is instability of, inactivating in aerobic conditions, commercially used copper(I) complexes. The most used way to stabilize copper(I) compounds is entering a N-donor ligands with π-system into an inner coordination sphere of a metal, for example, 1,10-phenanthroline, 2,2'-bipyridine etc. However, the more stable the complex, the lower it's reactivity, and, therefore, the worse is the initiation of the polymerization process. On another hand, the stabilizing ligands obstruct the process initiation.

In this work the complexation processes of copper(I) and copper(II) with 4-(pyridinyl)-1,2,3-thiadiazole (**L**) ligand series have been examined. The ligands can effectively stabilize low metal oxidation states. The main reason why L has been chosen to be examined is poorly studied complexes with this ligand. Also, one can use these complexes as ligands to polynuclear complexes because of lone pair of electrons on sulfur.

Ligands are the isomer series of 4-pyridinyl-1,2,3-thiadiazole (**3a-c**) were obtained by two-stage synthesis from acetylpyridines (**1a-c**), based on Khurda-Mori method (Fig. 1).

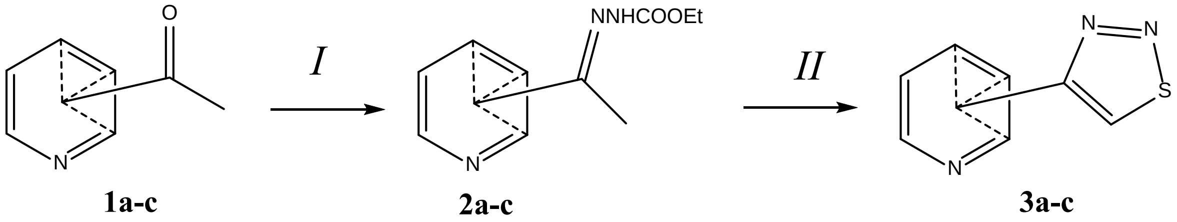

Fig. 1 - I: $NH_2NHC(O)OEt$, EtOH, 3 hours boiling; II: $SOCl_2$, 0-5^{0}C, 4-8 hours; 3a – 4-(pyridin - 2- yl)-1,2,3- thiadiazole; 3b – 4-(pyridin -3-yl)-1,2,3- thiadiazole; 3c – 4-(pyridin-4-yl)-1,2,3- thiadiazole.

The method, proposed in the research [2], has been modified: acetylpyridines **1** entered in the chemical reaction with the carbethoxyhydrazine in the ethanol solution in the presence of catalytic amounts of sulfuric acid. On cooling, obtained carboethoxyhydrazone was mixed with thionyl chloride and sustained with stirring at room temperate within a few hours. The reaction mixture was cooled and neutralized by a solution of sodium bicarbonate. The target compound extracted and evaporated under vacuum. The yields of compounds were **3a** – 88%, **3b** – 64%, **3c** – 86%.

The yellow $[Cu^{(I)}L_2]ClO_4$ and blue $[Cu^{(II)}L_2](ClO_4)_2$ suitable for structural analysis crystals have been obtained by reactions between $[Cu(CH_3CN)_4]ClO_4$ and $Cu(ClO_4)_2{\cdot}6H_2O$ with 4-(pyridine-2-yl)-1,2,3-thiadiazole in acetonitrile solutions. The yields of the both copper complexes are about to 80-90%. Complexes are examined by elemental analysis, electronic and IR spectroscopy.

Acknowledgements. The work was financially supported by Russian Science Foundation (grant 20-15-00332).

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VP-I-2

Synthesis of Fe(II)-LDH and Study of Its Activity in Radical Oxidation of Limonene

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Layered double hydroxides (LDH), also known as hydrotalcite-like materials or anionic clays, are synthetic compounds with general formula $M^{2+}_{1-x}M^{3+}_{x}(OH)_2[A^{n-}_{x/n} * mH_2O]$, where M^{2+} и M^{3+} are metal ions, A^{n-} is an anion or any anionic complex [1]. In recent years, due to their unique structure, LDHs are widely used in catalysis, pharmacy, photochemistry and etc. [2].

In this work, we investigated the oxidation process of D-limonene in the Fenton-like system with Fe-containing LDH.

Fe-containing LDH with following composition $Mg_{5.7}Fe_{0.3}Al_2(OH)_{16}CO_3$ was synthesized by co-precipitation method from mixed metal salts solution containing magnesium nitrate, aluminum nitrate nonahydrate and ferrous sulfate dissolved in distilled water (250 ml). The mixed metal solution was added dropwise to sodium carbonate solution at vigorously stirring with controlled addition of 1 M sodium hydroxide solution used to maintain pH of approximately 9-10. Precipitation was carried out in an inert atmosphere of argon in order to prevent Fe(ii) oxidation. Upon completion of the addition, the LDH sample was aged for 24 hours at 98°C. After that suspension war separated by centrifuging, washed with distilled water and dried in desiccator with inert atmosphere of argon for 7 days.

Structure of LDH was identified by powder X-ray diffraction. The XRD pattern of $Mg_{5.7}Fe_{0.3}Al_2(OH)_{16}CO_3$ exhibits the characteristic diffraction peaks of hydrotalcite, the sample is well crystalized (fig.1).

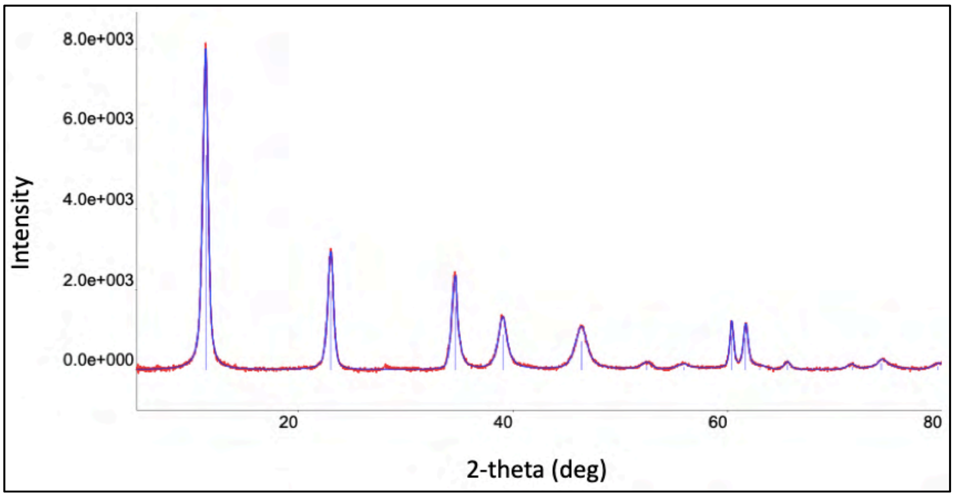

Fig. 1. X-ray diffraction pattern of synthesized LDH in carbonate form

The LDH sample was characterized by transmission electron microscopy as well.

Limonene oxidation in the presence of H_2O_2 was carried out under vigorous stirring in system consisting of a glass reactor with the capacity of 25 ml, equipped with a magnetic stirrer. In typical reaction D-limonene was used as reagent, H_2O_2 was added as a source of radicals (D-limonene:H_2O_2

ratio was 1:4) and the synthesized Fe-containing LDH (50 mg) was employed as a catalyst of radical decay of hydrogen peroxide. The solvent used was ethanol. The oxidation reaction was carried out in an inert atmosphere of argon. Reaction was performed at a temperature of 60°C for 24 h.

Products of the reaction were analyzed by gas chromatography with Agilent 7890a chromatograph equipped with an HP-5ms capillary column and a flame-ionization detector.

Maximum conversion of D-limonene was 25%, the content of the accompanying components of D-limonene decreased by 10-80%, and the appearance of new, previously undetectable peaks of compounds was also observed. The nature of the products and probable reaction pathways are discussed in the study.

These results are promising for further studies of the catalytic oxidation of D-limonene for obtaining products required in organic and pharmaceutical syntheses.

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VP-I-3

Novel Catalysts on the Base of α-Phosphino-α-Amino Acids: Synthesis, Properties and Catalytic Activity in the Ethylene Oligomerization Process

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Synthetic organophosphorus amino acids are interesting in various fields of chemistry, biochemistry and pharmacy. This is primarily due to excellent and widely tunable donor properties of trivalent phosphorus that can be combined with biogenic or artificial amino acids or even peptides, resulting in more or less good water-solubility and secondary controlling features. This was found useful in asymmetric reactions of transition metals [1-3] and organo-catalyzed reactions [4], bioinspired outer-coordination-sphere functionalized catalysis, mimicking redox-enzyme functions, allowing electrochemical oxidation of hydrogen, used in fuel cells, oxidation of formic acid, and hydrogenation of carbon dioxide to formate via coupled proton and electron transfer [5]. We systematically varied the nitrogen substituents of the α-phosphinoglycines to obtain more stable and effective α-phosphino-α-amino acids in catalytic processes of the ethylene oligomerization and report here about the novel derivatives α-phosphino-α-amino acids, their synthesis, structure and properties, and the first examples of their transition metal's complexes and their using in homogeneous catalysis.

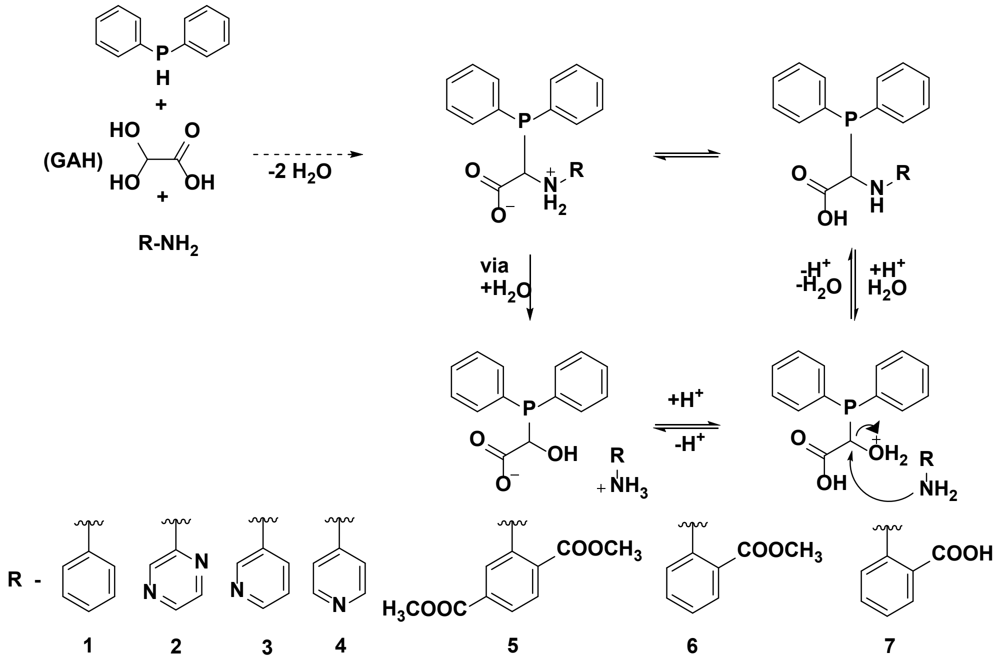

*Fig. 1. Preparation of α-phosphino-α-amino acids **1-7** by three-component condensation reaction of diphenylphosphine, glyoxylic acid, and primary amines*

Novel *N*-(phenyl)- **1**, *N*-(pyrazin-2-yl)- **2**, *N*-(pyridin-3-yl)- **3**, *N*-(pyridin-4-yl)– **4**, *N*-(2,5-dimethoxycarbonylphenyl)- **5**, *N*-(2-methoxycarbonylphenyl)- **6**, *N*-(2-carbonyl)- **7** α-diphenylphosphino glycines were obtain by a three-component condensation reaction of diphenylphosphine, glyoxylic acid, and primary amines (Fig.1).

Using ^{31}P NMR spectroscopy and electrospray ionization mass-spectrometry (ESI), the stepwise mechanism of the formation of α-phosphino-α-amino acids, passing through the main intermediate of the process - phosphinoglycolate, has been confirmed. The molecular structure and relative thermodynamic stability of non-ionized and zwitterionic forms of α-diphenylphosphinoglycine derivatives have been studied by the method of quantum chemical analysis. Based on the obtained data, it can be concluded that *N*-aryl and *N*- (hetero) aryl-substituted α-phosphino-α-amino acids in methanol presents in the non-ionized form due to their low basicity, which is due to the presence of a (hetero) aryl π-system capable of involving the lone a pair of nitrogen into the conjugation [6].

Novel catalysts, based on newly obtained α-phosphino-α-amino acids **1-7** in combination with the [Ni(COD)$_2$] complex, where COD = 1,5-cyclooctadiene leads to the formation of a main products of low α-olefins as a result of the ethylene oligomerization, and for the first time demonstrated the possibility of using an organophosphorus ligand in combination with a nickel complex in homogeneous ethylene dimerization reactions with selective formation of butene-1 more than 85% for example of *N*-(pyrazin-2-yl)-α-diphenylphosphinoglycine **2** [7].

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 19-29-08051.

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VP-I-4

About Ethanol Conversion over Mg-Zn-O Catalyst

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Ethanol is an initial raw material for production of various chemicals. One of the interesting ways of converting of ethanol is producing of acetone. In this regard, this work is devoted to studying of the reaction of conversion of ethanol over binary magnesium-zinc oxide catalysts.

Binary magnesium-zinc oxide catalysts of different compositions were prepared by co-precipitation method from aqueous solution of magnesium nitrate and zinc nitrate. The activity of the synthesized catalysts was studied on a flow-through installation unit with a quartz reactor in the temperature range of 250-600°C. X-ray study of the phase composition of the prepared catalysts was carried out on an automated powder diffractometer «D2 Phaser» of the «Bruker» company (CuKα radiation, Ni filter, $3 \leq 2\theta \geq 80°$).

Based on the X-ray studies, it was found that in the Mg-Zn-O catalyst system, the formation of two phases is observed, namely magnesium oxide and zinc oxide. We also found that the formation of chemical compounds between magnesium and zinc oxides is not observed. İt is found that calculated degree of crystallinity of the Mg-Zn-O catalytic system slightly depend on the catalyst composition.

Based on the conducted research we can say that over magnesium-zinc oxide catalysts main product of ethanol conversion reaction is acetone and acetic aldehyde. We found that the activity of Mg-Zn-O catalysts in the conversion of ethanol depends on reaction temperature and the atomic ratio of magnesium to zinc in the composition of the binary catalyst. At temperature until 400^{0}C main reaction product is acetaldehyde. In the reaction of formation of acetaldehyde are active catalysts reached with zinc oxide. Maximum yield of acetaldehyde (39.8%) is obtained over Mg-Zn=3-7 catalyst at 350°C. Increasing the reaction temperature above 400°C changes direction of conversion of ethanol to formation of acetone. Below in the table 1 it is shown the effect of the atomic ratio of magnesium to zinc on the activity of Mg-Zn-O catalysts. As can be seen from the table 1, the yield of acetone with an increase in the content of magnesium oxide in the composition of the catalyst decreases from 68,7% over catalyst Mg-Zn=1-9 until 6,4% over catalyst Mg-Zn=9-1. Conversion of ethanol and selectivity to acetone decreases to with increasing of the content of magnesium oxide in the composition of the catalyst.

Table 1. The conversion of ethanol over Mg-Zn-O catalysts at a temperature of 450°C.

The atomic ratios of magnesium to zinc	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
Yields of CH_3COCH_3, %	68,7	62	59,8	55,8	48,7	36,9	30,7	16,9	6,4
Selectivity of CH_3COCH_3, %	77,4	69,3	65,9	69,8	61,7	51,6	44,3	29	12
Ethanol conversion, %	88,8	89,5	90,8	79,9	78,9	71,5	69,3	58,3	53,5

Based on obtained results it can be said that binary magnesium zinc oxide catalysts have high activity in the reaction of the conversion of ethanol to acetone. Catalyst with the composition of Mg-Zn =1-9 is the most active in the reaction of acetone formation.

VP-II-1

Prediction of the Nickel Catalyst Activity in Hydrogenation Reactions via Calorimetry

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Until now, there is no unified theories of catalysis that would allow predicting the activity of transition metals based on their physicochemical properties for the selected reaction. There are a number of approaches to solving this problem. The originally appeared theory of intermediate compounds and electronic theories had a number of significant drawbacks and were not able to describe all the known facts. The multiplet theory and the theory of active ensembles were also developed earlier, which also have a number of significant disadvantages.

In the hydrogenation reaction over heterogeneous catalysts, one of the reactants is always hydrogen, which enters into the system in gaseous form, dissolves in the liquid phase, and is then adsorbed onto the catalyst surface. According to [1], hydrogenation is occurs by the adsorption mechanism, i.e. all the participants in the reaction must be adsorbed on the catalyst surface, while the adsorption state of the reactants may differ. The authors of [2] in their work eliminated the influence of such processes as external and internal diffusion, creating all conditions for the reaction on the surface to be limiting, while the adsorption state of substances becomes decisive.

The work was carried out on the example of the hydrogenation reaction of sodium maleate over a skeletal nickel catalyst in various aqueous-alcoholic solutions with sodium hydroxide additives.

A simple method was found for calculating the activity of a nickel catalyst for model hydrogenation reactions from the dependence of the heat of hydrogen adsorption versus the degree of filling. To calculate the activity, you need to know the parameters: $K_{H\to A}$, A_{max}, K_{pois}, $\rho(\Delta_a H(H_2))$, for this you need to solve the system of equations.

It is shown that the mathematical description of this correlation does not depend from the selected solvents. And also It was found that the parameters ($K_{H\to A}$, A_{max}, K_{pois}) included in this mathematical description do not depend from the nature of the solvent.

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The theoretical part was implemented with financial support from the Presidential grant for young PhD scientists (project MK-771.2020.3).
The study was carried out by using the resources of the Centre for collective use of scientific equipment FSBEI of HE “ISUCT”.

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VP-II-2

Bi-and Polynuclear Coordination Complexes of d-Elements as Prospective Catalysts of Selective Oxidation of Endogenous Thiols

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It is known that one of the types of redox regulation of cellular processes is carried out through the thiol groups of cysteine of evolutionarily conserved domains of proteins and oligopeptides [1]. The basis of this type of regulation is the selective oxidation of thiol groups to disulfide forms. In the human body, the balance between the forms of thiol groups ($2R\text{-}SH - 2e^- \rightleftarrows RSSR + 2H^+$) is characterized as a "thiol-disulfide status" and its violation leads to pathophysiological states of the cell, tissue, or organism as a whole [2]. Glutathione (GSH, L-γ-glutamyl-L-cysteinylglycine), an endogenous peptide present in all mammalian cells in significant concentrations [1, 3], as well as derivatives of 2-aminoethanethiol and cysteine, play a regulatory function concerning thiol-disulfide status. *In vivo* oxidation of thiol groups to disulfide crosslinks are controlled by enzymes, including metal-containing ones, whose active centers can be modeled by complexes of d-elements [4, 5].

It was previously established [6] that the binuclear compounds of Pd(II) and Pt(II) are efficient as selective catalysts for the oxidation of thiol groups to disulfides under mild conditions. It has been shown that the stages of the catalytic cycle (Fig. 1) are complementary in terms of both geometric parameters and electron transfer.

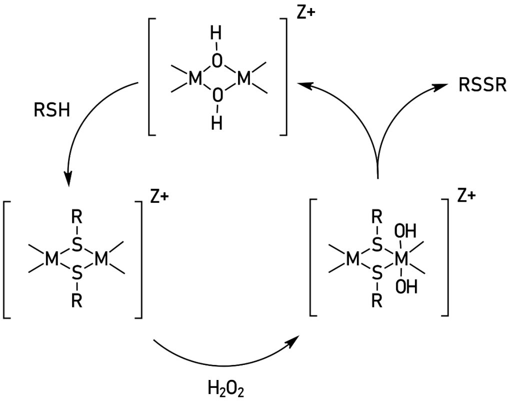

Fig. 1. Catalytic cycle of oxidation

In the search for other catalytic systems that have complementarity and the possibility of potential use in living systems, model systems were investigated - binuclear Pt(II) compounds with Cu(I), Ag(I), and Au(I). Within the framework of this work, we used the DFT quantum-chemical simulation method with the PBE0 functional and the def2tzvp basis set. Based on Pearson's theory of hard and soft acids and bases [7], thiols and thiolate ions should be classified as soft bases prone to the formation of the strongest bonds with such soft Lewis acids as easily polarizable metal ions - for example, Pt(II), Cu(I), Ag(I), and Au(I), while, in complexes, they can act as bridging ligands [8] that bind metal ions into polynuclear structures.

An analysis of the fragments' geometry of the model complexes made it possible to conclude that they are structurally inconsistent with the formation of a common binuclear core of $Pt(\mu\text{-}S)_2M$

(M: Cu(I), Ag(I), Au(I)), which makes it impossible for the catalytic system to function, similar to that shown in Fig. 1. It was found that in the heterometallic systems Pt(II)/Cu(I), Pt(II)/Ag(I), Pt(II)/Au(I), active centers have different directions of chemical bonds of metal ions and, therefore, are poorly compatible with each other. At the same time, the structure of the active center of the Pt(II)/Au(III) system turned out to be close to Pt(II)/Pt(II), which makes it capable of maintaining complementarity during reactions of the catalytic cycle of oxidation of thiol groups of the substrate. However, during the attempts of synthesis of a heterometallic complex of Pt(II)-Au(III), a darkening of the solution was observed, which was a consequence of the reduction of Au(III) to a colloidal precipitate of metallic gold. This is explained by the oxidation potential of Au(III)/Au(0), which is capable of oxidizing the initial platinum complex to the Pt(IV) state. So far, no single-crystal samples suitable for X-ray structural analysis have been isolated containing Pt(II) and Au(III) ions. In summary, the possibilities of the considered systems' behavior based on Pt(II), Cu(I), Ag(I), and Au(I) ions are shown in Fig. 2.

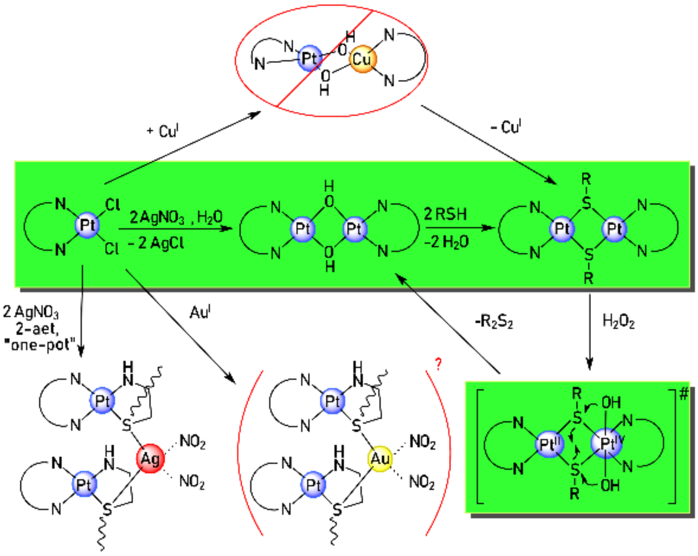

Fig. 2. Promising catalytic systems based on Pt(II), Cu(I), Ag(I), and Au(I) ions

The ability of coordination compounds to form complexes with coordinated OH-groups in redox processes with hydrogen peroxide and enter into reactions accompanied by the transfer of two electrons during the transformation of RS^- anions into R_2S_2 is unique for catalysts of the required type. However, the search for new low-toxic binuclear coordination compounds capable of forming catalytic systems with similar properties remains relevant.

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VP-II-3

Research of Morphology and Phase Composition of Autoclave Thermolysis Products of Chloropentaammincobalt (III) Tetrachloroplatinate (II)

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Catalysts containing noble metal are widely used in oil refining and chemical industry due to their high catalytic activity. Catalytically active phase is applied on various substrates in order to save expensive metals and increase the efficiency of their use. A binary complex compounds containing anion of platinum metal and cation of non-ferrous metal are promising precursor compounds for the preparation of supported catalysts.

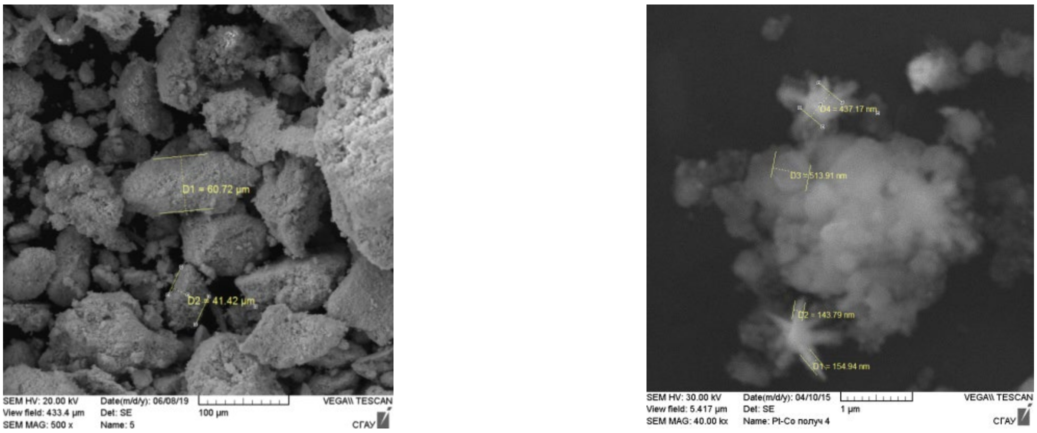
The products of reaction can be different compounds depending on the initial complex composition and thermolysis conditions. It is known that dispersed metal phases can be obtained from simple ammonia complexes of platinum metals in aqueous solution at elevated temperatures, the so-called autoclave conditions. The heteronuclear complexes decomposition of tetrachloroplatinate (II) with nickel or chromium ammonia leads to the formation of multicomponent phases consisting of non-ferrous metal oxide matrix and particles of metallic platinum embedded in it under the same conditions [1,2].

The aim of this work is research of morphology and phase composition of products autoclave thermolysis of binary complex chloropentaammincobalt (III) tetrachloroplatinate (II) $[Co(NH_3)_5Cl][PtCl_4]$.

The reaction was carried out in an autoclave at a solution 8-9 pH and a temperature of 190°C.

Powdered products of reaction were studied by scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDX), and X-ray phase analysis (XPA).

The SEM results (Fig. 1) showed that the product of autoclave thermolysis of the binary complex is a black powder consisting of irregularly shaped porous cobalt oxide particles several micrometers in size, including spherical platinum metal particles hundreds of nm in size. This is confirmed by EDX analysis. Surface-average atomic ratio of platinum and cobalt about 1 to 1, this corresponds to the complex stoichiometry.



500 times *40000 times*

Fig. 1. Electronic images of the autoclave thermolysis products of $[Co(NH_3)_5Cl][PtCl_4]$ at different magnifications

VP-II-3

The XPA results showed that powder contains two phase, one of which is metallic platinum, the other is mixed oxide of cobalt in the +2 and +3 oxidation states of Co_3O_4.

The obtained data are in agreement with the results of optical emission spectrometry with inductively coupled plasma.

A scheme of binary complex autoclave thermolysis, including a series of sequential transformations, such as ligand exchange between the anionic and cationic part, the cationic part hydrolysis, reduction of both partial cobalt and complete platinum was proposed. In this case, the platinum reduction occurs on the primarily formed porous cobalt oxide framework.

It is assumed that the product of autoclave thermolysis of tetrachloroplatinate (II) chloropentaamminecobalt (III) the double complex should have catalytic properties in redox reactions.

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VP-II-4

Ammonia-Carbonate Technology for the Synthesis of a Copper-Containing Catalyst with a Fixed Active Component

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Ammonia-carbonate complexes of one or more metals are widely used In the technology of catalysts, resulting in active component (AC) precursors formation in a fine-disperse state [1,2]. A copper-containing catalyst [3] utilizing pyrogenic silica (also known as Aerosil) as a carrier, has been developed in the Russian Federation for dehydrogenation of cyclohexanol to cyclohexanone, using the ammonia-carbonate technology (ACT). The catalyst shows high activity and selectivity values, but loses up to half of its activity in case of possible overheating. The low thermal stability of the catalysts is a consequence of weak precursor fixation over the Aerosil surface, so physically adsorbed nanoscale copper oxide particles are prone to migration and sintering, thus resulting in the active surface loss. «K-CO» Cu-Zn-based catalyst [4] is another result of the ammonia-carbonate technology usage, catalyst is obtained by mixing solutions of copper and zinc complexes, some of which form a cover of physically adsorbed nanoscale particles, and the other forms solid solutions of copper and zinc hydroxocarbonates. The K-CO catalyst resists thermal influences due to the part of the precursor that is fixed in the structure of solid solutions, but it is not selective enough. It was possible to obtain a MAK-K catalyst with a fixed active component [5] according to the ACT technology. The catalyst was prepared on a combined aluminum-silica carrier, where amorphous silicon dioxide in the form of white soot performs as a silica component, boehmite is the aluminum-containing phase, and copper hydroxocarbonate (CHC) is the precursor of AC. Hydroxylated silica usage leads to graft-phase formations of the AC precursor over the matrix material surface. Due to the strong adhesion to the carrier, nanoscale AC particles lose their overheating-caused tendency to migrate and become larger. Using IR spectroscopy, it has been shown that processing of amorphous silica with copper-containing ACR results in splitting of siloxane bonds on the silica surface, thus forming additional active silanol groups, suitable for the precursor of the active component fixing. On the contrary, the spectrum of the aerosil-based catalyst shows pyrogenic silica carrier lacks chemical interaction with CHC. It has been investigated, how thermal treatment conditions influences total precursor content, its phase state, chemical composition, and specific surface. Specific surface accelerated growth rate from 79 m^2 up to 340 m^2 followed by temperature increase from 25^0C to 90^0C indicates an ambiguous nature of the AC precursor sorption, and is explained by the mixed mode of its precipitation over a silica carrier. A relatively slow specific surface increase change takes place starting 70-75^0C, resulting in intensive growth. Part of the CHC from the solution precipitates in a physically sorbed state, bounds weakly to the carrier, and turns into copper oxide during subsequent heat treatment. The other part of the CHC is chemically fixed to the carrier utilizing its surface functional groups and retains its structure during heat treatment.

Bond strength between CHC and the carrier was confirmed by the differential thermal analysis. When a dried catalyst sample, prepared at 90^0C, is heated over white soot, the endoeffect is observed within 240 to 255°C range because of boehmite partial dehydration. The endothermic effect responsible for the decomposition of CHC within the catalyst has not been registered. The effect corresponding to the phase transition of boehmite to γ-Al_2O_3 with Tmax =400°C, which occurs when individual boehmite is heated, was also not detected. The absence of CHC decomposition effects inline with boehmite transition to γ-Al_2O_3 confirms aluminum oxide component of the carrier is involved in active cover formation over carrier surface. As for Aerosil sample, the effect of HCM decomposition is depicted as a relief, though confirming IR spectroscopy data on the precursor shown as a free phase within the catalyst. According to XRD analysis, no precursor in CHC form detected in calcined MAK-K samples prepared at 50^0C, 70^0C and 90^0C. On the other hand, in addition to boehmite, a well-crystallized copper oxide phase (d=2.52 Å (2θ=35.50), d=2.32 Å (2θ=38.70), and d=1.86 Å) with a dispersity of about 12 nm is clearly identified in the MAC-K70 and MAC-K50 samples, resulting from the free CHC decomposition. MAK$_{90}$ sample prepared at 90^0C proved to be completely x-ray amorphous relating to the active component precursor, that fits previous investigations. Catalyst on pyrogenic silica media with a precursor content of about 17 wt.% is represented exclusively by the copper oxide phase on the diffractogram. Results of prepared catalyst samples testing in the dehydrogenation reaction are shown in Table 1, for varying media/carrier and copper ACR treatment thermal conditions.

Table 1. The properties of the catalyst samples on different media

Catalyst	Conversion rate at 250°C, %	Selectivity at 250°C, %
МАК – К$_{90}$	53,5 – 55,8	99,3 – 99,5
	After overheating at 350°C for 16 hours	
	48,1	99,7
МАК – К$_{70}$	54,1 – 54,5	99,2 – 99,4
	After overheating at 350°C for 16 hours	
	32,8	99,5
Aerosil-based catalyst	52,8 – 54,5	96,9 – 97,6
	After overheating at 350°C for 16 hours	
	28,9	98,1

It has been shown, that after overheating the MAK-K90 catalyst, the conversion rate dropped from (53.5-55.8) % to 48.1 %, while the conversion rate of the aerosil-based catalyst conversion rate decreased from (54.5 - 52.8) % to 32.8 %.

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VP-II-5

Catalytic Properties and Kinetic Parameters of Molecularly Imprinted Macroporous Polymer Monolithic System Containing Artificial Active Sites of Chymotrypsin

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Chymotrypsin is an enzyme specific to C-terminal residues of L-tryptophan, L-phenylalanine and L-tyrosine and widely used in the chemical, food and medical industries. However, its practical application is severely limited due to their instability to organic solvents as well as pH and temperature differed from the optimal values [1]. In addition, laborious production and isolation of enzymes determines their high cost [2]. Thus, there is a need to develop modified enzymes capable of "working" in a wide variety of environments and conditions. An alternative solution to overcome that obstacle is the development of enzyme-like artificial catalytic systems, devoid of the above disadvantages [3].

In this work, a new type of organic catalysts based on high flow-through macroporous polymer monoliths containing artificial catalytic centers imitating an active center of chymotrypsin was developed using the molecular imprinting technique, which is based on the formation of the target molecule (template) imprints in the polymer matrix [4].

Preparation of molecularly imprinted monolithic catalyst (MIC) was carried out in 2 stages. Initially, using ethylene glycol dimethacrylate (EDMA) as a monomer and 1-dodecanol/toluene = 70/30 (% v/v) as porogens, a macroporous monolithic framework was synthesized. Then, on the surface of the framework a functional layer was grafted. For this purpose, the derivatives of amino acids forming the active center of chymotrypsin (N-methacryloyl-L-histidine, N-methacryloyl-L-aspartic acid, N-methacryloyl-L-serine) were used as functional monomers. EDMA and a compound similar in structure to the substrate used in the work, N-nicotinoyltyrosylbenzyl ester, were used as a crosslinking agent and template, respectively. Cobalt(II) chloride was applied to coordinate amino acids and provide their close arrangement in the resulting material. The average pore size of the material was about 1.5 µm, the total porosity was about 75% and the content of active sites was 2.6 µmol/monolith (1.2 µmol per 100 mg of polymer). According to the data of scanning electron microscopy, the obtained MIC was characterized by a homogeneous morphology and a branched network of flow-through macropores.

The catalytic properties of the developed system were evaluated by the hydrolysis of the ester bond in a low-molecular weight substrate (Z-L-tyrosine p-nitrophenyl ether) in the recirculation mode of the substrate solution through the MIC. The effect of an increase in the flow rate (0.5-1.5 mL/min) and temperature (37-65°C) on the efficiency of reaction was evaluated and the kinetic parameters (maximum reaction velocity (V_{max}) and Michaelis constant (K_m)) of hydrolysis were determined using a graphical approach based on linearization by Lineweaver–Burk or Hanes methods. The molar ratio [substrate]/[active sites] was varied in the range of 25-100 in reaction medium – acetonitrile/0.005 M sodium phosphate buffer (pH 7.8) = 60/40 (% v/v). It was shown, that both an increase in the flow rate and the reaction temperature led to a significant increase in the hydrolysis rate of substrate. The kinetic parameters of hydrolysis showed, that at a substrate solution flow rate of 0.5 mL/min (K_m = 0.037±0.002 M, V_{max} = 132±10 µmol/(L·min) by Lineweaver–Burk method) MIC has a better affinity for the substrate than at a rate of 1.5 mL/min (K_m = 0.065±0.004 M, V_{max} = 238±13 µmol/(L·min) by Lineweaver–Burk method), but the reaction rate was lower. The results obtained by Lineweaver–Burk and Hanes methods well correlated with each other. To assess the specificity of the developed MIC, its ability to hydrolyze the ester bond of other amino acids analogous derivatives, namely Fmoc-L-alanine p-nitrophenyl ether, at a flow rate of 0.5 mL/min was investigated. The hydrolysis of the tyrosine-based ester was more efficient in relation to the alanine analog. It was found that the hydrolysis rate and the maximum reaction velocity were almost 2 times higher for the tyrosine derivative that means a higher selectivity of MIC for substrates based on tyrosine. Evaluation of the MIC stability over time showed, that the catalytic activity remained constant even after 40 catalytic cycles, which indicates a high regeneration of the catalyst after use and good stability of artificial catalytic sites. Thus, the developed mimics can outperform natural biocatalysts in long-term stability and applicability under more severe reaction conditions.

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VP-III-1

Mathematical Modeling the H_2SO_4-Catalyzed Alkylation of Isobutane with Olefins

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The purpose of this work is to develop a mathematical model of sulfuric acid alkylation of isobutane by olefins, taking into account the physical and chemical laws of the process. Significant features of the technology that need to be taken into account when modeling are identified. The main schemes of transformations of sulfuric acid alkylation of isobutane by olefins are considered. The probability of all reactions is estimated from the Gibbs energy value. The foundations for further modeling of the entire chemical-technological process are laid.

Currently, there is a tendency to improve the environmental characteristics of automobile fuel while maintaining a high octane number. Sulfuric acid alkylation of isobutane with olefins makes it possible to obtain a high-octane component of gasoline with a minimum content of aromatic hydrocarbons. Therefore, it is a significant process of the modern refinery.

The main advantage of alkylate is the high octane number: according to the research method, it is 96, according to the motor method, it is 92. The alkylation product is non-toxic, does not contain benzene, and has a low saturated vapor pressure, hence it does not evaporate much during storage and transportation [1].

In the middle of the XX century, at the design and construction stages of most industrial installations, including reactors, insufficient attention was paid to in-depth study of the mechanism of most processes. Now the intensive development of information technologies, such as the theory of analysis and storage of large amounts of data, parallel computing technology, artificial neural networks, etc., has led to the creation of universal software systems that allow you to develop detailed kinetic models of production processes [2,3].

The most complete account of thermodynamic and kinetic regularities of target and side reactions during modeling will allow predicting the yield of the target product with the highest degree of confidence. What can be used in the future to find optimal technological conditions and intensify the process [4,5].

When modeling this process, it is necessary to take into account the properties of acid catalysts with high corrosion activity and low selectivity, which leads to the fact that along with the target alkylation reactions, a large number of side reactions occur. They lead to a loss of activity and an increase in the consumption of the catalyst, as well as to the formation of lighter and heavier hydrocarbons than the target product, which lowers the octane number of the alkylate. Figure 1 shows the effect of sulfuric acid concentration on the alkylate octane number. Figure 1 shows the effect of the sulfuric acid concentration on the octane number of the alkylation product [1,6].

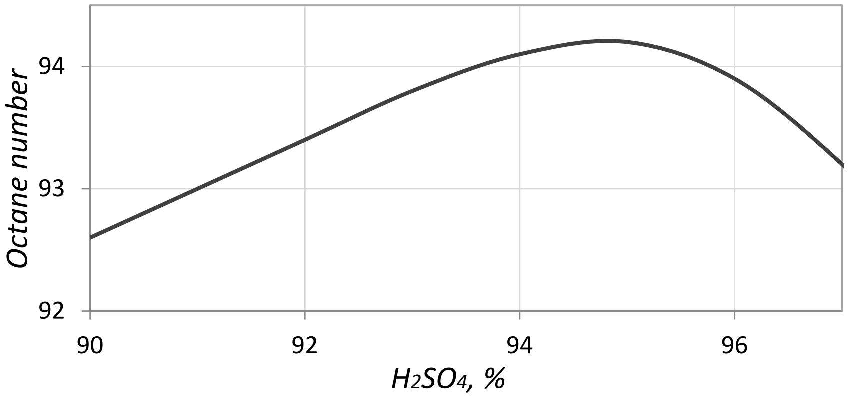

Fig. 1. Effect of sulfuric acid concentration on the alkylate octane number [1].

Thus, on the basis of the literature review a preliminary scheme of chemical transformations. We have developed a detailed kinetic model of sulfuric acid alkylation that takes into account the following reactions: alkylation of isobutane by olefins, olefin polymerization reactions, disproportionation, self-alkylation with H-transfer, and destructive alkylation.

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VP-III-2

Kinetic Study of Acetophenone Hydrogenation with Hydrogen Transfer Using Bis-Imine-Rhodium Complex

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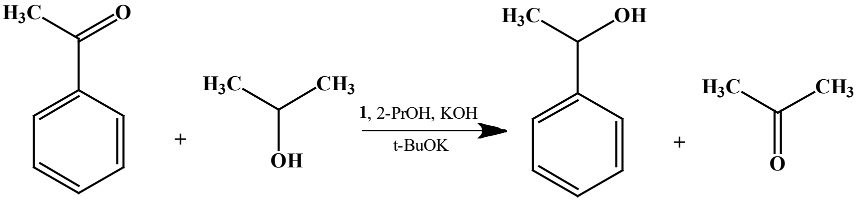
Asymmetric transfer hydrogenation (ATH) of acetophenone (APh) to 1-phenylethanol (PhE) was studied in 2-propanol solution in the presence of Rh(1,5-COD)(μ-Cl)]2+L,**1**, where 1,5-COD = cyclooctadiene and L is a bis-aldimine ligand based on (R,R)-1,2-cyclohexanediamine and pyridinecarboxaldehyde. The ATH reaction proceeds according to equation 1. Hydrogen transfer from 2-PrOH to APh produces 1-PhE and Ac as products, with no other products found in the system.



(1)

To propose a kinetic model, we first established the catalyst activation rate and 1-PhE formation rate at different reagent concentrations. To identify factors that influence the rates and directions of these reactions, kinetics experiments were conducted in the following concentration ranges: APh (1.7×10^{-5}–1.9×10^{-1}) M, Rh (3×10^{-4}–2.2×10^{-3}) M, KO*t*Bu (3×10^{-4}–8.8×10^{-3}) M, 1-PhE (4.7×10^{-2}–4.7×10^{-1}) M, and Ac (0–5×10^{-2}) M.

According to the results of typical experiments in the presence of the catalyst, the reaction proceeds with TOF_{max} up to 268 h^{-1} and with (*R*)-1-PhE as the dominant product in all cases. The introduction of *rac*-1-PhE (0.0476 M) into the initial reaction mixture led to a small decrease in W_{max} (by a factor of 1.2) and a slight increase in the *ee* of the product (to 40%). A decrease in W_{max} was also observed when ~3.3-times the amount of Ac was introduced, although this effect was already observed when 1/4 of the initial concentration of APh was used; this increased the *ee* of (*R*)-1-PhE to 49%.

Increasing the substrate concentration has a positive effect on the reaction rate, as indicated by a higher turnover frequency (TOF). The dependence of TOF on the initial concentration of APh deviates from linearity at C_{APh} > 100 mM (Fig 1). The maximum rate of this reaction is from the combined effects of various rate constants, and therefore it cannot be used to determine the activation parameters of the rate-deterimiting step.

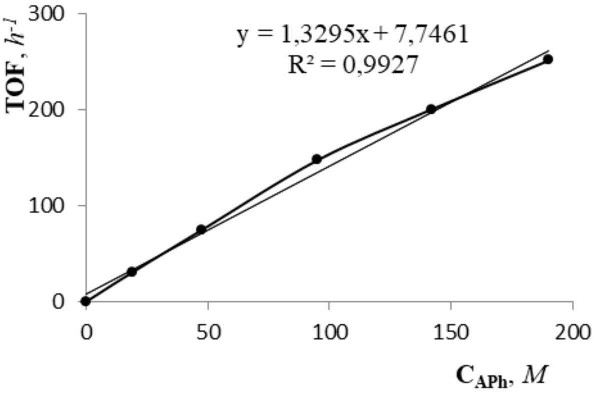


Figure 1. Dependence of TOF for 1-PhE formation on the initial concentration of APh, [Rh₀] = 5.5×10⁻⁴ M

VP-III-2

The substrate can bind to the chiral rhodium complex in two different ways (the *re*- or *si*-side of the prochiral C=O bond), and thus two diastereomeric complexes can be formed. The rates of these two competing reactions are d[(*R*)-1-PhE]/dt and d[(*S*)-1-PhE]/dt, respectively. The differential selectivity for the enantiomeric products, d[(*R*)-1-PhE]/d[(*S*)-1-PhE], is independent of the amount of active catalyst, when the products are formed on the same active component [1]. The phase trajectories for the products at different rhodium precursor concentrations are given in Fig 2. The almost overlapping phase trajectories indicate that the different enantiomers are indeed formed over the same type of catalyst.

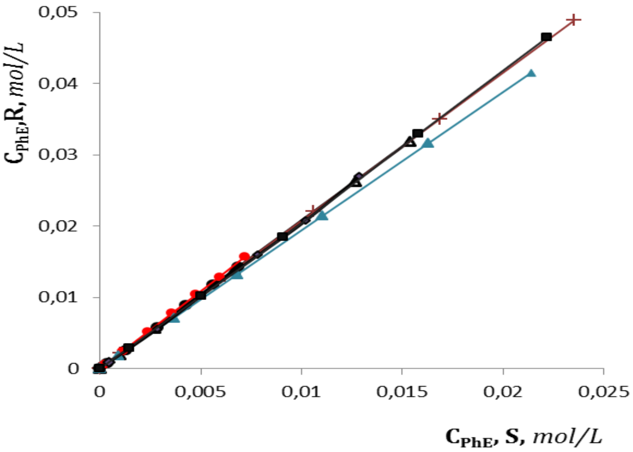


Figure 2. The phase trajectories of the (R)- and (S)-1-phenethanol formation at different concentrations of the rhodium precursor. Conditions: [APh] = ● – 0.048; ♦, Δ¸ – 0.095; ▲ – 0.143; ■, +, ● – 0.190 M; [Rh$_0$] = ♦, ▲, + - 5.5×10^{-4} ; ● – 5.9×10^{-4}; ● – 6.2×10^{-4}; ■ – 1.1×10^{-3}; Δ – 2.2×10^{-3} M; [KOtBu]/[Rh$_{0,init}$] = 6; [2-PrOH] ≈ 13 M; 78 °C.

Acknowledgement. This work was supported by Irkutsk National Research Technical University [grant number 04-FPK-19]

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VP-III-3

Quantum-Chemical Study of the Stages of Alkene Insertion into Zirconocene Alkylchloride–Trimethylaluminum Bimetallic Complexes $L_2ZrMeCl-AlMe_3$

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Catalytic di-, oligo- and polymerization of alkenes [1-3] are widely demanded in various fields, and give a wide variety of products, the structure of which depends on the type of catalytic system used. Despite the fact that a large number of complexes have been proposed, tested as catalysts for the homo- and copolymerization of olefins of various structures [3-9], nevertheless, it remains important to establish the relationship between the structure of the complexes and their catalytic properties (activity, selectivity). The aim of this work was to theoretically study the stereoselectivity of the propene dimerization reaction with the participation of the $L_2ZrMeCl-AlMe_3$ **1** complexes (where L_2 = Cp_2, Ind_2, Me_2CInd, Me_2SiInd_2, $C_2H_4Ind_2$, $C_2H_4Ind_2$, H_2CCpBu^t), key intermediates of the carbometallation reaction [10, 11].

As a result, a series of calculations was carried out using the quantum chemical method PBE/3ζ (Priroda 6 [12]), to determine the thermodynamic and activation parameters of two successive stages (Fig. 1) of the insertion of an alkene into zirconocene alkylchloride–trimethylaluminum bimetallic complexes containing cyclopentadienyl, indenyl and ansa-lidands with a different type of bridge.

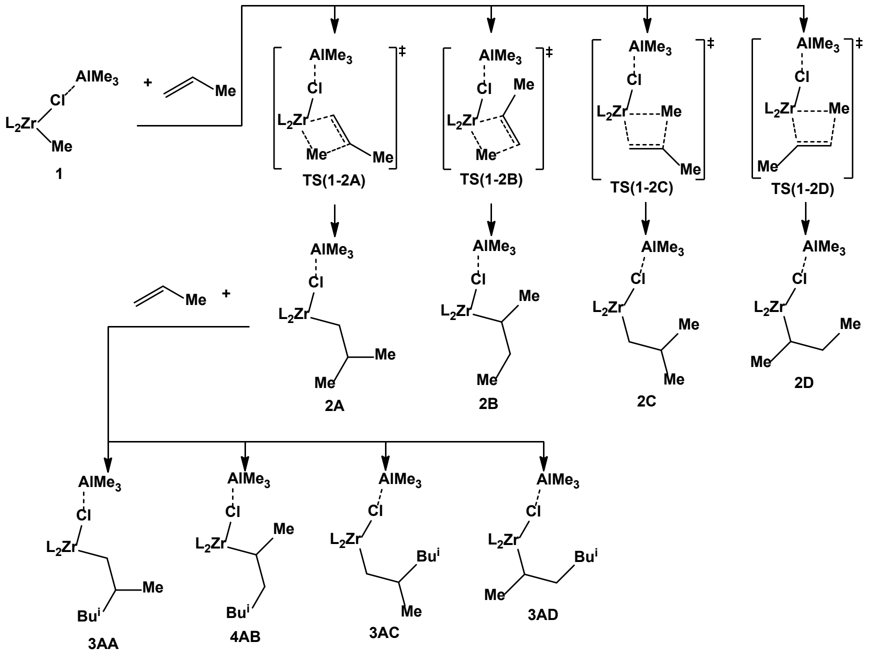

Fig 1. Two stages of olefin insertion into complexes of the $L_2ZrMeCl-AlR_3$ type

It was found that, for all complexes, the most energetically favorable pathroute for the insertion of an olefin molecule into the initial complex **1** is the pathroute of interaction by the type of 1,2-interaction with a metal alkyl, which is consistent with experiment. Comparative analysis of the energy parameters of reactions involving various complexes showed that the most reactive in the carbometallation reaction are indenyl $Ind_2ZrClMe$-$AlMe_3$ and cyclopentadienyl $Cp_2ZrClMe$-$AlMe_3$ complexes.

It was shown that the reaction of chain growth, i.e. the insertion of the second olefin molecule into the formed complex of the $L_2ZrAlkCl$-$AlMe_3$ **2** type, is thermodynamically more favorable, regardless of the structural features of the ligands. It was found that the regioselectivity of the complexes in oligomerization reactions largely depends on the structure of the ligand of the zirconium complex, for example, the bis(cyclopentadienyl)zirconium complex reacts with propene non-regioselectively, while comlexes with relatively bulky bis-indenyl and ansa-ligands exhibit a greater selectivity. For the latter conformationally determined bridged complexes, the direction of olefin insertion during chain growth is also determined by the conformational state of the oligomer chain.

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VP-IV-1

An Insight into Deactivation of Pd/Al_2O_3 Catalyst for Bioethanol Conversion

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Conversion of bioethanol to butanol-1 is a promising process for recycling of biooxygenats. This is a complex process, including the stage of hydrogenation-dehydrogenation catalyzed by metals and aldol-croton condensation catalyzed by acid-base sites. Therefore, the optimal catalyst for this process must possess metal sites and acid-base sites [1-2]. In our preliminary study it was found, that at 275 °C on Pd/Al_2O_3 (Pd = 0.1 wt.%), the ethanol conversion is 20%, and the selectivity of 1-butanol formation is 65% (Fig. 1). This is a rather high performance in comparison with other supported catalysts descried in [1]. However, the stability of Pd/Al_2O_3 is low and it demonstrates rapid deactivation during time-on-stream (Fig.1). In this work, we studied the probable mechanisms of deactivation of this catalyst.

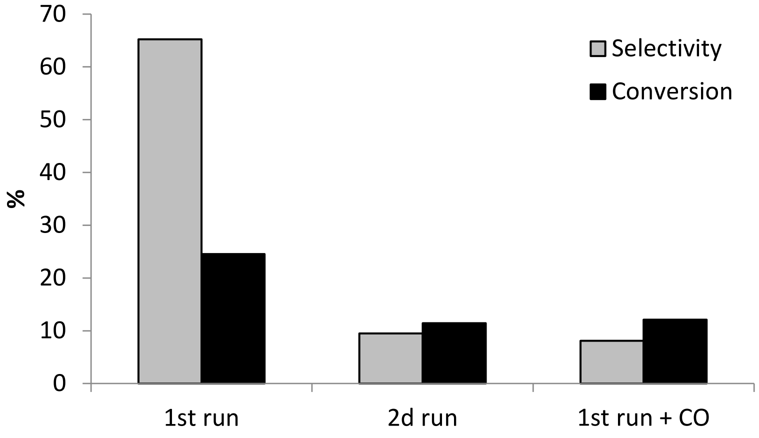

Fig. 1. *Bioethanol conversion and selectivity to 1-butanol on Pd/Al_2O_3 catalyst in sequential runs. (Standard Run - 275 °C, 5 h, 25 ml C_2H_5OH, 5 g catalyst; Run + CO - 275 °C, 5 h, 25 ml C_2H_5OH, 5 g catalyst, 1×10^{-4} mol of CO)*

Four probable reasons can be assumed for deactivation of Pd/Al_2O_3 during catalysis: oxidation of the Pd by side products; formation of soluble organopalladium compounds followed by leaching; sintering of Pd phases during heating in the reactor, and deactivation of Pd sites by CO produced via side reaction. The first reason can be ruled out, because the oxidation state of palladium in the catalyst determined via XPS before and after catalysis was Pd(0) (Fig. 2(a)). The second reason can be ruled out too, as the metal content in Pd/Al_2O_3 determined via AAS was the same before and after catalysis. According to TEM measurements (Fig. 2 (b)), sintering of Pd particles should also be excluded from consideration.

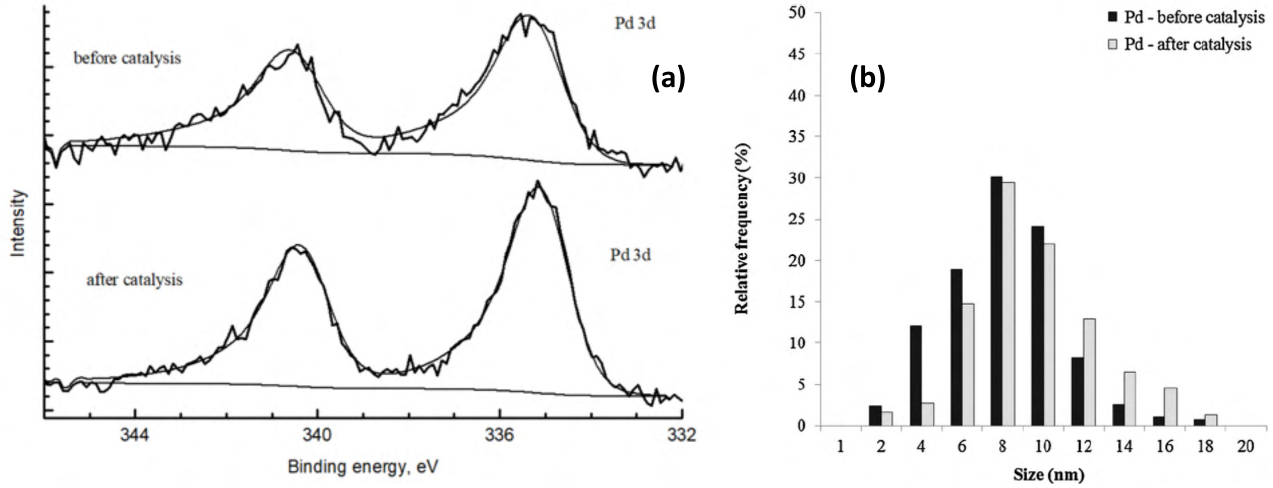

Fig. 2. *Pd 3p XPS spectra* ***(a)*** *and particle size distributions* ***(b)*** *of the Pd/Al_2O_3 catalyst before catalysis and after the 3rd run.*

According to GH-MS analysis, CO molecules produced via side reactions were accumulated in reaction media during conversion of ethanol on the Pd/Al_2O_3 sample. The amount of CO measured after 5 h of the reaction is about 1×10^{-4} mol. This is comparable with the total Pd amount in the catalyst loaded into the reactor (i.e., 5.2×10^{-5} mol).

In order to directly verify the inhibitory effect of CO, 1×10^{-4} mol of CO was injected into the reactor containing ethanol and the initial catalyst. Next, the standard test was performed. The results are presented in Fig.1. The addition of CO before the start of the reaction (Fig. 1, run 1 + CO) results in more pronounced decreasing of catalytic activity in comparison with the test performing under standard conditions (Fig. 1, run 1) . Consequently, CO chemisorption can be regarded as the most probable reason for deactivation of Pd component of the Pd/Al_2O_3 catalyst.

The elucidated reason of deactivation of catalyst allows to develop approaches of improving the stability of the Pd/Al_2O_3 catalyst, for example, by promoting the Pd component. This will be studied in our further work.

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VP-IV-2

Comparison of the Catalytic Behavior of Supported Mono- and Bimetallic Ag, Au and Pd NPs in HMF Oxidation

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There is an increase in the consumption of fossil raw materials within the growth of the world's population. Since the resources of Earth are finite, alternative sources of chemicals are becoming increasingly important. One of those sources is the biomass compound 5-hydroxymethylfurfural (HMF). By oxidizing HMF, various valuable products are obtained, such as 2,5-furandicarboxylic acid (FDCA). This compound is widely used in pharmaceuticals and in the production of succinic acid for chemical industry, and more importantly, as a potential precursor for the production of polyethylenefuranoate (PEF), biopolyester designed to replace the oil-derived polyethylene terephthalate (PET) [1].

The highest activity in HMF oxidation processes using molecular oxygen has been shown by catalysts based on noble metals, such as Pd, Pt or Au [2]. However, the catalytic activity of such supported catalysts is strongly sensitive to many factors, such as metal dispersion, preparation method, nature of the support, metal-support interaction, etc. Therefore, this research topic still requires further investigation. The present work aims at studying the effect of support for mono- and bimetallic catalysts based on noble metals (Ag, Au, Pd) for HMF oxidation yield FDCA.

HMF oxidation was carried out in a semi-batch reactor at 60 °C and 3 atm O_2. H_2O was used as a solvent. Samples were analyzed using a HPLC Agilent 1260. The catalysts were characterized by XRD, BET, ICP, HRTEM, XPS and Hammett indicator method. Titania was modified by impregnation with aqueous solutions of the corresponding nitrates. Sibunit carbon support (denoted as Cp) was treated by boiling in a nitric acid or ammonium hydroxide 20 wt% solutions (denoted as Cp-HNO_3 or Cp-NH_4OH, respectively). Catalysts were synthesized by deposition-precipitation method for titania and alumina-based samples, while sol immobilization was used for metal deposition on Sibunit supports.

Table 1 shows the screening of samples activity for HMF oxidation after 2 h. Full conversion (97-100%) and carbon balance (95-101%) is observed for all catalysts except Ag/CeO_2/TiO_2 (Table 1, entry 11). At the same time, deposition of silver on Sibunit leads to complete conversion, although carbon balance was still worse but at higher level (69%) than for Ag/CeO_2/TiO_2. This shows the low activity of silver, which cannot suppress HMF degradation towards polymeric products (humins), occurring under basic conditions (Table 1, entry 2), because no reaction occurred in the absence of NaOH (Table 1, entry 1).

In general, the order of FDCA formation for the remaining Au and Pd catalysts was as follows: Au/TiO_2 ≤ Au/Fe_2O_3/TiO_2 < Au/Al_2O_3-V < Au/La_2O_3/TiO_2 ≤ Au/Al_2O_3-V ≤ Au/MgO/TiO_2 < Au/CeO_2/TiO_2

< Au/AlOOH-S ≤ Au/Cp < Pd/AlOOH-S < Pd/Cp < PdAu/Cp < PdAu/Cp-HNO_3 < PdAu/Cp-NH_4OH. Thus, on both Au and Pd, the highest FDCA selectivity was obtained when metals were supported on Sibunit. Moreover, Pd-Au bimetallic systems on Sibunit supports were more active than the corresponding monometallic analogues (Table 1).

Table 1. Catalytic behaviour of Ag, Au, Pd and PdAu NPs on supported on different materials for HMF oxidation under basic conditions.

Entry	Catalyst	Conversion, % after 2h	Selectivity, %		Carbon balance,%
			HFCA	FDCA	
1	No catalyst	0	0	0	100
2	No catalyst +NaOH	30	100	0	31
3	4wt% Au/TiO_2	97	94	6	95
4	4wt% Au/Fe_2O_3/TiO_2	98	93	7	95
5	4wt% Au/La_2O_3/TiO_2	99	89	11	95
6	4wt% Au/MgO/TiO_2	99	87	13	95
7	4wt% Au/CeO_2/TiO_2	99	84	16	96
8	4wt% Au/AlOOH-C	99	90	10	95
9	4wt% Au/Al_2O_3-V	100	88	12	95
10	4wt% Au/AlOOH-S	100	80	20	95
11	2.3wt% Ag/CeO_2/TiO_2	36	100	0	30
12	4wt% Pd/AlOOH-S	97	50	50	100
13	1wt% Ag/Cp	98	98	2	69
14	1wt% Au/Cp	100	79	21	95
15	1wt% Pd/Cp	99	45	55	97
16	0.69wt% Pd 0.31wt%Au/Cp	99	40	60	101
17	0.69wt% Pd 0.31wt%Au/Cp-HNO_3	99	32	68	96
18	0.69wt% Pd 0.31wt%Au/Cp-NH_4OH	99	30	70	98

A deeper study of catalytic behavior of the most active bimetallic catalysts demonstrates the positive effect of the treatment in the activity of catalysts in HMF oxidation (Table 2). Thus, the highest FDCA yield (58%) was obtained on PdAu/Cp-NH_4OH already after 15 min.

The final work will present an explanation of the beneficial role of Sibunit treatments for FDCA production, on the basis of a comparative study of physicochemical and catalytic properties of the bimetallic systems.

Table 2. Activity of Pd-Au/Sibunit catalysts with different support treatments in HMF oxidation.

Entry	Catalyst	Conversion, % after 15 min	Selectivity, %		Yield, %		Carbon balance, %
			HFCA	FDCA	HFCA	FDCA	
1	PdAu/Cp	83	69	31	57	26	100
2	PdAu/Cp-HNO_3	80	57	43	46	34	100
3	PdAu/Cp-NH_4OH	93	38	62	35	58	95

Acknowledgements. This work was partially supported by FCT-Portugal (CEECINST/00102/2018) and Associate Laboratory for Green Chemistry—LAQV, financed by national funds from FCT/MCTES (UIDB/50006/2020) (Portugal), Tomsk Polytechnic University Competitiveness Enhancement Program project VIU-RSCBMT-197/2020, Russian Foundation of Basic Research, project 18-29-24037.

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VP-IV-3

Inorganic Binuclear Complex of Ruthenium with a Nitrogen Bridge and Lithium Countercations as a Precursor of the Water Oxidation Reaction in Artificial Photosynthesis

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At the present time the problem of environmental pollution by industrial production is quite important. This is due to the accumulation of carbon dioxide in the atmosphere, which leads to the greenhouse effect and can ultimately lead to global warming of the entire Earth. The most topical task of the XXI century is the search for ways to utilize solar energy (SE). Most of the world's modern energy sources came from sunlight that was converted into chemical energy by photosynthetic organisms. Therefore, many modern studies are focused on the so-called artificial photosynthesis - the photo-induced decomposition of water into oxygen and hydrogen, which is the most promising energy carrier in the future. Stable, highly efficient catalysts are required to create effective photocatalytic converters of solar energy into chemical energy.

Earlier well-studied ruthenium catalysts for water oxidation show low activity (TON = 30 - 40 sec^{-1}) due to the presence of organic ligands, which are oxidized more easily than water and contain labile Ru-O-Ru bonds, leading to catalyst destruction. In the present work the $Li_3[Ru_2NCl_8\times 2H_2O]$ complex was synthesized and its structure was studied by X-ray diffraction.The Ru-N bond (1.71Å) in this complex is shorter than that of its oxygen analogue Ru-O (1.86Å). The kinetic ESI-mass spectrometric investigation shows that the oxidation of water in an acidic medium proceeds according to the bimolecular law according to the reaction: $2[Ru^{IV}\text{-}N\text{-}Ru^{IV}] + 2\ H_2O = 2[Ru^{III}\text{-}N\text{-}Ru^{III}] + O_2 + 4H^+$ with reaction constant $k = 0.22\ M^{-1}\times min^{-1}$. The maximum peak of the reduction products of the complex with molecular weight m/z = 512.28 corresponds to the tetranuclear $Ru_4N_2O_5^+$ cluster, which is a catalyst for the four-electron oxidation of water with the formation of O_2. The effect of Li^+- cation is discovered. The turnover number the catalyst with Li^+ (TON = 356) is 3 times higher than that of a similar catalyst with K^+- cation (TON = 112) and 8-10 times higher than that of the complex *cis,cis*-$[(bpy)_2Ru(OH_2)]_2O^{4+}$ and its numerous analogs which contain organic ligands and labile Ru-O-Ru bonds.

VP-V-1

Influence of the Modifier on the Activity of the Catalytic Systems Pd (acac)$_2$-Mod-H_2 in the Reaction of Asymmetric Hydrogenation of Acetophenone

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The catalytic system Pd (acac)$_2$-Mod-H_2 in the reaction of asymmetric hydrogenation of a model substrate, acetophenone (APh), was studied. APh hydrogenation proceeds according to the scheme in Fig. 1.

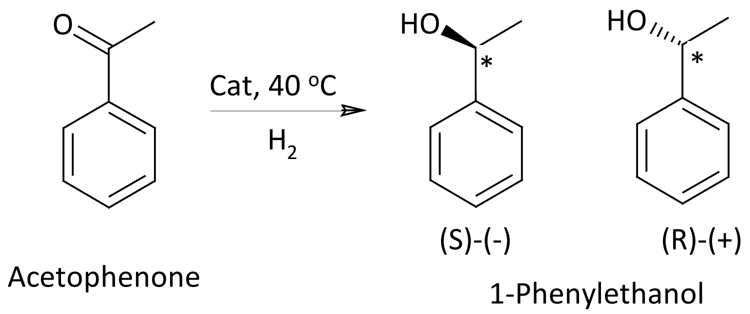

Figure 1. Scheme for APh hydrogenation over the catalytic system Pd (Acac)$_2$ – Mod-H_2

(-) - Cinchonidine (**1**), its biprotonated derivative (**2**) and (1S, 2S) - (+) - 2-amino-1-phenyl-1,3-propanediol (**3**) were used as modifiers. Polyvinylpyrrolidone (PVP), cross-linked polyvinylpyrrolidone (CLPVP), and cetyltrimethylammonium chloride (CTAC) were added to the system with modifier **1** for additional stabilization. Also we studied a system formed without stabilizer and modifier. The obtained data are presented in table 1.

Table 1 - Influence of the nature of the modifier on the activity of the catalytic system Pd-Mod-H_2 (Mod/Pd = 1; C_{sub}=140 mM; C_{Pd} = 3,3 mM; P_{H2} = 5 Bar; T = 40 °C).

№	Mod	AP conversion, %	W_{max}, mM/*h	TOF_{max}, mM/g at. Pd*h	ee (S)-(-), %
1	**1**	44	12	4	19
2	**1** + PVP	18	5	1	15
3	**1** + CLPVP	6	2	1	17
4	**1** + CTAC	27	6	2	23
5	**2**	100	38	11	12
6	**3**	80	16	5	2
7	-	14	6	2	0

The most active system was the one formed in the presence of the biprotonated derivative (-) - cinchonidine, it provides a hydrogenation rate of about 38 mM/h, the excess of the (S) -enantiomer was 12%. The system with (1S, 2S) - (+) - 2-amino-1-phenyl-1,3-propanediol (16 mM/h) exhibited a relatively high activity, but the *ee* of the product was also low (2%).

The systems formed in presence of (-) - cinchonidine were less active. The addition of cetyltrimethylammonium chloride (CTAC) to the system as a structural control agent is a common practice to improve the stability of the colloidal system [1], but in this case it is not effective. In this way, its introduction accelerated the formation of the system, reducing the induction period, but at the same time, the activity of the catalyst was almost halved. Systems formed in the presence of polymers showed low activity (5 mM/h and 2 mM/h using PVP and CLPVP, respectively). Thus, stabilization in the polymer matrix increases the catalyst system lifetime and allows the system to be reused [2]. Table 2 shows the results of experiments on the recycling of the catalyst formed in system Pd(acac)$_2$–**1**+CLPVP-H$_2$.

*Table 2 - Recyclization of the catalytic system Pd-**1**+CLPVP-H$_2$ (**1**/Pd = 1; C_{Pd} = 3,3 mM; P_{H2} = 5 Bar; T = 40 °C).*

№ exp.	AP conversion, %	W$_{max}$, мM/h	TOF$_{max}$, mol/g at. Pd*h
1	5,6	2	1
1-st recyclization	68,9	16	5
2-nd recyclization	70,5	17	5
3-rd recyclization	64,1	10	3

It can be noted that the development of the catalytic system is observed with reuse. This makes it possible to obtain a significantly higher activity already at the 1st and 2nd recyclization.

Acknowledgement. This work was supported by the Irkutsk National Research Technical University grant number 04-FPK-19.

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VP-V-2

A New Approach to the Synthesis of Synthetic Derivatives of Acetogenins - Promising Anticancer Drugs

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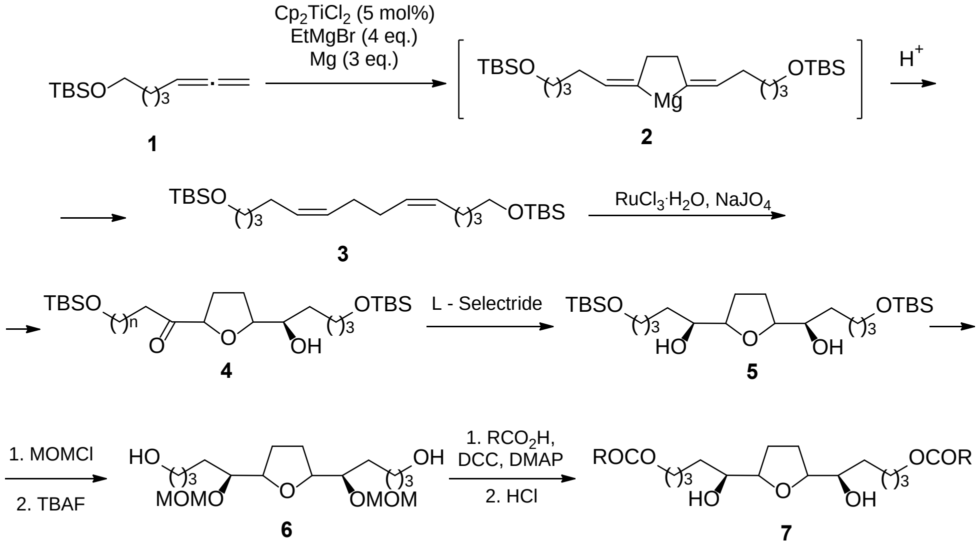
An efficient method for the preparation of synthetic analogs of acetogenins, based on Ti-catalyzed homo-cyclomagnesiation [1] of 5,6-heptadien-1-ol protected by tert-butyldimethylsilyl group **1** has been developed. Oxidative cyclization of the forming 5Z,9Z-diene **3** leads to substituted tetrahydrofuran **4**. Subsequent reduction the carbonyl group using L-Selectride gives compound **5**. Protection of hydroxyls with methoxymethyl group and further removal of tert-butyldimethylsilyl protecting groups leads to compound **6**. The esterification reaction and removal of methoxymethyl protecting groups in an acidic medium give the corresponding synthetic analogs of acetogenins **7**.



Scheme 1. Synthesis of synthetic derivatives of acetogenins

Acknowledgement. The study was supported by grants from the Russian Science Foundation (project No. 18-73-10030, No. 20-64-47019) and the Russian Foundation for Basic Research (project No. 19-03-00603, No. 18-29-09068)

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VP-V-3

Cobalt(I)-Catalyzed [6π+2π]-Cycloaddition of 1-Substituted 1,3,5-Cycloheptatrienes for the Synthesis of Bicyclo[4.2.1]Nonanes

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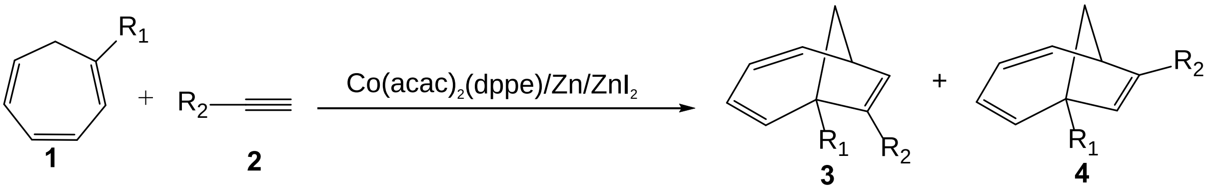
We have previously developed efficient methods for the synthesis of a wide range of substituted bicyclo[4.2.1]nonadi(tri)enes based on the catalytic cycloaddition of 1,3,5-cycloheptatrienes to 1,2-dienes and alkynes [1-3]. It is important to note that this research is highly relevant, since the bicyclo[4.2.1]nonane core is a key structural element of important terpenoids and their metabolites, such as mediterraneols A and B, longifolane, and seco-longifolenediol derivatives, which have pronounced antitumor activity. In the development of further research, we first studied the reaction of cobalt(I)-catalyzed cycloaddition of 1-substituted 1,3,5-cycloheptatrienes to alkynes. It was found that [6π+2π] cycloaddition of 1,3,5-cycloheptatrienes **1** to terminal alkynes **2**, including functionally substituted ones, under the action of the three-component catalytic system $Co(acac)_2(dppe)/Zn/ZnI_2$ developed by us [4] leads to the formation of substituted bicyclo[4.2.1]nona-2,4,7-trienes **3** and **4** in high yields (72-86%).



R_1 = Me, CH_2OH; R_2 = Alk, Ar, $(CH_2)nCN$, $(CH_2)nOH$ n = 2, 3

Scheme 1. *Cobalt-Catalyzed [6π+2π]-Cycloaddition of 1-substituted 1,3,5-cycloheptatrienes with Alkynes*

The obtained bicyclo[4.2.1]nona-2,4,7-trienes showed high antitumor activity in vitro against the Jurkat, K562, U937 and HL60 tumor cell lines.

Acknowledgement. This work was supported by the Russian Science Foundation (project № 19-73-10116) and the Russian Foundation for Basic Research (project № 19-03-00393, 18-29-09068).

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VP-V-4

Reaction of Ti-Catalyzed Homo-Cyclomagnesiation of 1,2-Dienes in the Synthesis of Acetogenin Analogs

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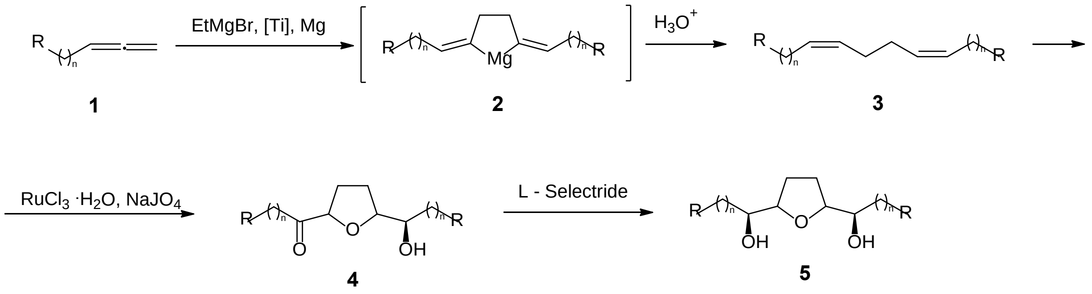
The acetogenins contained in the fruits of plants of the Annonaceous family exhibit a wide range of biological activities and are the subject of numerous studies [1, 2].

We have developed a new original method for the synthesis of symmetric analogs of acetogenins, using at the key stage Ti-catalyzed homo-cyclomagnesiation of alkyl- and aryl-substituted 1,2-dienes **1** (Dzhemilev reaction [3]). The symmetrical 1Z,5Z-dienes **3** obtained after hydrolysis were subjected to direct oxidative cyclization producing substituted tetrahydrofurans **4**. Subsequent stereoselective reduction of the carbonyl group with L-Selectride leads to the target symmetric analogs of acetogenins **5**.



Scheme 1. Synthesis of acetogenin analogs

Acknowledgement. The study was supported by grants from the Russian Science Foundation (project No. 18-73-10030, No. 20-64-47019) and the Russian Foundation for Basic Research (project No. 19-03-00603, No. 18-29-09068)

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VP-V-5

Stereoselective One-Pot Synthesis of Functionally Substituted Alkene Oligomers, Catalysed by Chiral Zirconocenes

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Being valuable precursors in the production of adhesives, lubricants, and other high-performance synthetic compounds, alkene oligomers can be obtained using homogeneous zirconocene catalytic systems. Further advances in such systems require precise control of their chemo- and stereoselectivity [1-4]. The idea on chemo- and stereoselective one-pot synthesis of functionally substituted alkene oligomers in the presence of chiral zirconocenes, organoaluminum compounds (OAC) and boron activator $[CPh_3][B(C_6F_5)_4)]$ is realized in the work (Fig.1).

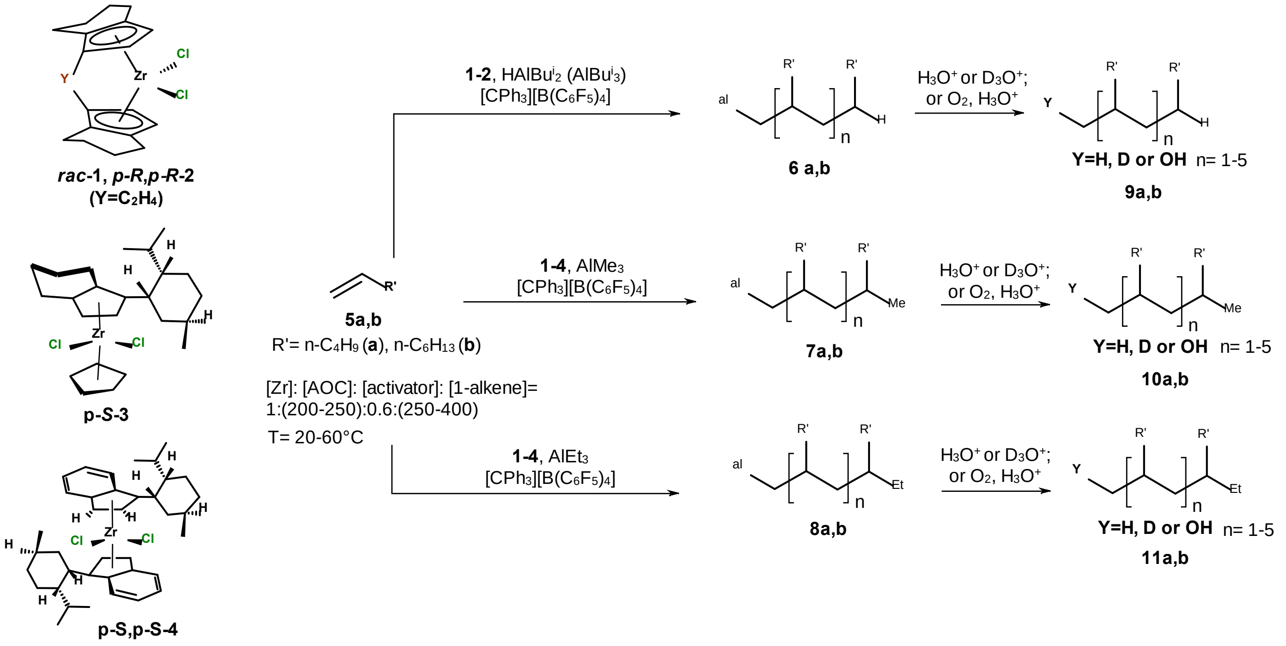
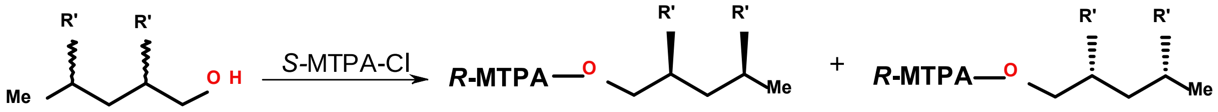


*Fig. 1. The oligomerization of terminal alkenes in the presence of complexes **1-4**, OAC, and $[CPh_3][B(C_6F_5)_4)]$.*

The highest activity, chemo- and stereoselectivity towards the formation of oligomers with a starting *n*-alkyl group, Me- or Et- substituted oligomers **6**-**8a,b** (yield 65-70%, >99%*de,* >95%*ee*) are achieved in the systems based on conformationally rigid *ansa*- complexes Zr **1** or **2**, $HAlBu^i_2$ or AlR_3 (R= Me, Et, Bu^i) and $[CPh_3][B(C_6F_5)_4$ at the ratio $[Zr]:[AlR_3]:[B]:[1\text{-alkene}]=1:(200\text{-}250):0.6:250$. The reaction of alkenes with AlR_3 (R= Me, Et) catalyzed by the C_1-symmetric complex ***p-S-3*** proceeded with the formation of Me- or Et-substituted oligomers **7,8a,b** with a yield of 50-71% and lower diastereoselectivity of 50-60%*de*. The C_2-symmetric conformationally labile complex ***p-S,p-S-4*** significantly reduces the diastereoselectivity of the reaction to 4%*de*; wherein the reaction products - Me- or Et-substituted dimers were obtained with the yield of 50-60%.

The enantioselectivity of the reactions was determined using NMR spectroscopy of MTPA derivatives of alcohols **9-11a,b** (Fig.2).



10a **12a**

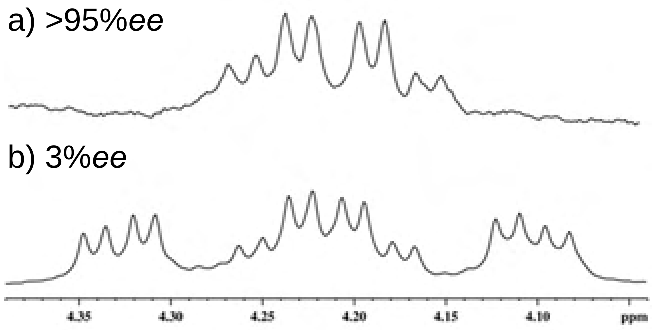


Fig. 2. ^{1}H NMR (400 MHz) signals (O-CH$_2$ group) of diastereomers **12a**: a)- alcohol **10a** was obtained in the reaction catalyzed by **p-R, p-R-2**; b)- alcohol **10a** was obtained in the reaction catalyzed by **rac-1**.

Thus, complexes with a rigid geometry *rac-*, *p-R*, *p-R-* [$C_2H_4(\eta^5-C_9H_{10})_2$]$ZrCl_2$ (**1**, **2**) in combination with a boron activator [Ph_3C][$B(C_6F_5)_4$] exhibit a higher selectivity towards the oligomers and provide high diastereomeric and enantiomeric purity of the products compared to catalysts ***p-S*-3** and ***p-S*-4**. The developed catalytic systems could be used in the one-pot synthesis of enantiomerically pure functionalized alkene oligomers as structural blocks of biologically active compounds.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 19-73-10122.

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VP-V-6

Solvent-Free Palladium-Catalyzed C-O Cross-Coupling of Aryl Bromides with Phenols

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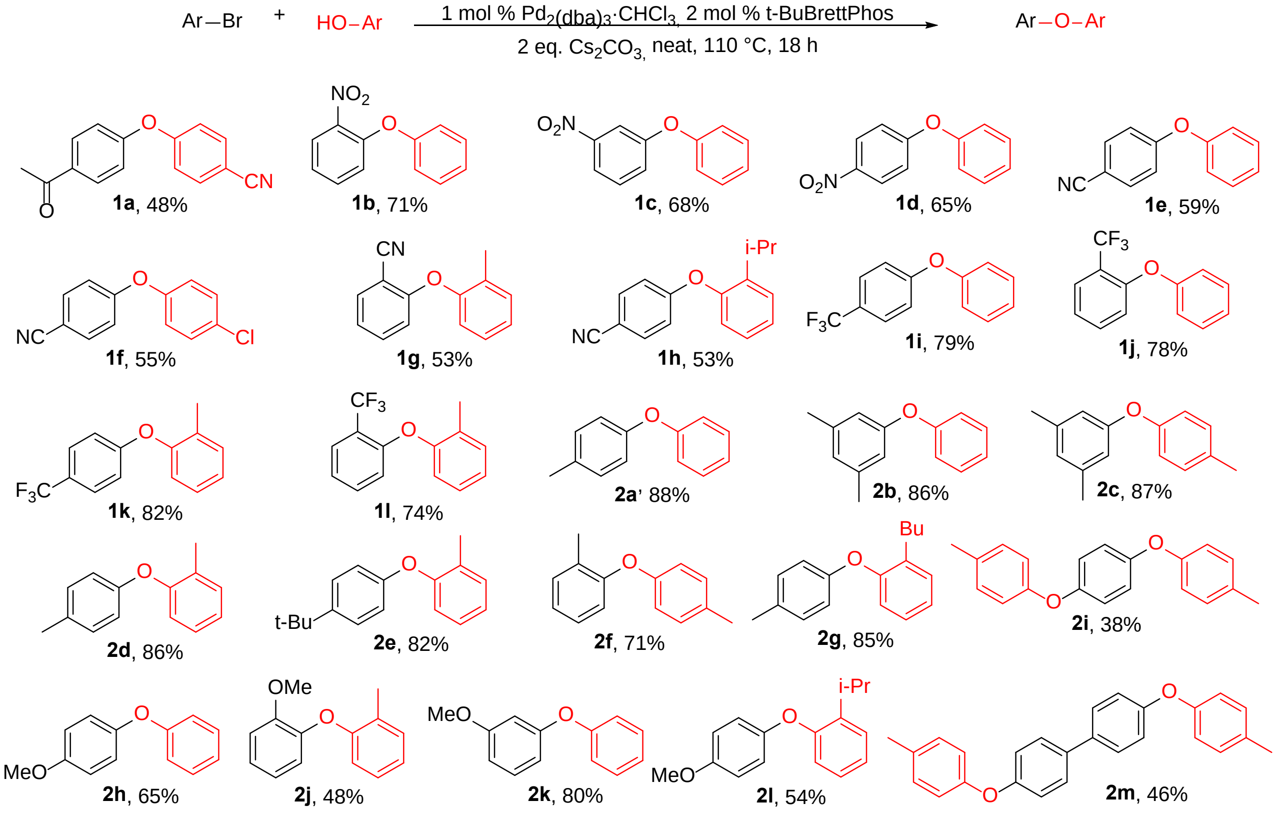
Palladium and copper-catalyzed cross-coupling methodologies has become an efficient tool for formation of C-O bond in these molecules both in academic and industrial laboratories. [1-7] There are many examples of successful application of solvent-free approaches to cross-coupling. [8-13] However there are no mentions of C-O cross-coupling reaction yet.

Herein we report on the development of a catalytic system for C-O cross coupling of (hetero)aryl bromides with phenols based on Pd/phosphine ligands system under solvent-free conditions. A series of bulky phosphine ligands were compared: tBuBrettPhos, tBuXPhos, RuPhos, $(tBu)_3P\text{-}HBF_4$. The highest yield was obtained in case of tBuBrettPhos. Base, ligand loading, and reaction temperature were varied to find optimal conditions. Eventually, we reached the highest yield of 88% using 2 eq. of Cs_2CO_3 as a base and 1:2 $Pd_2(dba)_3$ to ligand ratio at 110 °C. Notably, the obtained yields were lower for *p*-TolCl or *p*-TolI as coupling partners. We investigated the activity of solvent-free catalytic system on a variety of substrates (Scheme 1).



Scheme 1. Pd-catalyzed C–O cross-coupling of aryl bromides with phenols.

Substrates, bearing various electron-withdrawing groups at *o*-, *m*-, and *p*-positions were systematically tested: -NO_2 (**1b-d**), -CN (**1e-h**), -CF_3 (**1i-l**). Coupling of donor-substituted aryl bromides is usually a challenge. However, we were able to obtain diaryl ethers with yields over 80% for a series of substrates (Scheme 2, **2a-e**, **g**, **k**). We have also obtained good yields in cases of sterically hindered *ortho*-substituted substrates (**2f**, **j**, **l**) and in cross-coupling of dibromides (**2i**, **m**).

Acknowledgement. This work was supported by the Russian Science Foundation, grant № 17–13–01076.

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VP-V-7

Enantioselective Hydrogenation of N-Acetyl-α-Amidocinnamic Acid over Palladium Nanoparticles

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N-acetyl-α-amidocinnamic acid (α-AACA) was hydrogenated over Pd (acac)$_2$-mod-H$_2$ catalytic systems, where palladium nanoparticles are formed [1]. In the course of the reaction, the initial substrate is hydrogenated sequentially with the formation of a chiral product, N-acetylphenyl-L-alanine (N-APA), and its subsequent esterification to methyl ester of N-acetylphenyl-L-alanine (ME N-APA) (Fig. 1).

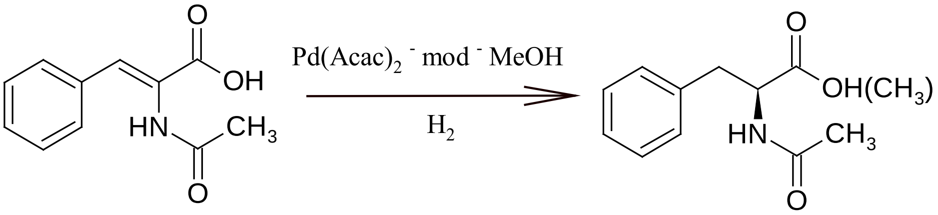

Fig. 1. Scheme for hydrogenation of α-AACA over Pd (acac)2–Mod-H$_2$ catalytic system with the formation of N-APhA (ME N-APhA).

Transition metal nanoparticles are widely used as catalysts for asymmetric hydrogenation [2]. They are highly active and increase the stability of nanoparticles, they use stabilizers, which are usually organic neutral molecules and macromolecular systems, or compounds of the ionic type. As a rule, Neutral stabilizers of metal nanoparticles are coordinated to surface metal atoms and provide steric stabilization [3]. Electronic stabilization can be achieved by using compounds of the ionic type, for example, quaternary ammonium or phosphonium salts.

In this study we used (8S, 9R) - (-) - cinchonidine (**1**) and its monoprotonated (**2**), biprotonated (**3**) derivatives, as well as (+) - 2-amino-1- (4 -nitrophenyl) -1,3-propanediol (**4**) as a modifying agents (mod). The research results are shown in the table.

Table. Effect of the nature of the modifier on the hydrogenation of α-AACA overcatalytic systems Pd(acac)$_2$-Mod-H$_2$ (C_{Pd} = 5 mmol/L; mod/Pd=1, Sub/Pd=50; T=25°C; P_{H2}=5 Bar, Solvent - toluene: methanol mixture =3:17).

№	Mod	Conversion, %		ee (R)-(-), %	W, mmol/L*h		TOF, mol/g-at Pd*h	
		α-AACA	N-APhA		α-AACA	N-APhA	α-AACA	N-APhA
1	**1**	57	8	35	25	5	5	1
2	**2**	100	9	3	31	8	6	2
3	**3**	100	34	10	48	6	10	1
4	**4**	68	33	9	33	1	7	0,2
5	-	100	1	0	56	-	11	-

In all cases, except for the experiment without the modifier (entry 5), the reaction proceeds with the formation of the methyl ester of N-APhA, and the esterification started even before the complete conversion of α-AACA. In the presence of protonated cinchonidine derivatives as stabilizers the activity of the system increased (entries 2-3), which may be associated with changing in the type of stabilization (electrostatic + steric) when going from neutral (-) - cinchonidine to its protonated forms. The largest excess of the (R) - (-) enantiomer was obtained in the presence of (-) - cinchonidine. The catalytic system with dextrorotatory (+) - 2-amino-1- (4-nitrophenyl) -1,3-propanediol also led to the formation of an excess of (R) - (-) - enantiomers of the products (ee 9.2%).

The figure 2 shows typical kinetic curves of α-AACA conversion and N-APhA formation in the first 6 hours. There is no esterification product. Its traces under similar reaction conditions are usually observed not earlier than 20 hours from the beginning of hydrogenation.

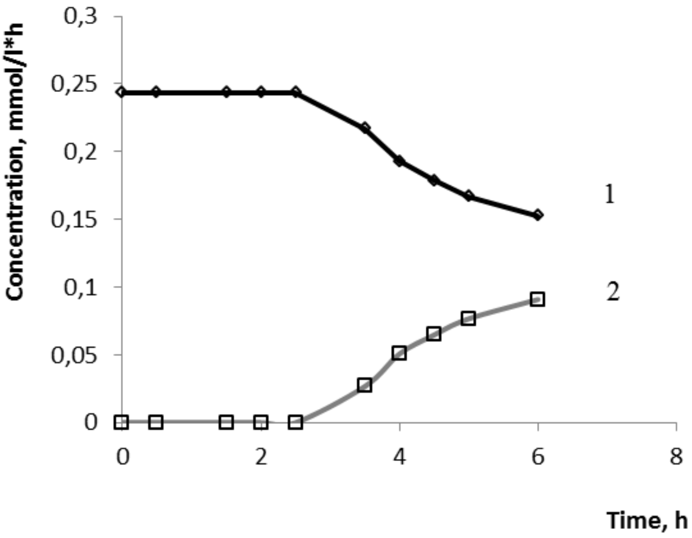

Figure: 2. Hydrogenation of α-AACA (1) over the catalytic system $Pd(acac)_2$-**3**-H_2 with the formation of N-APhA (2) (T=25°C; P_{H2} = 5 Bar, Solvent - toluene: methanol mixture =3:17)

Acknowledgement. This work was supported by the Irkutsk National Research Technical University [grant number 04-FPK-19

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VP-V-8

Solvent-Free NHC-Pd Catalyzed Head–to–Head Telomerization of Isoprene with Methanol

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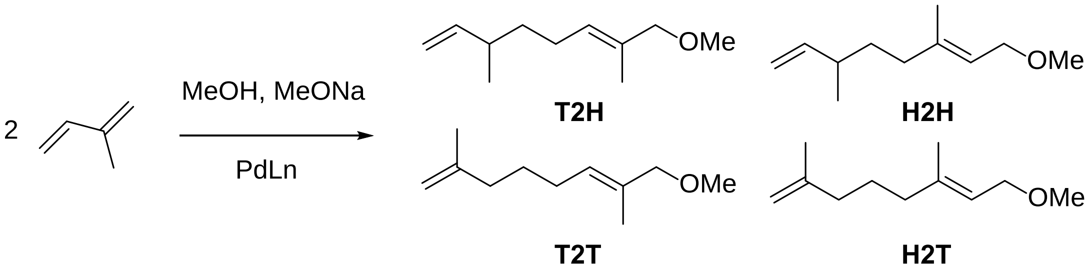
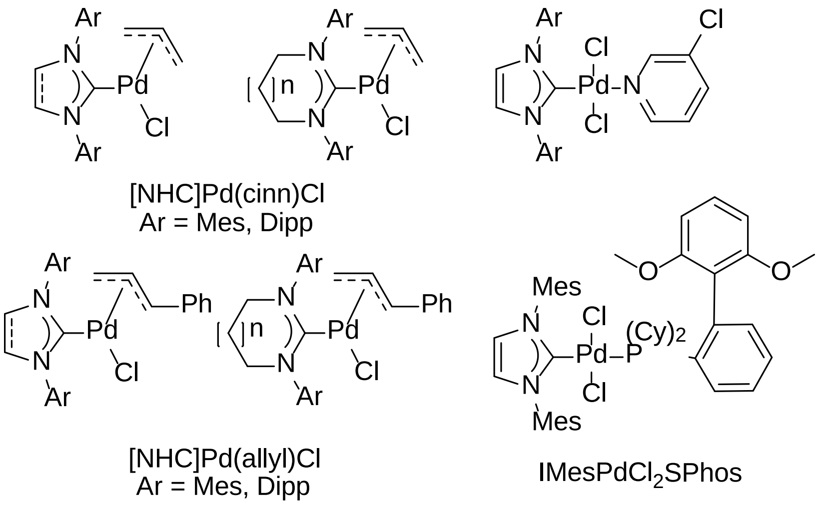
Palladium-promoted dimerization of dienes with a nucleophile, known as telomerisation, is a well-studied reaction with a significant synthetic potential in terpenoid synthesis.[1] In unsymmetrical dienes e.g. isoprene the ratio of the various products depends on solvent, temperature, and mostly on the catalyst system employed (Scheme 1). The classical systems for the telomerization of isoprene with alcohols consist in a combination of a palladium complex and a phosphine ligand.[2] Recently, it was demonstrated that isolated palladium(0) complexes containing N-heterocyclic carbenes provide reaction to obtain head-to-head (**H2H**) products, which were considered mostly as side-products before.[3-5]



Scheme 1. Products of Isoprene telomerization with methanol.

Herein we investigated a role of ring sizes and substituents in NHC ligands in some [NHC]Pd (0) complexes as well as influence of leaving group nature (Scheme 2) in isoprene telomerisation with methanol in presence of catalytic amount of base under solvent-free conditions.



Scheme 2. Structures of NHC-Pd complexes.

We analyzed the ratio of isomers and total conversion of isoprene and found **IMesPd(allyl)Cl** to be the most efficient complex.

Acknowledgement. This work was supported by the Russian Science Foundation, grant № 19-73-10185.

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VP-V-9

Ionic Liquids and Their Possible Applications in Desulphurization Processes

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This paper presents a study of catalytic systems based on ionic liquids to obtain more efficient catalysts for desulfurization processes in order to reduce the cost of using expensive catalysts. From a number of desulphurization processes, one was identified in which it is possible to use ionic liquids as a catalyst for clean- ing the diesel fraction. The advantages of ionic liquids over other catalysts are shown, namely, low melt- ing point and vapor pressure, but high thermal stability, density, viscosity, etc. X-ray fluorescence spectrometry was used to compare analytical cal- culations of the determination of sulfur in the oil product under study with their actual concentrations.

Preparation of ionic liquid. After analysis of literature sources, the ratio of quantity organic salt to metal halide was taken at a ratio of 1:2. The preparation of the ionic liquid triethylamine aluminum chloride hydrochloride was carried out in Engler flask without moisture access. Triethylamine hydrochloride and aluminum chloride were placed in a magnetic stirrer flask. It was stirred until the reaction was complete and the system was completely homogenized f. Activating agents were added to the resulting ionic liquid. The mixture was stirred.

During the experiment, ethyl mercaptan was charged into the reactor in the desired concentration of DT. The catalyst was then added to the reactor. When the desired temperature was reached, air was supplied to the reactor. This moment was taken as the beginning of the reaction. During the reaction, air was stopped every 15 minutes. 2 parallel samples were taken by the sampler in which the mercaptan sulfur content was determined by potentiometric titration. After completion of the test, the air supply and heating were switched off sequentially, and then the reaction mass containing no disulfides formed was discharged from the reactor.

Potentiometric titration method. This technique needed to be finalized in connection with the modern state of laboratory technology and the quality of chemical reagents. The calomel electrode was replaced with saturated silver chloride. Organic solvents - acetic acid, methanol, ethanol, benzene - were further purified and dehydrated. As part of the potentiometric titration plant, the instrumentation specified in Figure 2 was used:

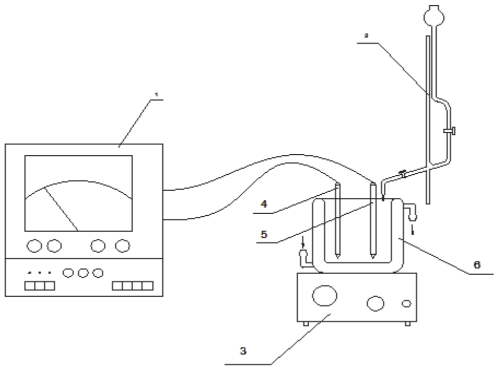

Fig. 2 Potentiometric Titration Unit
1 – potentiometer; 2 – microburette; 3 - magnetic stirrer; 4 - reference electrode;
5 - measuring electrode; 6 - thermostatic electrochemical cell.

VP-V-9

X-ray fluorescence method for determination of sulphur. Samples with known sulfur content were taken to construct the calibration curve. A calibration curve was drawn from these samples. The sulfur concentration in the sample was calculated automatically from the calibration curve (Fig. 3).

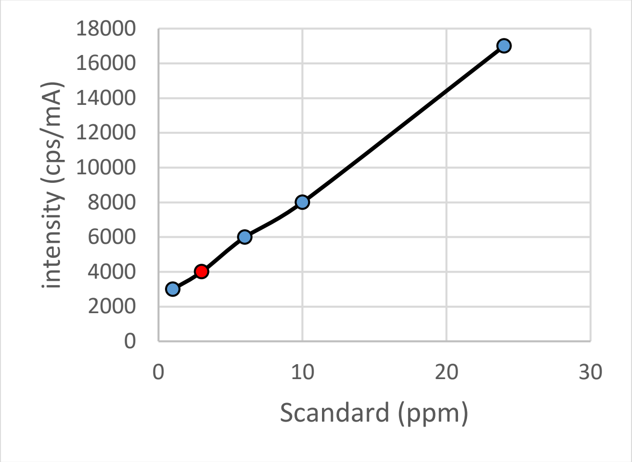

Fig.3 Diesel fuel calibration curve

According to the data obtained, the sulfur content in diesel fuel was determined - 0.1682%.

According to the readings of the universal X-ray fluorescence spectrometer: The initial sulfur content in the diesel fraction was: 0.3%. After the experiment, the sulfur content in the DT became: 0.1682%,

Including 0.00004% ethyl mercaptan and 0.0001% diethyl sulfide.

Therefore, ionic liquids are effective in sero cleaning!

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VP-VI-1

Influence of Modified Graphene Supports on the Oxygen Reduction Reaction in PEMFC

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Due to population growth, the consumption of electrical energy obtained mainly from traditional fossil fuels is also growing. However, this method of electricity generating is accompanied by various emissions, which include greenhouse gases and nitrogen oxides.

Fuel cells are one of the greenest power source. In particular, during the production of electricity using fuel cells with solid polymer electrolyte (PEMFC), only water is released as a by-product in the future.

Carriers in PEMFC electrodes are carbon materials on which catalytically active nanoparticles are applied. This approach allows to increase the catalysts's electrochemically active surface area and activity. Carbon blacks are most often support materials, but they have significant drawbacks, such as the presence of impurities, a high proportion of micropores, and insufficient electrochemical stability. Several alternatives as carbon nanotubes, nanofibers, mesoporous carbons and graphene-based materials have been proposed.

Key advantages of the graphene-based materials are its high specific surface, chemical stability, graphitic structure (providing high electrochemical durability), superior electronic conductivity and strong metal-support interaction which stabilize Pt nanoparticles from growth and detachment [1]. Their modification with heteroatoms, for example, nitrogen, can contribute to a more uniform distribution of platinum nanoparticles on the surface, to increasedactivity in the oxygen reduction reaction and to the increased catalyst stability due to metal-support interactions [2]. These advantages allow to increase the lifespan of PEMFC membrane-electrode assemblies and to reduce the Pt loadings on the cathode, but simple and easy-scaled approaches to produce heteroatom doped carbon nanomaterials are still necessary.

In this study, catalysts based on Pt and carbon nanomaterials doped with nitrogen are used to prepare a PEMFC electrode. Nitrogen embedding was carried out by carbon supports processing in a gas discharge plasma in a vacuum chamber of a magnetron-ion sputtering installation [3]. The achieved increased activity and stability of the obtained supported electrocatalysts are due to the high dispersion of Pt nanoparticles on the support surface, as well as their metal-support interaction revealed by X-ray Photoelectron Spectroscopy.

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VP-VI-2

Supercritical Water Oxidation of Industrial Waste of Propylene Oxide Production Using Heterogeneous Catalysts

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The existing methods of cleaning organic waste and industrial wastewater do not completely clean the environment. There are also difficulties associated with the separation of catalysts used in technologies from the reaction products, which leads to losses of often expensive catalysts and a large amount of toxic waste water when washing the reaction products from the catalyst. For example, one of the largest oil refining complexes, Public joint-stock company Nizhnekamskneftekhim annually loses raw materials worth 2.3 billion Russian rubles with water flows. The expensive molybdenum complex used at the enterprise, which accelerates the propylene epoxidation reaction in a large-tonnage industrial process, after washing the reaction product, is concentrated in the wash water, which undergoes only thermal treatment, as a result of which high-value molybdenum salts are lost, being distributed in the flue gases and the corresponding melt. The separation of expensive catalysts from industrial wastewater is also an equally urgent task. One of the solutions to overcome all these difficulties can be the carrying out of the oxidation reaction in a supercritical aqueous medium, where hydrogen peroxide, air or oxygen can act as an oxidizing agent. Waste oxidation in supercritical water has a significant advantage over the widespread thermal neutralization due to the reduction of the amount of emissions into the atmosphere, improvement of the quality of neutralization, and the possibility of recycling the neutralized water. With the appropriate composition of the waste, it is possible to use the heat of the exothermic reaction for internal production needs [1].

As part of the work on the development of the waste disposal process in supercritical fluid conditions of the reaction mixture, at the Department of Theoretical Foundations of Heat Engineering, Kazan National Research Technological University, an original experimental flow-through installation was created and is being operated, which is based on a catalytic unit with the possibility of placing heterogeneous catalysts in a fixed bed. [2]. Experiments were carried out on this installation to study the process of utilization of industrial aqueous waste from the production of propylene oxide. Air oxygen was used as an oxidizer, and iron hydroxides, iron acetates, and manganese oxides on a substrate made of a mixture of bentonite and kaolin clays were used as heterogeneous catalysts. During the experiments, the temperature range was T = 673-873 K at a pressure of P = 25 MPa. The chemical oxygen demand (COD) values were a qualitative indicator of the process efficiency. In fig. 1 shows the results of experiments in the form of the dependence of the COD value on temperature.

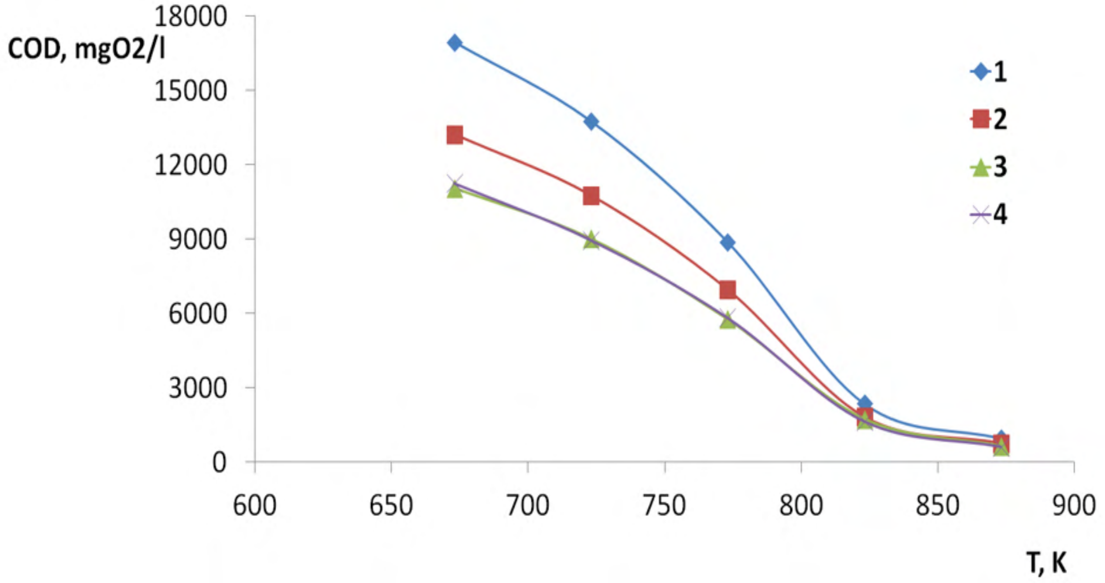

Fig. 1. Dependence of COD on the process temperature: 1 - without catalysts, 2 - using iron acetate, 3 - using iron hydroxide, 4 - using manganese oxides

It can be seen from the figure that the use of catalysts leads to a more intense oxidizability of the feedstock compared to the non-catalytic version of the process. An increase in the temperature parameters shows that in the range of the temperature range 825-875 K, the use of catalysts is not so effective than in the range up to 825 K. Among the presented catalysts, the greatest effect is observed when using manganese oxides and iron hydroxides.

The studies carried out by the authors show the possibility of implementing the process of supercritical water oxidation using heterogeneous catalysts for utilizing industrial effluents of propylene epoxidation, as well as obtaining water suitable for reuse in production.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, agreement No. 18-29-06041.

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VP-VI-3

Investigation of the Adsorption and Photocatalytic Properties of Mesoporous Titanium Dioxide Doped with Dysprosium

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Nowadays, the photocatalytic properties of titanium dioxide are promising for study, in particular the ability to purify air and water from toxic waste by their photocatalytic oxidation on the TiO_2 surface to water and CO_2. However, TiO_2 exhibits its photocatalytic properties only under UV radiation. Therefore, the development of photocatalysts capable of absorbing light in the visible region of the spectrum is of great interest. Doping titanium dioxide with dysprosium helps to solve this problem.

Samples of mesoporous titanium dioxide were obtained by the template method. To obtain samples doped with dysprosium (Dy/TiO_2), CTAB was dissolved in ethanol, the resulting solution was stirred for 30 minutes. Then to the solution with stirring acetic acid, titanium dioxide and aqueous solutions of dysprosium chloride of various concentrations were added and the reaction mixtures were stirred for 3 hours. The mixture was kept in air for ten days, after which the sample was subjected to temperature treatment at 500°C in a muffle furnace for two hours. Samples of titanium dioxide doped with different amounts of dysprosium were obtained. The presence of dysprosium atoms in the structure of mesoporous titanium dioxide was shown using X-ray fluorescence analysis (XRF).

The textural characteristics of the obtained materials were determined by the method of low-temperature nitrogen adsorption-desorption. In fig. 1 isotherms of nitrogen adsorption and desorption on mesoporous Dy/TiO_2 samples with different dysprosium contents are showed.

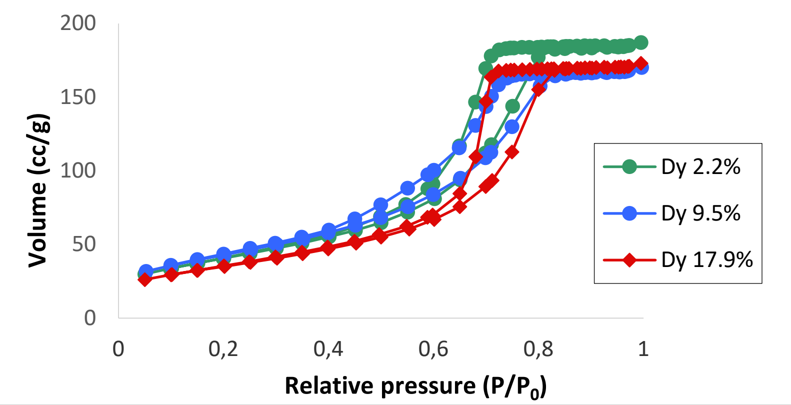

Fig. 1. Nitrogen adsorption and desorption isotherms for Dy/TiO_2 samples with different dysprosium concentrations.

The sample with a mass fraction of dysprosium of 9.5% has the largest specific surface area, its surface area is 156.3 m^2/g. According to calculations by the BJH and DFT methods, the effective pore diameters for all obtained Dy/TiO_2 are approximately 6.8 nm and 5.3 nm, respectively.

Photocatalytic activity was assessed by studying the decomposition of m-xylene and benzene in aqueous solutions. The experiments were carried out in a glass reactor with constant stirring under the influence of an LED lamp with a wavelength range of 400-700 nm. Substance concentrations were determined by gas chromatography. The concentrations were measured at regular intervals. To study the adsorption properties of Dy/TiO_2, aqueous solutions of m-xylene or benzene were placed in a glass beaker and stirred on a magnetic stirrer without access to light.

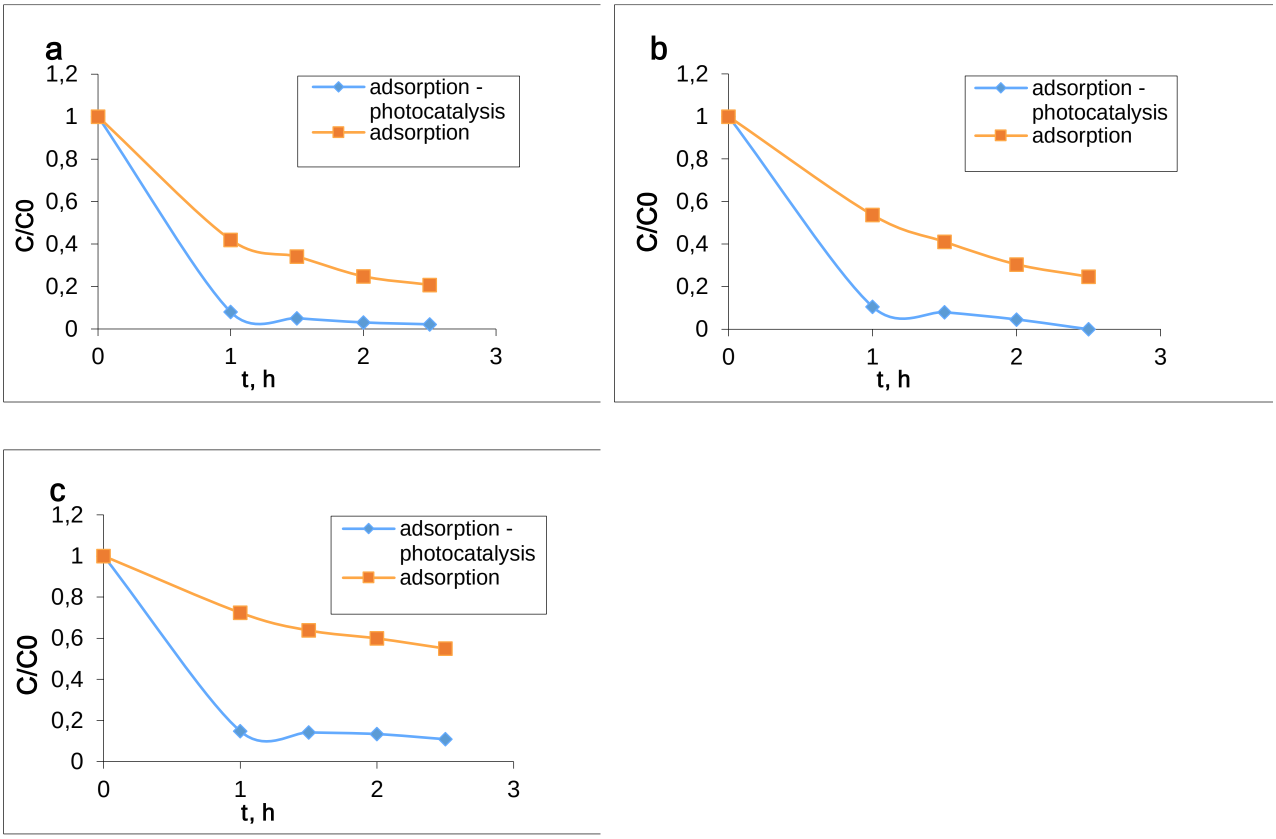

Fig. 2. Diagrams of photocatalysis and adsorption of m-xylene on Dy/TiO_2 (dysprosium concentration in the samples: a) 2.2%, b) 9.5%, c) 17.9%).

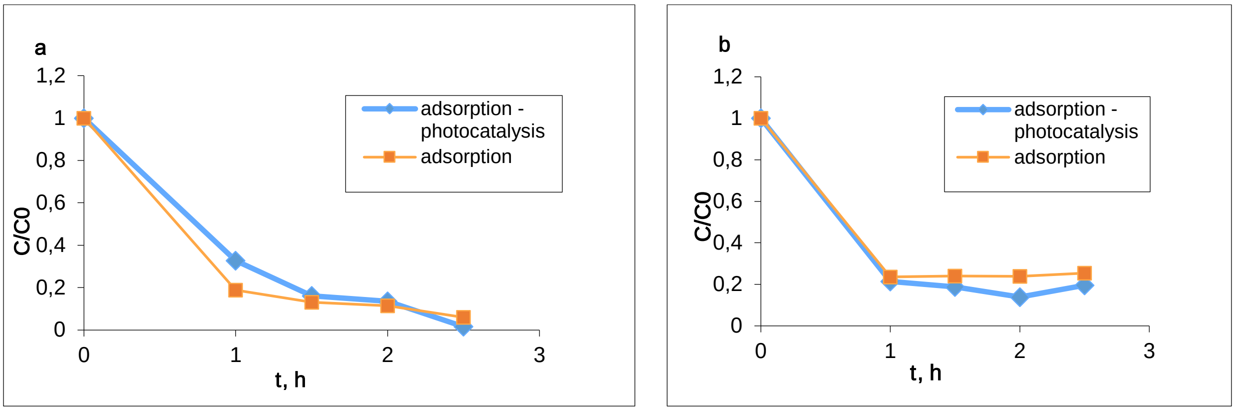

Fig. 3. Diagrams of photocatalysis and adsorption of benzene on Dy/TiO_2 (a) 2.2% Dy; b) 17.9% Dy).

After 2.5 hours, on samples with 2.2% and 9.5% of dysprosium, the conversion of m-xylene reaches almost 100%. For benzene, the most effective sample is Dy/TiO_2 with a 2.2% dysprosium content: after 2.5 hours, its 100% conversion is observed.

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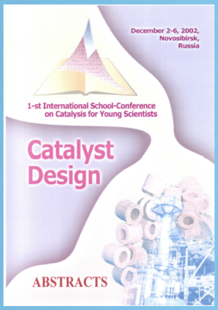

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