

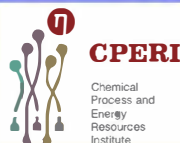
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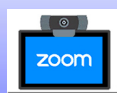


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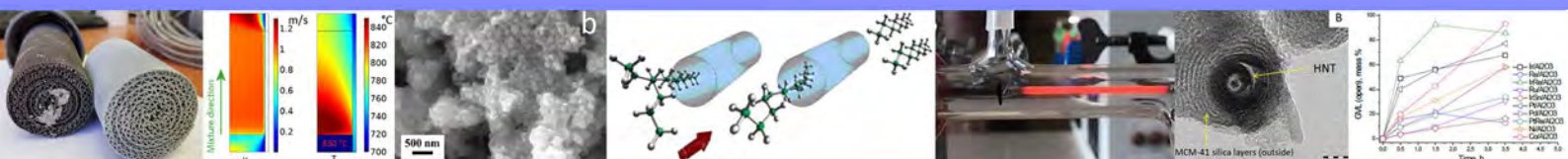
IV Scientific-Technological Symposium CATALYTIC HYDROPROCESSING IN OIL REFINING

April 26 – 30, 2021 Novosibirsk, Russia



ABSTRACTS

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IV Scientific-Technological Symposium

CATALYTIC HYDROPROCESSING IN OIL REFINING

April 26 - 30

**2021
RUSSIA**

**Novosibirsk
online**

ABSTRACTS

Boreskov Institute of Catalysis
Chemical Process & Energy Resources Institute (CPERI)
PJSC Gazprom Neft



IV Scientific-Technological Symposium

CATALYTIC HYDROPROCESSING IN OIL REFINING

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Novosibirsk, Russia
online

ABSTRACTS

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С 31

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Сборник включает тезисы пленарных, ключевых лекций, устных и стендовых докладов.

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The collection includes abstracts of plenary and keynote lectures, oral and poster presentations.

The main topics of the Symposium scientific program are:

- Fundamentals of hydroprocessing catalysis, new materials and approaches
- Perspective catalysts, adsorbents and hydroprocessing technologies for various applications (manufacturing of hydrocarbon fuels, hydrocracking, hydroprocessing of heavy oil, light hydrocarbon feedstock, alternative and renewable raw materials, preprocessing of hydrocarbon feedstocks)
- Mathematical modelling and simulation of oil refining and petrochemical catalytic processes
- Advanced methods for analysis of hydroprocessing feedstock and products
- Experience of industrial production and use of catalytic cracking, reforming, hydrotreatment and hydrocracking catalysts
- Economic aspects of the catalysts use in oil refining

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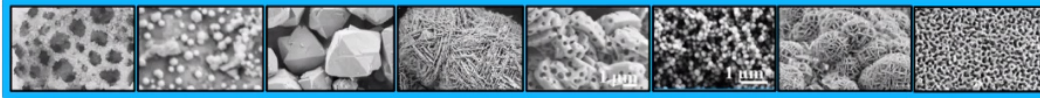
PLENARY LECTURES



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HIERARCHICAL ZEOLITES IN PROCESSING OF HYDROCARBONS

Concepts, Preparation Strategies and Application

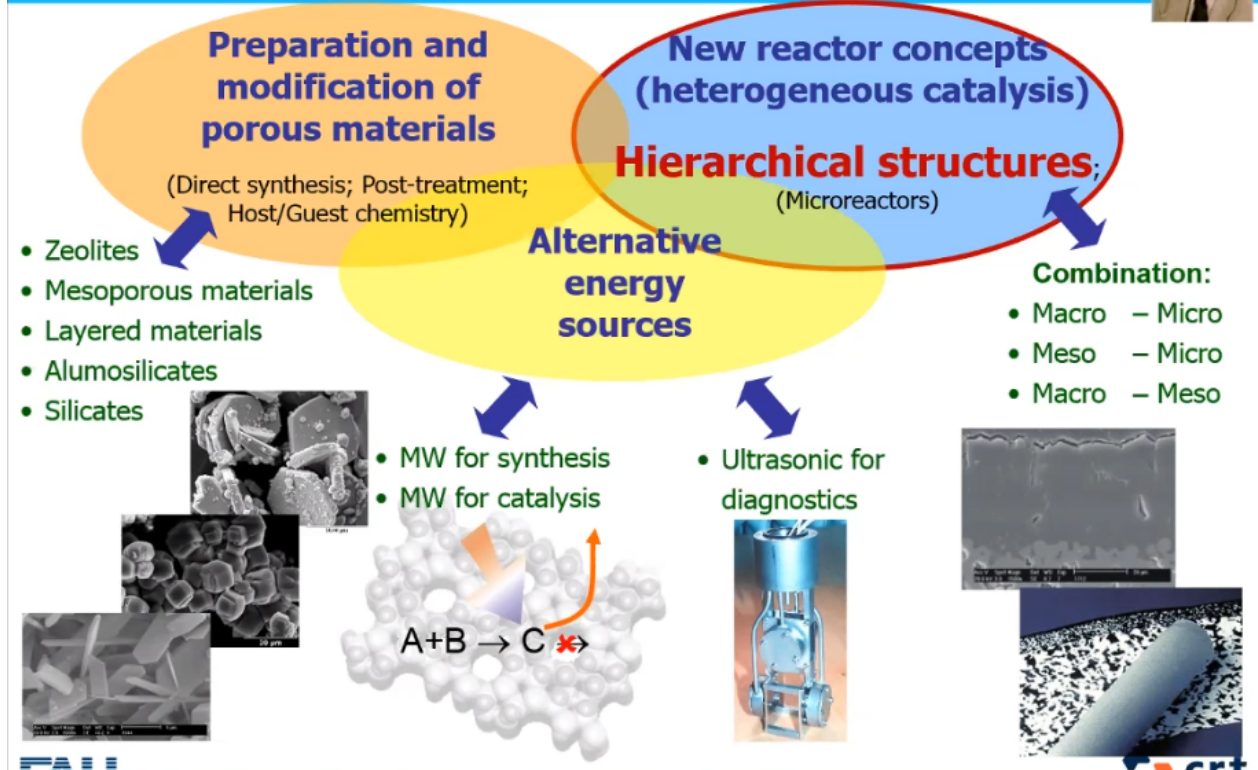
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IV Scientific-Technological Symposium CATALYTIC
HYDROPROCESSING IN OIL REFINING
26. – 30. April 2021



Research topics in my group



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The fossil fuel hydroconversion technology has been fundamentally excavated from a molecular level to an industrial scale. In recent years, heavy oil upgrading has gained considerable importance in the petroleum refining industry, mainly due to the decline in the availability of light crudes [1]. The heavy oils contain a large fraction of bottom of the barrel (residue) after distillation. In Kuwait, the oil industry has a strategy to expand production of heavy oil, *i.e.*, Lower Fars (LF), which has low API and high viscosity. At the same time, refineries are under a great deal of pressure to meet the market demand for high-quality fuels (*i.e.*, gasoline and diesel). Residue fraction has a very hefty matrix that contains high concentration of asphaltene and hetero-atoms (S, N, O, metals, etc.).

The complex structure of asphaltenes causes many problems during the upgrading of heavy oils, particularly during the hydroprocessing [2-3]. Thus, asphaltene composition is an optimal starting point to define or estimate feedstock properties and its processing options. During the residue hydrotreating, asphaltenes also carbonize the catalysts in two ways. In the first place, they are heat labile at the process temperature, and secondly, their large molecules adsorbed onto the catalytic sites. The conversion of asphaltenes in residue hydroprocessing is important as the asphaltenic fraction often contains the most refractive components. Not only that, during the processing of such feedstock, both the non-asphaltenic phase and the asphaltenes undergo chemical compatibility, which may lead to unstable products (sediment formation) as well as to increased coke lay-down on the catalyst. Thus, understanding the problem of asphaltene instability and its transformation during the hydroprocessing is not only important for high conversion but also vital to understand catalyst stability and sludge formation in the reactor. Globally, 5% residue is processed using hydroprocessing units; in which 82% units are operated in a fixed bed, 16% ebullated, and less than 2% as a slurry phase. The number of reactor concepts and catalyst formulation has been designed to achieve an active and stable catalyst with sustainable products, which has a high H/C (> 2) ratio. Therefore, catalysts were evaluated for their activities, stability and deactivation behaviours using LF-AR (350 °C+) and/or Ku heavy crude oils, which contains a high amount of metals (150-600 ppm) and asphaltene (7-15 wt%). The core competency of the study is to synthesize a fixed bed catalyst that has bimodal type pore size

PL-2

distribution, *i.e.*, both meso- and macro-porosity. An increase in the pore diameter is expected to lead effective penetration of supramolecular structures (asphaltene or CCR) of petroleum residue to catalytically active sites and sustain its hydroconversion (HDM, HDS, and HDAs) longer with TOS. This review discusses the impact of residue feed composition, process operating conditions, catalyst formulations, and catalyst properties on structural transformation and problems caused during hydroprocessing.

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INTENSIFICATION OF STEAM REFORMING FOR HYDROGEN PRODUCTION**Lemonidou A.A.**

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Hydrogen is one of the most important energy carriers of the future and an important raw material with wide use in the chemical and refining sector. The current industrial major technology for large scale production of hydrogen is steam reforming of natural gas, which although a mature process, remains very energy intensive. The thermodynamically limited reaction is industrially operated at temperatures higher than 800 °C in the presence of supported nickel-based catalysts. High operating temperatures negatively affect the economic and environmental performance of the process, due to requirements for expensive materials, high energy consumption and CO₂ emissions resulting from demands of strongly endothermic reforming reaction. It becomes therefore a necessity to introduce new environmentally friendly, low-energy consumption technologies with high hydrogen efficiency. In this context, research efforts have focused on new concepts for hydrogen production that operate at milder conditions and have lower carbon footprint. Sorption-enhanced steam methane reforming (SE-SMR) is an advanced environmentally friendly process for pure H₂ production in a single step by combining reaction and separation together by means of a solid CO₂ sorbent [1]. In an effort to further intensify the process and reduce the energy demands for the sorbent regeneration, the combination of SE-SMR with chemical looping has been proposed. In this novel concept, the reformer contains, in addition to the sorbent, an oxygen carrier which during reforming is reduced by CH₄ into metallic Ni, serving as the reforming catalyst [2]. In this work, we report on the efforts to develop the materials and to demonstrate experimentally the feasibility of the sorption enhanced chemical looping methane reforming (SE-CL-SMR) over NiO-based oxygen carriers combined with CaO-based sorbents along with the investigations on the influence of various operating variables.

The oxygen carrier-reforming catalyst NiO/ZrO₂ and the CaO/ZrO₂ CO₂ sorbent developed were proved very promising materials in terms of activity and stability under cyclic operations. The experiments over mechanical mixing of the two materials demonstrated the feasibility and high potential of the proposed process in a range of operating conditions [3,4]. At reforming temperature of 650°C, CH₄ is almost completely converted to a gas stream with a very high H₂ concentration (~95%). CO₂ capture is over 90%. More importantly, the highly exothermic Ni oxidation during regeneration releases enough heat to increase the temperature of the reactor

PL-3

and to supply substantial part of the heat required for the endothermic regeneration of the sorbent. Further testing using non isothermal reactor with temperature profile along the reactor axis demonstrated that it is possible to further increase the purity of hydrogen to over 99%, thus allowing its direct use in many industrial processes without any further treatment [5]. A preliminary conceptual design using two interconnected fluid bed reactors serving as reformer and regenerator and operating under different fluidization regimes revealed the feasibility and the potential for scale up of sorption enhanced chemical looping methane reforming process for hydrogen production [6].

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CONTENT

KEYNOTE LECTURES

CATALYTIC HYDROPROCESSING: AN EFFECTIVE MODE FOR DIRECT FUELS DECARBONIZATION



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The decarbonization of transportation fuels is a key strategic policy towards energy security and sustainable growth. However, the 2020 EU target on replacing 10% of all transport fossil fuels with biofuels has been characterized as an over-ambitious goal, due to the technical constraints and unfavourable properties of biogenic feedstocks. Catalytic hydroprocessing of raw and residual lipids is foreseen as a key biofuels technology that renders high-quality and fully compatible with their fossil counterpart fuels, which are being commercially employed as transportation fuels' renewable alternatives. However, as an established refining technology, catalytic hydroprocessing can also be employed for the direct decarbonization of transportation fuels by enabling co-processing refinery fractions with bio-based feeds and intermediates.

This presentation will focus on key R&D perspectives, challenges and potential for integrating residual lipids and lignocellulosic bio-based intermediates in conventional catalytic hydroprocessing units. The presentation will provide practical and useful information for the refiners, in order to enable a fast integration of biomass within existing conventional refineries for the production of high bio-content fuels.



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Chemical transformations often involve more than a single reaction, either as undesired side or consecutive reaction which is chemically similar to the desired reaction or not, or as an extensive reaction network of elementary steps in mixtures of components. The number of reaction steps to be accounted for and, correspondingly, the number of kinetic parameters required for the modeling of such chemical transformations, potentially increases quickly and enhances the model's complexity.

Various techniques have been developed for simulating the conversion of mixtures of components, the most straightforward one being lumping [1]. While decent simulation results can be achieved with such lumped models, intrinsic disadvantages are that the number of model parameters inherently increases with the number of lumps and typically also are feedstock dependent. A particular type of lumping, i.e., so-called continuous lumping, has been developed for complex mixtures, considering that they comprise a wealth of components with chemical properties that are very close to each other, such that the reaction behavior can be expressed as a continuous function of the components properties such as the boiling point [2-3]. Even more advanced types of models aim at considering the elementary steps, recognizing that the innumerable reactions and components can be classified into a limited number of reaction families and types of components. E.g., for paraffin hydrocracking a distinction can be made between alkyl-shifts (non-branching isomerization), so-called PCP-branching isomerization (Protonated CycloPropane) and β -scissions (C-C bond breaking in β position with respect to the charged carbon atom. Structured Oriented Lumping [4] and Single-Event MicroKinetic [5] modeling are the two most renowned techniques in this respect.

Starting from the SEMK model for hydrocracking and, more generically, for the transformation of hydrocarbon streams, this work will address the more recent evolutions in this area, among others considering the use of renewables. A tool for automated reaction network generation is being adapted for use against glycerol hydrogenolysis data [6], showing the benefits and the constraints of the methodology. A further extension towards lignin depolymerization will also be discussed.

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ALUMINUM OXIDES AS SUPPORTS FOR HYDROTREATING CATALYSTS



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The most suitable and frequently used support for hydrotreating catalysts is γ - Al_2O_3 , which is obtained by thermal treatment of boehmite AlOOH or pseudoboehmite $\text{AlOOH}\cdot n\text{H}_2\text{O}$, where $n < 1.5$.

There are two main industrial methods for producing boehmite or pseudoboehmite used for the preparation hydrotreatment catalysts:

- 1) reprecipitation of gibbsite or precipitation of aluminum salts;
- 2) sol-gel method.

These methods have both advantages and disadvantages. In the first case, the synthesized alumina support may have optimal textural and mechanical properties, but the method involves a high consumption of reagents and the formation of a large number of effluents. The second method is extremely expensive, but the pore size distribution in the supports is better than in the first case.

In the Boreshkov Institute of Catalysis a new eco-friendly and accessible method was developed for the synthesis of pseudoboehmite by hydrothermal treatment of active aluminum hydroxyoxide, obtained via flash calcination of gibbsite $\text{Al}(\text{OH})_3$. The particle morphology of such pseudoboehmite is diverse (fig. 1) and depends only on three synthesis conditions: T , pH and τ .

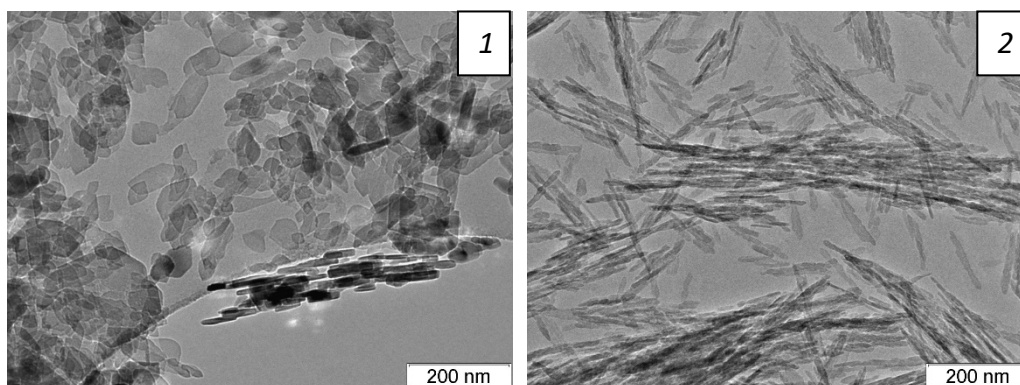


Figure 1 – HRTEM images of boehmite. 1 – particles in the form of boats, 2 – needle-like particles

The typical specific surface area of alumina supports obtained by new technology is 200-220 m^2/g , the average pore diameter is 10-13 nm, and the pore volume is up to 0.92 cm^3/g .

The introduction of modifying additives at the stage of pseudoboehmite synthesis containing, for example, boron, silicon or sulfur, allows serious changes to be made not only in the textural

KL-3

characteristics of the supports, but also to modify the acid-base surface properties, which ultimately are reflected in the catalytic activity of hydrotreating catalysts.

The method has serious advantages, namely: the consumption of reagents is minimal, the amount of effluent is much less, and the degree of pseudoboehmite purity is high. γ - Al_2O_3 based on such a pseudoboehmite meet the requirements for a supports for hydrotreating catalysts.

The lecture will talk about alumina supports obtained through different methods and the catalytic activity of catalysts based on them in the hydrotreating reaction of diesel fuel or vacuum gasoil.

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CONTENT

ORAL PRESENTATIONS

INFLUENCE OF Si DOPING TO HYDROTREATING CATALYSTS OF FCC FEED PRETREATMENT



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Hydrotreating of vacuum gasoil (VGO) is the key process to prepare FCC feed before further conversion [1,2]. The main goal of the process is to decrease sulfur and nitrogen contents to reduce deactivation speed of FCC catalysts. In recent years, there is the tendency to involve heavier fractions to FCC process. It results in an increase of sulfur and nitrogen containing compounds in the feed. Therefore, it is necessary to find new solutions to develop hydrotreating catalysts with higher activity in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions.

Hydrotreating catalysts of VGO are preferentially the composition of active Ni(Co)MoS phase supported on alumina oxide. In this case, the active phase plays hydrogenating/HDS/HDN roles, while alumina oxide is used as almost inert material for dispersion of active metals, transferring of the feed to active component and so on. Such catalytic system is characterized by small quantity of acid sites with mild strength. If we consider kinetics of transformation of sulfur and nitrogen containing compounds in VGO, it will be obvious that hydrogenation of aromatic rings of these compounds is the limiting reaction. Therefore, it is necessary to increase hydrogenation activity of hydrotreating catalysts. One of the solution of this goal is to change acidity of hydrotreating catalysts. It can be achieved by modification of alumina support by silica compounds, for example at the stage of the alumina precursor preparation.

In present work, modification of the alumina support by silica compounds during boehmite preparation will be studied. Boehmites for alumina support preparation were prepared via hydrothermal treatment of gibbsite as it is described in [3]. Silica compound was doped at the stage of hydrothermal treatment of alumina monooxide. Molar ratios of Si/Al were 0.02, 0.03, 0.04. Alumina supports were prepared by peptizing of modified boehmites with ammonia solution followed by extrusion via fluoroplastic sinneret with trilobe holes, drying at 120°C and calcination at 550°C. Catalysts were prepared by impregnation of alumina supports with the solution containing Ni and Mo compounds, citric and phosphoric acids. Boehmites, supports and catalysts were studied by XRD, nitrogen adsorption-desorption, NMR, TGA, IR CO, HRTEM.

OP-1

XRD studies of the boehmites show similar data for all samples except of the one with Si/Al=0.02. For that sample, there is broadening of the peaks at small angles. Such tendency remains unchanged for the alumina supports. ^{29}Si MAS NMR spectra of boehmites and alumina supports show the formation of $\text{Si}(\text{OSi})(\text{OAl})_2(\text{O}^-)$ and $\text{Si}(\text{OSi})(\text{O}^-)_3$ fragments, observed for different aluminosilicates or silicate anions. Textural characteristics changes significantly after Si addition. The support and catalysts with Si/Al=0.02 have smaller surface areas than the samples without Si. The increase of Si content results in the increase of the surface area from 210 to 290 m^2/g . It was noted that Si addition resulted in the increase of stacking number and slab length that is typical for catalysts containing alumina-silicates. It was interesting that addition of Si results in the decrease of Lewis acidity of the supports that could indicate blockage of basic OH groups of alumina. These groups are known to be involved in strong interaction with NiMoS phase.

Catalysts have been tested in hydrotreating of FCC feed at the following conditions: P=5,0 MPa, WHSV=1 h^{-1} , T=360, 375°C, H_2/feed =1000 nl/l. Figure shows residual sulfur and nitrogen contents in the liquid products after reaction. Introduction of Si in small quantities (Si/Al=0.02) significantly improves HDS activity. Further increase in Si content resulted in the decrease of the activity. While HDN activity does not practically changed, when Si quantity is small. The catalyst with Si/Al molar ratio 0.02 showed the best combination of HDS and HDN activities. This effect could be due to the formation of alumina-silicate species, which improves interaction of sulfide active component and the support.

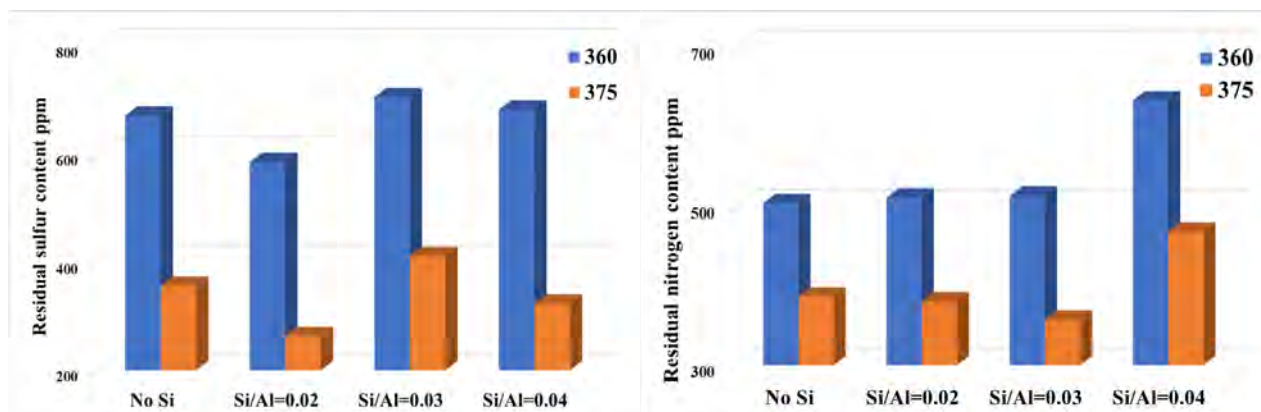


Figure – Residual sulfur (left) and nitrogen (right) contents hydrotreating products

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INFLUENCE OF THE TRANSITION METAL AND CATALYST DRYING PROCEDURE ON THE CATALYTIC PERFORMANCE OF Re/Pd, Co/Mo AND COMMERCIAL CATALYSTS SUPPORTED ON HEXAGONAL MESOPOROUS SILICAS DOPED WITH Ti-IONS DURING THE HDS OF DIBENZOTHIOPHENE AND 4,6-DIMETHYLDIBENZOTHIOPHENE



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Diesel fuel is a complex mixture of hydrocarbons containing varying amounts of heteroatoms with the most containing sulphur presented in a variety of compounds: thiols, sulphides, disulfides, thiophenes, benzothiophenes, and dibenzothiophenes. The most difficult to be removed from diesel fraction is 4,6-dialkyldibenzothiophenes because of its high aromatic character and these compounds constitute the bulk of the remaining sulphur compounds in diesel fraction. Removal of sulphur through “deep desulphurisation” process and obtaining ultra low sulfur diesel, ULSD, is a most demanding task and hydrodesulphurization represent a key process for producing clean engine fuels. There are many formulations for deep HDS catalysts, and the selection depends on the content of the distillates being treated in petroleum refineries. Nowadays, in practice, most HDS units use catalysts based on Co/Mo disulfide or Ni/W supported on alumina. Many other metal sulphides are active in HDS catalysis, but those at the middle of the transition metal series, Ru, Os, Rh, Ir, are most active and provide maximum activities [1-5]. However, there are few critical obstacles for their application in deep hydrodesulphurisation reactions since pore diameter directly influence the conversion of sulphur compounds and asphaltenes and catalysts deactivation due to blockage of reactive internal pore surface. Therefore, much research is focused on catalysts pore size enlargement to mesopore range providing advantages like: high surface areas, enhanced pore volumes, tuneable pore size; excellent mechanical properties and hydrothermal stability for demanding reaction conditions, bifunctionality of the active metal together with base or acid function of the support [4-6].

In the present work, a series of deep hydrodesulphurisation catalysts Re/Pd supported on Ti doped hexagonal mesoporous silicas and Co/Mo supported on silica/alumina was prepared, characterized and tested in DBT and 4,6-DMDBT HDS and compared with a commercial catalyst.

Mesoporous silica with pore sizes from 3.5 to 4.5 nm and surface areas between 950 and 1150 m²/g were synthesized using tetraethyl ortosilicate, Ti sec-butoxide, 1-propanol or ethanol and mesitylene as structure directing agent. The synthesis method for Ti doped hexagonal

mesoporous silica is made as combination of two procedures: procedure for the synthesis of pure hexagonal mesoporous silica by Tanev and Pinnavaia and incorporation of the Ti heteroatom was done following the procedure published by Gontier and Tuel with following conventional, thermal evaporation in air and the supercritical drying in excess of solvent [6]. Support with more than three times increased mesopore volume and with finer morphology is obtained with supercritical drying, while additional ten times larger mesopore volume is obtained with mesitylene addition and with reduction of larger macropores (pore size bigger than 1000 nm) coupled by simultaneous development of smaller macropores (50-100 nm). Prior the reaction, sulphidization of catalyst was performed in reactor with CS₂ at 30bars and 603K during 4h. The catalytic activity was tested in 300 mL batch reactor (Autoclave Engineers BTRS-Jr, Division of Snap-title, Inc., Erie, PA, USA) at pressure of 60 bar and temperature of 603 K, during 6 h. Ration of DBT/4,6-DMDBT was 0,800 g / 0,100 g (cca 2000ppm of sulphur) dissolved in mixture of dodecane/hexadecane 1:1(V/V) with 1 wt%. The obtained mixture of reactant and product was analysed using GC-MS.

The Re/Pd catalyst obtained with supercritical drying exhibited significantly higher catalytic activity in the model reaction of DBT and 4,6-DMDBT compared to conventional hydrotreating catalyst and Co/Mo catalyst. In addition, it was shown that the resulting hydrodesulphurization activity strongly depends on the preparation procedure of the final catalyst and the extremely high surface area of mesoporous silica favours the dispersion of the active species, which result in very high HDS activity.

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TUNING METAL-ACID PROPERTIES OF ZEOLITE HYDROCRACKING CATALYSTS BY SUPPORTING NiMo WITH IMPREGNATION SOLUTIONS OF DIFFERENT COMPOSITION



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Bifunctional catalysts based on zeolites and hydrogenation component (Ni-Mo(W)-S or Pt) are widely used for hydrocracking (HC) providing remarkable activity and stability. The balance between acid function and hydrogenation (metal) function determines the activity and selectivity of HC catalyst and products distribution. Catalysts with higher acidity but weaker hydrogenation function will tend to produce light products such as naphtha and gases, whereas catalysts with lower acidity and enhanced hydrogenation activity will produce middle distillates. Much effort was dedicated to the development of the approaches for the adjustment of metal-acid properties of HC catalysts. The aim of this study was to investigate the influence of the composition of impregnation solution on physicochemical and catalytic properties of NiMo-zeolite hydrocracking catalysts. For this purpose, a series of samples was prepared using various impregnation solutions (Ni and Mo precursors, phosphoric acid, citric acid, diethylene glycol).

Support for HC catalysts containing 30 wt% of zeolite was prepared by mixing USY zeolite (CBV-720, Zeolyst; SiO₂/Al₂O₃ = 30) and AlOOH powders followed by peptization, extrusion, drying and calcination. NiMo/USY-Al₂O₃ catalysts (10.0 wt.% Mo and 3.0 wt% Ni) were obtained by incipient wetness impregnation with aqueous solutions containing Ni and Mo precursors with different additives (see Table 1 for catalysts description). Impregnated catalysts were dried and calcined. The samples were studied by nitrogen adsorption, ICP-AES, XRD, HRTEM, ²⁹Si MAS NMR, XPS, UV-Vis, TPR, IR spectroscopy of adsorbed pyridine. For evaluation of metal function the samples were tested in the model reactions of dibenzothiophene (DBT) hydrodesulfurization and naphthalene hydrogenation (240°C; 3.5 MPa; 20 h⁻¹; H₂/feed 200 v/v). For evaluation of acid function the samples were tested in the model reaction of decane hydrocracking (330 and 350°C; 3.5 MPa; 8 h⁻¹; H₂/feed 500 v/v).

Description and textural characteristics of support and corresponding catalysts are presented in Table 1. According to the obtained results, the catalysts have similar metals content and quite similar textural properties. It should be noted that there is no significant decrease in micropore volume after metals incorporation for all studied catalysts.

Table 1. Characteristics of the studied samples

Sample	NiMo impregnation solution	Content, wt%			S _{BET} , m ² /g	Pore volume, cm ³ /g	
		Ni	Mo	P		V _{total}	V _{micro}
Support	-	-	-	-	415	0.70	0.07
NiMo	Successively Mo→calcination→Ni	2.7	9.4	-	328	0.54	0.06
NiMo+CA	Ni + Mo + CA	2.6	9.4	-	357	0.57	0.06
NiMo+PA	Ni + Mo + PA	2.9	10.0	2.0	306	0.50	0.06
NiMo+CA+DEG	Ni + Mo + CA + DEG	2.7	9.6	-	356	0.58	0.07
NiMo+CA+PA	Ni + Mo + CA + PA	2.6	9.5	1.8	328	0.51	0.07

CA – citric acid; PA – phosphoric acid; DEG – diethylene glycol

The results obtained by HRTEM, XPS, UV-Vis and TPR suggest that the state and morphology of the supported Ni and Mo is different for the catalysts obtained with impregnation solutions of various composition. At the same time, the acidic properties are also affected by the impregnation with different solutions. According to ²⁹Si MAS NMR the presence of citric acid in the impregnation solution may affect the Si/Al ratio in zeolite framework.

Table 2. Catalytic properties of the studied samples

Sample	Metal function		Acid function	
	Conversion, %		n-Decane conversion, %	
	DBT	Naphthalene	330°C	350°C
NiMo	41.7	48.2	32.2	45.3
NiMo+CA	46.1	48.6	33.8	46.9
NiMo+PA	31.9	50.3	37.9	51.7
NiMo+CA+DEG	45.7	54.4	35.7	47.5
NiMo+CA+PA	33.7	53.4	37.5	50.9

Changes in the properties of metal and acid functions of HC catalysts obtained using various impregnation solutions cause a change in the catalytic properties (Table 2). Thus, using of impregnation solutions of different composition on the stage of metals incorporation may affect both metal and acid functions of bifunctional hydrocracking catalyst. This approach may be considered for adjusting metal-acid properties of zeolite hydrocracking catalysts.

Acknowledgements

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NEW DIRECTION IN THE HYDROPROCESSING OF GASOLINE FRACTIONS: INTEGRATION OF C₅-C₆ AND C₇-PARAFFIN HYDROCARBONS ISOMERIZATION PROCESSES



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Improving of the environmental properties of commercial gasoline is one of the priority directions of oil refining. The light gasoline fractions isomerization process allows to obtain environmentally friendly high-octane components of gasolines.

The pentane-hexane fraction isomerization process on sulfated zirconia catalysts has been successfully implemented in industry [1]. The expansion of the feed base of isomerization process is of practical interest, therefore isomerization of a heptane fraction with a higher molecular weight is currently studied. Selective catalysts for the isomerization of C₇ hydrocarbons should have less acidity compared with SO₄²⁻/ZrO₂ systems, due to the higher reactivity of heptanes to cracking reactions.

WO₃-ZrO₂ catalysts for selective isomerization of C₇ alkanes are proposed [2, 3]. Due to the different requirements to the acid function for C₅-C₆- and C₇-alkanes isomerization catalysts, these two directions of isomerization are currently considered as two separate processes. However, the practical interest is integration of two processes into one technological unit using only one catalyst.

In this work catalytic studies on the isomerization of individual hydrocarbons (n-heptane, n-hexane) and their mixtures (mass ratios of n-heptane / n-hexane are 70/30, 50/50, 30/70) on Pt/WO₃-ZrO₂ catalysts were carried out. In table 1 the main reaction parameters of n-heptane, n-hexane and their mixtures isomerization reactions on catalyst Pt/WO₃-ZrO₂ with tungsten oxide content of 15 wt.% are shown (the data are given at the reaction temperatures, allowing to achieve the highest yields of C₇ isomers). It is seen that in the presence of a tungstated zirconia catalyst, the octane number of isomerate when using individual n-heptane as a feed is 54 (RON), for n-hexane – 73 (RON). The octane number of isomerate obtained in isomerization of n-heptane / n-hexane mixtures is 62-68 (RON) depending on feed composition. RON for mixtures of C₇ isomerate and C₆ isomerate is also 62-68 (RON).

OP-4

Table 1 – The isomerization of n-heptane, n-hexane and their mixtures on Pt/WO₃-ZrO₂ catalyst

Indicator	Feed				
	n-heptane	n-heptane / n-hexane mixture (wt.%)			n-hexane
		70/30	50/50	30/70	
T, °C	200	220	200	200	240
Conversion, %:					
n-heptane	87,8	91,9	92,1	90,8	–
n-hexane	–	77,4	74,4	70,8	84,4
Yield, wt. %:					
iso-C ₇ [*]	62,7	41,6 (59,4)	29,7 (59,4)	20,8 (69,3)	–
DTMS ^{1*}	25,0	17,8 (25,4)	12,8 (25,6)	8,8 (29,3)	–
iso-C ₆ [*]	–	24,3 (81,0)	36,2 (72,4)	48,6 (69,4)	80,5
DMB ^{2*}	–	6,1 (20,3)	7,7 (15,4)	9,7 (13,9)	29,6
C ₅₊ -hydrocarbons	78,4	79,3	83,1	92,9	97,2
RON of isomerate	54	62	63	68	73
RON of mixing product **	–	62	64	68	–

¹ Dimethyl and trimethyl substituted isomers of heptane

² Dimethyl butanes

* In parentheses is calculation for individual components

** RON for mixture of C₇ isomerate (RON of 54) and C₆ isomerate (RON of 73)

Thus, the results of the isomerization of n-heptane / n-hexane mixtures show that the isomerization of C₅-C₇ hydrocarbons can be carried out by using only one catalyst in one technological unit. The octane number of the isomerate of the joint isomerization reaction is not inferior to the octane characteristics of the mixed component obtained by separate isomerization of C₆ and C₇ hydrocarbons.

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EFFECT OF BENTONITE ADDITION ON PROPERTIES OF NANOSTRUCTURED PtPd-ZEOLITE HYDRODESULFURIZATION CATALYST



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Requirements of EURO-5 specification of the content of sulfur and aromatic compounds in motor fuels encourage the search of novel catalysts for ultra-deep desulfurization and dearomatization of hydrocarbon fuels. Pt-zeolite catalysts were found to be excellent for hydrodesulfurization of diesel fractions with low sulfur content (< 50 ppm) [1], but they are subjected to considerable deactivation by high concentration (> 500 ppm S) of sulfur compounds [2]. According to the Song concept [3], to improve the sulfur-resistance of hydrotreating Pt-catalysts, their design has to satisfy the following requirements: bimodal pore texture, two types of active Pt-sites, and optimal proton acidity. Besides, adding Pd to Pt enhances the catalytic hydrotreating activity in the sulfur presence [4].

Current communication is devoted to the study of catalytic properties and sulfur-tolerance of PtPd-zeolite catalysts which satisfy the Song concept as the function of catalyst proton acidity. The acidity was regulated by the addition of a bentonite clay to a trefoil-shaped support containing Al₂O₃-H/ZSM-5. The morphology of Pt(Pd) particles and Pt(Pd) state in these catalysts will be also discussed.

The unmodified Pt(Pd)-zeolite catalyst demonstrates high efficiency in deep desulfurization of low-sulfur straight-run gas oil (SRGO) at 280-320 °C, but its activity with respect the secondary diesel fraction is insufficiently high (Table, cat. 1). The modification of Pt(Pd)-zeolite catalyst by bentonite has a positive effect on its efficiency in deep HDS of SRGO with LCO (Table, cat. 2). However, the observed effect depends on bentonite properties, in particular on the content of alkaline and alkaline-earth elements and Fe. For example, the use of bentonite with a high content of Ca and K (1.8 and 0.5 wt. %, respectively) results in a substantial decrease of the catalytic activity of Pt(Pd)-zeolite catalyst in HDS of secondary diesel fraction (Table, cat. 3). It was shown the catalysts 1 and 2 have a high sulfur resistance, when sulfur content in SRGO is 1000-2000 ppm. Their catalytic properties are totally recovered after regeneration.

For more active catalysts 1 and 2, the finely dispersed particles (3-5 nm) of PtPd-alloy on zeolite and alumina surface were observed by TEM (Fig. a) and as ν_{CO} at 2075-2090 cm⁻¹ by FTIR. These PtPd particles probably provide high activity in hydrogenation of alkylsubstituted DBT with their subsequent hydrogenolysis. The electron-deficient Pt particles (1-3 nm) located close to Bronsted acid sites inside the zeolite channels were suggested only for the catalyst 2, based on FTIR data

OP-5

($\nu_{\text{CO}} = 2105\text{-}2125 \text{ cm}^{-1}$ and excitation lack of $\nu_{\text{CO}} = 3610\text{-}3615 \text{ cm}^{-1}$). They ensure high sulfur-tolerance. In case of the catalyst 3, which has the lowest activity and sulfur tolerance, the bimodal size distribution of PtPd-particles was observed, with the maxima at 3 nm and 15-22 nm (Fig. b). Most likely, the anchoring of PtPd-complexes on BAS prevents sintering of PtPd-particles during catalyst activation under reducing conditions.

So, for high efficiency and sulfur resistance in desulfurization of the secondary diesel fraction, the PtPd-zeolite catalyst must have optimal proton acidity, which has a substantial effect on the size of PtPd-particles and their location.

Table. Performance of Pt(Pd)-zeolite catalysts in HDS of straight-run and secondary diesel fraction, at 300 °C. Conditions: 4 MPa, LHSV 0.5 h⁻¹, H₂/fuel – 500 l/l, and 300 °C.

Characteristics	SRGO	HDS Product of SRGO over			SRGO/ LCO, 70/30	HDS Product of SRGO/ LCO over		
		cat 1	cat 2	cat 3		cat 1	cat 2	cat 3
Density, d_4^{20} , kg/m ³	847	844	848	826	866	848	859	859
Simulated distillation, °C, 10%	185	184	75	85	184	173	118	119
50%	270	275	299	270	280	270	277	274
96%	360	355	365	347	360	350	360	345
S content, ppm	1065	45	28	10	1320	155	58	530
Aromatic CH content, wt %	20	14	12	11	27	22	22	22
Cetane number	45	45	44	45	44	44	42	42

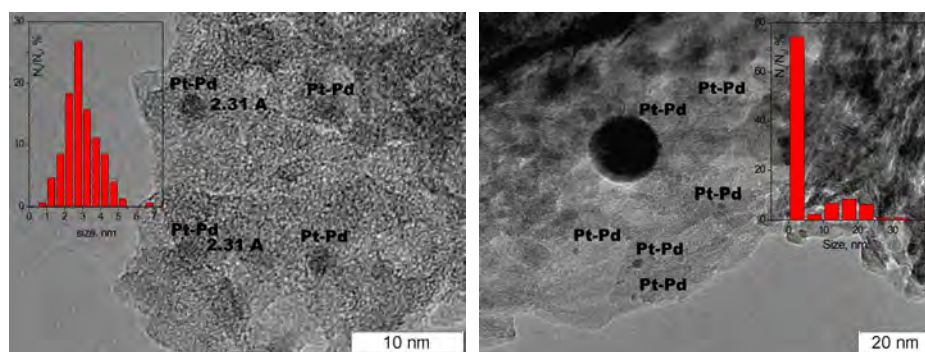


Fig. EM images of PtPd-catalyst 2 (a) and 3(b)

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NEW METHODOLOGY COUPLING RAMAN AND XAS FOR THE SPECIATION OF ADDITIVATED Mo-BASED HDS CATALYSTS AND CHARACTERIZATION BY QUICK-XAS OPERANDO OF THEIR LIQUID SULFIDATION



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There is a continuous challenge to increase the performances of the HDS catalysts, cobalt-promoted MoS₂ supported on alumina, in order to meet the increasingly stringent global environmental standards concerning the reduction of pollutant in exhaust gas such as sulfur. To do so, organic additives are nowadays largely used to increase the catalytic activity. An abundant literature exists on this matter to describe the impact of the additives both on the oxide state or during the sulfidation. However there is a crucial lack of quantification of the various and numerous molybdenum oxide species which coexist at the support surface. Besides, most of the activation studies have been done using gas phase sulfidation, whereas the industrial sulfidation of gas oil HDS catalysts is mainly performed using a liquid feedstock. The few works which have been comparing both sulfidations have highlighted differences on catalytic properties [1-3]. Therefore it is important to be able to study the liquid sulfidation of the additivated catalysts.

In order to answer these two issues, we have first developed a new methodology coupling Raman and XAS which for the first time gives a quantification of Mo-species both in the impregnation solution (MoO₃, Co(OH)₂ and H₃PO₄) and at the catalyst surface upon impregnation on γ -alumina and drying. Two types of additives have been used in co-impregnation: a dispersing one (Triethyleneglycol) and a chelating one (Citric acid). Figure 1 highlights the species differences in the solutions according to the additive used. These differences are even more pronounced on the dried catalysts, in line with what was observed in previous works [4-6].

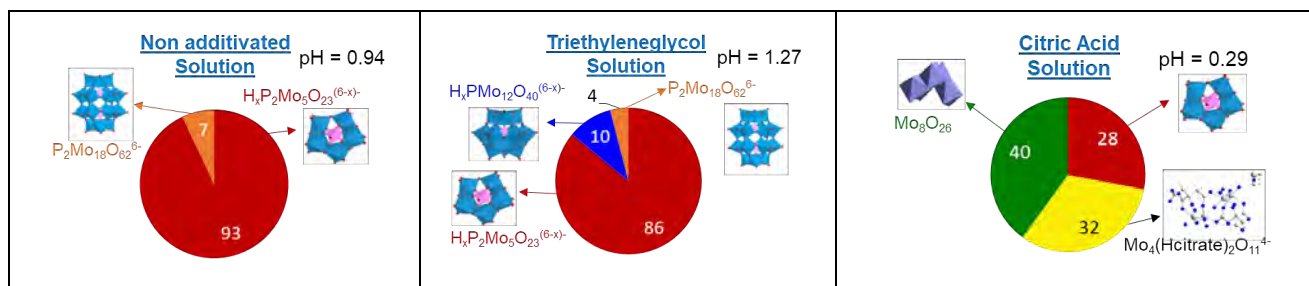


Figure 1: Speciation of the solution (non-additivated, TEG additivated and citric acid additivated) using a methodology coupling Raman and XAS

OP-6

These catalysts (non additivated and additivated CoMoP) were then studied during their liquid sulfidation using a new tubular reactor which allows the sulfidation until 350°C and 30 bar and at the same time the simultaneous Mo and Co K edges Quick-XAS spectra recording thanks to the unique properties of ROCK beamline at SOLEIL Synchrotron [7]. Powerful chemometric tools, such as Multivariate Curve Regression with Alternating Least Square fitting (MCR-ALS) approach, have been used for isolating and identifying the intermediate species involved in the activation process (Figure 2). Sulfidation in liquid conditions with dimethyldisulfure delays the formation of H₂S at 230°C. This brings new insights on the role of additives which have been used in the past in gas sulfidation activation to retard the sulfidation of promoter and improve the formation of the CoMoS active phase. Therefore the role of both additives on the sulfidation mechanism and on the final sulfided phase will be discussed and linked to the activity improvement on real gas oil feedstock.

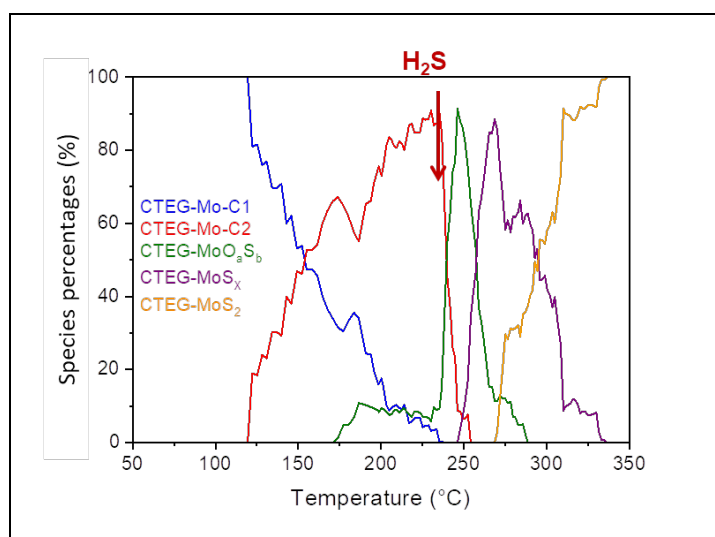


Figure 2 : Evolution of the concentrations of the Mo species identified by MCR-ALS during the liquid sulfidation process of TEG CoMoP catalyst

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AN ALTERNATIVE APPROACH FOR LCO UPGRADING



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It is well known that Light Cycle Oil (LCO) upgrading is a difficult task, as there are some inhibitory properties of LCO such as high-refractory sulfur species' content and high aromatic content. [1] Until now, neither hydroprocessing of LCO nor co-hydroprocessing of LCO with petroleum fractions or/with liquid biomass could lead to a product which entirely meets the diesel specifications. [2] In this study, fractionation and co-hydroprocessing with Waste Cooking Oil (WCO) are combined to enable effective and sustainable LCO upgrading. On the one hand, the fractionation of LCO up to 350 °C was realized with the objective of exploiting only the light fraction (LCO_cut), which presented improved properties as the heavy sulfur species and polyaromatic compounds are isolated in the residue (heavy) fraction. [3] On the other hand, the LCO_cut was mixed with WCO in a 90/10 ratio and led for hydroprocessing for producing liquid products attaining diesel specification.

The LCO fractionation took place in a batch distillation unit of the Chemical Process & Energy Resources Institute (CPERI) of the Centre for Research and Technology Hellas (CERTH), enabling the separation of the lighter than 350 °C LCO fraction. Moreover, all co-hydroprocessing tests of the lighter LCO fraction with WCO were performed in the small-scale hydroprocessing pilot plant of CPERI/CERTH. (Figure 1)

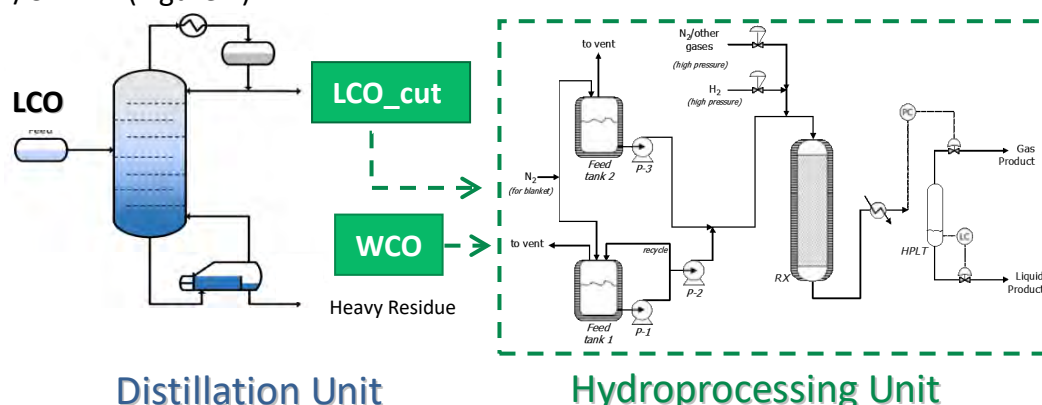


Figure 1: The experimental steps combining distillation and co-hydroprocessing technology

In total, three test runs of co-hydroprocessing of 90/10 v/v LCO_cut/WCO were carried out, employing three different hydroprocessing temperatures (340, 360 and 380 °C), employing the same commercial NiMo/ γ -Al₂O₃ catalyst. The quality of the total liquid products was compared

OP-7

with the corresponding ones produced from the preceding study where the whole LCO stream was co-hydroprocessed with WCO. [2] In order to evaluate the quality of the final liquid products, all necessary analyses were performed in the Laboratory of Fuels Technology and Lubricants of the School of Chemical Engineering of the National Technical University of Athens.

The results showed that distillation contributed positively to the co-hydroprocessing of LCO with WCO. The most intense improvement of properties corresponds to high temperature (380 °C) and the improvement percentage (%) of each property is depicted in Figure 2. More specifically, the distillation increased HDS effectiveness about 2% and it rendered a product with significantly low sulphur content, not too far from the EN590 diesel specification (10 mg/kg). Moreover, an intense improvement of the density value (1.6%) and cetane number (12%) is also observed when distilled LCO is co-hydroprocessed with WCO instead of LCO/WCO. Moreover, the LCO fractionation allows the saturation reactions to be more dominant, leading to a reduced aromatic content, while the polyaromatic improvement content reaches 6%. Finally, co-hydroprocessing of LCO_cut with WCO has rendered a nearly 100% yield for mid-distillates, in contrast with the co-hydroprocessing of LCO/WCO (≈94%). [2]

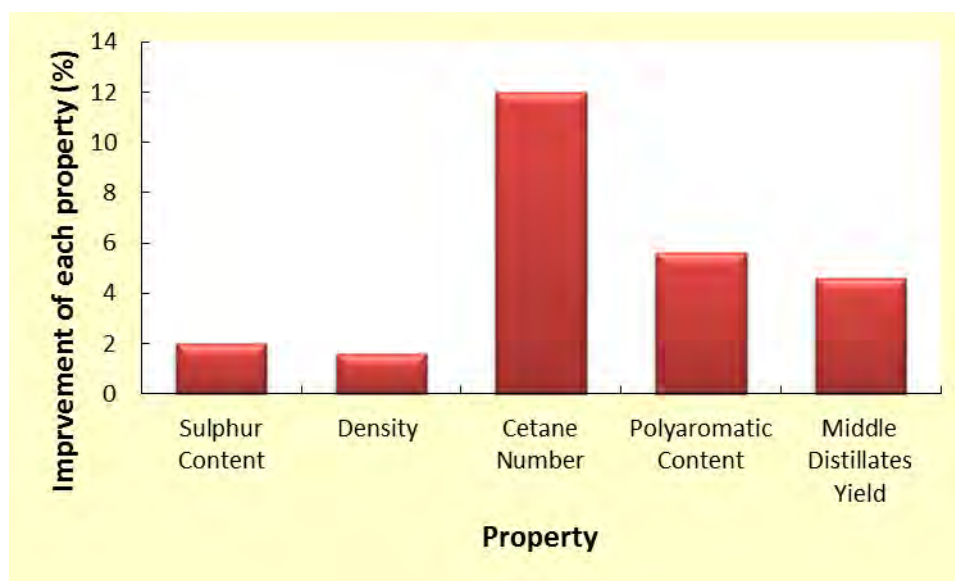


Figure 2: The improvement content (%) of each property of LCO_cut/WCO product in comparison with the corresponding one of LCO/WCO at 380 °C

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HYBRID DIESEL PRODUCTION VIA CATALYTIC CO-HYDROPROCESSING OF BLENDS GASOIL-WASTE COOKING OIL

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The refining process technology includes the hydrotreatment, which is used to remove pollutants content in the petroleum and their products. The main pollutants are sulfur, nitrogen, and metals like vanadium, nickel and chrome [1]. In recent years this process had been using to produce biofuels and other biochemical products. The biofuels produced via hydrotreatment have an interval from C₁₂ to C₁₈, compatible with the intermediate's fossil fuels (diesel and jet fuel) [2]. The present work studies the production of a (hybrid) diesel using a blend of light gasoil and waste cooking oil (LGO-WCO) with a low sulphur content respect to the initial value of the gasoil. For the hydrotreatment the main evaluation parameters are the temperature, pressure and flow [3]. The reaction performed into a micro reaction system at 613, 633 and 653 K, with a constant pressure of 56.0 Kg/cm². There were evaluated three blends, whose content 5, 10 and 20% of WCO. A space velocity of 1.5 h⁻¹ has used in this hydrotreatment. The catalyst used had a composition CoMoP/γAl₂O₃, a typical catalyst for the hydrodesulfurization (HDS). The characterization of the liquid product includes the sulphur content, density, viscosity (kinematic and dynamic) and the total acidity number. The results obtained shows a good conversion up to 90%, which increase in temperature function (effect over the conversion). The catalytic activity in the BET analysis shows a good surface area after the reaction. The better results occur at high temperatures, so is important to consider other aspects as the catalyst used, type of reactor, pressure and space velocity, to have a good conversion and a high-quality fuel [3].

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Acknowledgements

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PRODUCING LOW CARBON FUELS BY CO-HYDROCRACKING HTL BIOCRUDE WITH VACUUM GAS OIL

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With the increasing requirement for renewable transportation fuels, co-processing biogenic feedstocks with petroleum streams in existing refinery units is gaining more attention and interest given its potential to deliver fuels with bio-based content at competitive prices. Biocrudes originating from thermochemical conversion of waste biomass, such as forestry residues and agricultural wastes, are a promising class of biogenic feedstocks owing to the abundance of such resources. Having typically less than 15% oxygen and being thermally stable, biocrudes produced by hydrothermal liquefaction (HTL) are attractive candidates for co-processing [1]. In this study, we investigate the potential of co-processing HTL biocrude with vacuum gas oil (VGO) in a hydrocracking process with hydrotreating at the front.

Experiments were conducted in a continuous hydroprocessing pilot plant having an upflow tubular reactor (length 105 cm and diameter 0.9 cm), a high-pressure separator, an atmospheric stabilizer column, and an on-line GC instrument for gas analysis. The co-processing feed was constituted of 92.5 vol% VGO (3.6 wt% sulfur and 13°API) from Canadian bitumen and 7.5 vol% HTL biocrude (10.5 wt% oxygen and 2.7°API) from woody biomass. Prior to blending with VGO, the biocrude was filtered and distilled to remove sediments and high boiling components.

The test plan consisted of two stages – hydrotreating and hydrocracking. In each stage, two feeds were tested, pure VGO first to establish a baseline and then the biocrude blend feed. In the first stage, the pure VGO and biocrude blend were sequentially hydrotreated over a commercial NiMo/Al₂O₃ catalyst to meet the sulfur and nitrogen specification of the hydrocracking catalyst. The operating conditions for hydrotreating were the following: temperature 375°C, pressure 97 bar, liquid hourly space velocity (LHSV) 1.5 h⁻¹, and H₂/oil ratio 800 NL/L. The second stage consisted of hydrocracking in once-through mode the two products from the first stage, using a commercial zeolite-based catalyst at the following conditions: temperature 382–390°C, pressure 110 bar, LHSV 1.5 h⁻¹, and H₂/oil ratio 800 NL/L. The hydrocracked liquid products were fractionated using an ASTM D1160 distillation setup. Products were characterized using standard methods. The biogenic carbon distribution across the co-processed products was measured using radiocarbon analysis.

For both feeds, the hydrotreating step achieved sulfur and nitrogen removal levels, exceeding 99% and 93%, respectively. Hydrogen consumption was estimated at 1074 scf/bbl for pure VGO and 1099 scf/bbl for the biocrude blend. An important difference observed during this stage was that oxygen removal from the biocrude blend (89%) was not as high as that of sulfur and nitrogen, resulting in a product having ~1,500 wppm oxygen. This is believed to have drastically impacted catalyst activity during the hydrocracking stage, an indicator of this being that the biocrude blend required a higher reaction temperature than VGO (390°C for the biocrude blend vs. 382°C for VGO) to achieve the same conversion.

Table 1 presents a comparison of the overall product distribution and hydrogen consumption resulting from the hydrocracking of pure VGO and the biocrude blend. Product yields are noted to be quite comparable for both scenarios, whereas hydrogen consumption is virtually the same. Co-processing shows a slightly lower naphtha yield with respect to the baseline, but is higher in diesel to a small degree. These differences can be attributed to the effect of oxygen compounds that persisted in the biocrude blend after hydrotreating. Radiocarbon measurements confirmed the retention of biogenic carbon in the co-processed products: 8% in naphtha, 10% in diesel, and 8% in the jet fuel fraction (180–270°C) which is not reported in Table 1.

Table 1. Hydrocracking product distribution and hydrogen consumption.

Product distribution	VGO	7.5 vol% biocrude blend
Gases (H ₂ S, C ₁ –C ₄), wt%	7.02	6.95
Naphtha (IBP–204°C), wt%	48.58	44.76
Diesel (204–343°C), wt%	30.34	32.82
Unconverted oil (343°C+), wt%	17.71	19.07
Total, wt%	103.64	103.59
Hydrogen consumption, scf/bbl	2,343	2,310

In conclusion, this study suggests that co-processing HTL biocrude in a VGO hydrocracking unit is technically feasible within a delimited range of operation parameters. Further research is needed to optimize co-processing performance, particularly in the initial hydrotreating step to have a better control on the quality of the feedstock going to the hydrocracking stage.

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NiMoS NANOCUBES FOR HYDRODESULFURIZATION OF LIGHT HYDROCARBONS

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Oil is currently the primary source of energy; the industry should support efforts to reduce emissions from the development of new technologies to produce fuels with less environmental impact [1]. One of the methods to improve the performance of the hydrodesulfurization (HDS) process is to improve the efficiency of the catalyst; for this reason, there are several studies focused on improving catalysts for hydrotreatment. To improve an HDS catalyst, some parameters are typically studied and modified to have better performance. These key parameters are, for example, the catalytic precursor of the active phase, the nature of the active phase, the support, and the synthetic procedures to which the catalyst is submitted. For this kind of process, the catalysts consist of Ni(Co)-Mo(W) oxides supported on alumina, which are usually transformed in sulfides under kerosene enriched with dimethyl disulfide on the liquid phase and high pressure [2]. Also, there are unsupported catalysts that have shown high activity performance as the NEBULA (New Bulk Activity) [3]. In the present work, we seek to synthesize NiMo unsupported catalysts with specific morphology of nanocubes prepared by the hydrothermal method and apply it in the HDS process. The synthesized materials were characterized by several techniques, and their catalytic behavior was evaluated in the hydrodesulfurization of 3 methyl thiophene (3MT), a naphtha type model molecule.

Nanocubes synthesis and characterization

We use controlled quantities of nickel nitrate, distillate water, and thioacetamide to prepare a solution that was left at 200 rpm for 2 hours to be mixed after we add sodium molybdate, and we wait for another 30 minutes to grant the mixed of all precursors. The resulting solution was added to a Teflon vessel and then in a sealed autoclave at 200°C for 5 hours. Then the system was left cold down to ambient temperature, and the black product was filtered and washed four times. The product was dried at 60°C for 1 hour after that, calcined at 400°C for 4 hours, and then characterized. We varied the molar ratio between Ni and Mo (Ni/Mo=x) with x=0,0.25,0.5,0.75,1.0; then the samples were labelled as nC-S-x-cal. Samples were characterized by SEM, TEM, XRD and tested in the HDS of 3MT in a continuous flow reactor from 260°C to 320°C with increments of 10°C after 2 hours of stationary state stabilization.

Results

The samples were analysed first by SEM and presented well-defined nanocubes morphology, as seen in Fig. 1 for the nC-S-x-cal

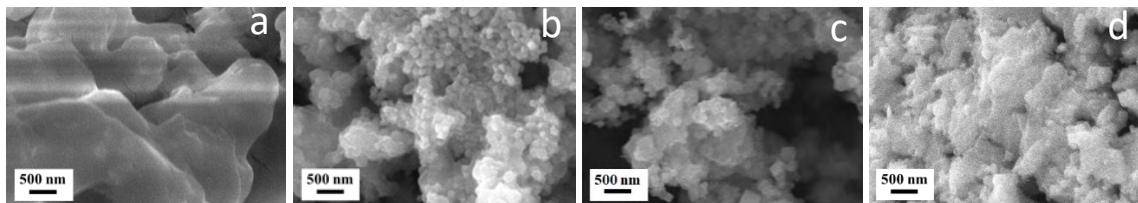


Fig. 1. Typical micrographs obtained for the NiMoS nC-S-x samples from left to right, a) nC-S-0.25-cal, b) nC-S-0.5-cal, c) nC-S-0.5-cal, d) nC-S-1.0-cal.

Samples presented high activity in the HDS reaction at atmospheric pressure, as seen in fig.2; the nC-S-0.50-cal showed the highest performance. Also, samples presented high stability as seen in the catalytic activity and in the images of a nanocube before and after the activity test of the nC-S-0.5-cal sample.

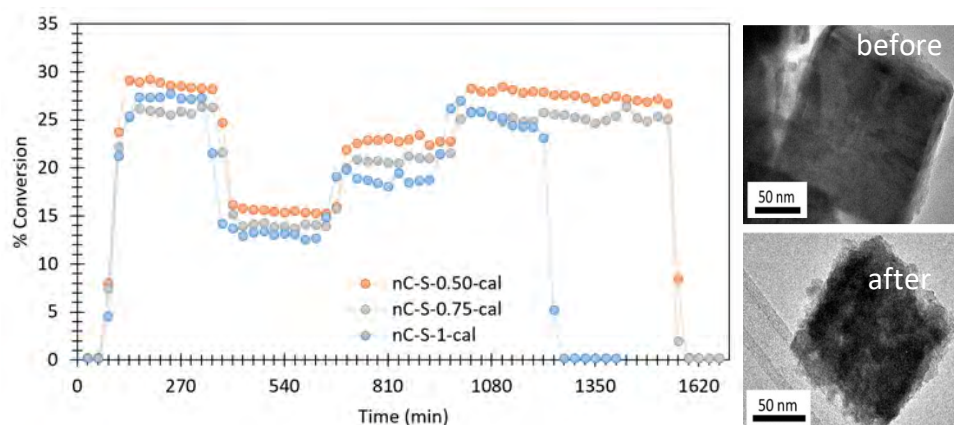


Fig 2. Catalytic conversion of 3MT at steady state for the most active samples and typical TEM micrographs of a nanocube in the nC-S-0.5-cal sample before and after the reaction.

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INFLUENCE OF NITROGEN CONTAINING COMPOUNDS OF DIFFERENT NATURE IN HYDROTREATED VGO ON PRODUCT COMPOSITION OF FCC PROCESS FOR LIGHT OLEFINS PRODUCTION

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Fluid catalytic cracking (FCC) is one of the key processes in oil refining. The typical feeds for FCC are high-boiling vacuum fractions (350-530÷580°C). Along with hydrocarbons, FCC feed contains nitrogen and sulfur organic compounds, which invariably lead to deactivation of FCC catalysts [1]. Sulfur containing compounds have a relatively small deactivating effect on the cracking catalyst compared to nitrogen compounds. The latter lead to a strong deactivation of cracking catalysts due to the partial blocking of active sites [2]. Therefore, FCC is previously hydrotreated to decrease sulfur and nitrogen contents. However, residual contents of these compounds still remain hundreds of ppm. Currently, there is no clear correlations between the content and composition of sulfur- and nitrogen-containing components in the FCC feedstock and the composition of the products of the FCC process. The establishment of such dependences is very important due to the definition of the possibilities of variability of FCC process in relation to obtaining different types of products and in relation to the deactivation of cracking catalysts.

In present work, the influence of content and nature of nitrogen compounds in previously hydrotreated feed on the composition of FCC products was determined. To obtain hydrotreated product, two catalytic systems were used. The first system consisted of two layers of Co-Mo/Ni-Mo catalysts, the second one was Co-Ni-Mo catalyst. The use of different catalytic systems was made to change ration of nitrogen compounds with different nature at the same content of sulfur compounds. Vacuum gasoil (0,75 wt.% S, 1100 ppm N) was hydrotreated in a pilot unit in the following conditions: P=5,0 MPa, T=340-370°C, WHSV = 0,65 h⁻¹, H₂/feed = 625 nl/l. As a result, 8 products with different nitrogen and sulfur contents were obtained for further testing of products in catalytic cracking. The obtained products were subjected to FCC process in a laboratory unit with fixed bed of the catalyst (Micro-activity test, ASTM D3907) at a temperature of 527 °C and catalyst/oil ratio = 2-6. Bizeolite catalytic system (HREY, P/ZSM-5) was used as a catalyst.

For the quantitative determination of basic nitrogen in hydrocarbons by the method of titrimetric analysis, the method of UOP 269-10 is used. Also, the method of ISO 9702 is used for determination of primary, secondary and tertiary amino groups in hardeners of epoxy resins. These methods were adapted for VGO analysis: concentration of titrant, weight of the samples,

OP-11

conditions of dissolution and acylation and reagents were selected. The characteristics of hydrotreated products are given in Table 1. The hydrotreated products with different nitrogen contents were obtained. The content of basic nitrogen compounds was lower for Co-Ni-Mo system. Calculated N basic/N total was sufficiently lower for Co-Ni-Mo system.

Table 1. Composition of hydrotreated FCC feed

Parameter	Feed	Co-Mo/Ni-Mo				Co-Ni-Mo			
		340	350	360	370	340	350	360	370
Process temperature, °C	-	340	350	360	370	340	350	360	370
S content, ppm	7500	704	437	256	144	819	527	312	155
Total N content, ppm	1100	775	660	556	480	749	603	491	372
Content of basic N compounds, ppm	336	179	148	108	76	173	126	83	42
Nitrogen of tertiary groups	334	159	141	106	73	167	121	75	39
N basic/N total, %	30,5	23,1	22,4	19,4	15,7	23,1	20,9	16,9	11,3

The decrease of nitrogen compounds in the feed results in the increase of the activity of FCC catalyst (conversion of the feed, gasoline yield, yield of light olefins). The greatest effect of hydrotreating the feedstock on the cracking material balance is achieved at low catalyst / oil ratios. This effect is accounted for by relatively higher degree of blockage of acid sites of the catalyst at lower ratio of catalyst/nitrogen compounds. The increase of the catalyst/oil ratio does not significantly change the product composition at the change of hydrotreating depth. The total yield of the sum of C₂-C₄-olefins at 527°C and catalyst / oil ratio - 4 is about 26 wt.%.

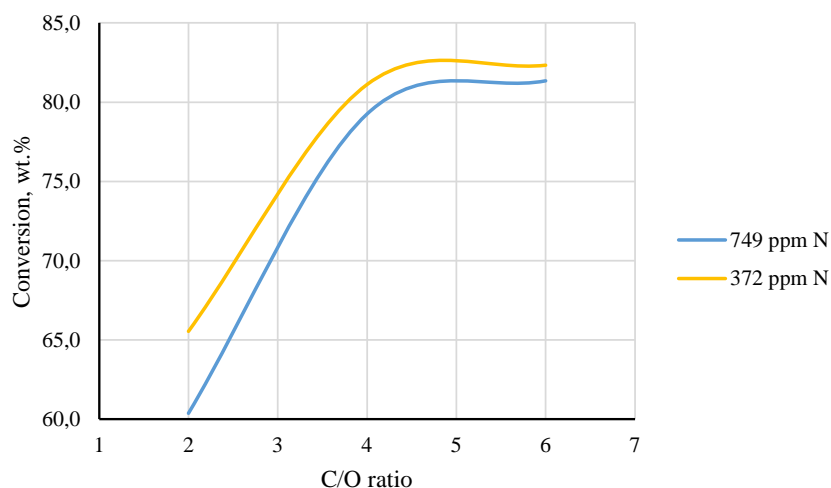


Figure 1. Conversion of the feed with different nitrogen and sulfur compounds

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DETERMINATION OF VARIOUS CHEMICAL STRUCTURES IN BASE OIL USING MULTIDIMENSIONAL NMR SPECTROSCOPY

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Base oil is mainly composed of normal and isoparaffins, naphthenes and tiny amount of stable aromatics after catalytic hydroprocessing, of which the various chemical structures and their contents determine the lubricant properties such as visococity index (VI), pour point (ppt), cold cranking simulation (CCS) viscosity. In base oil, components with methyl/ethyl-branching structures are crucial, and their quantification is important in feedstock and hydroprocessing selection. However, restricted by available analytic techniques, current hydroprocessing optimization such as isodewaxing only simply relies on measurement of VI and ppt parameters. Mass spectroscopy and nuclear magnetic resonance (NMR) are two useful tools in base oil analysis, but they have respective defects in obtaining precise information of the branching structures in mixtures. For NMR, it is not only suffered from serious signal overlapping, but also, it is unable to distinguish naphthenes and paraffins in the complex of base oil.

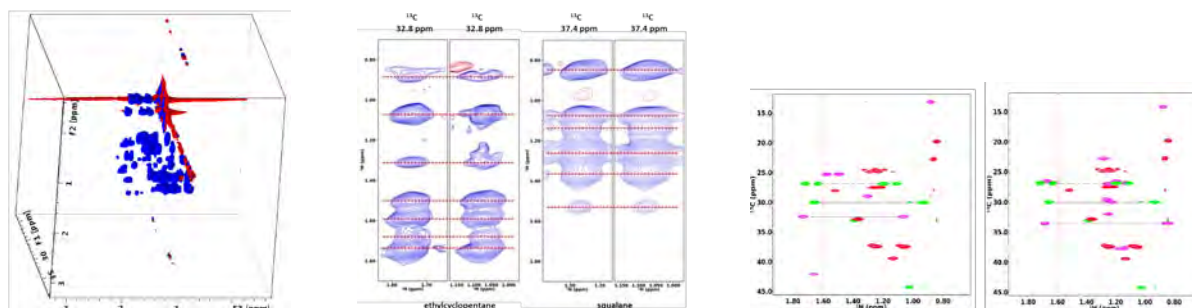


Fig. 1 Typical 3D HSQC-TOCSY spectrum and analysis of a mixture of naphthenes and paraffins.

In the present study, three-dimensional (3D) HSQC-TOCSY spectroscopy was applied to resolve the NMR problem in distinguishing naphthenes and paraffins, with the help of the ¹³C dimension to separate overlapped peaks. From the 3D data of a mixture of naphthenes and paraffins, extracted ¹H-¹H TOCSY signals could be used to differentiate different molecules, while ¹H chemical shift large than (or close to) 1.6 ppm for one of the pairwise ¹H-¹³C signals, which have same ¹³C chemical shift and same TOCSY correlation, is a indication of existence of naphthene (Fig. 1). Our finding is in accordance with the suggestion from the work of Mäkekä [1]. Next, this 3D NMR technique was used to analyze real paraffinic base oil samples. Although naphthene was

OP-12

not observed as expected, six different structures including methyl/ethyl-branching and normal paraffins were undoubtedly determined, and their contents counted for 79% of the total base oil (Fig. 2). Such a multidimensional NMR method sheds light on molecular engineering in catalytic hydroprocessing of base oil.

Finally, our progress on the average structure analysis of heavy oils will be introduced briefly.

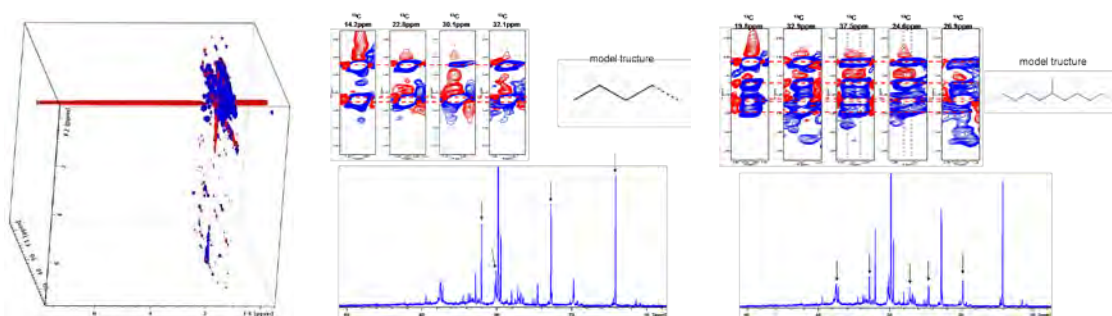


Fig. 2 3D HSQC-TOCSY spectrum and analysis of paraffinic base oil.

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IS IT POSSIBLE TO REACTIVATE HYDROTREATING CATALYST POISONED BY SI?

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Hydrotreating catalysts used in industrial scale are poisoned by different contaminants, for example, such as Si. It is known, that Si compounds interact with OH groups of the support and block active component particles. However, there is no answer, is it possible to reactivate such poisoned catalysts and which content of Si is critical?

In present work, commercial CoMoP/Al₂O₃ catalyst catalyst was used to estimate Si influence on catalytic properties after regeneration and reactivation processes. Catalysts with Si contents 3.2, 4.5 and 5.3 wt.% (table 1) has been obtained during hydrotreating of straight run diesel fraction (S=3684 ppm, N=121 ppm) poisoned by Si compound (300 ppm Si) for 24 h, 72 h and 168 h, respectively. Reduction of a surface area and a pore volume of catalyst is noted due to a sorption of Si (table 1). Catalytic activity in hydrodesulfurization (HDS) and hydrodenitrogenation reactions decreases with the increase of Si content, the exception is the sample with 3.21 wt.% of Si (table 1). It is also noted in [1], that then Si sorbed, the activity of NiMo-catalysts decreases. Si compounds are localized occurs near active component particles and restrict an access of feed molecules to active sites.

Table 1 —Characteristics of obtained samples

Si content in catalyst, wt.%	Surface area, m ² /g	Pore volume, cm ³ /g	Residual S content, ppm	Residual N content, ppm
0	135	0.34	44	5
3.2	117	0.30	40	3
4.5	120	0.30	51	4
5.3	123	0.31	59	10

Catalysts after testing in hydrotreating of straight run diesel fraction poisoned by Si were calcined at 550 °C. Then the catalysts were reactivated by a citric acid solution using methodology described in [2]. The obtained catalysts were tested in hydrotreating of model mix, which contained dibenzothiophene (DBT) (2500 ppm S) and quinoline (200 ppm N) as model S- and N-containing molecules. The reaction constants of hds of dbt has been calculated for each catalytic tests (Figure 1-A). Decrease of activity in HDS of DBT is noted after regeneration (Figure 1). It has been shown in [2], that the reduction of activity relates to the decrease of CoMoS phase content

due to the formation of β -CoMoO₄ and CoAl₂O₄ on catalyst surface. In addition, there is the significant increase in HDS activity of DBT (by 1.4-1.7 times) after reactivation in comparison with the initial catalyst (Figure 1-A). It can be accounted by the formation of CoMoCitr complex on the catalyst surface during impregnation of a calcined catalyst by citric acid solution. Also, the dispersion of active metals on the catalyst surface increases, as was shown in [2]. In addition, the initial and reactivated catalysts were tested in hydrotreating of diesel fraction (S=3289 ppm, N=43 ppm). According to catalytic test results, presented in figure 1-B, reactivated catalyst with Si content 3.2 wt.% is more active in HDS reaction in comparison with initial catalyst. It can be explained by the restructuring of catalyst surface and blocking of some basic OH groups of the support and formation of aluminosilicate compounds that decrease of interaction between active component and support. Further growth of Si content resulted in irreversible blockage of active component particles. Thus, it is found, that successful reactivation of catalyst poisoned by Si is possible at Si content less than 3 wt.%.

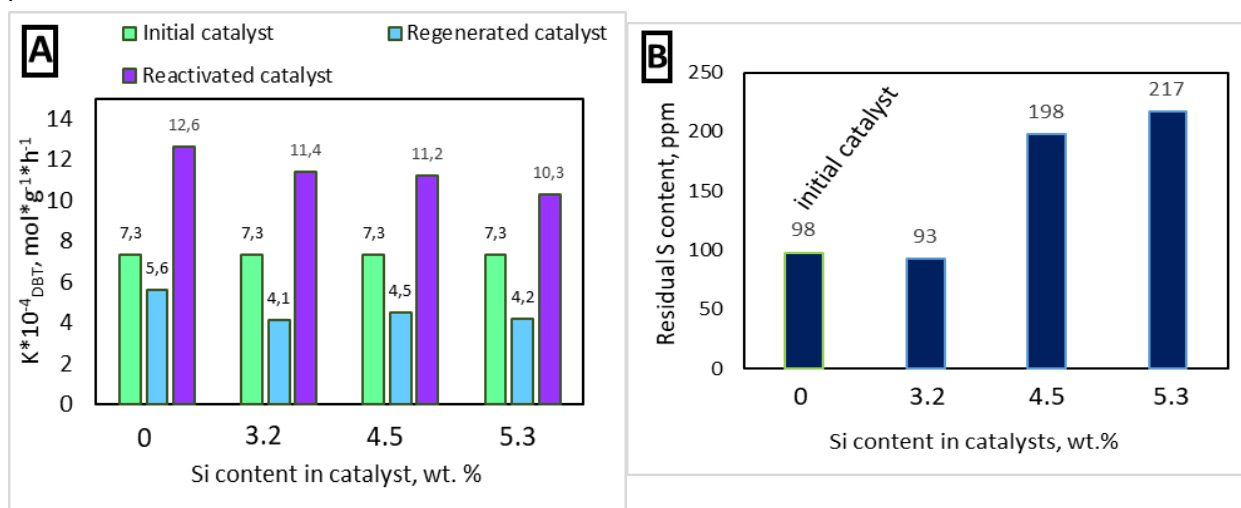


Figure 1 – **A**-Results of catalytic test in hydrotreating using model mix of initial catalyst, regenerated and reactivated catalysts ($K \cdot 10^{-4}_{\text{DBT}}$ – constant of HDS, $\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$). **B**-Results of catalytic test in hydrotreating using diesel fraction of initial and reactivated Si poisoned catalysts.

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THE INFLUENCE OF FRAMEWORK AND EXTRAFRAMEWORK ALUMINIUM SPECIES IN FAUJASITE ZEOLITES ON VGO HYDROCRACKING OVER NiMo/USY CATALYSTS

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Ultrastable zeolites Y (USY) are widely used for catalytic cracking, hydrocracking and isomerization in the petroleum refinery process. It is generally accepted that strong Brønsted acid sites, the framework bridging SiOHAl groups of zeolites, are the active sites for these reactions [1]. The role of the extraframework aluminium (EFAl) species in the catalytic transformation of hydrocarbons has been vividly debated. Several forms of the EFAl species have been proposed: cationic (Al^{3+} , AlO^+ , $\text{Al}(\text{OH})_2^+$, AlOH^{2+}) and neutral or polymeric species. Since the Brønsted acidity of the catalysts is determined by properties of the initial zeolites [2], the aim of this study was to find relationships between the acidity of zeolites (including variety of EFAl species) and performance of the Ni-Mo catalysts in vacuum gas oil (VGO) hydrocracking.

A series of USY zeolites (Si/Al~12-15) in the cation-decationated form denoted as REY-(%Ln) ($\text{Ln}_2\text{O}_3=0.35-3.3$ wt%, where Ln is a lanthanide) and H-form (commercial CBV-720, Zeolyst) were used to catalysts preparation. Zeolite powders were characterized by XRD, SEM and N_2 adsorption. The combination of solid state NMR and IR techniques has been successfully employed to determine the framework and the existence of different EFAL species in zeolites. The acidity of zeolites was studied by TPD- NH_3 and IR spectroscopy of adsorbed CO, quinoline and pyridine.

Several types of Brønsted (BAS) and Lewis acid sites (LAS) were found on the zeolites surface, the concentration and strength of which depended on the Ln content. The concentration of strongest BAS (the value of the low frequency shift of OH vibrations with adsorbed CO ($\Delta\nu_{\text{OH/CO}}$) was 340-380 cm^{-1}), the framework Si-O(H)-Al groups, declined with increasing Ln content. An increase in the content of Ln in REY zeolites leads to a decrease in the concentration of the strongest BAS by almost 2 times. Apparently, this is due to blocking of cages by Ln_2O_3 . Three types of medium strength BAS ($\Delta\nu_{\text{OH/CO}} = 190-280$ cm^{-1}) deal with EFAL species were found on the REY surface: the bridging Al-O(H)-Al groups with ν_{OH} 3670 and 3690-3695 cm^{-1} (2.7-3.1 and 3.7-3.5 ppm) and defect silanol groups Si-O(H)... Al^{3+} with ν_{OH} 3735 cm^{-1} (2.1 ppm). The concentration of the Al-O(H)-Al groups on the REY surface was unusually high and close to the concentration of framework BAS in

contrast to H-USY fajausite (CBV-720) (Table). Excess aluminum in REY zeolites does not lead to an increase in the concentration of LAS. It was found that washing the zeolites from EFAl ions by tartaric acid (TA), accompanied by a sharp decrease in the content of 6- and 5-coordinated extraframework Al atoms according to ^{27}Al NMR, led to a predominant removal from the surface of two types of OH groups - with ν_{OH} 3690 and 3735 cm^{-1} (Table). In addition, the concentration of strong LAS deal with extraframework Al^{3+} ions reduced significantly.

NiMo catalysts (3 wt% Ni and 10 wt% Mo) were prepared by co-impregnation of supports (30%USY+70% Al_2O_3) with solutions containing precursors of active metal and citric acid. Testing of stacked beds in the one-through hydrocracking of VGO was carried out in a fixed-bed flow reactor under 16.0 MPa at 390-410°C [3]. It was shown that the maximum middle distillates fraction (130-360°C) yield (48%) was achieved at 410°C for REY-(1.2% Ln)-based catalyst. REY-based catalysts are characterized by higher selectivity to gasoline compared to a H-USY based catalyst. The washing of the zeolites from some EFAl species by tartaric acid (TA) drastically reduced the middle distillates

selectivity and yield (Table). It was

Table. The effect of REY-(0.5% Ln) zeolite washing.

Zeolites		CBV-720	REY-0.5	REY-0.5 TA
Properties				
^1H NMR, $\mu\text{-mol/g}$	Si-O(H)-Al (FAI)	555	610	630
	Al-OH (EFAl)	150	480	350
^{27}Al NMR	AlO_4 (FAI)/ $\text{AlO}_6+\text{AlO}_5$ (EFAl)	1.7	0.92	1.5
IR CO, $\mu\text{-mol/g}$	LAS (EFAl)	47	60	16
IR	BAS (FAI)/ all BAS	0.62	0.28	0.34
Middle distillate fraction	Selectivity (at X=50%)	76.6	77	70.6
	Yield (410°C)	46	46.9	44.3

found that hydrocracking activity of the Ni-Mo/USY- Al_2O_3 catalysts did not correlated with the concentration of framework BAS. The better zeolite acidity probably deal with the optimal ratio of the concentration of the strongest BAS (the framework Si-O(H)-Al groups) and concentration of less acidic BAS deal with EFAL species (defect silanol groups located in the close vicinity of the LAS (Si-O(H)... Al^{3+} , ν_{OH} 3735 cm^{-1}) and the bridging Al-O(H)-Al groups (ν_{OH} 3690-3695 cm^{-1})).

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NEW NAPHTHA-REFORMING Pt/Al₂O₃ CATALYSTS WITH Mo OR In

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Reformate is one of the main gasoline components. It contains up to 65 %wt. aromatic hydrocarbons and up to 35 %wt. paraffins. The paraffin part includes n-paraffins with a low octane values. It is possible to reduce the content of C₇₊ n-paraffins in reforming products due to the intensification of isomerization reactions. The reforming catalyst selectivity must be adjusted to produce iso-alkanes with higher octane numbers from n-alkanes. To modify the aromatization and isomerization functions of the traditional Pt/Al₂O₃ catalytic reforming system the In and Mo metals addition is used.

According to the literature [1] the conversion of n-hexane increases with the In₂O₃ addition to the Pt/SO₄²⁻/ZrO₂ catalyst. The indium modification of the Pt/WO₃/ZrO₂ and Pt/H-beta systems leads to an increase in activity and selectivity in the isomerization of n-heptane and the one-stage conversion of n-butane to isobutene, respectively [2, 3]. It is reported [4] that for MoC₂ catalyst is active for the dehydrocyclization of n-hexane and n-heptane to yield benzene, toluene and xylene. The patent [6] describes modern reforming catalysts — Mo-zeolite-containing systems, characterized by reduced coke formation. Thus, there is no unambiguous opinion in the literature on the effect of indium and molybdenum on the properties of Pt/Al₂O₃.

Alumina-platinum catalysts were synthesized with a Pt (0.25 %wt.), In (0.0-2.0 %wt.) or Mo (0.0-0.1 %wt.). The samples were characterized by elemental analysis, low-temperature nitrogen adsorption-desorption, IR spectroscopy of adsorbed CO, pulsed chemisorption of CO, and others. The catalytic experiments were carried out on a flow-through microcatalytic stand with an isothermal reactor at a ratio of hydrogen:n-heptane = 5:1 (mol), LSHV 3-h⁻¹, temperatures 460, 480, 500 and 520°C, pressure 1 MPa for Pt/Mo/Al₂O₃ systems and the ratio hydrogen: n-heptane = 5:1 (mol), LHSV 3 h⁻¹, temperatures 460, 480, 500 and 520°C, pressure 1 MPa for Pt/In-Al₂O₃ systems.

For the first time the IR CO data for Pt-In/Al₂O₃ and Pt-Mo/Al₂O₃ is given.

In n-heptane reforming for 0.1-0.3% wt. In doped alumina-platinum system it was achievement the increasing of the *i*-C₅₊ and C₃-C₄ gases yield by 1.4 and 4 %wt., respectively, the reducing of the aromatic hydrocarbons yield by 5 %wt., the conversion decreasing by 2%. Pt-Mo/Al₂O₃ demonstrates the aromatic hydrocarbons yield decreasing by 19 %wt., the iso-paraffins and C₁-C₄

OP-15

hydrocarbon gases yield increasing by 11.1 and 3.6 %wt., respectively, and the n-C₇ conversion reducing by 3%.

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COMPARATIVE STUDY OF Ni-PHOSPHIDE CATALYSTS SUPPORTED ON GRANULATED Al_2O_3 IN HYDROTREATING OF STRAIGHT RUN GAS OIL**Shamanaev I., Suvorova A., Gerasimov E., Pakharukova V., Bukhtiyarova G.***Boreskov Institute of Catalysis, Novosibirsk, Russia**E-mail: i.v.shamanaev@catalysis.ru*

The search for new active hydrotreating catalysts is one of the strategies of R&D branches in modern companies [1]. Ni_2P containing catalysts were shown to have higher activity in hydrodesulphurization, hydrodenitrogenation and hydrogenation. But most of the works are made using model compounds and powder catalysts [2]. There is no study of Ni-phosphide catalysts supported on granulated Al_2O_3 .

The aim of this work is to study preparation of granulated Ni-phosphide catalysts and their catalytic activity in hydrotreating of straight run gas oil.

The catalysts were prepared by incipient wetness impregnation of granulated Al_2O_3 ($S_{\text{BET}} = 215 \text{ m}^2/\text{g}$, $D_p = 103 \text{ \AA}$, $V_p = 0.56 \text{ cm}^3/\text{g}$). Two different methods were used to prepare the catalysts – temperature-programmed reduction (TPR) and temperature-programmed phosphidation (TPP). For TPR phosphite ($\text{Ni}(\text{OH})_2$ and H_3PO_3 – I) or hypophosphite ($\text{Ni}(\text{NO}_3)_2$ and H_3PO_2 – H) were used as precursors. After impregnation the samples were dried and reduced in situ in catalytic reactor at 400–600 °C. For TPP Al_2O_3 was impregnated by aqueous solution of $\text{Ni}(\text{NO}_3)_2$ dried and calcined at 400 °C, reduced to $\text{Ni}/\text{Al}_2\text{O}_3$ at 400 °C in hydrogen flow and phosphidized by PPh_3 in hydrogenated gas oil at 380 °C. Straight run gas oil (sulfur content = 7740 ppm, nitrogen content = 116 ppm) hydroprocessing was carried out in continuous flow fixed bed reactor at 340 °C, 4 MPa, LHSV = 1,5 h^{-1} .

According to XRD results TPR method allowed us to obtain Ni_{12}P_5 phase after reduction at 600 °C ($D_{\text{XRD}} < 3 \text{ nm}$). Catalysts prepared by TPP method contained Ni_2P phase ($D_{\text{XRD}} = 7.5 \text{ nm}$). TEM analysis showed broad distribution for TPR samples (5–20 nm) and narrower distribution for TPP samples ($D_{\text{TEM}} = 3.4 \text{ nm}$). The beneficial effect of decreasing reduction temperature and using TPR method was found. Nevertheless, all samples showed relatively low activity in hydrodesulfurization – sulfur content after reaction was 2400–4500 ppm (Figure 1, for NiMoS catalysts it is about 50–60 ppm). In hydrodenitrogenation the activity was quite high – 3–7 ppm of nitrogen after reaction.

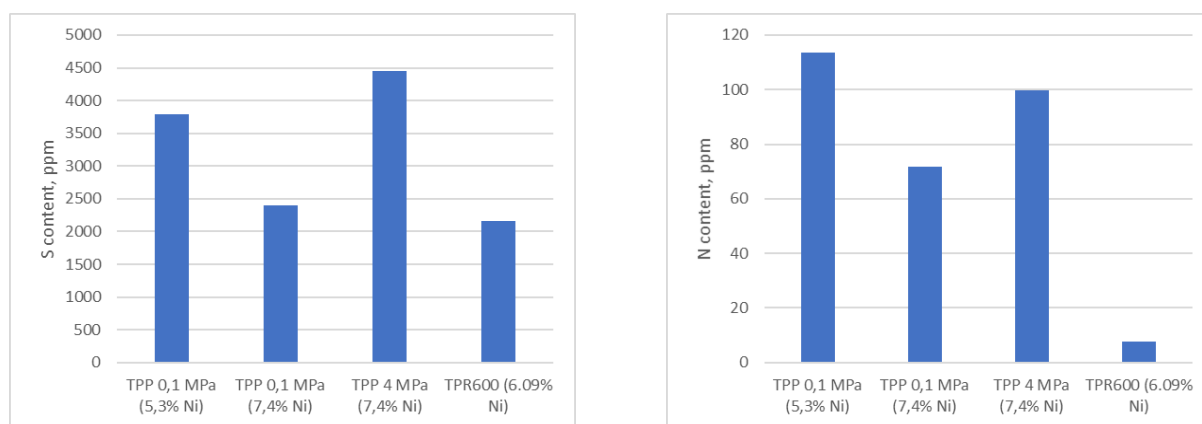


Figure 1. Sulfur and nitrogen content after hydrotreating over different Al_2O_3 -supported Ni-phosphide catalysts. $T=340\text{ }^\circ\text{C}$, $P=4\text{ MPa}$, $\text{LHSV}=1.5\text{ h}^{-1}$.

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REFORMING CATALYST FOR PRODUCING OF A LOW AROMATICS GASOLINE COMPONENT

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The work presents studies of a new fluorine-promoted catalyst for a reforming process using a technology with a fixed bed catalyst bed in order to produce a gasoline component. The new catalyst should provide reduction the content of aromatic hydrocarbons in reformat by 3-5 wt.% in comparison with modern industrial analogues in the mode with RON 95-97. A minimum decrease of reformat yield is allowed no more than 1-1.5 wt.%.

The technology for preparing a new catalyst was developed [1], and its physicochemical and catalytic studies were carried out. Comparative pilot tests of the new catalyst and the industrial reforming catalyst PR-81A were carried out on a hydrotreated fraction of 105-183 °C and under the conditions of PJSC Gazpromneft-MNPZ. Key indicators are presented in table 1.

Table 1. Key performance indicators for pilot testing of the new catalyst and PR-81A

Conditions: P - 1.5 MPa, liquid hourly space velocity (LHSV) = 3.0 h⁻¹, the hydrogen-rich gas circulation ratio = 1400 m³/m³ of raw material.

Catalyst	PR-81A		New	
Temperature, °C	490	500	480	485
Reformat C ₅₊ yield, wt.%	85,0	83,9	84,3	83,6
Hydrogen yield, wt.%	2,5	2,6	2,5	2,5
Aromatics in C ₅₊ , % mac.	67,7	69,4	63,9	66,4
RON	95,3	97,4	95,0	97,2

It can be seen that RON reaches 95–97 for the PR-81A catalyst at 490–500 °C versus 480–485 °C for the new catalyst (decrease by 10–15 °C). The yield of reformat C₅₊ was 83.9-85.0 versus 83.6-84.3% wt. (decrease by 0.3-0.7 wt.%), and the content of aromatic hydrocarbons in C₅₊ is 67.7-69.4 against 63.9-66.4% wt. (decrease by 3-3.8 wt.%) at that temperatures respectively. It should also be noted that the difference in the yield of hydrogen does not exceed 0.1 wt.%, and the content of benzene in the reformat is not more than 0.2 wt.%.

Comparative resource tests of the new catalyst and industrial catalyst PR-81A were carried out for 100 hours in the mode of accelerated deactivation (hydrogen-rich gas circulation ratio is

OP-17

300 m³/m³, P = 1.5 MPa, LHSV = 3.0 h⁻¹, RON = 96). The test results showed that a decrease in the octane number of the reformat as a result of deactivation for both catalysts occurs symbatically. Thus, the new catalyst provides in the 95-97 RON mode the reduction of the content of aromatic hydrocarbons in the reformat by 3-4 wt.% in comparison with the industrial analogue PR-81A, with a minimal decrease in the yield of reformat by 0.3-0.7 wt.%.

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NiW/Y-ASA-Al₂O₃ CATALYSTS FOR SECOND STAGE HYDROCRACKING: INFLUENCE OF Si/Al RATIO IN ZEOLITE

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Hydrocracking is one of the key processes in oil refinery for the conversion of vacuum distillates into high-quality products. Conversion and the yield of middle distillates are higher for two-stage hydrocracking than for one-stage hydrocracking. To avoid the accumulation of condensed polyaromatic compounds in recycled feedstock catalysts containing amorphous silica-alumina (ASA) in addition to zeolite Y are used for second stage hydrocracking [1]. It is well known that the Si/Al ratio can affect the acidity of zeolites. Therefore, in this study, the influence of Si/Al ratio of zeolite Y on activity and selectivity to middle distillates of hydrocracking catalysts for two-stage hydrocracking were investigated.

Commercially available zeolites Y (Zeolyst) with different Si/Al, ASA (Si/Al = 0.9) and pseudoboehmite (AlOOH) were used for supports preparation. Four supports containing 5 wt % of zeolite Y, 45 wt. % of ASA and support containing 50 wt. % ASA were prepared by extruding of wet mixture of zeolite and ASA with AlOOH, followed by drying and calcination at 550 °C. Catalysts containing 3.5 wt. % of Ni and 16.0 wt. % of W were prepared by impregnation with aqueous solutions of nickel hydroxide, ammonium paratungstate and citric acid. Impregnated catalysts were dried and calcined. The obtained catalysts were denoted as NiW/Y(x), where x - Si/Al ratio of zeolites (from XRD data).

The samples of zeolite and catalysts were studied by nitrogen adsorption, XRD, HRTEM, TPD-NH₃, XPS, IR spectroscopy of adsorbed pyridine. From the XRD data for each zeolite, the unit cell sizes were calculated. Si/Al ratio of zeolites was calculated from unit cell size according to [2]. FTIR spectroscopy of adsorbed pyridine revealed that the increase Si/Al ratio is accompanied by decreasing concentrations of Bronsted (BAS) and Lewis (LAS) acid sites in zeolites (Table 1).

The catalysts were tested in hydrocracking of model feed (squalane, dimethyl disulfide, tert-butylamine) under the following conditions: temperature 320-390 °C, pressure 6.0 MPa, feed rate 2.0 h⁻¹. Catalytic tests showed that activity of the catalysts increases with decreasing of zeolite Si/Al ratio in zeolites but the selectivity of the catalysts to middle distillates was close and no conclusion can be drawn.

Table 1. Characteristics of zeolites Y

Zeolite	Concentration, $\mu\text{mol/g}$		unit cell size, \AA	Si/Al
	BAS	LAS		
CBV-720	290	82	24.314	13
CBV-760	153	27	24.257	24
CBV-780	121	37	24.235	37
CBV-901	29	30	24.226	47

To determine catalysts selectivity hydrocracking of unconverted oil from first-stage VGO hydrocracking was carried out using fixed-bed reactor at a pressure of 6.0 MPa, a LHSV of $1,4 \text{ h}^{-1}$ and H_2 to oil ratio of 750 (v/v).

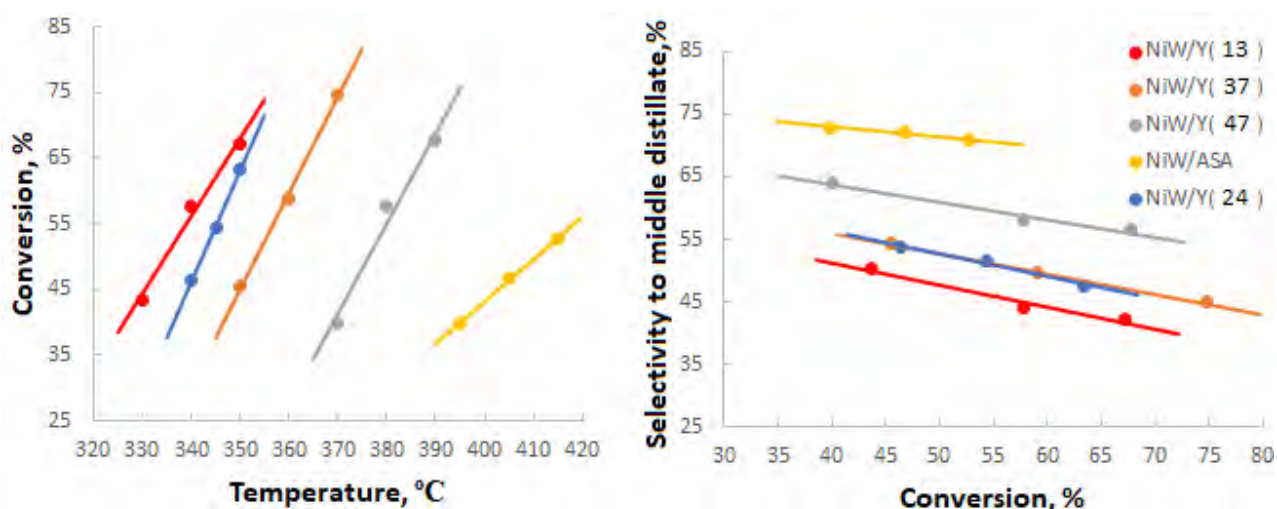


Figure 1. Activity and selectivity of NiW/Y-ASA- Al_2O_3 catalysts with different zeolite in second stage hydrocracking.

Catalytic tests (Figure 1) in hydrocracking showed that the activity of the catalysts decreases with an increase in the Si/Al ratio in zeolites due to a decrease in the concentration of acid sites, which is confirmed by FTIR spectroscopy of adsorbed pyridine. An increase in selectivity to MD with an increase in the Si/Al ratio in zeolites was established. This result may be explained by the balance between hydrogenation and cracking functions of the catalysts: hydrogenation function is similar for all the catalysts but an increase of zeolites acidity leads to secondary cracking reactions, higher yields of gas and naphtha and, hence, to drop of selectivity to middle distillates.

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DEVELOPMENT OF THE APPROACH TO MODELLING OF THE DESTRUCTIVE CATALYTIC HYDROPROCESSES OF ATMOSPHERIC AND VACUUM DISTILLATES CONVERSION

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In recent decades, there has been a tendency to depletion of easily recoverable oil reserves. As a result, oil production growth is provided due to heavy, hard-to-recover oil. Heavy oil is characterized by high viscosity and density, high content of paraffins, resins and asphaltenes, sulfur and metals (vanadium, nickel). These factors significantly complicate the processing of heavy oil into light oil products with high added value and lead to the need to setting into operation new and increase the capacity of existing catalytic processes for advanced and deep oil refining, such as hydrodewaxing and hydrocracking.

Under the current conditions of the need to process heavy oil fractions, which contain a significant amount of long-chain n-paraffins with positive pour points, oil refiners also face another urgent problem – production of diesel fuel that meets winter and Arctic grades for low-temperature properties, the demand for which is growing due to development of the Arctic territories and the development of the economic potential of the regions, most of which are located in cold climatic zones. The process of hydrodewaxing allows processing middle distillates (including atmospheric gas oil) into components of low-freezing varieties of diesel fuel [1]. Hydrocracking process allows the processing of high boiling fractions (vacuum gas oil, atmospheric residue) into more valuable products (gasoline, kerosene and low sulfur diesel fuel) [2]. Diesel fuels are the most valuable products of the hydrocracking process.

The processes of hydrodewaxing and hydrocracking are similar. These processes occur in the presence of hydrogen on bifunctional catalysts. The main reaction in both processes is the selective hydrocracking of long chain paraffins. Constantly changing composition of the raw materials and the continuous deactivation of the catalyst during the operation of industrial processes determine the unsteady nature of these processes.

To study the processes of hydrodewaxing and hydrocracking, models based on the grouping of reacting substances into fractions [3], as well as more detailed models based on the combination of reacting substances into groups: paraffins, naphthenes, aromatic hydrocarbons [4], have been developed. However, the developed models do not take into account the distribution of the content of n-paraffins and their reactivity in the target hydrocracking reaction. Thus the

approach [5], based on the component aggregation into pseudo components according to their reactivity and taking into account the catalyst deactivation, which was created and applied for light fraction conversion processes, is reasonable to expand and apply for hydroprocesses of heavier oil distillates.

A new approach to modeling of the destructive catalytic hydroprocesses of atmospheric and vacuum distillates conversion includes:

1. identification of the distribution function of the long-chain n-paraffins content in raw materials;
 2. identification of the probability of bond cleavage in a particular position in n-paraffin molecules by calculating the values of the thermodynamic probability of bond cleavage in a different position using quantum chemical methods;
 3. development of mathematical model equations of hydrodewaxing and hydrocracking processes taking into account reactions proceeding without the participation of hydrogen, reactions involving hydrogen, hydrocracking reactions of n-paraffins;
 4. identification of the functional relationships between the composition of the obtained diesel fuel and its low temperature properties;
 5. development of an algorithm and a computer modeling system for determination of the model parameters (kinetic parameters, deactivation coefficients) and conducting predictive calculations.
- The developed models according to this approach provide prediction of product yield and composition, activity and service life of the catalyst, low-temperature properties of the obtained diesel fuel as well as optimization of the processes.

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Ni AND Pt CATALYSTS SUPPORTED ON SILICOALUMINOPHOSPHATES FOR n-HEXADECANE HYDROISOMERIZATION



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Introduction

Hydroisomerization is catalyzed by bifunctional catalysts that provide the necessary functionalities for the reaction to occur: metal sites for dehydrogenation/hydrogenation and acid sites for the skeletal re-arrangement of the carbon chain. The structure and pore size of the support can guide the process either to the selective hydroisomerization of the paraffin or its further cracking to lighter products. In this study, we use Pt and Ni catalysts supported on micro/mesoporous SAPO11 zeolites with SiO₂/Al₂O₃ ratio of 0.3 and varied pore structures to investigate the effect of the active metal (Pt or Ni) and the structural and acidic properties of the support on the activity and selectivity in n-C₁₆ hydroisomerization. The ultimate goal is to use the optimum catalyst to improve the octane number and cold flow properties of kerosene and diesel-range fuels under mild operating conditions.

Experimental

Silicoaluminophosphates were synthesized via two synthetic methods in order to study the effect of porosity characteristics. **SAPO-11** was synthesized via hydrothermal route by using a structure directing agent, while in-situ solid synthesis method was also used with (**Ni-SAPO-11S**) or without (**SAPO-11S**) in-situ substitution of Ni in zeolite framework. Tetraethoxysilane (TEOS), orthophosphoric acid (85%), pseudoboehmite (Catapal B) and di-n-propylamine (DPA) were used as starting materials. Metal-modification of SAPO supports was applied with 0.5 wt.% Pt or 5-10 wt.% Ni via wet impregnation in appropriate amounts of ethanol solution, followed by calcination at 500 °C (for Ni) and 400 °C (for Pt) for 4 hours under air flow. The catalysts were characterized with ICP, XRD, N₂ adsorption/desorption, TPD-NH₃, TPR-H₂ and pyridine-FTIR. Catalytic performance was investigated in a high-pressure fixed bed reactor unit at constant conditions (WHSV= 4 h⁻¹, T= 300 °C, P= 30 bar and H₂/n-C₁₆ molar ratio 15). Catalysts were pre-reduced in situ in H₂ at 300 °C for Pt and 400 °C for Ni.

Results/Discussion

All catalysts present characteristic diffraction peaks at 2θ 8.1°, 9.4°, 13.1°, 15.6°, 20.3° and 21.123.2°, indicative of the typical crystal phase with AEL structure. Depending on the synthesis

method, textural and porosity characteristics can be modified by inducing mesoporosity or/and textural porosity in the silico-alumino-phosphate support. N₂ adsorption/desorption isotherms are typical of microporous zeolitic structures, with generated secondary mesoporosity with average pore diameter of 6.5 - 8 nm. The SAPO supports retain their general porous and structural characteristics after modification either with Pt or Ni (Fig. 1). Acidity measurements reveal mild acidity, reaching up to 78 $\mu\text{mol/g}$ Brönsted and 33 $\mu\text{mol/g}$ Lewis acid sites, with equal distribution in acid site strength, ranging from very weak to strong.

Testing of both Pt/SAPO-11 and Ni/SAPO-11 catalysts demonstrate high activity in the nhexadecane hydroisomerization reaction, with high selectivity to the desired isomers (Fig. 2). Among Ni catalysts, deposition on microporous SAPO-11 with enhanced mesoporosity of 8 nm pore size (5Ni/SAPO-11) shows similar catalytic performance with that achieved over Pt. On the contrary, the in-situ substitution of Ni in the silica framework via solid synthesis method (Ni-SAPO11S) exhibits much lower hydroisomerization activity. The major by-products are cracked linear alkanes, with extremely low formation of dry gases (C₁-C₄). Optimum catalyst is the 0.5 wt.% Pt/SAPO-11, combining both the highest conversion (85.3 wt.%) and highest selectivity (91.9 wt.%), reaching thus a high iso-hexadecane yield of 78.4 wt.%.

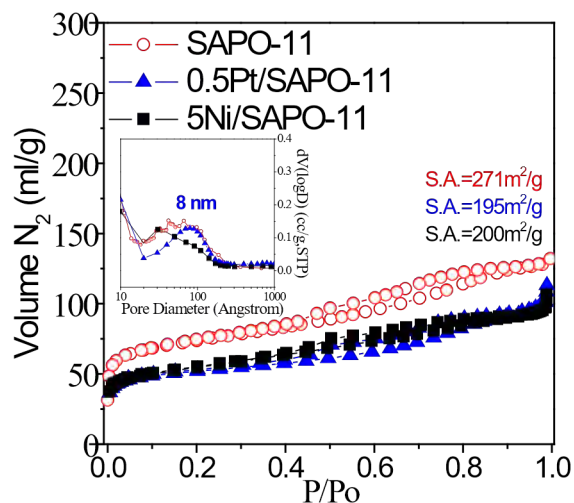


Figure 1. N₂ adsorption/desorption

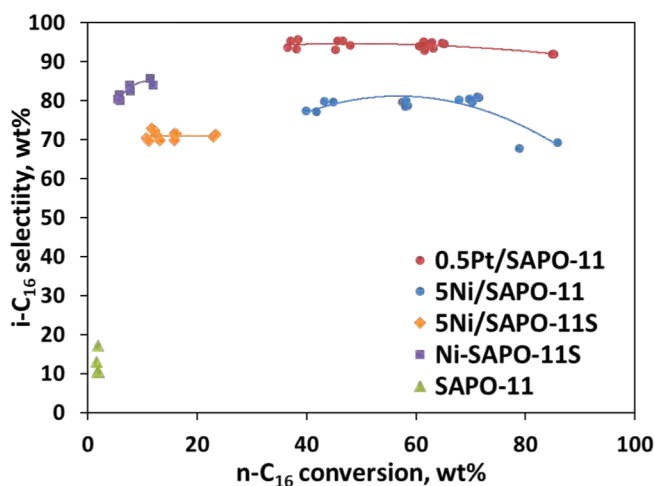


Figure 2. i-C₁₆ selectivity versus n-C₁₆ isotherms conversion

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**EFFECT OF Mo/W RATIO ON THE CATALYTIC PROPERTIES OF ALUMINA
SUPPORTED HYDROTREATING CATALYSTS PREPARED FROM MIXED $\text{SiMo}_n\text{W}_{12-n}$
KEGGIN TYPE HETEROPOLYACIDS**

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Development of more active hydrodesulfurization (HDS) catalysts remains a challenge for the deep refining of lower quality feedstocks. Therefore, active development of new catalytic systems is underway for the production of ultra-pure diesel fuel. Recently, there has been a steady tendency toward the development of catalysts including both molybdenum and tungsten [1-3]. The synergistic effect between Mo and W was found to be enhanced by using mixed MoW oxide precursors of the active phase, such as $\text{H}_4[\text{SiMo}_n\text{W}_{n-12}\text{O}_{40}]$ Keggin type heteropolyacids (HPAs) [4]. Catalysts prepared from $\text{H}_4[\text{SiMo}_3\text{W}_9\text{O}_{40}]$ HPA were superior in activity compared to a sample obtained from a mixture of $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]$ and $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ monometallic HPAs with the same Mo(Mo+W) ratio, due to the formation of a highly active mixed MoWS_2 phase, which presence was evidenced by HAADF and EXAFS [5].

In order to study the effect of the Mo/W ratio on the formation of the mixed active phase, synthesis of $\text{H}_4[\text{SiMo}_6\text{W}_6\text{O}_{40}]$ and $\text{H}_4[\text{SiMo}_9\text{W}_3\text{O}_{40}]$ HPAs was developed. The structure of prepared compounds was confirmed by Raman and IR spectroscopy, as well as by XRD. MoW/ Al_2O_3 catalysts were then synthesized by incipient wetness impregnation of alumina support with water solutions of prepared mixed Keggin HPAs. Their corresponding counterparts based on mixture of monometallic $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]$ and $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ HPAs with Mo(Mo+W) atomic ratio of 0.5 and 0.75 were also prepared for comparison purpose. Determination of the precursor structure after deposition on the support was performed by Raman spectroscopy. The gas phase sulfided samples were characterized by HRTEM, HAADF and XPS and were tested in co-hydrotreating of dibenzothiophene (DBT) and naphthalene.

It was found that the Mo/W ratio has a direct effect on the structure of the active phase, and therefore on the catalytic properties. According to the HAADF results, it was noted that at a Mo(Mo+W) atomic ratio of 0.5, a similar core-shell structure than the one previously evidenced on

the Mo₃W₉ sample is observed, with Mo mainly located in the core and W on the outer part of the sulfided slabs. A further increase in the molybdenum content to a Mo/(Mo+W) ratio of 0.75 led to the formation of a more disordered structure of the active phase. We found that the highest catalytic activity is achieved for Mo₆W₆/Al₂O₃ sample with an equal atomic ratio of metals, in both HDS and hydrogenation reactions (Fig 1). This was attributed to the type of mixed MoWS₂ phase evidenced on this sample, which was not further retained on the Mo₉W₃ sample, exhibiting greater hydrogenating activity as well as a large number of mixed active centers.

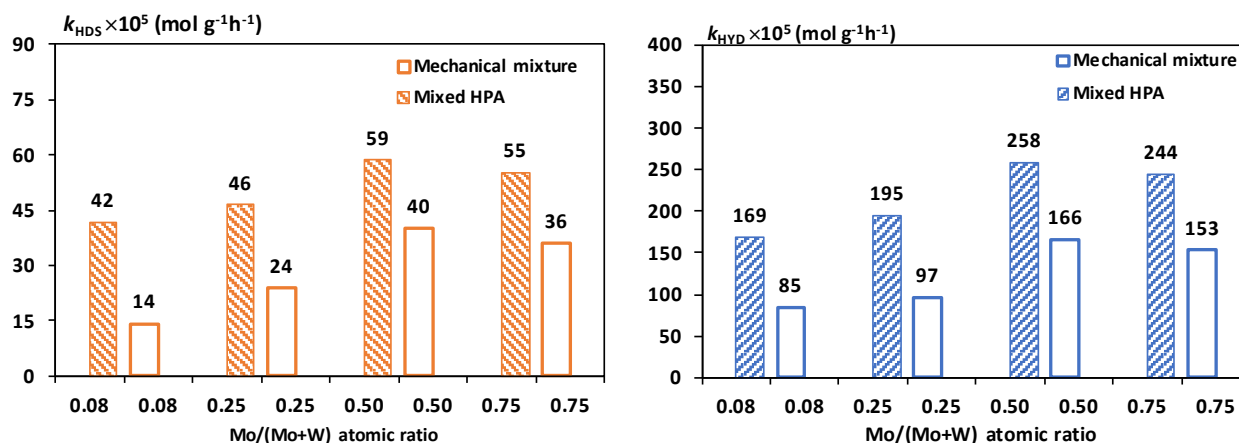


Fig. 1. Dependence of reaction rate constants in DBT HDS and naphthalene HYD on Mo/(Mo+W) atomic in MoW/Al₂O₃ catalysts

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FUELS OBTAINED FROM HYDROCRACKING OF DIFFERENTS BLENDS OF VGO AND POLYOLEFINIC WASTES



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Introduction

In the last decades, plastic has become indispensable in our daily life because of its high number of uses and good features. Indeed, several industries, e.g., packaging, building & construction or automotive industries [1], have intensified its use in the recent years. However, an increasing demand followed by an improper waste management in almost every country, are causing one of the most important environmental issues ever. In this context, scientific community is searching for high-scale solutions capable of valorize this waste in an economically profitable way. Among the range of alternatives proposed, the possibility of co-feeding this waste to already depreciated refinery units appears as a promising route to face this problem. Among the units available in refineries, hydrocracking is the most suitable one to treat blends of municipal solid wastes and the standard refinery stream (vacuum gasoil, VGO) [2]. Hence, the present work tackles a comprehensive study of the possibility of co-feeding plastic-derived to hydrocracking units and how yields and the composition of the products are affected by these.

Experimental

The materials used in this work have been: (i) VGO, supplied by Petronor refinery and with a boiling point range of 314–519 °C; (ii) HDPE pyrolysis oil (LP), provided by GAIKER Technological Center and with boiling point range of 70–513 °C; and (iii) virgin HDPE (46,200 g mol⁻¹ and 940 kg m⁻³), supplied by Dow Chemical. With them, five different feeds have been prepared (i) VGO; (ii) LP; (iii) a blend of 20 wt% LP and 80 wt% VGO (Blend 1); (iv) a blend of 20 wt % HDPE and 80 wt% VGO (Blend 2); and (v) a blend of 10 wt% LP, 10 wt% HDPE and 80 wt% VGO (Blend 3). A commercial bifunctional catalyst has been used in this work (NiW/HY), which has been sulfurized prior to reactions. The catalyst has been characterized by several techniques.

Runs have carried out in a 100 cm³ stirred autoclave reactor at 400, 420 and 440 °C, at a pressure of 80 bar, for 120 min long, stirring at 1300 rpm and with a continuous flow of H₂ (200 ml min⁻¹). The catalyst to feed ratio used in the reactions have been of 0.1 g_{cat} g_{feed}⁻¹. At the end of the runs, both gaseous and liquid products have been collected and analyzed by chromatographic means.

Results and discussion

Figure 1 depicts the yields of the lumps of products (gas (C₁-C₄), naphtha (C₅-C₁₂), diesel (C₁₃-C₂₀), HCO (+ C₂₃), unconverted plastic (wax) and coke), the hydrocracking conversion in black squares and the conversion of HDPE in white triangles. Attending to pure feeds (VGO and LP), it can be seen that the best hydrocracking conversion has been achieved with LP (80 wt%), nevertheless, an excessive production of gases has been obtained (46 wt%). On the other hand, the lowest conversion has been obtained with the VGO (69 wt%), with a reduced gas production (19 wt%). Focusing on the results obtained with the blends, the higher hydrocracking and HDPE conversion has been obtained with Blend 2 (79 and 81 wt%, respectively), maximizing the production of gases again (26 wt%). The hydrocracking conversion of Blend 1 was slightly lower than that of Blend 2 (76 wt%), but the gas fraction was reduced in to 16 wt% and the naphtha yield was the

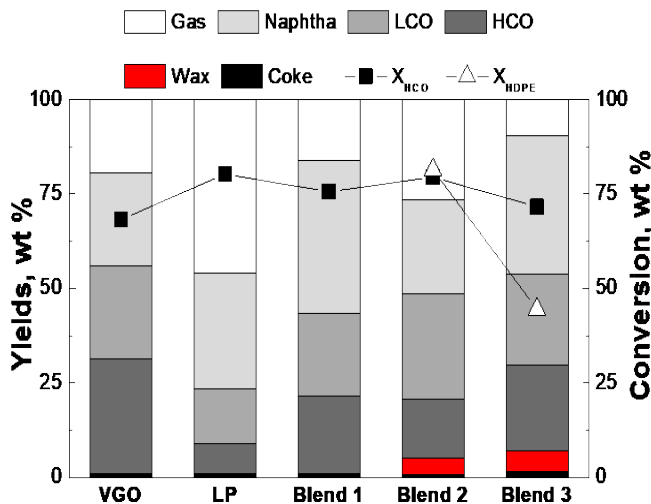


Figure 3. Product distribution and hydrocracking and HDPE conversions in the hydrocracking of the different feeds
Reaction conditions: 440 °C; 80 bar and C/F ratio, 0.1.

highest (40 wt%). Finally, the lowest hydrocracking and HDPE conversions of the blends have been obtained with Blend 3. A change in the composition of naphtha was appreciated depending on the feed used in each run. From VGO, the naphtha analysis reveals that the composition is mainly aromatic and i-paraffinic (34 and 30 wt%, respectively). Meanwhile, LP produces a strongly increase in i-paraffins (40 wt%) and a decrease in aromatics (26 wt%). According to the blends, blend 2 obtains the higher content in aromatics and i-paraffins (35 wt% and 34 wt%, respectively) and the lowest n-paraffin content, similar behavior to VGO run.

Therefore, enlightening results have been obtained since they reveal promising results in the co-feeding of plastic-based feeds with the current one (VGO) to hydrocracking unit. This way, Blend 1 and Blend 2 offer the most promising results in matter of conversion and naphtha production. Furthermore, this work opens the way to new studies with the best two blends to optimize the operating conditions and maximize the production of automotive-like fuels.

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FROM BULK PROPERTIES TO SINGLE EVENT MICROKINETICS FOR VGO HYDROCRACKING



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Hydrocracking (HCK) units are an essential part of a modern oil refinery. Fuels, synthetic crude oil, lube oils and even chemicals are produced using HCK units as part of the refining scheme. Increasingly heavy feeds are currently being processed. This goes in line with a higher heteroatom and metal contents as well as higher final boiling points. The use of HCK units in recently developed schemes denoted as 'Crude-Oil-To-Chemicals' (COTC), implies that they need to fit within a wide range of feeds and configurations. For the corresponding design, the extrapolative capabilities of a fundamental approach to feedstock reconstruction and microkinetic models are necessary.

The available developments at LCT related to molecular reconstruction of hydrocarbons and Relumped Single Event Micro-Kinetics (RSEMK) have been tested as robust approaches to evaluate important scenarios for steam cracking [1] and hydrocracking [2] respectively. SIMCO is a tool developed to perform molecular reconstruction of hydrocarbon mixtures, taking as input variables commercial indexes used to describe these feeds in an operational context (e.g. ASTM D2887, API gravity, PIONA) [1]. On the other hand, the RSEMK uses a fundamental micro-kinetic approach specially designed to model hydrocracking and hydroisomerization reactions [3].

In this work, the combination of both methodologies is presented in the context of a HCK process for heavy vacuum gas oil. First, the reconstruction of the feed is performed to determine a molecular based composition. The result is fed to a reactor model with the RSEMK engine embedded. Using the molecular representation of the reactor effluent, bulk properties are calculated for the product such as boiling point curve and API gravity.

As shown in Figure 1, the distillation curve was built for each of the outlet stream. A significant reduction in the average boiling point is observed, mainly in the lighter cuts due to hydrocracking reactions. The hydroisomerization reactions also play an important role in the shape of the boiling point curve mainly for lighter fractions. Heavier fractions in the inlet stream shows minor changes in the boiling point in comparison to lighter fractions.

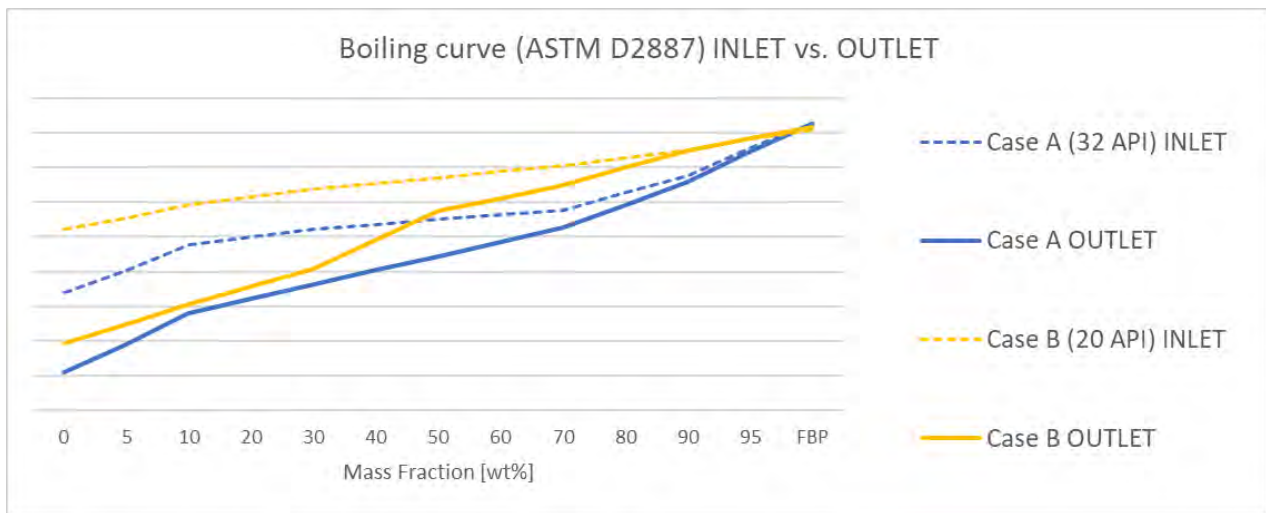


Figure 1. Boiling point curve for reactor Inlet and Outlet using feeds with different API gravity. The molecular detail considered in the kinetic engine results in a molecularly detailed product. That feature allowed to inspect with high reliability the change in the density between feed and products as it is shown in Figure 2. In this case it is observed that an important increase in the API gravity (decrease in density) is reached in all cases. The API increase (delta API) is higher in the heavier feed where some polyaromatic molecules get partially hydrogenated.

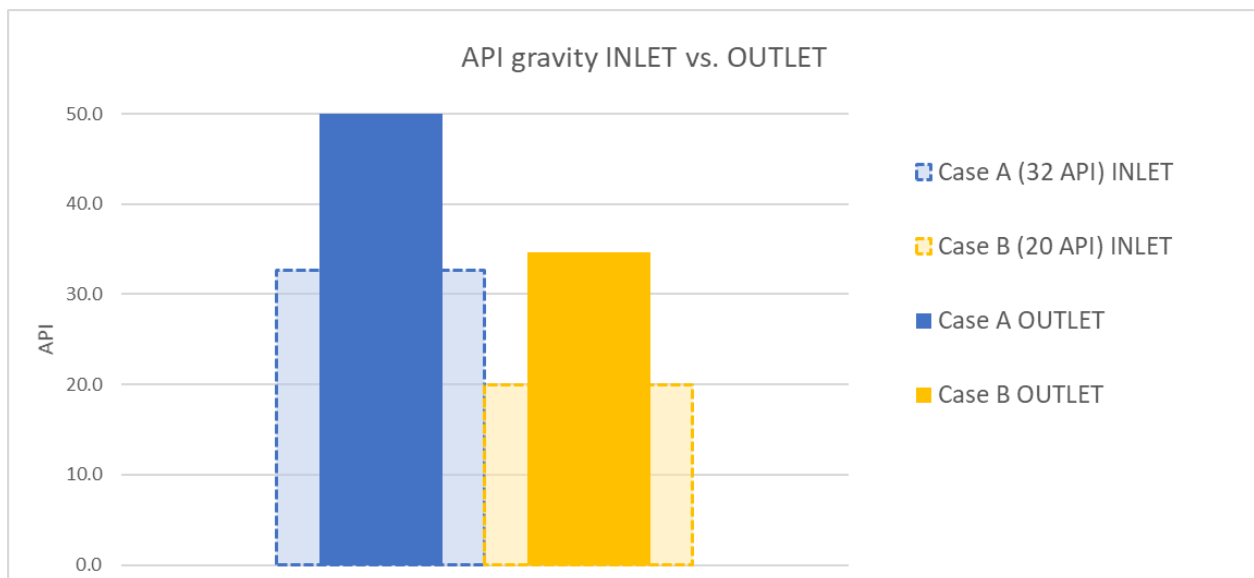


Figure 2. API gravity of feed and product for the hydrocracking of feeds with different API gravity

These results demonstrate that, given the fundamental approach of both steps, a very detailed insight of the process and its products can be obtained.

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THE EFFECT OF THE SUPPORT PRECURSOR ON THE PROPERTIES OF BIMETALLIC CATALYSTS Pt-Au/MgAlO_x IN THE PROPANE DEHYDROGENATION



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Heterogeneous catalysts containing gold as an active component are the subject of intensive research for several decades. It is well known that the catalytic systems where gold is anchored on TiO₂, CeO₂, Fe₂O₃, Al₂O₃, ZrO₂ are active in different reactions of oxidation, hydrogenation of nitro compounds, hydrogenolysis, isomerization. The use of bimetallic catalysts containing additional active metal (Pt, Pd, Ni) besides gold allows increasing significantly activity and selectivity of these catalysts compared to monometallic catalysts.

The aim of this work was the synthesis of monometallic catalysts Pt/MgAlO_x and Au/MgAlO_x and bimetallic catalysts Pt-Au/MgAlO_x, where layered double hydroxides (LDH) were support precursors, studying of effect of the support precursor on the composition of anchoring of metal complexes as well as on the properties of active sites formed in the reaction of propane dehydrogenation.

MgAl-LDH with CO₃²⁻ anions into interlayer space (MgAl-LDH-CO₃), MgAl-LDH with OH⁻ anions into interlayer space (MgAl-LDH-OH) and MgAl-mixed oxides (MgAlO_x) were used to the active metal complexes fixing. MgAl-LDH-CO₃ were synthesized by coprecipitation by adding of water solution of magnesium and aluminum nitrates to water solution of sodium carbonate at constant values of pH = 10 и T = 60 °C. MgAlO_x were formed by calcination of MgAl-LDH-CO₃ at 550 °C. MgAl-LDH-OH were prepared by hydration of the mixed oxides in distilled water. Mg/Al was varied from 2 to 4, content of the active metals was 0.3 wt.% in monometallic catalysts and 0.6 wt.% in bimetallic catalysts (Pt/Au = 1). Anchoring of the [AuCl₄]⁻ and [PtCl₆]²⁻ complexes on the MgAl-LDH-CO₃, MgAlO_x и MgAl-LDH-OH was made by adsorption from excess of an aqueous solution. Structural properties of the samples was carried out by X-ray diffraction (XRD) analysis on a D8 Advance (Bruker) diffractometer using a parallel Cu-Kα radiation in the 2θ angle range of 5 to 80°. The electronic diffuse-reflectance spectra (DRES) of the supported metal complexes were measured on a UV-2501PC spectrophotometer (Shimadzu, Japan) with an ISR-240A attachment in a range of 11000– 54000 cm⁻¹. TEM images of the samples were made using a high resolution transmission electron microscope (HRTEM) JEM-2100 "JEOL" (accelerating voltage 200 kV, resolution 0.145 nm). Platinum dispersion in the reduced samples was estimated by pulse chemisorption of H₂ and CO probe molecules at room temperature assuming the stoichiometry of [Pt]:[H] = 1:1 (AutoChem-2920 (Micromeritics) chemisorption analyzer). The

catalytic properties of the systems were investigated in propane dehydrogenation (sample loading 0.5 g., $T = 550\text{ }^{\circ}\text{C}$ the molar ratio $\text{H}_2/\text{C}_3\text{H}_8 = 0.25$, atmospheric pressure, feed space velocity of 8 g h^{-1}).

It was determined that adsorption of chloride gold and platinum complexes on MgAl-LDH did not lead to destruction of layered structure. It was found by using of DRES that hydrolyzed forms of Au-complexes were formed at a contact with the basic MgAl-supports and composition of adsorbed gold complexes changes in time.

It was found that both the Mg/Al ratio in the support and the form of the support precursor substantially affect the activity of the catalysts in the reaction of propane dehydrogenation. The activity of monometallic catalysts Au/MgAlO_x in the reaction is negligible. As for monometallic platinum catalysts Pt/MgAlO_x for bimetallic systems $\text{Pt-Au}/\text{MgAlO}_x$ propane conversion decreases with increasing Mg / Al ratio. In both cases, it can be explained by the decrease of the platinum dispersion with an increase in the Mg/Al ratio in the support. The dispersion of gold particles by chemisorption could not be determined.

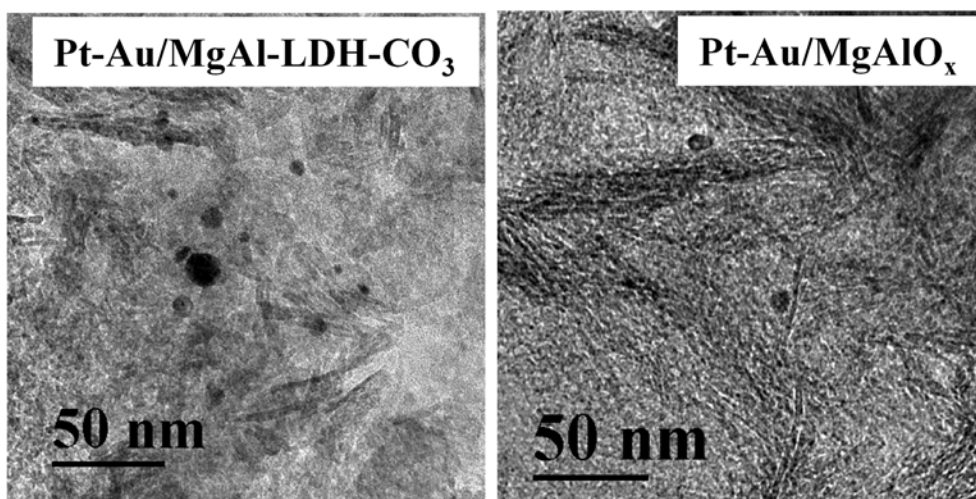


Fig. 1. TEM images of the bimetallic catalysts.

More active catalysts are formed when metal complexes are fixed in the interlayer space of the LDH (when the support precursor were MgAl-LDH-OH or MgAlO_x), than when complexes are fixed on the external surface of the support (when the support precursor was MgAl-LDH-CO_3). The highest propane conversion, as well as the lowest degree of deactivation is observed for catalysts prepared using a MgAlO_x as support precursor. This is probably due to the less size of gold particles formed during the anchoring of the $[\text{AuCl}_4]^-$ complexes on the MgAlO_x (Fig. 1). Moreover, the activity of bimetallic catalysts $\text{Pt-Au}/\text{MgAlO}_x$ exceeds the activity of monometallic catalysts Pt/MgAlO_x , regardless of the form of the support precursor.

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CATALYTIC HYDROGENOLYSIS OF LIGNIN TOWARDS THE PRODUCTION OF PHENOLIC BIO-OILS



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Lignin is the most abundant, natural, aromatic/phenolic polymer composed of p-coumaryl, coniferyl, and sinapyl alcohols as primary building blocks, linked with ether (C-O) and carbon-carbon bonds. Lignin is widely available in Mtonnes as by-product from the Kraft process in the pulp and paper industry (Kraft lignin), as well as from the production of 2nd generation bioethanol (hydrolysis lignin). The chemical structure of lignin offers numerous exploitation opportunities towards the production of aromatic and phenolic monomers while its direct use as reactive additive in epoxy or phenolic resins is also of great importance. In addition, the lignin derived bio-oils that contain phenolic monomers and oligomers, via fast pyrolysis, liquefaction or hydrogenolysis, can be utilized as bio-crude for the production of (cyclo)alkane hydrocarbon fuels. Catalytic hydrogenolysis of lignin can be achieved at low reaction temperatures with a hydrogen source, usually H₂ gas or hydrogen donor solvents [1]. In the present work, we investigated the catalytic hydrogenolysis of lignins derived from different types of hardwood and softwood biomass, including commercially available softwood Kraft lignin and hardwood lignins isolated from agricultural wastes via the combined hydrothermal-extraction procedure [2-3].

Catalytic hydrogenolysis experiments were carried out in an autoclave batch reactor, with external H₂ (30 bar) and/or ethanol as hydrogen donor solvent to induce transfer hydrogenolysis/hydrogenation, on metallic catalysts supported in micro/mesoporous carbons. The present study focused on the effect of reaction parameters (temperature, time), catalyst properties (acidity/basicity, porosity, mass, metal loading) and lignin type/nature on the final composition and properties of bio-oil.

Indicatively, in the hydrogenolysis of Kraft lignin, low reaction temperatures (<260°C) or prolonged reaction time resulted in lower monomer yields either due to the mild reaction conditions or due to the re-polymerization of monomers in the latter case. Furthermore, catalysts (i.e. carbon supports) with alkaline surface enhanced the depolymerization to monomers, in contrast to the more acidic materials which led to lower monomer yields and conversion. Considering the lignin nature, organosolv hardwood lignin showed higher reactivity and phenolic

monomers yield (30-40%) compared to the softwood kraft lignin (5-15%). It was also shown that the composition profile of the feedstock lignin, can be actually transferred to the produced bio-oil, in terms of the type of monomers produced (i.e. guaiacol or syringol type). All the hydrogenolysis derived bio-oils contain mainly alkoxy-phenols (>85%) and acids (<15%), as can be observed in Figure 1A. The compounds distribution and ratio were proved to be influenced by the overall process parameters. Finally, the combination of GC-MS and 2D HSQC NMR techniques provided information with regard to the cleavage of linkages existing in the parent lignin which were reduced or minimized in the bio-oil (Figure 1B).

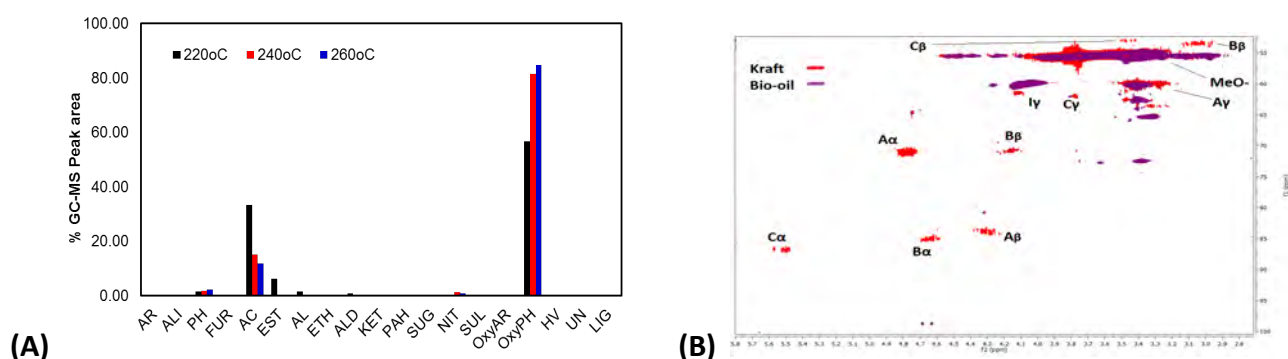


Figure 1. (A) Effect of reaction temperature on the product distribution of bio-oil and (B) effect of hydrogenolysis process on the cleavage of linkages existing in parent lignin.

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Acknowledgements

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Gamma-valerolactone (GVL) accessible from renewable lignocellulosic biomass is a promising platform for the sustainable production of fuels and antiknocking additives (RON 100). It is expected that 20% of transportation fuel and 25% of chemicals by 2030 will be produced from lignocellulosic biomass [1-3]. One-step fructose to levulinic acid (LA) conversion on sulfonated H- β zeolite under mild conditions was reported [4] giving the product which can be converted into 1,4-pentanediol [5]. The current study is aimed at LA into GVL hydrogenation (Fig. 1) over VIII group metals (Ru, Ir, Re, IrRe, IrSn, Pt, Pd, PtRe, Ni, Co) supported on carbon, alumina and silica under comparable reaction conditions. LA (6.9 mmol) in 1,4-dioxane (15 mL) was typically hydrogenated at 165°C, under 16 bar of hydrogen in a batch reactor. Ru on zeolites (HZSM-5, H-Beta, H-Y, H-USY) prepared by impregnation followed by reduction in H₂ at 450°C were also tested [6].

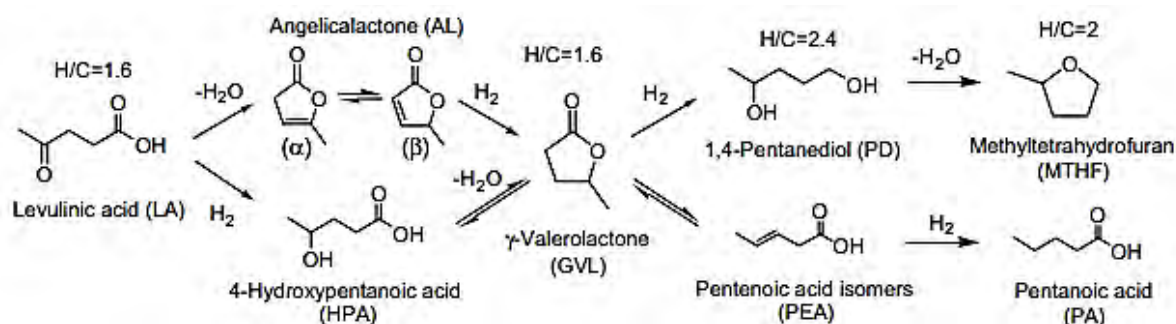


Fig. 1. Scheme of levulinic acid conversion into GVL, 2-MTHF, 1,4-pentanediol and pentanoic acid

Screening of mono- and bimetallic catalysts based on alumina showed that IrRe/Al₂O₃ is one of the most active and selective catalysts (Fig. 2, 3). Activity and selectivity to GVL of VIII group metals supported on Al₂O₃ increase in the following order: IrSn < Ru < Pd < PtRe < Ni < Re < Co < Pt < Ir < IrRe. Significant deactivation was observed over Ir, PtRe, Pt and Re after 30 min. On the contrary, in the case of Pd, an acceleration of the reaction was observed, which may be due to its reduction during hydrogenation. Activity and selectivity to GVL of metals on SiO₂ follow the order: Ir < Pt < PtRe < IrRe (Fig. 3). The kinetic regularities of LA hydrogenation in the presence of the most selective IrRe/Al₂O₃ catalyst were investigated. A reaction scheme was proposed including step-wise hydrogenation of LA to GVL followed by conversion of the latter to 2-MTHF and pentanoic acid. This network is in a good agreement with several series of experiments data obtained under different reaction conditions, namely 135°C, 150°C, 165°C and 180°C and total pressures of 20, 25, 30 bar at each temperature. The kinetic model allows an adequate description of the catalytic behaviour in LA into GVL hydrogenation depending on the operation conditions.

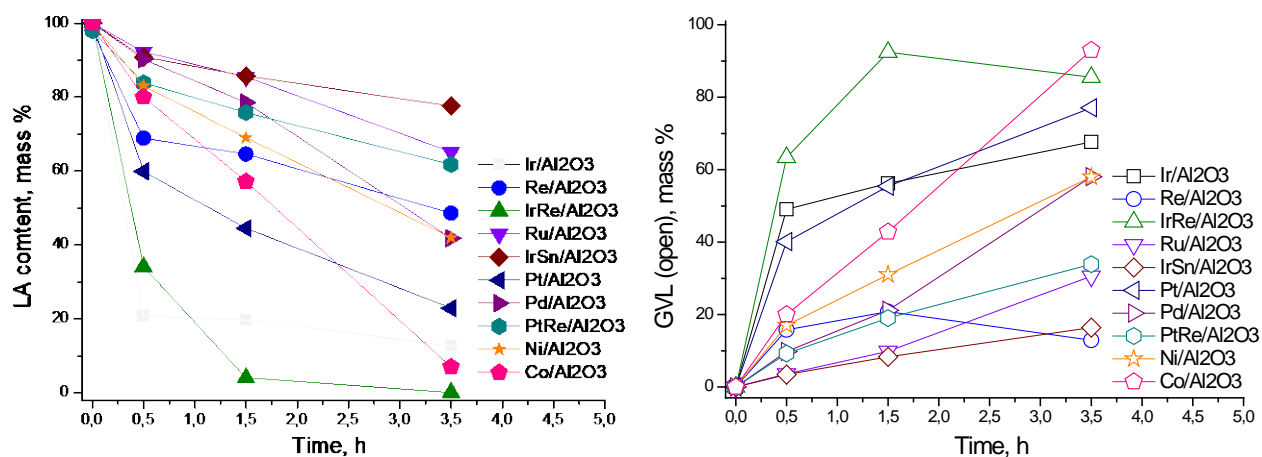


Fig. 2. Screening of LA hydrogenation over alumina based VIII group metals catalysts, kinetic profiles - LA (left), GVL (right)

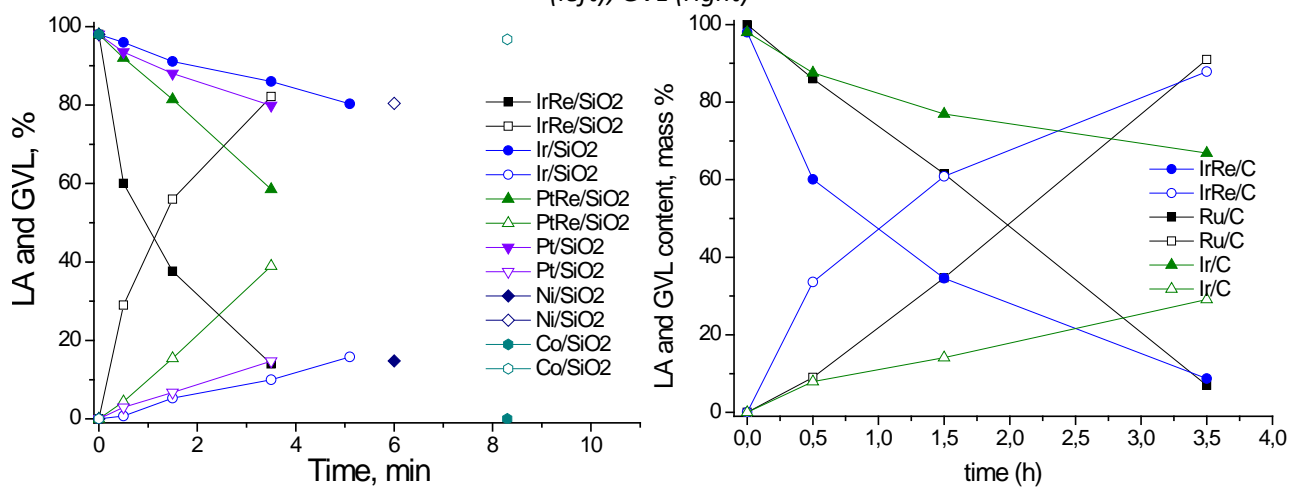


Fig. 3. Screening of LA hydrogenation over silica (left) and carbon (right) supported VIII group metals catalysts, LA – solid symbols, GVL – open symbols

The obtained results highlight a possibility to develop a simple catalytic technology for the production of novel antiknocking additives from industrially available multi-tonnage biomass-derived oxygenate – levulinic acid, even if challenges for scaling up and commercial implementation should not be underestimated.

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DECOMPOSITION OF HYDROGEN SULFIDE INTO ELEMENTS IN THE CYCLIC CHEMISORPTION-CATALYTIC REGIME



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Active development of hydroprocessing technologies and hydrogen energy require the development of new efficient ways for production of hydrogen, preferably from non-hydrocarbon feedstocks.

Hydrogen sulfide is the very attractive feedstock for this purpose. First, it is the conventional waste from oil and natural gas processing facilities. Second, the bonding energy of hydrogen in H₂S is the lowest among all hydrogen-containing compounds met in nature.

Unfortunately, the reaction of hydrogen sulfide decomposition



is characterized with severe equilibrium limitations. The complete H₂S decomposition requires the extra-high temperatures (above 1500°C), leading to high energy consumption, necessity to apply expensive thermostable materials and risk of backward element recombination at cooling stage. In (very typical) case, when the carbonaceous compounds (CO₂, hydrocarbons) are present in the gas feedstock, such temperatures may also cause side reactions with formation of undesired products (coke, CO, COS and CS₂). Due to these reasons, still there is no feasible technology for H₂S decomposition in wide practical application.

The new process approach [1] is based on the chemisorption enhancement of the decomposition reaction (1). The process, involving metal sulfide chemisorbent-catalyst, includes cyclic alteration of two reaction stages technologically separated in time and space:



As shown by thermodynamic calculations [1], the reaction (2) is exothermic and the corresponding equilibrium conversion of H₂S may reach 100% at ambient temperature. The regeneration reaction (2) require higher temperatures, but the backward formation of H₂S is completely excluded by hydrogen absence in the reaction media during the regeneration stage.

The earlier work [2] stated the possibility of hydrogen sulfide decomposition at ambient temperatures, but it contained no quantitative data on hydrogen yield. The aim of the current study was experimental check of this possibility.

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The performed experiments showed that under cyclic alteration of chemisorption and regeneration stages, the formation of hydrogen at ambient temperatures is negligible at all tested sulfides, most probably, due to kinetic limitations. The conversion of H_2S with emission of hydrogen at the chemisorption stage becomes visible starting from $200^\circ C$ and it rises with temperature increase reaching maximum at $\sim 350^\circ C$ (see Fig.1), this rise caused by kinetic factors. With further temperature rise the influence of backward reaction of H_2S formation becomes significant and the observed conversion decreases. At the same time, it is seen that H_2S conversion in all presented temperature range significantly exceeds the equilibrium value, this is caused by the chemisorption enhancement of the H_2S decomposition reaction.

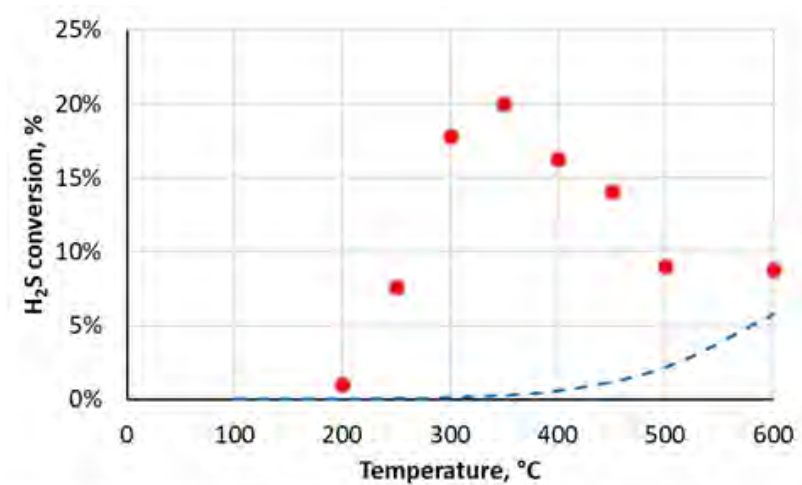


Fig.1. Conversion of H_2S at the chemisorption stage under the chemisorption-regeneration cycling. Points – experimental data, dashed line equilibrium for reaction (1). Chemisorbent – FeS , reaction media – 5% H_2S in nitrogen.

High-temperature ($600^\circ C$) regeneration completely restores the chemisorbent properties, showing no degradation of this material during 20 cycles.

Though the received results appeared to be less optimistic than it was expected in respect to reaction temperatures, the propose process approach is still feasible for practical application in hydrogen manufacturing purposes. The presentation discusses the possible process flow sheets.

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LINEAR ALKANES HYDROISOMERIZATION OVER CoMoS CATALYSTS SUPPORTED ON MODIFIED ALUMINOSILICATES

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The isomerization of linear alkanes in petroleum cuts is of great importance to modern oil refinery industry. This reaction allows to increase octane number of gasoline and decrease pour point of diesel fuels and engine oils. Noble metals based catalysts supported on acidic carrier are commonly used ones for hydroisomerization reaction of alkanes. High cost and low stability to catalytic poisons, such as sulfur and nitrogen are major disadvantages of this type of catalysts. It was shown previously, that transition metal sulfides can be used to prepare bifunctional catalysts and play the role of hydrogenation/dehydrogenation active sites [1].

The presented research is devoted to the investigation of the new modified aluminosilicates application for bifunctional hydroisomerisation catalyst synthesis. New composite supports based on alumina and mesoporous materials such as MCM-41, Al-MCM-41, SAPO-31 have been studied as CoMoS-based bifunctional catalysts carrier and tested in n-hexadecane isomerization.

CoMo catalysts have been prepared from cobalt carbonate, phosphomolybdic acid and citric acid as chelating agent, by the wetness impregnation technique.

All solids have been studied by powder X-ray diffraction, transmission and scanning electron microscopy, low-temperature N₂ adsorption, temperature-programmed desorption of NH₃ and reduction with H₂. Catalytic tests have been performed in bench-scale flow reactor under 15 bar of hydrogen, WHSV = 1÷3h⁻¹, temperature range from 260 to 360°C and H₂/feedstock ratio equal to 200 nl/l. Catalysts were activated at 400°C in H₂S/H₂ flow (10/90 %vol.) for 2h.

It was found, that new composite supports modified with mesoporous material with a hierarchical structure can improve catalytical properties of the CoMo-based bifunctional catalysts.

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NEW CATALYSTS BASED ON LAYERED DOUBLE HYDROXIDES FOR THE FURFURAL HYDROGENATION



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One of the large-capacity biomass processing products, furfural is widely used in the petrochemical industry as a solvent and raw material for the preparation of solid resins and pharmaceuticals. Derivatives of furfural as a result of its hydrogenation are no less demanded. Therefore, the process of catalytic hydrogenation of furfural is significant and it requires both environmentally friendly conditions for carrying out the reaction, and modern catalysts that provide selective production of desired products. One of the main challenges is selectivity, which is determined by the nature of the metal and the support. Traditional oxide and carbon supports, as a rule, possess functional groups of an acidic nature and are capable of initiating side reactions reactions both between transformation products and with a solvent. Therefore, in this paper, we consider non-acidic supports based on aluminum-magnesium layered double hydroxides (MgAl-LDHs). MgAl-LDHs consist of brucite-like layers in which part of Mg^{2+} is substituted by Al^{3+} . The excess positive charge of the layers is compensated by anions located in interlayer spaces. The non-acidic properties of this support allowed us to carry out the reaction in the most environmentally friendly aqueous medium, since in their presence no reactions of furfural with water.

Hydrogenating metals palladium and nickel were used as active metals. Supported palladium is the most successful catalytic system for this type of reactions and the directions of substrate transformations can be regulated by a change in the electronic and dispersed state of Pd, which depends on the nature of the support. Variation of the nature of interlayer anion, the composition of hydroxide layers makes it possible to control acid-base properties of the support, location of Pd precursor and palladium properties. Nickel was introduced by embedding its cations in the structure of brucite-like layers by isomorphic substitution of Mg^{2+} for Ni^{2+} . The distribution of nickel at the atomic level in the LDH structure made it possible to ensure a high dispersion of supported nickel in the catalyst.

Mg(Ni)Al- CO_3 (LDH with CO_3^{2-} - interlayer anions) were synthesized by co-precipitation. MgAl-OH (LDH with OH^- - interlayer anions) was obtained after calcinations of MgAl- CO_3 at 550 °C and subsequent hydration of mixed oxides. Anchoring of Pd(II) chloride complexes was carried out on MgAl- $CO_3(OH)$. Pretreatment of the catalysts includes calcination and reduction with hydrogen at

823-873 K. Structural features of LDH and mixed oxides were studied by XRD (D8 Advance, Bruker). Adsorption–desorption isotherms of nitrogen were measured using ASAP-2020M (Micromeritics). CO chemisorption (AutoChem II 2920, Micromeritics) and STEM-HAADF electron microscopy (JEM-2100, JEOL) were used to estimate the Pd particle size. EXAFS spectra were measured at the ID26-beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The catalytic hydrogenation of furfural was performed in an autoclave with controlling volume of absorbed hydrogen. Reactions were carried out in aqueous solution at 363 K and a hydrogen pressure of 2.0 MPa with products examination by ^1H and ^{13}C NMR spectroscopy (Avance-400, Bruker), and GC.

The use of MgAl-LDHs with different interlayer anions MgAl-CO₃(OH) allowed varying the method of fixing and localization of Pd complexes. As a result catalysts of identical chemical composition were obtained, but differing in size and morphology of palladium particles: Pd particles of a dendritic structure (up to 100 nm) when the precursor is intercalated into the LDH interlayer space and highly dispersed palladium particles with sizes less than 1 nm while fixing the complexes on the support surface. A difference in the hydrogenation activity and selectivity of such Pd/MgAlO_x catalysts was found. It has been shown that the use of the basic supports leads to a change in the route of the aqua-phase hydrogenation of furfural: when using traditional Pd/C catalysts, furfuryl alcohol is the main product, and the use of Pd/MgAlO_x leads to the predominant hydrogenation of the furan ring and tetrahydrofurfuryl alcohol is formed with high selectivity and the products of the interaction of furfural with water are absent. The effects detected are associated with different adsorption geometry of furfural molecules on the catalyst surface.

The proposed synthesis method by introducing nickel into the LDH structure has shown significant advantages compared to traditional methods of impregnating the support with a nickel precursor. The resulting Ni/Mg(Ni)AlO_x catalysts contained nickel particles in a highly dispersed state and ensured high hydrogenation activity of the catalyst.

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CHARACTERIZATION AND HYDROISOMERIZATION PERFORMANCE OF Mg-PROMOTED Pt/ZSM-23/Al₂O₃ CATALYSTS



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The importance of n-paraffins isomerization is related to the manufacturing of diesel fuels and lubricants with improved cold-flow properties. The bifunctional catalysts based on noble metals and zeolites with 10-ring pore system (TON, MTT and AEL topologies) are usually used for such isomerization processes. It is generally accepted that the structure of medium-pore monodimensional zeolites limits multibranching and therefore inhibits the undesired cracking reactions. The additional way of improving isomerization performance of zeolite-based catalysts is magnesium addition, which results in better selectivity and higher Pt dispersion of Pt/ZSM-23 samples [1]. In this paper, we investigate the effect of different platinum precursors (H₂PtCl₆ (PtCl) and [Pt(NH₃)₄]Cl₂ (PTA)) and Mg concentration on the behavior and physicochemical properties of Pt-Mg/ZSM-23/Al₂O₃ catalysts.

Pt-Mg/ZSM-23/Al₂O₃ catalysts were prepared by a incipient wetness co-impregnation of 70% ZSM-23 (Zeolyst Int., SiO₂/Al₂O₃=48)/30% Al₂O₃ support with a solution containing Mg(NO₃)₂ and Pt precursor. Pt loading was 0.5 wt%; MgO concentration was varied over a range of 0.25-1.25 wt. %. The impregnated samples were dried and calcined at 400°C. All prepared catalysts were denoted as PTA(PtCl)-X, where X - MgO content. Nitrogen adsorption, HRTEM, CO chemisorption, H₂-TPR and IR spectroscopy of adsorbed pyridine were used for the characterization of the prepared catalysts. Hydroconversion of n-decane was carried out at a pressure of 3.5 MPa, a weight hourly space velocity of 2.35 h⁻¹ and H₂: feed molar ratio of 60. The reaction temperature was varied in the range of 250-350°C. Prior to the experiment, the catalysts were reduced *in-situ* at 400°C under flowing H₂.

The catalytic performance of Pt-Mg/ZSM-23/Al₂O₃ catalysts with different MgO content prepared by using PTA precursor is shown in Fig. 1. The addition of promoter results in the decrease in activity and slightly improved yield of C₁₀ isomers, which demonstrates a rather low dependence on promoter content. PtCl-1 sample prepared using another Pt source exhibits a similar activity but a lower selectivity in comparison with PTA-1 catalyst. This fact can be explained by the decrease in the intimacy between metal and acid sites due to Pt distribution between zeolite and alumina binder observed for PtCl-1 sample (Fig. 2).

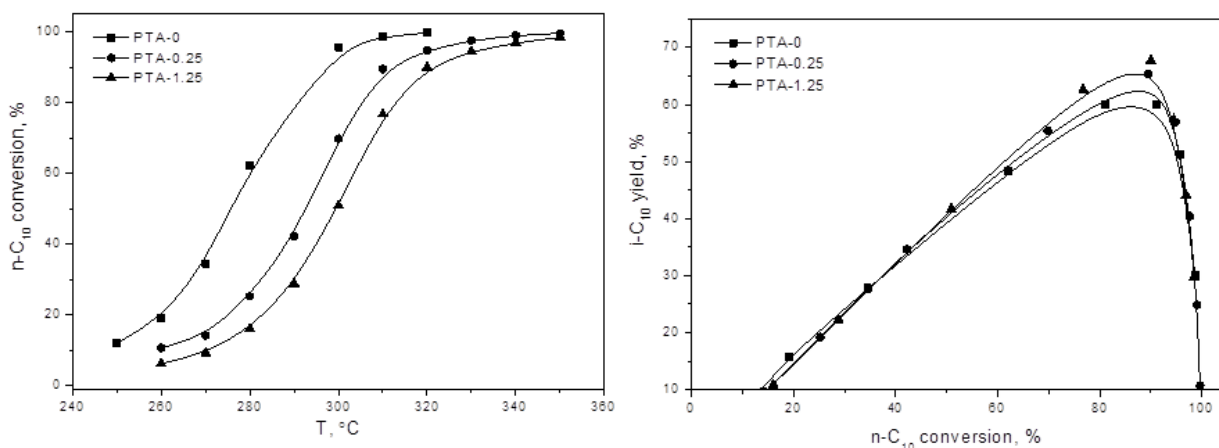


Fig. 1. Activity and isomers yield obtained over in n-decane conversion

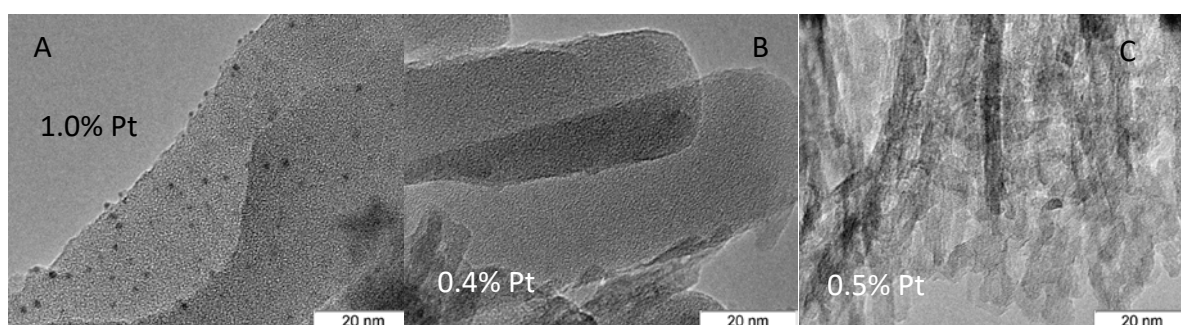


Fig. 2. HRTEM images of PTA-1 (A) and PtCl-1 (B, C) samples

As can be seen from Table 1, magnesium addition leads to a significant increase in Pt dispersion with simultaneous drop in acidity, especially in Brønsted acid sites concentration (BAS), that is more pronounced in the case of PTA-X samples. Both of these tendencies result in a higher metal/acid sites ratio, which favors a fast hydrogenation of intermediate olefins. According to the literature [2], the balance between hydrogenation and acidic functions is responsible for the increase in isomers yield due to cracking suppressing.

Table 1. Pt dispersion and acidic properties of Pt-Mg/ZSM-23/Al₂O₃ catalysts

Catalyst	BAS ₁₅₀	LAS ₁₅₀	D(Pt), %	BAS ₁₅₀ /LAS ₁₅₀	BAS ₁₅₀ /BAS ₄₅₀
ZSM-23/Al ₂ O ₃	167	61	48	2.8	2.0
PTA-1	42	31	90	1.3	1.3
PtCl-1	69	45	79	1.5	1.4

The results obtained in the present study provide insight into the magnesium promoting effect that could be useful for the development of isodewaxing catalysts with improved Pt dispersion and isomerization selectivity.

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KINETIC PATTERNS OF VACUUM DISTILLATE CATALYTIC CRACKING ON DIFFERENT CATALYST



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The catalytic cracking efficiency, the products distribution and quality are significantly determined by the catalyst composition used. The issue of the optimal catalyst selection is relevant since the cracking catalysts compositions have features depending on the feedstock composition and the process purpose (gas, gasoline or diesel fuel productions). The mathematical modeling method ensures the consideration of the differences in activity and selectivity of industrial catalysts by the numerical values of the reaction rate constants [1-3].

This paper presents a comparative analysis of the catalytic cracking kinetic patterns for the various catalysts using the mathematical model developed at the Tomsk Polytechnic University. Table 1 shows the estimated kinetic parameters of the catalytic cracking main reactions during the industrial catalysts operation with different compositions.

Table 1. Kinetic parameters of catalytic cracking reactions for KAT-1 and KAT-2 catalysts (temperature 791 K, pressure 146119.1 Pa)

Reaction	CAT-1	CAT-2	Degree
Cracking of C ₁₃ –C ₄₀ alkanes to C ₅ –C ₁₂ isoalkanes	0.6	0.27	s ⁻¹
Dealkylation of high molecular weight cycloalkanes	0.32	0.18	s ⁻¹
Dealkylation of high molecular weight aromatics	0.27	0.11	s ⁻¹
Cracking of high molecular weight cycloalkanes	0.25	7.3·10 ⁻²	s ⁻¹
Cracking of C ₅ –C ₁₂ alkanes	2.6·10 ⁻²	3.2·10 ⁻²	s ⁻¹
Cracking of C ₅ –C ₁₂ isoalkanes	2.9·10 ⁻²	3.5·10 ⁻²	s ⁻¹
Cracking of C ₅ –C ₁₂ unsaturated hydrocarbons	6.9·10 ⁻²	7.2·10 ⁻²	s ⁻¹
Cracking of C ₅ –C ₁₂ unsaturated hydrocarbons to BBF	5.8·10 ⁻²	6.5·10 ⁻²	s ⁻¹
Cracking of C ₅ –C ₁₂ unsaturated hydrocarbons to PPF	6.9·10 ⁻²	8.0·10 ⁻²	s ⁻¹
Hydrogen transfer	28.8	20.4	ls ⁻¹ mol ⁻¹
Coke formation	0.57	0.2	ls ⁻¹ mol ⁻¹

The cracking catalysts efficiency analysis by the catalytic cracking target product yield and composition was performed using the developed mathematical model (Figure 1). We used the high-paraffin vacuum distillate (the saturated to aromatic hydrocarbons ratio is 1.83 units, the resins content is 3.8% wt.) as a catalytic cracking feedstock under the other equal conditions (the catalyst temperature at the regenerator outlet is 967.6 K, the feedstock consumption and temperature are 378.2 m³/h and 586.9 K, the sludge consumption to the reactor is 10.44 m³/h, the

steam consumption for the feedstock spraying is 2400 kg/h, the steam consumption to upward flow creation is 5697.4 kg/h, the catalyst circulation rate is $5.46 \text{ t}_{\text{kat}} / \text{t}_{\text{feed}}$).

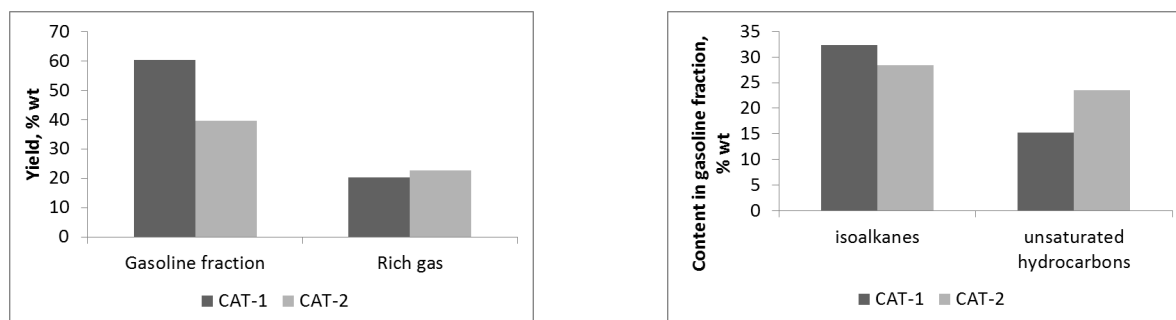


Figure 1 – Comparative analysis of the different catalyst application (model-based calculation)

It has been established that a high of gasoline fraction yield (60.1% wt.) is ensured by CAT-1 catalyst composition, which is due to high primary reactions rates: alkanes cracking (0.6 s^{-1}), cycloalkanes and arenes dealkylation (0.32 and 0.27 s^{-1}) and cracking (0.25 s^{-1}) of), also the hydrogen transfer and coke formation secondary reactions (0.57 and $28.8 \text{ ls}^{-1} \text{ mol}^{-1}$) compared to CAT-2catalyst. Moreover, the coke content is higher (0.9% wt.) for CAT-1 catalyst relative to CAT-2 catalyst (0.6% wt) by cause of a high polycondensation reactions rates.

Decreasing the hydrogen transfer reaction rate and rising the rate of gasoline hydrocarbons cracking to form gases are provided by CAT-2 catalyst composition: the rates of $\text{C}_5 - \text{C}_{12}$ alkanes, isoalkanes and unsaturated hydrocarbons cracking are $3.2 \cdot 10^{-2}$, $3.5 \cdot 10^{-2}$, $7.2 - 8.0 \cdot 10^{-2} \text{ s}^{-1}$. As a result, the gasoline composition is less enriched in isoalkanes and arenes (by 3.94 and 2.92% wt.) and is characterized by a high content of unsaturated hydrocarbons (by 8.22% wt.) using CAT-2 catalyst. A high selectivity of gasoline cracking secondary reactions gives a greater yield of richy gas using the CAT-2 catalyst (22.62% wt.).

It is found that the catalyst composition influences significantly the industrial catalytic cracking unit performance, along with the feedstock composition and the reactor-regenerator unit process conditions. The catalyst testing with transferring the catalytic system to other industrial conditions and feedstock is possible using the mathematical model. Further it will allow us to select the optimal catalyst for industrial catalytic cracking plants depending on these factors.

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CO-PROCESSING OF RAPESEED OIL – STRAIGHT RUN GAS OIL MIXTURE: PECULIARITIES OF ULSD PRODUCTION WITH IMPROVED COLD FLOW PROPERTIES



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The growing demand in transportation fuels, along with the decrease in available fossil fuel resources and vital tendency to reduce the greenhouse gas emissions have caused ascending interest in the involvement of renewable feeds for their production. Hydrotreating of the triglyceride-based feedstocks gives linear hydrocarbons which are the excellent components of diesel-range fuels being fully compatible with the petroleum-derived products and having the improved cetane number, gravity, aromatic and sulfur contents. But the main drawback of linear hydrocarbons is poor low-temperature flow property. The cold flow properties can be adjusted by hydrocracking/hydroisomerization process of n-alkanes over zeolite-containing catalyst.

The scope of the present work is to investigate the effect of reaction conditions on conversion of alkanes produced from co-processing of rapeseed oil-straight run gas oil mixture (RSO-SRGO) over dual bed catalytic system (sulfide $\text{Mo}/\text{Al}_2\text{O}_3$ + $\text{NiMo}/\text{Al}_2\text{O}_3$ -SAPO-11 catalysts). Hydrodeoxygenation of RSO will occur over selective nonpromoted sulfide catalyst ($\text{Mo}/\text{Al}_2\text{O}_3$) in the first layer via “direct hydrodeoxygenation” route with negligible formation of CO_x gases: the main products will be n-alkanes and water. And hydrotreating of SRGO and hydrocracking/hydroisomerization of n-alkanes, produced from HDO of RSO, will be performed in the second layer over sulfide $\text{NiMo}/\text{Al}_2\text{O}_3$ -SAPO-11 catalyst.

Experimental

The support Al_2O_3 -SAPO-11 was prepared from AlOOH powder (Pural SB, Sasol GmbH, Germany) and SAPO-11 (Zeolyst International Co.) to get 30 wt.% SAPO-11 content on the dry basis.

The catalysts were prepared by impregnation of support granules with a water solution containing requirable amounts of the active components (Mo, Ni), H_3PO_4 and diethylene glycol. Precursors of Mo and Ni were molybdenum oxide MoO_3 and nickel hydroxide $\text{Ni}(\text{OH})_2$.

The hydroprocessing of 30 wt.% of RSO in SRGO was performed using a pilot plant with a trickle-bed reactor at 4.0-7.0 MPa, 350-380°C, LHSV 1-2 h^{-1} , H_2 /feed ratio 600-1000. The liquid and gases products were quantified using gas chromatographs, ANTEK 9000NS and Vario EL Cube were used to follow total S, N and O contents using the corresponding ASTM methods. The cloud point of the hydroprocessing products (Tcloud) was determined with automated device TPZ-LAB-22 (LOIP AO, Russia) according to ASTM D5771 standard procedure.

Characterization of the catalysts in the sulfide state by means of XRD and HRTEM confirmed that the applied preparation and sulfidation procedures provide the formation of highly dispersed MoS₂ and Ni-MoS₂ nanoparticles (3-5 nm) on the support surfaces.

Results and discussion

It should be noted that in whole range of process conditions complete conversion of oxygen-containing compounds was observed and sulfur content in final products did not exceed 10 ppm. It was found that the temperature increase from 350 to 380°C led to increasing of C₁₈+C₁₇ alkanes conversion and, consequently, decreasing of cloud point of the final products. In addition lower LHSV and higher H/C ratio resulted in increasing of alkanes conversion, but in lower extent than temperature increase. The influence of pressure on co-processing of RSO-SRGO mixture was quite unusual: pressure increase resulted in decreasing of C₁₈+C₁₇ alkanes conversion. We supposed that the reason of lower activity of catalytic system at high pressure was the inhibition of hydrocracking/hydroisomerization reactions by by-products of SRGO hydrotreating (H₂S, NH₃ gases) due to their higher concentration in liquid phase. To verify this observation we performed additional experiments. We investigated influence of dimethyldisulfide, as source of H₂S, and dihexylamine, as source of NH₃, in co-processing of 30 wt.% of RSO in hydrotreated SRGO (HT SRGO), containing 6 ppm of N and 8 ppm of S. The sulfur and nitrogen contents in the feed RSO-HTSRGO were adjusted to their contents in RSO-SRGO mixture. It was observed that C₁₈+C₁₇ alkanes conversion sharply decreased with the addition of nitrogen (dihexylamine). Effect of hydrogen disulfide on hydrocracking/ hydroisomerization reactions was less noticeable.

Conclusion

Thus, the concentrations of S and N-containing compounds in the petroleum feed could effect on the hydrocracking/hydroisomerization reactions, and, consequently, on cold flow properties, and should be taken into account when co-processing of SRGO with renewables is undertaken.

Acknowledgements

The authors would like to thank Dr. E. Gerasimov for characterization of the catalysts by TEM. The work was supported by Ministry of Science and Higher Education of the Russian Federation.

**STRUCTURED CATALYSTS FOR HYDROCARBONS AND OXYGENATES MIXTURES
CONVERSION TO HYDROGEN-RICH GAS**

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Over the past decades, a number of research projects aimed to the search and study of oxidative conversion catalysts (steam, autothermal conversion or partial oxidation) for gaseous fuel (natural gas, propane-butane mixtures, dimethyl ether) along with liquid fuel (kerosene, diesel, renewable natural raw materials - biodiesel and glycerin - a by-product of biomass processing), as well as engineering design of fuel processors for syngas or hydrogen-rich gas (an attractive fuel for fuel cells) production has increased significantly.

The production of standardized fuels from renewable plant feedstock also needs hydrogen for bio-oil hydro processing. In this case, standardized hydrocarbon fuels (components of biodiesel and bio kerosene) produced from renewable plant feedstock are a very effective hydrogen carriers (with gravimetric capacity more than 15 wt.% of hydrogen).

This study focuses on the development of catalysts and technologies for producing hydrogen-rich gas from various vegetable-derived sources, namely, bio-oxygenates and vegetable oils. An efficient and widely used method for producing hydrogen-rich gas is the steam or autothermal reforming of organic compounds, carried out in special devices - reformers, which are reactor systems integrated with heat exchangers containing catalysts. The catalyst composition can vary depending on the feedstock.

To avoid hot spot formation during the autothermal conversion of hydrocarbons and oxygenates, which arises due to the high exothermic effect of the oxidation reactions, which occur mainly in the frontal layer of the catalytic module, and the high endothermicity of the steam and carbon dioxide conversion reactions which occur in its outlet part, it was proposed to use metal foams and meshes with a higher thermal conductivity instead of cordierite ceramics [1,2]. The main problem that arises when using metal substrates is the difference in the thermal expansion coefficients of the metal and the deposited oxide layer. The use of standard suspension techniques leads to nonuniform deposition, poor adhesion and low mechanical strength of the catalytically active coating. In the conditions of thermal cycling, where the temperature difference can reach 1000 °C and more, its degradation, delamination and destruction occurs.

This problem was elegantly solved by developing a technique for growing aluminum hydroxide crystals on a metal surface, which, during calcination at a temperature above 600 °C, first goes into η -Al₂O₃, and then into θ -Al₂O₃ phase at a temperature above 900 °C [2]. This composite material was used as a primary support for preparation of catalysts for the all stages of hydrogen production: fuel conversion to syngas, CO water gas shift reaction, and CO clean-up. A large number of catalysts of various compositions were studied: Rh, Ru, Pd, Pt, Ni and Co, their bimetallic compositions in combination with various supports made of individual or mixed oxides of Zr, Ce, Gd, Al; doping with alkali and alkaline earth metals.

The peculiarity of the obtained coating is in the columnar (needle) structure of alumina crystals with a length of 30-60 μ m, which are chemically bonded to the metal substrate. The structure is “breathing”; during the thermal expansion of the metallic material, the alumina crystals are spatially moved relative to each other without disrupting the interaction with the metal.

The prepared catalysts have superior catalytic performances in laboratory and pilot scale reformers for syngas or hydrogen-rich gas production.

The study also focuses on mathematical modeling of the catalytic processes for hydrogen production in 2D axisymmetric geometry. The catalyst module was simulated as homogeneous porous medium. The reaction model included hydrocarbon oxidation, steam reforming, water-gas shift reaction, CO methanation, CO oxidation and hydrogen oxidation. Simulation of the experimental results including product distribution and temperature profile allowed defining the kinetic parameters corresponding to the best fit. The suggested simple quasi-homogeneous model describes experimental results (module temperature and outlet gas composition) with a good accuracy and could be used for process optimization and up-scaling.

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MATHEMATICAL MODELING OF THE HYDROTREATING PROCESS USING BI-FUNCTIONAL CATALYSTS



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Currently, the process of hydrotreating diesel fractions is one of the basic processes in the oil refining industry [1, 2]. This is due to an increase in the extraction of heavy petroleum with a high content of nitrogen- and sulfur-containing compounds, as well as a change in standards towards stricter environmental requirements [3, 4].

The aim of this work is to develop mathematical model of diesel fuel hydrotreating process using experimental data, obtained from laboratory desulfurization unit.

The catalytic hydrotreating of the diesel fraction was carried out under the following conditions: pressure 4.0 MPa; the ratio of hydrogen to feedstock 320 : 1; feed rate 2 h⁻¹, process temperature 340, 360 and 380 °C. The catalyst used was the Russian nickel-molybdenum of hydrotreating catalyst. The characteristics of the distillate feed are presented in Table 1.

1 – The composition of the original diesel fraction

Component	% wt.
Saturated hydrocarbons (paraffins + cycloparaffins)	53,8
Aromatic hydrocarbons	44,2
Sulfur-containing compounds (benzothiophenes, dibenzothiophenes)	0,95
Sulfur-containing compounds - sulphides	0,45
Olefins	0,6

Based on the results of a thermodynamic analysis of the reactions, a formalized scheme of hydrocarbon conversions in the process of hydrotreating diesel fractions is compiled. formalization of the process hydrocarbon conversion can simplify the mathematical description by account the main reactions without loss of sensitivity of the model to the composition raw materials. The kinetic model of the hydrotreatment process of diesel fractions is a system of differential equations.

Hydrotreating at T = 340 ° C, the proportion of dibenzothiophene sulfur decreased by 97.8%, the proportion of benzothiophene sulfur by 93.8%, and sulfide sulfur by 90.5%. The total hydrotreatment degree was 94%. With increasing temperature process, the degree of hydrotreating increases. The rate constants of the reactions are presented in Table 2.

Table 2 - Values of the reaction rate constants

Reaction	Value of speed constant , s ⁻¹
Hydrogenolysis of sulfids	0,3114
Hydrogenolysis of benzthiophenes	0,1090
Dehydrogenation of benzothiophenes	0,0218
Hydrogenolysis of dibenzothiophenes	0,0722
Dehydrogenation of dibenzothiophenes	0,0052
Hydrogenation of Olefins	0,0934
Dehydrogenation of saturated hydrocarbons	0,0990
Hydrogenation of of aromatic hydrocarbons	0,0078
Dehydrogenation of aromatic hydrocarbons	0,0012

The relative error for sulfur-containing compounds did not exceed 5%, for the main hydrocarbon did not exceed 1.5%.

The study of the influence of temperature using mathematical model showed that the degree of conversion of sulfides, benzothiophenes and dibenzothiophenes with an increase temperature from 350 to 425 °C increases by 2.1, 2.5 and 1.2 %, respectively. The most dependent on temperature was the degree of conversion of benzothiophenes, in contrast to dibenzothiophenes and sulfides.

The developed kinetic mathematical model can be used to calculate the degree of desulfurization when changing the contact time, temperature, and flow rate of a hydrogen-containing gas.

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**NEW ACHIEVEMENTS OF THE CRACKING CATALYSTS DEVELOPMENT
FOR PETROCHEMICAL DIRECTION OF PJSC «GAZPROMNEFT»**

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Catalytic cracking is one of the major processes of oil refining, providing valuable products such as high-octane component of marketable gasolines, light catalytic gas oil a component of diesel fuel and light olefins, which are a valuable raw material for petrochemical. The ratio of the resulting products determines the direction of the process - fuel or petrochemical. Constantly increasing demand for light olefins (primarily propylene) leads to a sharp increase in the consumption of FCC petrochemical catalysts.

PJSC «Gazpromneft» and the Center of New Chemical Technologies BIC have developed several series of FCC catalysts to increase the selectivity of petrochemical feedstocks. The first series of Olefin-1 catalysts is designed to process hydrotreated vacuum gas oils at elevated cracking temperatures. These catalysts are supposed to be used on DCC (deep catalytic cracking) units. These catalysts provide a yield of light olefins up to 35 wt. %. The second series of catalysts involves the joint processing of heavy (vacuum gas oils) and light (low-grade gasoline fractions) raw materials. These catalysts can be used in catalytic cracking units equipped with two reactors (2R-1R). The yield of C₂-C₄ olefins on low-grade gasolines can reach 50 wt. % when processing olefinic types of raw materials (for example, coking gasoline). The third series of catalysts "Olefin-2" allows you to produce up to 25 wt. % of light olefins in the processing of heavy types of raw materials significantly differ in the degree of hydrotreatment. It is also possible to process the hydrocracking residue, hydrotreated and non-hydrotreated (with a sulfur content of at least 15,000 ppm) vacuum gas oils. Another feature of the Olefin-2 series catalysts is the possibility of their use in conventional FCC units operating at relatively low temperatures. A small increase in the yield of light olefins (up to 25 wt. %) in combination with a high yield of cracked gasoline (up to 40 wt. %) with an octane number of about 95 points is often a more profitable option for many oil refineries.

All presented series of catalysts are bizeolite catalytic systems based on zeolites Y and ZSM-5. The main differences are in the conditions of zeolite modification and the ratio of components in the catalyst. The role of each component of the petrochemical cracking catalyst can be estimated by the hierarchical scheme of hydrocarbon cracking, shown in Figure 1. Large molecules of the initial

hydrocarbons undergo primary cracking on the components of the active catalyst matrix (based on amorphous silica-alumina). Further, the intermediates undergo transformations on wide-porous zeolite Y with the formation of gasoline hydrocarbons. That hydrocarbons, turning on the small-porous zeolites ZSM-5, form light olefins.

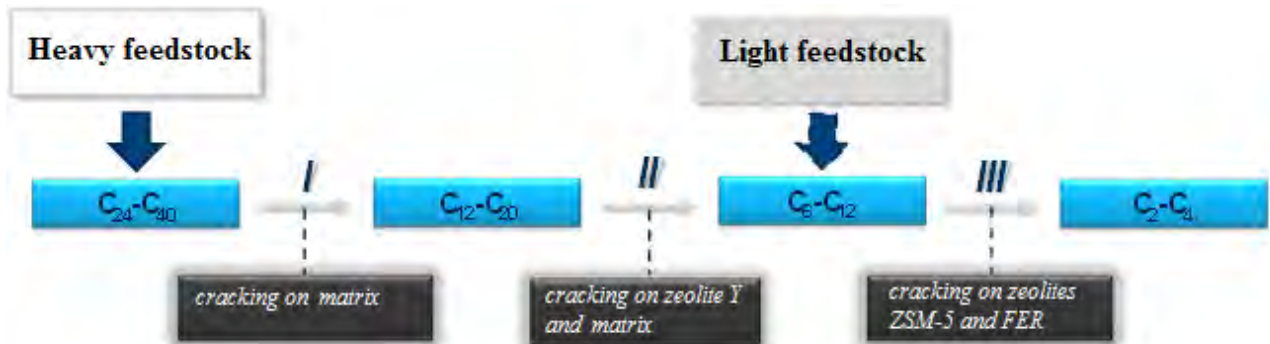


Figure 1. Hierarchical scheme of cracking of C₂₄-C₄₀ hydrocarbons on catalyst components

Regulation of the ratio between the components allows synthesis of the cracking catalyst to obtain the required composition of products, taking into account the processed raw materials.

The modification of the components of the petrochemical cracking catalyst is concentrated in the direction of minimizing the contribution of hydrogen transfer reactions with at the same time high activity in cracking, which will ensure high feed conversion and high selectivity for the formation of light olefins.

Acknowledgements

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A STEPWISE FABRICATION OF MORDENITE FRAMEWORK INVERTED (MFI) NANOSHEETS IN ACCELERATED MODE



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Micro-mesoporous materials have several advantages over zeolites (the lack of diffusion limitations, high specific surface area and pore volume) and mesoporous materials (high stability under hydrothermal conditions, high acidity).[1–3] The design of micro-mesoporous materials for specific processes requires the development of materials that combine pores of different diameters in a certain ratio. The most promising micro-mesoporous materials are zeolite nanosheets, which over the past decade have been well studied for several types of zeolites.[4–8] With a decrease in the thickness of zeolite layer, the availability of the external surfaces to the catalytic activity becomes significant. It was shown that 2.5-nm thick MFI nanosheets exhibited high catalytic activity in contrast to amorphous mesoporous materials and crystalline micro-mesoporous aluminosilicates.[9] Despite the fact that the synthesis of zeolite nanosheets is an effective way to create micro-mesoporous materials with improved catalytic properties, the mechanism of this process is not well studied: there is little information in the literature regarding the main stages of the formation, and all conclusions are based mainly on hypotheses.

The mechanism of MFI zeolite nanosheets formation was established under accelerated conditions using different promoters. The results indicated that the particles after pretreatment were initially formed as an ordered amorphous assembly that stepwise converted into zeolite nanosheets. The MFI nanosheets fabrication occurs through the transformation from MCM-41-like to KIT-1 like structure, lamellar structure, disordered lamellar structure and MFI nanosheets. The application of uniform microwave heating with addition of promoters made it possible to obtain the assembly of all types of structures in 6 hours. The MFI nanosheets generation process was analyzed by X-ray powder diffraction, IR spectroscopy, N₂ adsorption isotherms, SEM and TEM. A linear function of selectivity for bulky products in the solid acid alkylation process on the concentration of Brønsted acid sites has been determined for the materials possessing mesophase.

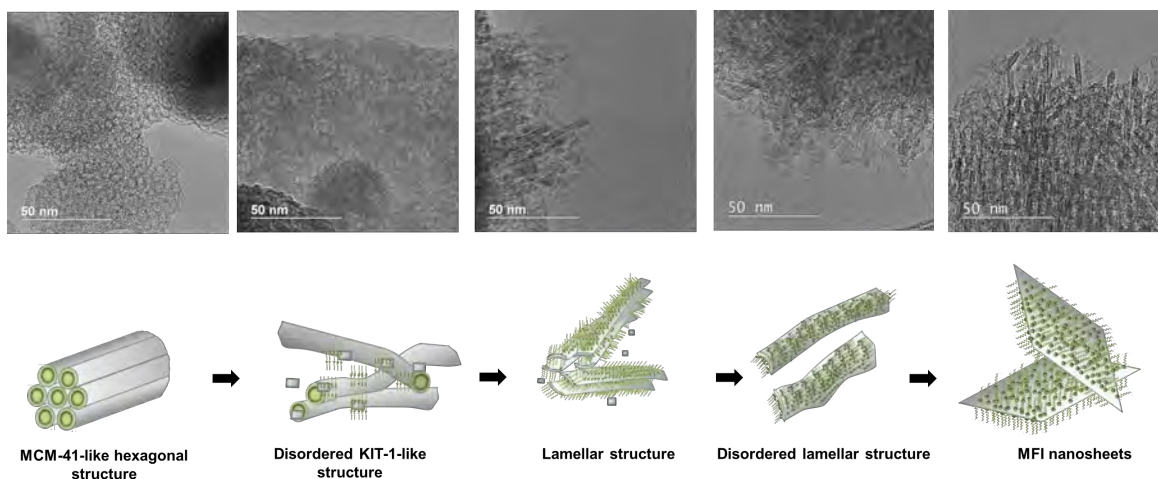


Fig. 1. TEM images of MFI zeolite nanosheets and mechanism of MFI nanosheets formation

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INDUSTRIAL HYDROCRACKING UNITS: NEW R&D CHALLENGES AND OPPORTUNITIES AS A WAY FORWARD TO IMPROVE REFINERY MARGINS



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Nowadays, refineries worldwide need to be prepared for a near future where flexibility vs continuous evolving raw materials and products is a must, considering the current energy model transition towards lower carbon dioxide (CO₂) emissions. Renewable raw materials as well as newer, and cheaper, crude oils baskets, will have to be taken into account. The limited information about their chemical properties, poisoning and deactivation impacts as well as derived product characterization, create some uncertainties regarding the possible operational consequences for existing refinery units.

Hydrocracker units are currently recognized as one of the most flexible conversion units intended to convert low valuable streams (such as vacuum gas oil, deasphalted oils (DAO), coker gas oil) and low-value aromatic streams (such as light cycle oil (LCO) from FCC unit and residues from the vacuum tower), into lighter and higher added value products (such as middle distillates). In commercial configurations, there is a pretreatment step to remove metals, heterocompounds (sulphur, nitrogen, oxygenates), and some aromatics. The main catalyst for the first reactor is usually nickel-molybdenum supported on alumina (NiMo/Al₂O₃). The second step, in which the cracking process takes place, uses an acid catalyst. Several reactions occur at the same time (aromatics hydrogenation, ring opening and isomerization) over the same catalyst [1].

Commercial catalyst suppliers are continuously improving their catalytic systems performance by feedback-feedforward strategies, which consider apart from the upgrading of catalytic synthesis, the commercial data operation as part of the core process that firmly contributes to a practical improvement such as more active catalysts or more selective ones with controlled energy savings (hydrogen, natural gas or fuel savings for the furnaces).

However, even selecting the best catalytic system in the market, it is of vital importance to determine the potential risk of these unknown contaminants through advanced Research and Development (R&D) collaboration with the commercial operation and the commercial catalyst

OP-37

suppliers. In the case of hydrocracking industrial operation, unexpected shutdowns or reduction into throughput can cause an important reduction into refinery margins.

As a first approach, considering the layout of the commercial unit, it is very important to identify the most critical points of the unit (heat exchangers, tanks, pipelines, reactor, etc). By planning different set of samples linked to different moments of the commercial operation, it can be known which type of contaminants we have and also if there is a clear relationship with the feedstock or any other operational parameter (temperature, pressure, hydrogen purity, hydrogen to oil ratio, among others).

Secondly, R&D need to decide about the appropriate analytical techniques, which allow determining the main chemical properties. By analyzing a suitable sequence of residue and origin, new recommendations are sent to the refinery and therefore, some practical actions can be set up as a way forward.

Finally, regarding the catalysts loaded at the unit, it has to be analyzed the possible relationship between activity and poisons by collecting samples at the end of the cycle. This approach has become a key driver to determine a possible malfunction of the catalyst due to these poisons as well as a possible maldistribution flow into the reactor due to the presence of these contaminants.

A business case study based on a Hydrocracking unit will be shown in which a root cause analysis among R&D, refinery and the commercial catalyst supplier allows the refinery business to balance the relationship between these new crudes and their impact into the refinery margins.

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MESOPOROUS ALUMINOSILICATES BASED ON NATURAL CLAY NANOTUBES FOR HYDROPROCESSING: SYNTHESIS, PROPERTIES, APPLICATION



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Structured mesoporous silicates and aluminosilicates are prospective functional materials for different catalytic processes, including hydrotreating, hydrocracking, catalytic cracking, hydroisomerization, selective hydrogenation. In comparison with zeolites, structured mesoporous silica or aluminosilicates have larger pores (2–10 nm in diameter) with 2-3D or wormhole channel structures and high surface area (ca. 1000 m²/g). Depending on synthesis procedure one can adjust textural properties, acidity. Moreover, the modification of inorganic walls through the incorporation of heteroatoms allows for tunable acidic or redox properties of supports and catalysts based on it. Commercial applications of structured mesoporous silica and aluminosilicates are limited due to their low temperature and steaming stabilities.

In this work, we are focused on the design and creation of new functional nanomaterials based on natural clay nanotubes (halloysite) and synthetic mesoporous aluminosilicates with enhanced thermal and mechanical properties compared to mesoporous MCM-41 type silica. We also propose nanoreactors for aromatics hydrogenation in aqueous systems.

Halloysite (HNT) is a natural kaolinite clay of unique scrolled structure with the tube length of 0.5 - 1.5 μm, outer diameter of 50-60 nm and inner lumen of 10-20 nm [1]. It's surface electrical potential is ca. -30 mV and the specific surface area is around 65 m²/g. Due to differently charged outer/inner surfaces, these nanotubes provide different site-dependent chemistry. This makes halloysite based core-shell nanosystems promising as catalysts carriers for wide range of applications.

We synthesized mesoporous aluminosilicates of MCM-41 type selectively inside/outside of halloysite nanotubes by the organic surfactant (cetyltrimethylammonium bromide) templating method [2] (Figure). Textural, structural, elemental composition were investigated by N₂ adsorption, XRD, SEM, TEM and XRF techniques. It was shown that both samples have a high specific surface area (ca. 400-800 m²/g), bimodal pore-size distribution with 2.4 nm (MCM-41) and 6-20 nm (halloysite). MCM-41 (outer)/Halloysite showed essentially improved thermo-mechanical characteristics compared to pristine MCM-41 (thermal stability up to 1110 °C and twice higher mechanical stability). Such improvement is due to armoring of mesoporous silica with embedded strong ceramic nanotubes.

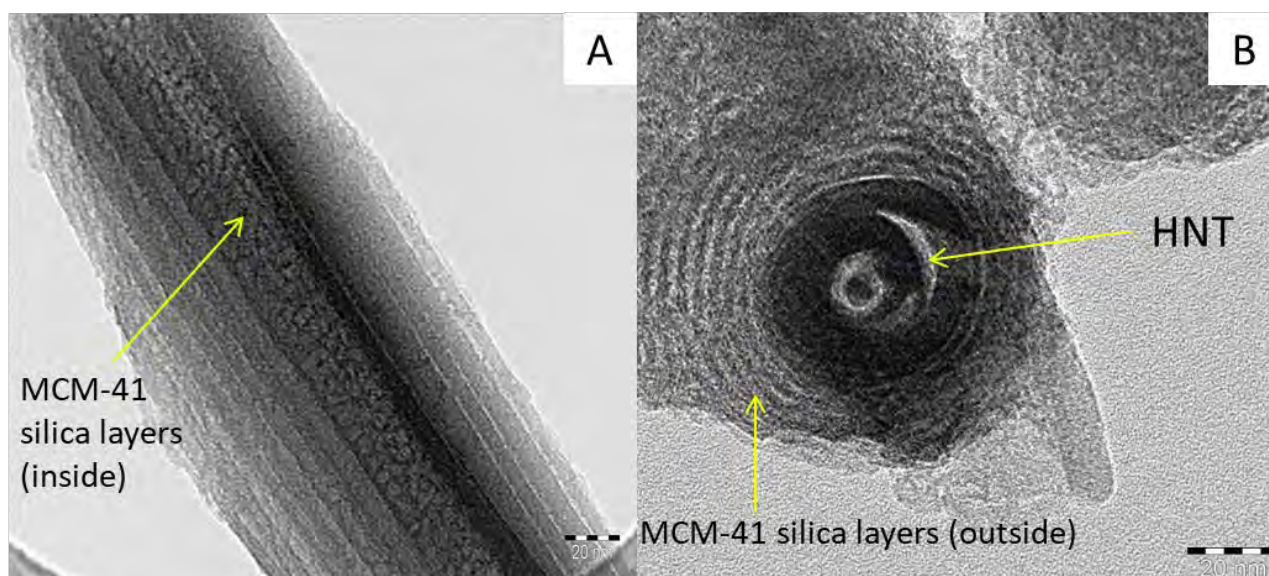


Fig. TEM images of MCM-41 inside (A) and outside (B) halloysite nanotubes

Developed aluminosilicate nanomaterials could be useful for application in mesoporous composites as bulk industrial catalyst carriers and adsorbents, especially in high-temperature reactions such as hydroprocessing and catalytic cracking.

Also, we present here a new strategy on the control of ruthenium deposition both on and inside halloysite nanotubes by modification of HNT with various C_3 - C_{18} -alkyltriethoxysilanes having increased hydrophobicity. Catalysts were investigated in aromatics hydrogenation at a temperature of 80°C and hydrogen pressure of 3 MPa both in the hydrocarbon medium and aqueous mixture. It was found that samples modified with C_{18} -alkyltriethoxysilane with Ru nanoparticles inside act as nanoreactors providing fully aromatics conversion with high water tolerance.

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ANIMAL FATS: A PROSPEROUS FEED FOR 2ND GEN BIOFUELS PRODUCTION

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The current work is focused on investigating the production of 2nd generation green transportation fuels via hydrotreating of animal fats produced from slaughter house wastes [1]. To that purpose, two feeds were examined (Table 1), one from pork fats and another from beef fats. The main objective of the work was to define the optimum operating window with respect to product quality and economic performance of the process. As a result various operating conditions were investigated for both feedstocks. More specifically three reaction temperatures (300°, 330° and 360°C), two reaction pressures (1000 and 1500 psi) and two H₂/feed ratios (3000 and 5000 scf) were tested, as presented in table 2. All the experiments were performed in the small-scale hydroprocessing pilot plant of the Centre for Research & Technology Hellas in Greece (CERTH), which is depicted in figure 1, employing a commercial NiMo/ γ -Al₂O₃ catalyst. The properties of the two feeds are presented in table 2.

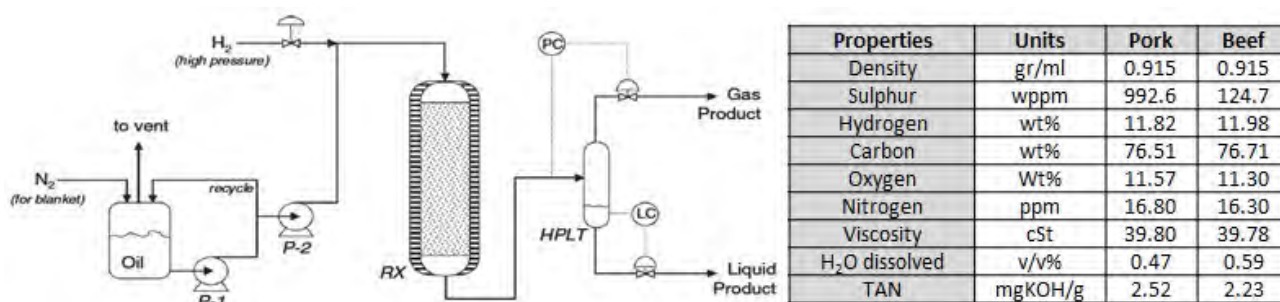


Figure 1: Hydrotreatment pilot plant diagram and Table 1: Feed properties

Table 2 Operating parameters tested for both feeds

Conditions	1	2	3	4	5
Pressure (psi)	1000	1000	1000	1000	1500
Temperature (°C)	300	330	360	330	330
H ₂ /oil ratio (scf)	3000	3000	3000	5000	3000
⁻¹ LHSV (hr)	1	1	1	1	1

The findings indicate that primarily diesel- and jet- range hydrocarbons can be produced after mild hydrotreating of both types of animal fats. Product recovery of both feeds is shown in figure 2 for the following operating conditions: Temperature=330°C, pressure=1000 psi and H₂/oil ratio=3000 scf. The resulting product consists of a water phase (up to 7 % v/v) and an organic liquid phase (up to

93% v/v). The organic liquid phase characterized by low density (~0.786 g/ml), almost zero oxygen content (<0.2 wt%), low viscosity (<3.5 cSt), and small amounts of dissolved water (<0.002 wt%), as presented in table 3.

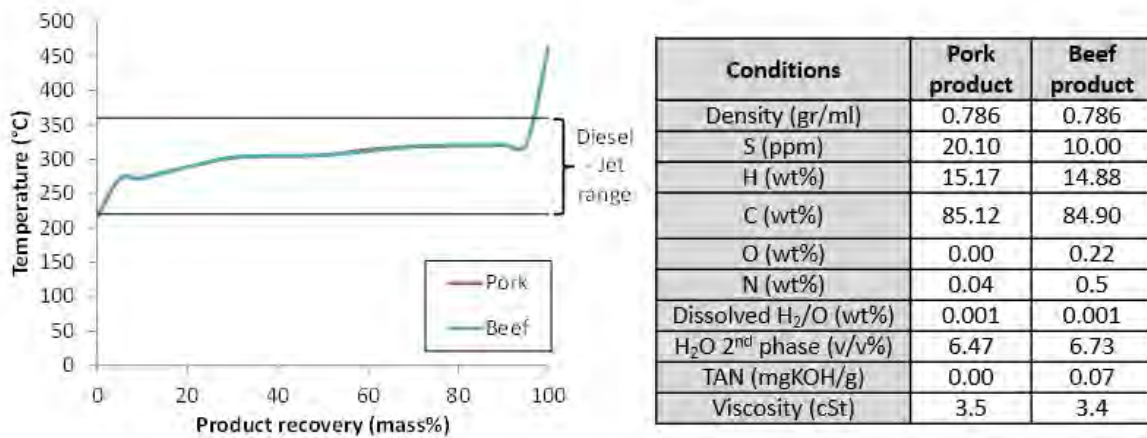


Figure 2 Product recovery and Table 3: product properties (at T=330°C, P=1000 psi and H₂/Oil ratio=3000 scf)

Besides the advanced properties of the produced green fuel, the suggested technology is extremely appealing as it employs existing refinery infrastructure and expertise, offers feedstock flexibility, and leaves no byproduct [2]. Figure 3 presents the hydrogen consumption for the 5 conditions studied. It is observed that severe conditions leads to increase of H₂ consumption, as a result mild conditions are preferable from hydrogen consumption viewpoint.

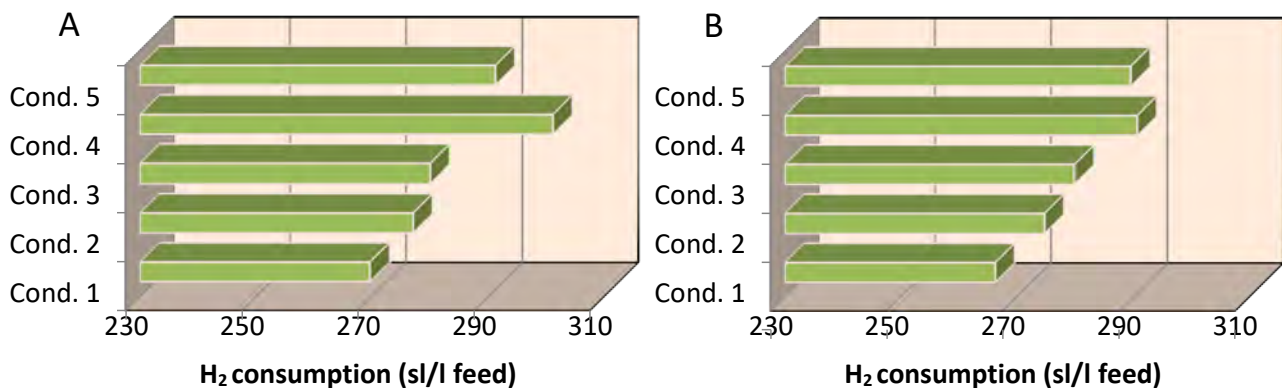


Figure 3 Hydrogen consumption: (A) is for pork fats feed and (B) is for beef fats feed

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MODELING OF MOTOR GASOLINE COMPONENTS COMPLEX PRODUCTION

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One of the most complex and multifactorial tasks in the field of crude oil processing is to determine the optimal ratios of mixing flows, taking into account their quality and quantity in the production process of care gasoline. Determination of mixing component ratios taking into account changes in the composition and properties of hydrocarbon raw materials entering the processing, as well as optimal technological regimes at the stages of catalytic processing of raw materials will reduce the cost of commodity products by reducing their stock in quality. Figure 1 shows a simplified scheme of production of motor gasoline of different brands.

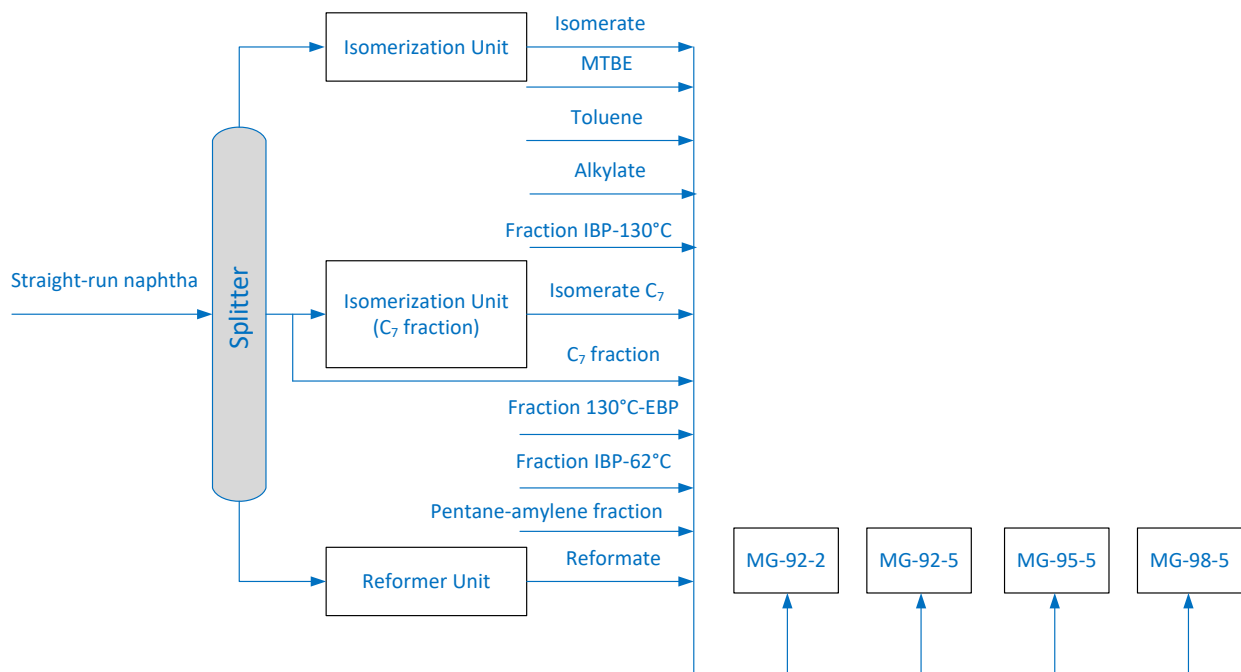


Fig. 1 Scheme of production of motor gasoline of different brands.

The hydrocarbon composition of the broad gasoline fraction, namely, the content of benzene and benzene-forming components, as well as C7+ components, depends on both the operating mode of the column-splitter and the optimal ratios of the mixing components, which must be strictly maintained to ensure sustainable production of marketable products with a minimum margin for the required quality and in a given quantity.

To determine the composition and properties of commercial gasoline of different brands, the proposed mathematical model of the compounding process was used, taking into account the laws of nonadditivity when mixing octane numbers and the pressure of saturated vapors of the

OP-40

mixing components [1]. The initial data for the mixing model are hydrocarbon compositions of the components entering the compounding. The results of the calculations are presented in tables 1,2.

Table 1- Composition of gasoline

MG-92 (5 class)

Component	Ratio of components, wt. %		
	1	2	3
alkylbenzene	2,23	2,23	2,23
Isomerizate	30,93	33,03	34,93
MTBE	4,88	4,88	3,28
Reformat	40,62	23,02	34,62
Toluene	3,00	12,85	6,00
Fraction 130° C-CC	7,11	7,71	7,11
Fraction NK-130 °C	0,93	0,93	0,93
Fraction NK-62 °C	10,30	15,35	10,90

Table 2-Composition of gasoline

MG-95 (5 class)

Component	Ratio of components, wt. %		
	1	2	3
alkylbenzene	1,70	1,70	1,70
Isomerizate	25,42	30,42	28,42
MTBE	10,25	7,65	10,25
Pentane-amylene fraction	3,53	3,53	3,53
Reformat	38,67	23,27	34,67
Toluene	2,85	12,85	3,30
Fraction 130° C-EBP	9,88	10,28	9,88
Fraction IBP-130 °C	1,40	1,40	1,40
Fraction IBP-62 °C	6,30	8,90	6,85

1-Project raw materials;

2-raw Materials with high content of benzene and benzene-forming components;

3-raw Materials with high content of hydrocarbons C₇₊

Thus, including the stage production of the components of commercial gasoline blending allows you to adjust the optimum ratio of threads in the process of commodity production in terms of changes in their quality indicators. The proposed technical solution for the selection of the lateral shoulder strap and its further processing in the process of isomerization of the C₇ fraction with recirculation of unbranched heptanes allows to increase the use of low-octane fractions by 4.5% by volume by increasing their operational properties.

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HIGHLY DISPERSED CATALYSTS FOR OIL HYDROPROCESSING IN SUPERCRITICAL CONDITIONS



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Oil is a complex mixture of organic compounds that can contain such heteroatoms as O, N, S, P, and metals. The oil composition is mainly represented by linear hydrocarbons with carbon number 4-30 as well as aromatic and naphthenic compounds. Besides the rectification, oil processing requires the heteroatom removal and cracking of heavy hydrocarbons. Catalytic hydrotreatment of oil fractions is a widely used technique that includes such reactions as catalytic hydrocracking and hydrodesulfurization [1].

Nowadays, the studies focused on the development of novel approaches for oil hydroprocessing are of great interest. These researches are divided into two main groups: (i) the search of novel highly effective catalysts and (ii) the search of process conditions allowed the process feasibility to be increased.

The use of supercritical fluids in the oil fraction hydrotreatment is one such perspective ways. Water is one of the widely used supercritical solvents because of its unique properties in the supercritical state allow the petroleum hydrocarbons to be effectively dissolved. Because of the oxidizing capacity, supercritical water (SCW) can be applied in desulfurization [2, 3]. Hydrocracking in SCW results in the high feedstock conversion and high yield of light petroleum fractions because of the hydrothermal decomposition of heavy oils. Besides, SCW can serve as a hydrogen donor that allows the process to be carried out in an inert atmosphere [4, 5]. Other hydrogen-donors are supercritical tetraline [6], hexane, dodecane [7] and light alcohols [8]. All studies conclude that the use of supercritical solvents, in addition to the complete removal of heteroatoms and high conversion of feedstock, leads to a decrease in the viscosity and density of the resulting product, as well as prevents coking of the catalyst [6].

The second direction of hydroprocessing development is the use of sulfur-free oxide catalysts. The activity of oxide catalysts in hydrodesulfurization and hydrocracking processes directly depends on the dispersion of the active phase and the presence of hydroxyl groups on the catalyst surface [9]. High dispersion of the active phase can be achieved by special methods of synthesis of supported catalysts, in particular, the use of solvothermal deposition [10].

In this work, the study of hydroconversion of model compounds of oil (dibenzothiophene and anthracene) was performed in the medium of supercritical solvents. Two types of SCF (hexane and propanol-2), as well as their mixture, were used. The influence of solvent composition as well as the presence of hydrogen was investigated. Transition metal catalysts deposited hydrothermally on the polymeric matrix of hypercrosslinked polystyrene were used for this study.

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MAGNETICALLY RECOVERABLE CATALYST BASED ON HYPERCROSSLINKED POLYSTYRENE FOR CELLULOSE HYDROCONVERSION INTO GLYCOLS**Manaenkov O.V., Kislitsa O.V., Ratkevich E.A., Matveeva V.G., Sulman M.G., Sulman E.M.***Tver Technical University, Tver, Russia**E-mail: ovman@yandex.ru*

Glycols are an important feedstock; they are commonly used in different branches of modern industry [1, 2]. It is obvious that the demand for these polyols is extremely high. New possibilities in catalysis are offered by the use of magnetically recoverable catalysts [3]. In this research, a novel catalysts on the base of hypercrosslinked polystyrene (HPS) with magnetic properties are proposed for the one-pot processes of the cellulose conversion into ethylene glycol (EG) and propylene glycol (PG). Synthesized magnetically recoverable supports and catalysts were characterized by different physical-chemical methods. The magnetic properties of the supports $\text{Fe}_3\text{O}_4/\text{HPS}$ MN270 and the corresponding catalysts were studied. The use of this catalyst in the process of microcrystalline cellulose hydrogenolysis in subcritical water allows PG and EG selectivities of 20.0 and 22.6%, respectively, at 100% of cellulose conversion.

HPS-based magnetically recoverable Ru-containing catalysts were synthesized according to the following procedure. 0.3 g of HPS was placed to the 10 mL of EtOH with preliminarily dissolved calculated amounts of FeCl_3 and CH_3COONa . Then, the sample was heated up to 200 °C in argon medium and maintained at this temperature for 5 h. Resulting $\text{Fe}_3\text{O}_4/\text{HPS}$ was washed with distilled water and then with EtOH. Washed sample of magnetically separable $\text{Fe}_3\text{O}_4/\text{HPS}$ containing *ca.* 20 wt. % of Fe.

For the synthesis of Ru- $\text{Fe}_3\text{O}_4/\text{HPS}$ catalyst, $\text{Fe}_3\text{O}_4/\text{HPS}$ MN270 was impregnated according to moisture absorption capacity with the solution of the calculated amount of ruthenium (IV) hydroxochloride in a complex solvent consisting of tetrahydrofuran, methanol. Then the catalyst was reduced in hydrogen flow (flow rate 100 mL/min) at 300 °C for 2 hours, cooled in nitrogen and kept under air. In this way, Ru-containing system with calculated ruthenium content of 3 wt.% was synthesized.

The experimental samples were shown to have a high saturation magnetization (4.0 ± 0.5 emu/g, Figure 1). The magnetization curves no remanence or coercivity is observed, demonstrating superparamagnetic behavior which is characterized for magnetite. A high value of saturation magnetization allows for fast magnetic separation of the $\text{Fe}_3\text{O}_4/\text{HPS}$ MN270 particles (Figure 2).

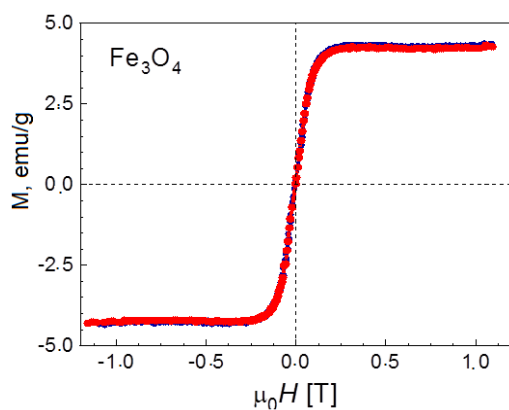


Figure 1: Magnetic properties of $\text{Fe}_3\text{O}_4/\text{HPS}$ MN270.



Figure 2: $\text{Fe}_3\text{O}_4/\text{HPS}$ MN270 before and after magnetic separation.

The synthesis method of catalyst (3 % Ru- $\text{Fe}_3\text{O}_4/\text{HPS}$ MN270) was developed. Synthesized magnetically recoverable supports and catalysts were characterized by different physical-chemical methods. The use of this catalyst in the process of microcrystalline cellulose hydrogenolysis in subcritical water at 255 °C, 60 bar hydrogen pressure in 50 minutes allows PG and EG selectivities of 20.0 and 22.6%, respectively, at 100% of cellulose conversion. The catalyst is stable under hydrothermal conditions of the process; it is easily separated from the liquid phase with the external magnetic field and can be reused. Therefore, the results of the research prove the advantages of the use of magnetically retrievable catalysts in biomass processing into chemicals.

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THE DEVELOPMENT OF NICKEL MEMBRANES FOR HYDROGEN PURIFICATION

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Hydrogen is a perspective and important energy carrier for development of renewable energy technologies. At the present time, the main method of hydrogen synthesis is the steam reforming of hydrocarbon fuels, especially steam methane reforming. During the synthesis, hydrogen is contaminated with other gaseous components of the reaction medium, such as carbon monoxide (II), nitrogen, methane, etc. To obtain hydrogen, being suitable for energy and industrial applications, with a high degree of purification, it is necessary to separate hydrogen from impurities. The hydrogen industry actively developing, development of hydrogen separation technologies with a high degree of purification and low cost is required [1].

Membrane separation is a promising method for hydrogen purification. One of the advantages of hydrogen selective membranes is the possibility of their direct implementation into a reformer. In addition to the purification of hydrogen from gas impurities, membranes allow increasing the hydrogen yield by removing the product from thereaction medium according to the Le Chatelier's principle [2]. Membranes for hydrogen purification can be made from various materials, but dense metallic membranes are most widely used.since metals, due to the dissolution of hydrogen in them, can provide high selectivity. This is explained by the fact that hydrogen passes through metals by the adsorption / dissolution / desorption mechanism, which provides high selectivity. The most studied metal membranes are palladium-based membranes, since palladium has the highest hydrogen permeability and also has catalytic properties. However, a number of significant drawbacks limit the use of palladium membranes in large-scale industrial production. In this regard, cheap palladium analogue is being developed. One of the promising substitutes for palladium in metal membranes is nickel. The advantages of nickel-based membranes include low cost and high resistance to toxic substances. In addition, nickel is also a catalyst for methane steam reforming. However, the disadvantage of nickel-based membranes is low hydrogen permeability compared to palladium [1].

Hydrogen flowing through nickel are limited by diffusion, one way to increase the yield of separating hydrogen is to obtain a developed surface. Traditionally, industrial nickel capillaries were used as nickel membranes. However, nickel capillaries have a massive structure, which reduces hydrogen permeability. Thus, to modify the surface in our work, we propose a method for producing nickel hydrogen selective membranes by controlled oxidation-reduction of industrial nickel capillaries.

According to estimates, nickel oxide after reduction by hydrogen loses about 41% of the volume, which turns into a open porous structure with channels in the volume and radial direction [3]. In addition, the study [4] showed that nickel oxidation is limited by the diffusion of nickel cations to the outside, which means that the nickel oxide front moves linearly. Thus, the mechanisms of nickel oxidation and nickel oxide reduction make it possible to modify the surface partially oxidizing and reducing it with a creation of a developed porous surface along the edges and a dense layer in the middle. In the present work, the influence of oxidation and reduction conditions of industrial nickel capillaries on their structural organization and morphology is shown. The resulting membranes will be characterized by a complex of physicochemical research methods. Thus, the selection of synthesis conditions will be carried out, ensuring the optimal structure from the point of view of hydrogen purification.

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CONTENT

POSTER PRESENTATIONS



GUARD BED CATALYST: ROLE OF TEXTURAL PROPERTIES AND THEIR CHARACTERIZATION

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The objective of this work is to develop an improved HDM guard-bed catalyst for residue/heavy oil hydrotreatment that has high HDM activity and large metal capacity, which will enable the catalyst to operate for a longer period. This objective was achieved by designing new catalyst support with optimized textural and mechanical properties. The new support was prepared by using different Al₂O₃/activated carbon ratios, which pores were further modified during the controlled calcination. The utilization of carbon in support increased the pore volume and the macro-pores in the catalyst. The large pore volume positively contributed to the higher metal retention capacity, while macro-pores reduced the diffusion limitation, which allowed the large hydrocarbon molecules (i.e., asphaltene) to reach the inner catalytic sites and enhanced their conversions [1-2]. The utilization of carbon support also reduced the coke and metal depositions on catalytic sites. Such selective deposition on the support surface, rather than pore mouth and catalytic sites, significantly contributed to the catalyst stability. The active phase assessment indicated that the most active catalyst is the FeMo, while the optimum textural and mechanical properties for support are obtained when the Alumina-Carbon ratio is 1:1 [3]. The activity and the stability of the prototype catalysts were assessed by using the atmospheric residue of Lower-Fars crude oil (one of Kuwait's heaviest crudes) and Mexican Ku crude oil. Both feedstocks are known for their high asphaltene and metal contents, where LF-AR has 7.3 wt% asphaltene and 212 ppm metals while Ku crude oil has 13.4 wt% and 579 ppm, respectively.

To characterize the catalyst texture, N₂ physisorption and mercury (Hg) porosimetry were used, which covers micro-/meso- and macro-pores. N₂ physisorption showed substantially lower pore volume, average pore diameter (APD), and pore size distributions (PDS) from Hg-intrusion. Hence, the focus has been given to the techniques that can identify meso- and macro-pores satisfactorily. Major structural changes of the pores were observed based on the Hg intrusion-extrusion results of the fresh and spent catalysts (**Figs. 1a** and **1b**). The fresh and spent catalysts textural results illustrated significant changes in the catalyst morphology that is mainly due to the metal and carbon depositions during the processing. The pore volume and the pores of diameter smaller than 100 nm significantly decreased in spent catalysts indicating selective deposition of metal and

carbon around the pore, which usually close smaller pores. The catalyst has an average pore diameter of 20-1000 nm, a total pore volume of 0.3-1.5 ml/g. The hydroprocessing activities of the catalyst were reported with time-on-stream (TOS) for various reactions such as HDS, and HDAs. The physical characterization and activity results indicated that the smaller the pore diameter, the shorter the catalyst's life.

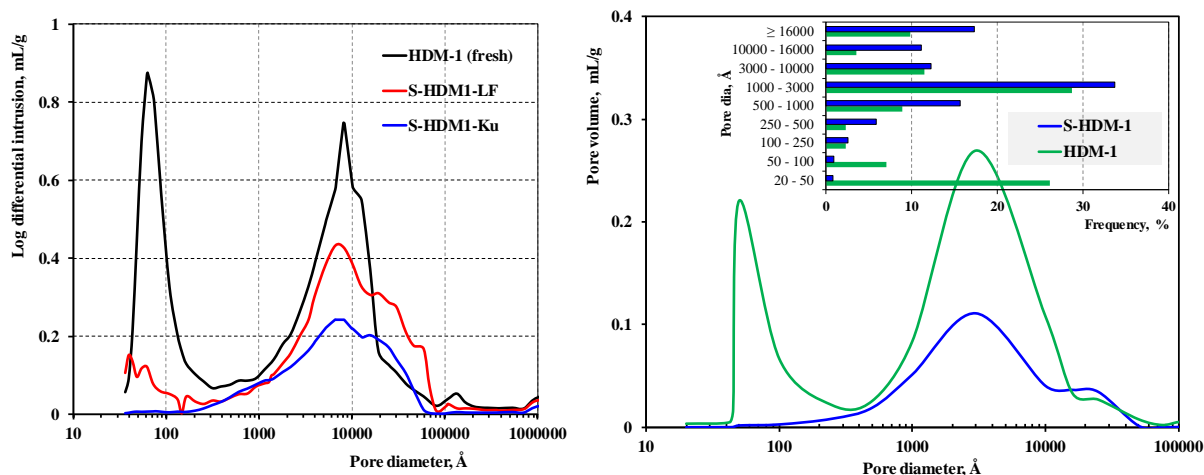


Fig. 1. Fresh and spent catalysts pore diameters (a) changes with two different feeds during the treatment and (b) variation in specific pore diameter measured by Hg porosimetry

However, types of pores vary with different catalysts as a function of support composition and feed treated. Fig. 1a, shows the comparison between the pore intrusion of fresh and the corresponding spent catalysts that were deactivated due to the catalyst tested against LF-AR and Ku crudes. Catalyst treated with Ku crude was highly deactivated compared to LF-AR treated catalyst. Moreover, these catalysts were active and performing their reactivities with respect to time-on-stream (TOS). This study is leading toward an improved guard-bed catalyst for feed that contains large amount of metals and asphaltene, which is being treated using large pore carbon-alumina support with optimized textural properties that have high metal and carbon retention capacity to ensure satisfactory run durations with TOS (1200 hrs).

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INVESTIGATION OF THE INFLUENCE OF STABLE GAS CONDENSATE ZEOFORMING PROCESS TECHNOLOGICAL PARAMETERS ON THE OBTAINED PRODUCTS CHARACTERISTICS

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Presently one of the most actively developing areas in the field of catalysis is the use of zeolite catalysts. Zeolites are used in the processes of cracking, alkylation, isomerization, dewaxing, also studies, the possibility of their use in other oil refining processes, are actively being [1]. It is important to note that advantages of zeolite catalysts are their environmental friendliness, profitability, and also resistance to catalytic poisons. The process of producing high-octane motor fuels components, using a zeolite catalyst, is called zeoforming. The advantage of this process is the possibility of using a fairly wide range of light hydrocarbons feedstock, including stable gas condensate [2] for the production of gasoline components.

The aim of this work is to study the influence of stable gas condensate zeoforming process technological parameters on the obtained products characteristics. In the course of work zeoforming of stable gas condensate was implemented at the laboratory catalytic unit. Samples of stable gas condensate, using in the work, is being obtained as a by-product in the processing of commercial gas at one of the oil and gas fields in Siberia. A block diagram of stable gas condensate production is shown in Figure 1. Test conditions are presented in Table 1.

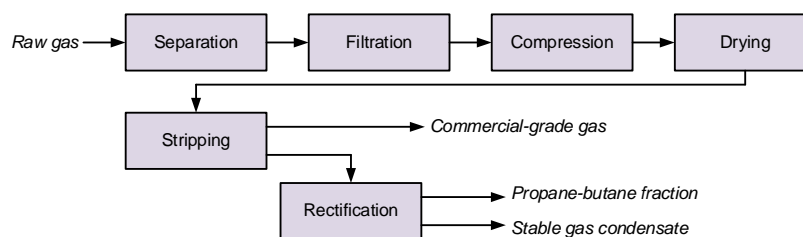


Figure 1. Block diagram of stable gas condensate production

Table 1. Test conditions

No.	Temperature, °C	Pressure, MPa	Feedstock space velocity, h ⁻¹
1	325	0.25	2
2	350	0.25	2
3	375	0.25	2
4	375	0.35	2
5	375	0.45	2
6	375	0.25	3
7	375	0.25	4

The characteristics of feedstock and obtained products were calculated using the “Compounding” software package and results of a chromatographic analysis [3]. The results of the calculation are

PP-2

presented in Table 2 (RON – research octane number, MON – motor octane number, SVP – saturated steam pressure).

Table 2. Characteristics of feedstock and products obtained on different test conditions

Characteristics	Feedstock	1	2	3	4	5	6	7
RON	67.2	73.7	81.7	85.1	87.4	76.5	84.2	83.1
MON	64.0	70.4	77.2	79.9	82.6	71.8	79.7	78.8
SVP, kPa	65.5	85.8	119.6	117.2	151.1	62.7	139.8	134.7
Density, kg/m ³	692.5	684.2	696.8	713.5	706.9	724.9	694.8	692.9
Olefins, % vol.	1.68	2.33	2.68	2.19	5.02	6.14	4.33	4.76
Isoparaffins, % vol.	44.40	49.92	47.35	45.33	44.67	41.84	47.14	46.55
Aromatics, % vol.	3.26	5.99	11.93	19.08	16.02	13.29	11.29	10.06
Benzene, % vol.	0.17	0.25	0.63	1.42	0.06	0.6	0.06	0.07

From the results presented in Table 2 it follows that with an increase in the process temperature, the content of aromatic hydrocarbons sharp increases and the product octane number increases. With increasing process pressure, the content of aromatic and isoparaffin hydrocarbons in the product composition decreases, which entails a decrease in the octane number.

With an increase in the feedstock space velocity, the residence time of the feedstock in the reaction zone decreases and, as a result, the content of isoparaffinic increase and the content of aromatic hydrocarbons decrease. The obtained results indicate that at a feedstock space velocity of more than 2 h⁻¹, the residence time of the feedstock-catalyst is insufficient for the formation of aromatic hydrocarbons. With an increase in the feedstock space velocity to 4 h⁻¹, the content of isoparaffins in the product also decreases, which indicates that at a feedstock space velocity of more than 3 h⁻¹, the contact time is also insufficient for isomerization reactions.

From the point of view of gasoline production, it is important that the obtained product has a high octane number and at the same time low SVP and benzene content, since these indicators are strictly regulated [4].

Thus, from the point of view of gasoline components production, the most promising of the presented products is the product obtained in the test No. 2. This product is characterized by a sufficiently high octane number and a relatively low SVP and benzene content.

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HYDRODESULFURIZATION OF SULFUR-CONTAINING AROMATIC COMPOUNDS VIA WGSR OVER DISPERSED Ni–Mo SULFIDE CATALYSTS

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Hydrodesulfurization (HDS) is of a great importance on producing high quality fuels with lower sulfur and aromatics contents meeting strong ecological requirements [1]. Thus, more active and efficient catalysts should be developed.

Conventional HDS catalysts are usually bimetallic systems containing Mo or W promoted by Co or Ni and supported on γ -Al₂O₃, zeolites, etc [2, 3]. Generally, supports used to provide high dispersion of active metal phase and mechanical stability. However, for conventional catalysts, based on microporous zeolites or aluminium oxide, mass transfer and diffusion limitation lead to pore blocking and coke formation followed by sintering of active phase and catalysts deactivation, especially for feedstocks with high asphaltenes and organometallic compounds content [4]. Dispersed unsupported catalysts could effectively solve this problems [5].

The promising way to obtain unsupported sulfide catalysts is the high-temperature decomposition of oil- or water-soluble metal precursors in the presence of sulfiding agent and surfactant stabilising invert emulsions [6]. This method ensures the formation of stable nanoparticles with a high content of the active phase in the reaction medium [7]. At the same time, transition metal sulfides being the main component of conventional HDS catalysts, also active in water gas shift reaction (WGS) [8, 9]. Thus, the Mo-sulfide catalysts could be used for HDS via *in situ* hydrogen generation through a WGS in CO/H₂O system [10].

The present work is devoted to testing of dispersed unsupported Ni-Mo sulfide catalysts in HDS of organosulfur compounds (benzothiophene, dibenzothiophene and its derivatives) in aqueous medium under CO pressure. These unsupported catalysts were *in situ* formed during HDS through high temperature decomposition-sulfidation of water-soluble metal precursors ((NH₄)₆Mo₇O₂₄·4H₂O and Ni(NO₃)₂·6H₂O) using elemental sulfur as a sulfiding agent and surfactant (SPAN-80) to stabilize W/O emulsion. The structure of Ni-Mo-sulfide catalysts were revealed by XRF, TEM and XPS. The catalytic testing was performed over the temperature range of 380-420°C, CO pressure of 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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DEVELOPMENT OF THE FORMALIZED SCHEME OF CHEMICAL CONVERSIONS IN THE PROCESS OF VACUUM GAS OIL HYDROTREATING FOR THE PROCESS MODELLING

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Due to an increase in the share of heavy oils in the production structure and toughening environmental requirements for motor fuels worldwide, the catalytic cracking process and the preceding stage of vacuum gas oil hydrotreating have taken the leading role as the main processes for upgrading and increasing the depth of oil refining.

The quality of the catalytic cracking process products (the content of sulfur and nitrogen compounds, and olefins), as well as the activity and service life of the catalyst, which is poisoned by heavy metals, present in vacuum gas oil, largely depend on the quality of the feedstock preparation at the hydrotreating stage [1].

The industrial process of vacuum gas oil hydrotreating is characterized by high demand for hydrogen-containing gas, severe technological conditions, and rapid deactivation of catalysts, which makes mathematical modeling more relevant to further optimize the process, taking into account these mutually affecting factors, to reduce production costs while maintaining the required degree of treating of raw materials for subsequent processing in catalytic cracking process.

This work is aimed at studying the physicochemical laws of the process of vacuum gas oil hydrotreating and developing a mathematical model based on the identified physicochemical laws of the process.

The object of the study is vacuum gas oil with boiling limits of 180 – 550 ° C, the sulfur content of which, according to the results of experimental studies by spectroscopy, ranges from 1.040% wt. up to 1.655% wt.

The initial stage in the development of the vacuum gas oil hydrotreating process mathematical model is the determination of key reactive substances based on the studies of vacuum gas oil composition and identification of the patterns of conversion of hydrocarbons and heteroatomic compounds during the process, on the basis of which a chemical reaction scheme is developed. Due to the complexity of the chemistry of the deep processing of hydrocarbon feeds, as well as the large number of individual components of the reaction mixture and individual reactions, their complete kinetic models are very complex, therefore various simplifications are used based on the

grouping of individual reagents and individual reactions into group pseudo-reagents and group reactions, respectively [2].

The developed scheme of chemical transformations in the hydrotreating process consists of 14 pseudo-components and 15 reactions (Fig. 1).

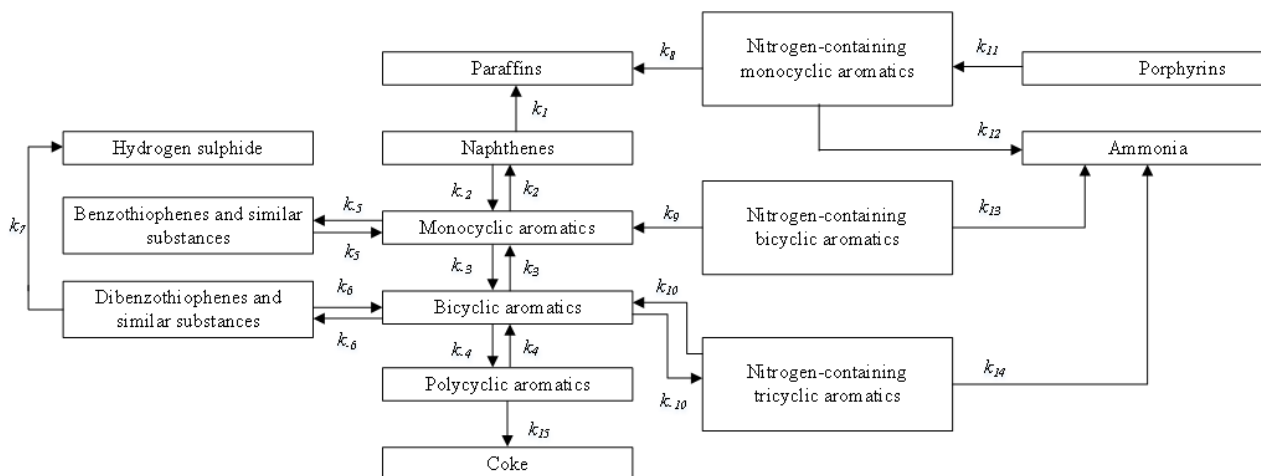


Fig. 1. The formalized scheme of chemical conversions in the process of vacuum gas oil hydrotreating

The chosen level of formalization of chemical transformations implies the occurrence of both target and side reactions in the hydrotreating process and allows, on the one hand, reducing the dimension of the mathematical model and the number of experimentally determined parameters, and on the other hand, preserving the sensitivity of the model to the composition of raw materials and makes it possible to predict the composition and product quality.

The developed mathematical model will make it possible to predict the degree of vacuum gas oil hydrotreating process, the degree of catalyst deactivation and its service life, and to optimize the process of vacuum gas oil hydrotreating and the associated catalytic cracking process.

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HYDROCARBONS CONVERSION REGULARITIES OF DIESEL FRACTION WITH ATMOSPHERIC GAS OIL DURING HYDRODEPARAFFINIZATION

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With the involvement in the refining an increasing amount of heavy paraffin oil, hydrodewaxing processes takes on greater and greater importance [1]. The choice of the hydrodewaxing process conditions by the means of mathematical modeling in order to improve a diesel fuel cold flow properties under industrial conditions on the change of the processed feedstock composition and the catalyst activity is an urgent task for the winter and arctic fuels production.

The diesel fraction yield functional dependency of temperature, the feedstock hydrocarbon composition and feed space velocity, the catalyst acid and metal activity balance, represented by the partial differential equations system, allows to predict the compounded diesel fuel low-temperature properties.

To determine the influence pattern of the hydrodewaxing process conditions on the unit performance and to verify the mathematical model adequacy, the results of pilot industrial tests were used at various feed space velocities and different processed feedstock hydrocarbon compositions. For the yield of a diesel fraction with certain cold flow properties an extreme dependence of temperature and feed space velocity is established. With increasing temperature and a decrease in the feed space velocity, the diesel fuel yield decreases and the yield of hydrocarbon gas and gasoline fractions increases. At high temperatures ($T = 340-370$ ° C) and low feed space velocities, mainly increases the high molecular weight paraffins ($C_{22} +$) hydrocracking reaction intensity.

It was found that the extremum position in the graph also depends on the catalyst acid and metal activity balance, since coke is deposited on the reaction surface as a result of polycondensation reactions. On a bifunctional catalyst selective hydrocracking of the feedstock takes place during dewaxing. Only unbranched normal paraffins can enter the catalyst pores and be transformed into smaller molecules by cleavage (Fig. 1).

Selective hydrocracking target reactions proceed at acid sites through intermediate stage of olefin formation at metal sites. In this case, a change in the acidic and metal active centers number ratio occurs, which affects the rates of hydroisomerization, hydrocracking and unsaturated aliphatic hydrocarbons hydrogenation. Faster deactivation of metal centers compared with acid centers

PP-5

occurs due to coke deposition, sulfur poisoning and Ni-containing catalyst particles sintering. Whereas the acid sites deactivation occurs only as a result of coking.

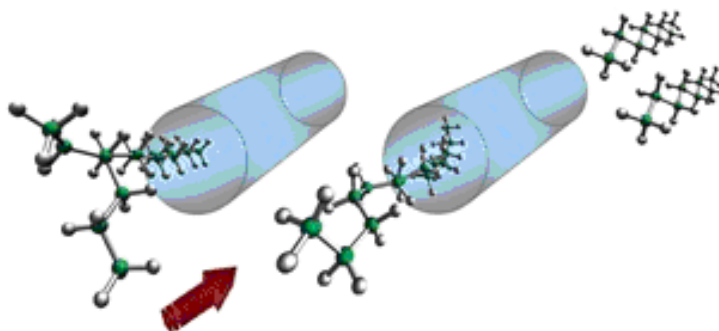


Figure 1 - The hydrodewaxing catalyst action principle

The calculations also showed that the hydrodewaxing process product cold flow properties are determined not only by the high melting point paraffins content and their crystallization rate, but also by the aromatic hydrocarbons content, which is confirmed by the Schröder – Le Chatelier solubility equation:

$$\ln(x) = A - B / T \cong A + BT,$$

where x is the solubility of n-alkanes (g/kg);

T is the temperature.

The bifunctional dewaxing process mathematical model, taking into account the coke formation rate, allows us to evaluate the catalyst deactivation degree, as well as to predict the its activity depending on the processed feedstock volume.

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INVESTIGATION OF THE SYNTHESIS PARAMETERS INFLUENCE ON THE PRODUCT YIELD AND CHARACTERISTICS OF THE PRODUCED BIODIESEL FUELS

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Over the past century, human consumption of energy, such as oil and gas, has increased by several times, while the natural resources are being run low, whereas the demand for various motor fuels is constantly increasing. In addition, ecological issues regarding the burning of petroleum fuels are being in hot discussion. [1, 2]. In this vein, the issue targeted at finding alternative energy sources and fuels, which will be renewable and environmentally friendly, is one of the most relevant challenges in our age.

The most prospective among the alternative fuels is biodiesel. Biodiesel is a mixture of fatty acids monoalkyl esters (most often methyl or ethyl) obtained from transesterification reaction of renewable biological resources, such as vegetable oils, animal fats, algae, etc. [3].

The characteristics of the synthesized end product – biodiesel – depend on many parameters: a type of feedstock, a ratio of source reagents and their chemical composition, purity of source reagents, moisture content of feedstock, conditions in which a reaction is conducted (temperature, reaction time, pressure), a type of catalyst used, and etc. Thus, the parameters affecting the biodiesel synthesis remain under high attention of many scientists around the world.

As a feedstock for the biodiesel synthesis, widely available unrefined sunflower oil was used. The temperature of the transesterification reaction was 45 °C; reaction time – 1 hour; the ratio of oil: alcohol was taken equal to 1: 9; ethyl alcohol was the transesterifying agent [4]; NaOH was used as a catalyst; concentration varied from 0.5 to 3.0 %wt. by oil weight. The main physicochemical characteristics of the obtained products are presented in Table 1.

Table 1 – Characteristics of the obtained biodiesel

Characteristic	Synthesis 1	Synthesis 2	Synthesis 3	Synthesis 4
Catalyst concentration, %wt.	0.5	1.0	2.0	3.0
Density at 15 °C, kg/m ³	896.3	901.9	905.9	901.4
Dynamic viscosity at 40 °C, mPa·s	4.758	8,648	7.092	6.943
Kinematic viscosity at 40 °C, mm ² /s	5.437	9,815	8.009	7.865

As can be seen the products obtained at the catalyst concentration of 0.5 wt% is characterized by the lowest density and viscosity. The results are explained by the fact that with a catalyst lack, the most reactive substances will react, the intermediates formation will be small, and the product separation will be as clear as possible. The products obtained at a catalyst concentration of

PP-6

1.0 %wt. characterized by highest viscosity, which is associated with a intermediates high yield and with the impossibility of a product mixture clear separation. The product obtained at a catalyst concentration of 2.0 %wt. characterized by highest density, which is explained by the fact that the feedstock reacted most fully with the formation of heavier substances in the target product.

The biodiesel yields at various catalyst concentrations are presented in Table 2.

Table 2 – Biodiesel yields at various catalyst concentrations

Characteristic	Synthesis 1	Synthesis 2	Synthesis 3	Synthesis 4
Catalyst concentration, %wt.	0.5	1.0	2.0	3.0
Initial components mass, g	511.7	513.5	517.2	520.9
End product mass, g	32.6	402.1	499.1	102.6
Yield, %wt.	6.4	78.3	96.5	19.7

As seen from Table 2, the feedstock conversion increases with increasing the catalyst concentration, however, to a certain limit. At the catalyst concentration of 3.0 %wt. the biodiesel yield decreases harshly, in addition, significant soap formation is observed, which complicates the products separation.

Thus, from the viewpoint of physicochemical characteristics and yield of biodiesel, the optimal catalyst concentration is 2.0 %wt. by oil weight.

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IMPROVEMENT OF STRAIGHT-RUN DIESEL FUEL LOW-TEMPERATURE PROPERTIES ON THE ZEOLITE CATALYST

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Today, the oil refining industry is dynamically developing, motor fuel production processes are being modernization and optimization, new methods and approaches in the field of industrial catalysis are being developed. One of important field is the development of process that improve the low-temperature properties of motor fuels. From this viewpoint, the most promising is use the processes of improving on zeolite catalysts, that is gaining increasing popularity. Zeolites are microporous aluminosilicates that have found many industrial applications due to several advantages, such as low capital investment and operating costs, explosion and fire safety, high activity and low sensitivity to the feedstock quality and catalytic poisons [1, 2].

Based on the above advantages, a study of the feasibility and effectiveness of using these catalysts for improve diesel fuel operational characteristics was conducted. The improving process on the zeolite catalyst was carried out on a laboratory catalytic unit at a temperature of 375 °C, a pressure of 0.35 MPa and a feedstock space velocity of 3 h⁻¹. As a feedstock, a sample of straight-run diesel fuel was used. The fractional composition (FC) of the sample, the main physicochemical and low-temperature characteristics are presented in Table 1 (CP – cloud point, CFPP – cold filter plugging point, PP – pour point).

Table 1 – Characteristics of a straight run diesel fuel sample

Characteristic	Value	Characteristic	Value
IBP, °C	134	Density at 15 °C, kg/m ³	836.5
FC _{10%} , °C	183	Dynamic viscosity at 20 °C, mPa·s	3.455
FC _{50%} , °C	263	Kinematic viscosity at 20 °C, mm ² /s	4.148
FC _{90%} , °C	342	CP, °C	-4
Cetane index, points	49.2	CFPP, °C	-9
Sulfur content, mg/kg	3911	PP, °C	-16

As can be seen from the data presented in Table 1, the straight-run diesel fuel sample has a high sulfur content and poor low-temperature properties (according to CFPP it can be used only as A-C grades summer diesel fuel, according to the requirements of [3]).

Fractional composition, the main physicochemical and low-temperature characteristics of the obtained product are presented in Table 2.

From the presented data it can be seen that the obtained product, in comparison with the feedstock straight-run diesel fuel, is characterized by a lower density (by 1.5 kg/m³), dynamic viscosity (by 1.652 mPa·s), kinematic viscosity (by 1.981 mm²/s) and sulfur content (by 170 mg/kg).

PP-7

The obtained product is characterized by lower *IBP* and *FC*_{50%}, which indicates the occurrence of cracking reactions with the formation of gases and light hydrocarbons, and the cetane index value decreased (by 2.9 points). In addition, the improving process on the zeolite catalyst allowed to significantly improve the low-temperature properties of the fuel, so the *CFPP* of the product compared to feedstock decreased by 42 °C.

Table 2 – Characteristics of the obtained product

Characteristic	Value	Characteristic	Value
<i>IBP</i> , °C	39	Density at 15 °C, kg/m ³	835.0
<i>FC</i> _{10%} , °C	123	Dynamic viscosity at 20 °C, mPa·s	1.803
<i>FC</i> _{50%} , °C	254	Kinematic viscosity at 20 °C, mm ² /s	2.167
<i>FC</i> _{90%} , °C	356	<i>CP</i> , °C	below -70
Cetane index, points	46.3	<i>CFPP</i> , °C	-51
Sulfur content, mg/kg	3741	<i>PP</i> , °C	below -70

As can be seen from the data presented in Table 2, the obtained product for all characteristics, except for the sulfur content (not more than 10 mg/kg), meet the requirements of [3] for Arctic diesel fuels (class 4).

Thus, the process of improving the straight-run diesel fuels on a zeolite catalyst is an effective and promising process, that can significantly improve the feedstock low-temperature properties and produce Arctic diesel fuel without the addition of depressant additives. However, for fully meet the requirements of [3], hydrotreating of obtained product is required.

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MICRO-MESOPOROUS Pt-CONTAINING CATALYSTS FOR XYLENES HYDROISOMERIZATION

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Hydroisomerization of C-8 aromatic fraction is one of the most effective ways to obtain p-xylene (PX), which in turn is the main raw material for the production of terephthalic acid further converted to polyethylene terephthalate. During gas-phase isomerization two basic reaction mechanisms can take place: intermolecular (1,2-alkyl shift in a benzenium ion) and intramolecular (disproportionation, trimethylbenzene formation, and its further transalkylation) [1]. The latter makes a significant contribution to the conversion of ethylbenzene, which is the least desirable component in C-8 aromatic fraction. However, the most commercialized ZSM-5-based catalysts essentially contribute to intermolecular mechanism suppressing intramolecular pathway due to the steric hindrance of the transition state in small zeolite pores. Hence, to facilitate both inter- and intramolecular routes, micro-mesoporous materials with bimodal pore distribution may be applied as isomerization catalysts support.

In this work new functional materials based on microporous ZSM-5 zeolite in conjunction with mesoporous ZSM-12 and MCM-41 aluminosilicates were synthesized and investigated as catalyst components for the isomerization process. Micro-mesoporous MCM-41/ZSM-5 composite was synthesized by a double-template method using TPAOH and CTAB as templates. Zeolite of ZSM-12 was prepared with TEABr as a template and then mechanically mixed with commercial ZSM-5 zeolite. The resulting material is referred to as ZSM-12/ZSM-5. Based on the materials obtained, extrudates with a diameter of 1 mm and 2–5 mm in length were prepared using boehmite (40% wt.) as a binder. The supports were loaded with hexachloroplatinic acid by a standard incipient wetness impregnation to achieve 0.5 % wt. metal loading. Textural, structural properties, acidity, elemental composition and micro-mesopores retention during the synthesis steps were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), N₂-adsorption-desorption, ammonia temperature programmed desorption (NH₃-TPD), X-ray fluorescence (XRF) and thermal gravimetric analysis (TGA). According to the data obtained from nitrogen adsorption/desorption isotherms, all the materials had ordered micro/mesoporous system, which didn't collapse after carriers formation and Pt deposition. The catalysts also possessed relatively high acidity – up to 1400 μmol NH₃/g.

PP-8

The activity and selectivity of the synthesized catalysts were investigated in hydroisomerization of the xylene reforming fraction in a flow-type laboratory unit with a fixed bed and compared to the same of a commercial catalyst. The process conditions: H₂:feed molar ratio 5, LHSV 1-6 h⁻¹, catalyst volume 5 mL, hydrogen pressure 1.0 MPa, and temperature range 350–400°C. Liquid and gaseous products were analyzed by gas chromatography.

As it had been predicted, the synthesized catalysts were found to provide better feed conversion in comparison to the industrial catalyst. It was proven that the pore size affects the reaction mechanism, and mesopores make a large contribution to intramolecular reaction pathway providing fuller EB transformation. As compared to the commercial catalyst, the EB conversion increase achieved 4 % on Pt/(ZSM-12/ZSM-5) and 40 % on Pt/(MCM-41/ZSM-5). Though on MCM-41/ZSM-5-based catalyst the substrates conversion raised significantly, dealkylation also took place at higher temperatures giving undesirable toluene and benzene. However, ZSM-12/ZSM-5-based catalyst decreased the number of dealkylation products and demonstrated excellent selectivity to PX which is up to 12% higher than the same on the industrial catalyst.

The optimal temperature range providing high *p*-xylene selectivity and ethylbenzene and *m*-xylene conversion was 320-340°C at LHSV = 1h⁻¹. Under these conditions the catalysts' stability was evaluated during 100 hours of continuous operation and it decreased only by 1.4 %.

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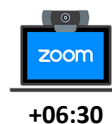
Acknowledgements

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INFLUENCE OF FLOW RATE OF LINEAR ALKYL BENZENE IN FILM SULFONATION REACTOR ON CONCENTRATION OF TARGET PRODUCT AND TETRALINES AND SULFONES CONCENTRATION

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The obtaining of linear alkylbenzenesulfonic acid (ASA) which is used for the production of synthetic detergents is the final stage of a multi-stage chain, including the processes of linear alkane dehydrogenation, hydrogenation of polyolefins and their subsequent alkylation to linear alkylbenzene (LAB) sulfonated with sulfur trioxide.

LAB sulfonation reactor is represented by vertical reaction tubes with an inner diameter of 25 mm and a length of 6 meters located as in shell-and-tube heat exchanger. A stream of a mixture of gaseous sulfur trioxide and air is passed through a vertical pipe, where organic liquid feed flows simultaneously along the wall in the form of a pipe film. When liquid and gas flow through the pipe, sulfur trioxide is absorbed by the liquid and reacts to form a sulfonated product.

The accumulation of viscous components resulting from the occurrence of side reactions leads to clogging of the reactor tubes, as a result of which the hydrodynamic regime of the film flow is disturbed and the yield of the target product is reduced. Upon reaching a critical concentration of highly viscous components in the reactor, it is washed with water, which allows the removal of viscous compounds [1-2].

Thus, the aim of this article is to study the influence of the consumption of raw materials on the duration of the periods between reactor washings and the yield of the target product based on long-term data on industrial operation using the method of mathematical modeling.

Based on the performed thermodynamic calculations, a formalized scheme of transformations in the process of sulfonation of LAB with sulfur trioxide was compiled (Figure 1).

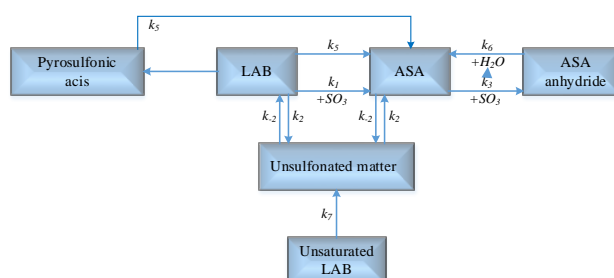


Figure 1 – The scheme of transformations in the process of sulfonation of LAB

Based on the above scheme of the conversion of substances, a mathematical model of the process in a film reactor has been developed, which allows quantifying the conversion rates of hydrocarbons depending on the contact time, the composition of the initial mixture, temperature and pressure in the system under the assumption of the ideal displacement mode. The rate constants of chemical reactions are determined by solving the inverse kinetic problem on the basis of experimental data.

To study the effect of reagent consumption, a calculation was carried out using the developed mathematical model of the process for one period between reactor washings.

Table 1 shows the results of calculations of changes in contact time, film thickness and Reynolds criterion from the mass flow rate of the liquid.

Table 1 – Variation of LAB consumption

Mass flow rate of LAB, kg/h	3500	4000	4500	5000	5500	6000	6500
Contact time, sec	27,0	24,7	22,8	21,2	19,9	18,8	17,8
Liquid film thickness, mm	0,57	0,60	0,62	0,65	0,67	0,69	0,70
Reynolds criterion	96,0	109,7	123,4	137,2	150,9	164,6	178,3
Mass transfer coefficient $\cdot 10^2$	1,73	2,21	2,75	3,33	3,97	4,66	5,39
Average ASA concentration, % mass.	97,13	97,17	97,21	97,22	97,23	97,24	97,24
The concentration of the viscous component on the last day of the period, % mass. $\cdot 10^2$	1,74	1,58	1,45	1,33	1,24	1,17	1,10

Mass transfer coefficient (1), influences the intensity of substance transfer inside the film and depends on the Reynolds criterion of liquid film and gas velocity: $\beta_l = 0,55 \cdot 10^{-6} Re_{film}^{\frac{1}{3}} w_g^{\frac{3}{2}}$.

An increase in the mass flow rate of LAB leads to a decrease in the contact time and an increase in the film thickness. At the same time an increase in the concentration of the target product and a decrease in the concentration of the viscous component takes place due to an increase in the mass transfer coefficient [3].

Thus, an increase in the consumption of raw materials supplied to the reactor leads to a decrease in the contact time, as a result of which the concentration of the highly viscous component is reduced, which allows to increase the duration of the periods between reactor washings. In this case, the yield of the target product does not decrease.

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SIMULATION THE CATALYTIC PROCESS OF ISOMERIZATION REACTION OF PENTANE-HEXANE FRACTION TO MAXIMIZE THE OCTANE NUMBER OF REACTION PRODUCTS



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The object of the study is the reactor unit of the catalytic isomerization unit of the pentane-hexane fraction, consisting of a cascade of three reactors. The first stage of the mathematical description of the object is the building of the scheme of hydrocarbon reactions during the process. In all known models [1–3] of the catalytic isomerization process of the pentane–hexane fraction, all the hydrocracking gases are combined into one product component, as a result of which it is impossible to predict the exact composition of hydrocarbon gases. In this work, an attempt was made to more detailed analysis of the transformation scheme based on the mechanism, including the reactions of hydrocracking products formation.

The mathematical model of the three-cascaded reactor block, adequately describing the chemical transformations within the reactors has been built and 102 kinetic parameters have been obtained [4]. Compared to the previous work, we added 3 reaction stages, this was done in order to examine the process in more detail and obtain greater accuracy of the calculations. Thus, we have obtained a refined kinetic model consisting of 108 kinetic parameters (54 activation energies and 54 preexponential factors).

The inverse problem of chemical kinetics belongs to the problems of continuous global optimization. Features of such problems are often nonlinearity, undifferentiability, multiextremality (multimodality), lack of analytical expression and high computational complexity of optimized functions, as well as high dimensionality of the search space. These features of chemical kinetics problems explain the lack of a universal algorithm for their solution. In this paper, we consider a harmony search method, which is one of the population algorithms. All population algorithms belong to the class of heuristic algorithms, that is, algorithms for which convergence to a global solution is not proven, but it is experimentally established that in most cases they give a good enough solution.

To solve the direct problem, the integration method ‘Radau’ was chosen; it’s an implicit Runge-Kutta method of the Radau IIA family of order 5 [6]. The error is controlled with a third-order accurate embedded formula.

In addition to solving the inverse problem, the conference will present the results of optimization of the reactor block in order to obtain dimethyl substituted components (2,2-dimethylbutane, 2,3-dimethylbutane), which affect the octane number of catalytic isomerization gasoline.

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GRAVITY SEARCH ALGORITHM FOR DETERMINING THE OPTIMAL KINETIC PARAMETERS OF LOW-TEMPERATURE STEAM CONVERSION OF C₂ + HYDROCARBONS

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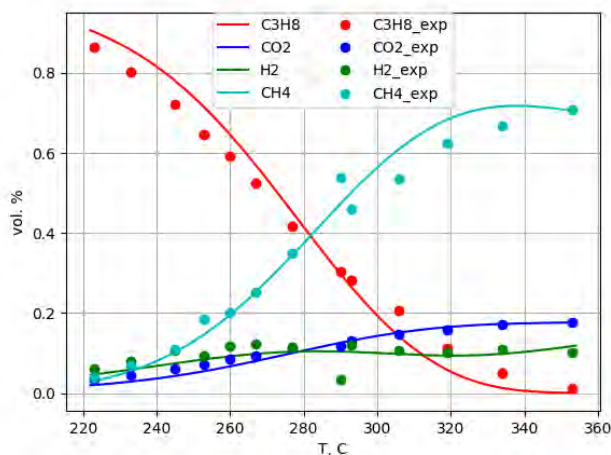
The Gravitational Search algorithm (GS) was proposed by E. Rashedi and other authors in 2009. The algorithm uses the analogy of the motion of heavy bodies due to their gravitational interaction. The gravitational force between two such bodies having masses m_1 , m_2 is determined by the law of universal gravitation, according to which this force is equal to $F = \gamma \frac{m_1 m_2}{r^2}$, where γ is the gravitational constant, and r is the Euclidean distance between the centers of mass of gravitating bodies. According to Newton's second law, the acceleration that a body of mass m acquires under the influence of this force is $a = \frac{F}{m}$.

In recent years, various heuristic optimization methods have been developed. Many of these methods are based on similar phenomena in nature, including the gravitational search algorithm. Since its appearance in 2009, GSA has attracted the attention of many researchers from a wide variety of fields [1]. In the case of GSA, it has been widely applied to real-world problems, ranging from power or electrical engineering to the water industry or biology. Thus, GSA has been widely applied in many problems of electrical engineering [2, 3], machine learning [4, 5], etc.

The gravitational search algorithm in this work was used to determine the optimal kinetic parameters of the reaction of low-temperature steam conversion of C₂ + hydrocarbons in a mixture with a high methane content [6]. A program was developed for modeling a process using the gravitational algorithm. The program is written in the programming language *Python 3* using modules such as *numpy*, *pandas*, *scipy*. The mathematical model described in work [7] was used, except that the inverse problem was solved within the framework of the power law kinetics.

Figure shows the results of calculations for experiments on propane pre-reforming at 1 atm.





In conclusion, we note that mathematical modeling of the propane pre-reforming process was carried out at pressures of 1 atm and temperatures of 220 - 360 °C. The inverse problem was solved by the gravitational search algorithm. To simulate the experiment, a solution to the inverse problem was found in the form of a fractional dependence by the power law kinetics. It is shown that the model correctly describes the experimental data and can be used to describe the process of propane pre-reforming and prediction of propane conversion under given reaction conditions.

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TWO STEPS SYNTHESIS OF BULK Ni/W CATALYSTS FOR 3-METHYL THIOPHENE DESULFURIZATION

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The HDS process with the conventional metal sulfides catalysts are effective in eliminating the sulfur present in aliphatic hydrocarbons like sulfides, disulfides and mercaptans normally at high hydrogen pressures [1]. In the case of supported catalysts, alumina is the most common support since it provides mechanical strength and high dispersion of the active phase. However, alumina has no catalytic role in the HDS mechanism, occupy large part of reactors volume and often is not an total inert carrier capturing promoter atoms in the sub-surface network [2]. The unsupported catalysts avoids these issues and could be alternative for the traditional supported catalysts. Recently with the increasing interest in the “nano” field, new possibilities are being explored to obtain properties that could help to improve the catalytic behaviour of HDS catalysts.

In this study, we focus on the preparation of nanoscale efficient Ni/W catalysts for selective hydrodesulfurization via the direct desulfurization route of 3-methyl thiophene (3-MT) under mild pressure conditions. Hydrochloric acid (HCl) and nitric acid (HNO₃) were used to modify the hydrothermal synthesis of WO₃ in order to know its effect on the physicochemical and catalytic properties. Also, Sodium nitrate (NaNO₃) salt was used combined with HCl for the hydrothermal synthesis to know the influence of the conjugate anion on catalyst structure and activity.

Catalysts synthesis

A series of W and Ni/W catalysts was prepared in two steps. WO₃ was obtained from ammonium metatungstate (AMT) using acid (HCl and HNO₃) by hydrothermal method followed by impregnation of Ni. In a typical synthesis procedure controlled quantities of AMT were dissolved in 30 mL of 5M HCl and stirred for 1 h at 320 rpm. Then the solution was transferred into a static autoclave and treated at 180°C for 24 h. After cooling the autoclave to room temperature, the obtained precipitate was washed with deionized water several times, dried at 100 °C for 12 h and calcined at 450 °C for 4 h with a ramp of 1 °C per minute. The resultant WO₃ sample was indicated as WH-24. In the next step, aq. NiCl₂ solution with a Ni/W ratio of 0.52 was impregnated on the WH-24 sample and calcined at 350 °C for 2 h. The obtained Ni/W catalysts was denoted as Ni/WH-24, where H indicates the acid type used and integer 24 is the hydrothermal treatment time in hours. Samples were characterized by X-ray diffraction (XRD) Raman spectroscopy, UV–Visible, Nitrogen adsorption-desorption isotherms, High-resolution SEM images and HRTEM analysis. The catalysts were activated by in-situ sulfidation in the reactor. The 3-methyl thiophene (3MT) HDS reaction

was carried out in a biphasic continuous microflow reactor operating under atmospheric pressure. The spent sulfided catalysts were recovered and suspended in n-heptane to carry out the HRTEM analysis.

Results

Peaks detected in the XRD profiles correspond well to the orthorhombic and monoclinic phases. The Ni impregnated materials do not present the presence of NiO (ICDD-001-1239) or Ni₂O₃ (ICDD-014-0481). Raman spectra of the WH-x samples showed characteristic bands of WO₃ at 137, 188, 275, 329, 717, 808 cm⁻¹. The TEM images of Ni/WH-24-Na sample small particles corresponding to nickel oxide over the WO₃ rod like structure was clearly observed. After in situ sulfidation Ni based particles remain almost of the same size than in the oxide phase samples. Almost similar activities were observed for the Ni/WH-24 and Ni/WN-48 catalysts. Low conversion of 3-MT were observed at 320°C i.e., 38 and 35% for Ni/WN-48 and Ni/WH-24 catalysts. Moderate conversion (48%) were obtained for the Ni/WH-24-Na catalyst and highest conversion of 3-MT found to be maximum up to 56% in the case of Ni/WN-24 catalyst. This behaviour can be correlated to the shorter slab lengths, smaller particle sizes, presence of large number of WO₃ octahedral species observed in the Ni/WN-24 catalyst. The HDS activity results showed that the reaction do not proceed through hydrogenation steps. Therefore, the only possible mechanism for formation of isopentane is the DDS followed by a secondary HYD.

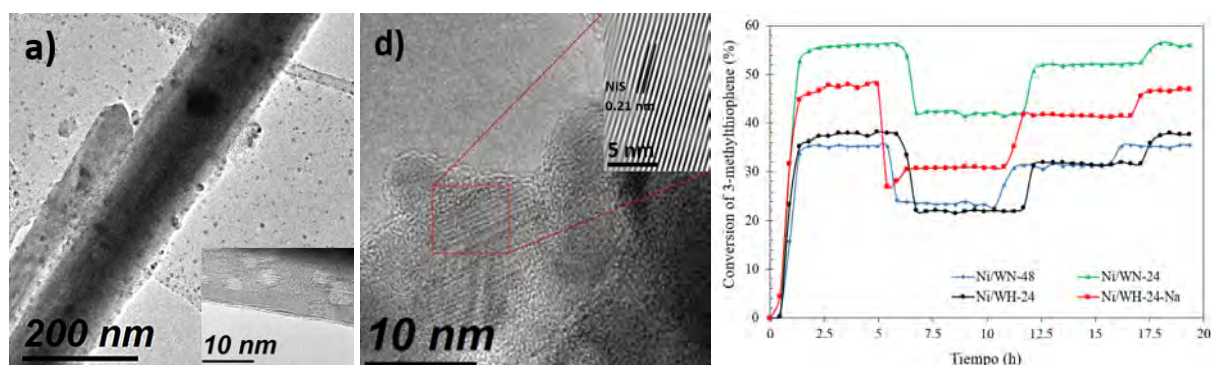


Figure 1.- Conversion of 3-methylthiophene over sulfided Ni/W catalysts.

Furthermore, it was indicated that low consumption of hydrogen in the reaction are highly desirable for catalysts in refineries for production of sulfur free fuels. Therefore, these catalysts expected to be have excellent performance for other refractive model compounds such as dibenzothiophene and its derivative or real fuels.

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CONNECTION BETWEEN STRUCTURE ATTRIBUTES AND ANALYTICAL METHODS USED FOR STOCHASTIC RECONSTRUCTION OF VACUUM GASOIL



+21:30

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The refining industry is currently facing increasing market demand for light fuel while crude oil is becoming heavier. Moreover, the quality of fuel must improve to meet environmental regulations. To do so it is necessary to optimize the conversion processes that require the development of reliable kinetic models. In order to account for the difference in reactivity of various species kinetic models require molecular description of the feed. Unfortunately, heavy petroleum cuts composition too complicated to be obtained directly from analytical data.

To overcome this problem a molecular description can be obtained using “molecular reconstruction” methods. Those methods generate a discrete set of molecules whose properties mimic the properties of the petroleum cut. “Stochastic reconstruction”[1] is one of these methods. Although molecular composition is unknown but structure attributes of molecules is well-known. Thus, probability of appearance structure attribute in arbitrary molecule can be considered. The substantial structure attribute should be defined, allowing to distinguish various species with different reactivity in concern process, as well as probabilistic distributions for them. After that the set of distribution sampled by a Monte Carlo method to obtain an equimolar mixture of molecules. Distribution parameter can be estimated using optimization. Estimated parameters allow to generate set of molecules which mixture properties similar to real cut. However, optimization process yield parameters whatever analytical data used. It can lead to unreasonable parameters due to lack of analytical information. To avoid it a criterion to define which analytical data influence distribution should be developed.

Understanding the behavior of calculated properties when changing distribution parameters can help solve this problem. The following steps were performed to verify the effect of parameters on output properties:

1. Set initial parameters close to mean of acceptable value. It is necessary to make sure that slight change in the parameter on average affect several molecules.
2. Sweep parameters one by one over a little range around initial value and track the calculated properties. Unfortunately, calculated properties change after regenerating set of molecules due to stochastic nature of Monte Carlo. This is why calculated properties must be averaged over a plenty of recalculation in order to reduce noise. Usually it's enough to average

PP-13

500-5000 times (depends on properties) to make noise as little as possible. At this point, it's clear that some relations are well established, while others are just noise.

- To distinguish these two cases Spearman correlation coefficient and p-value for properties-parameters relationship were calculated. Pearson correlation coefficient also can be applied, but it's less reasonable because those dependences are not linear in general.
- Use Holm-Bonferroni correction to account of multiple comparisons.

These criteria allow us to find connections between distribution parameters and properties. It's still not enough to be sure that each individual parameter is estimated correctly, but at least this allows to find a set of analytical methods to find a specific distribution or to reveal an unreasonable distribution.

Applying these methods to a set of distributions from [2] we get the next table. It shows that some distribution parameters can turn random without NMR data.

		Properties					
		Density	Mol. Mass	Elemental composition	PNA analysis	Distillation	NMR
Distribution	Class	1	1	1	1	1	1
	Parafin chain length	1	1	1	1	1	1
	Iso-parafin	0	0	0	0	1	1
	Alkyl branch carbons	0	0	0	0	0	0
	Alkyl branches (parafin)	0	0	0	0	0	0
	Naphthenic ring	1	1	1	1	1	1
	Number of benzen ring	1	1	1	1	1	1
	Heteroatomic ring	0	0	1	0	0	1
	Alkyl branch carbon	1	1	1	1	1	1
	Alkyl branches (cyclic)	0	0	0	0	0	1
	Sulfide substituent	1	1	1	0	1	1
	Amine substituent	1	1	1	0	1	1

1 means correlation between properties and distribution is significant while 0 means not.

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SYNTHESIS OF ACETYLENE ALCOHOLS BY CATALYSTS $\text{ZnEt}_2/\text{Ti}(\text{O}^i\text{Pr})_4/\text{PhMe}$ AND $\text{Sn}(\text{OTf})_2/\text{NEt}_3/\text{MeCN}$

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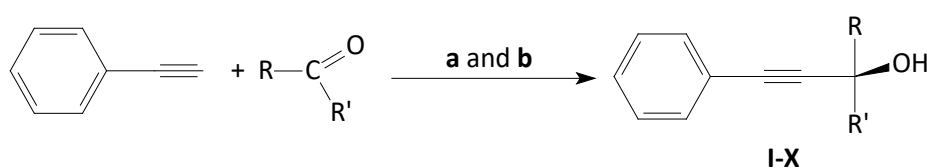
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For the first time, Osamu Hoshino synthesized acetylene alcohols of cyclohexanecarbaldehyde or benzaldehyde with zinc alkynyls and the chiral ligand of 2-[2,2-dimethyl-1-(2-pyridyl) propoxy]-1,1-diarulethanol via enantioselective alkylation as a catalyst [1]. The synthesis process of biologically active acetylene alcohols based on the reaction of nucleophilic addition of terminal acetylenes with aldehydes and ketones using a number of catalytic components have been studied. In particular, (+) - or (-) -N-methylephedrine, (R) - or (S) - BINOL, β -sulfonamide alcohols, derivatives of acetylene alcohols containing several reaction centers in the molecule with approximately weight substituents, secondary and tertiary acetylene alcohols and diols with a high yield on coordination nano selective catalysts for homogeneous catalytic reactions as bifunctional catalytic compositions of ProPhenol [2-6].

This work was the first time to study alkylation reactions based on phenylacetylene and some aliphatic, aromatic aldehydes and ketones in the presence of $\text{ZnEt}_2/\text{Ti}(\text{O}^i\text{Pr})_4/\text{PhMe}$ and $\text{Sn}(\text{OTf})_2/\text{NEt}_3/\text{MeCN}$ catalysts. Reaction scheme is proposed below, that is based on literature sources [7-9].



Where: R= -Me, R¹= -H (**I**); R= -MeCHCH, R¹= -H (**II**); R= -cHe, R¹= -H (**III**); R= -Ph, R¹= -H (**IV**);
R= -Me, R¹= ^tBu (**V**); R= -Ph, R¹= -Me (**VI**); R R¹= cHe (**VII**); RR¹= MecHe (**VIII**); RR¹= MeⁱPrcHe (**IX**);
RR¹= Me₃bicHe (**X**). **a**- $\text{ZnEt}_2/\text{Ti}(\text{O}^i\text{Pr})_4/\text{PhMe}$, **b**- $\text{Sn}(\text{OTf})_2/\text{NEt}_3/\text{MeCN}$

As objects of study, from the selected acetic and crotonaldehydes, cyclohexanal, benzaldehyde, pinokolin, acetophenone, cyclohexanone, 2-methylcyclohexanone, menthone and camphor with phenylacetylene based on the enantoselective reaction, respectively, new acetylene alcohols-4-phenylbutin-3, were synthesized (I), 1-phenylhexen-4-yn-1-ol-3(II), 1-cyclohexyl-3-phenylpropin-2-ol-1 (III), 1,3-diphenylpropin-2-ol-1 (IV), 3,4,4-trimethyl-1-phenylpentin-1-ol-3 (V), 2,4-diphenylbutin-3-ol-2 (VI), 1- (2-phenylethynyl) cyclohexanol (VII),

PP-14

2-methyl-1- (2-phenylethynyl) cyclohexanol (VIII), 2-isopropyl-5-methyl-1- (2-phenylethynyl) cyclohexanol (IX) and 1,7,7-trimethyl-2- (2-phenylethynyl) bicyclo [2,2,1] -heptanol -2 (X). The selectivity, stability and activity of the used catalysts in the process of alkynylation of selected aldehydes and ketones were studied. The additional reactions taking place that form intermediate and additional products were determined, the effectiveness of the selected catalyst composition was analyzed, and the influence of various factors — temperature, reaction time, and the nature of the solvents — was systematically studied. The optimal reaction conditions were determined based on the obtained results. According to this, when carrying out the process on the $\text{ZnEt}_2/\text{Ti}(\text{OiPr})_4/\text{PhMe}$ catalytic system, at a temperature of $-10\text{ }^\circ\text{C}$, with a reaction duration of 360 minutes, the molar ratio of the reagents $\text{PhCCH}:\text{RCOR}':\text{ZnEt}_2:\text{Ti}(\text{OiPr})_4$ is 3:1:3:0,25 or on the complex catalyst system $\text{Sn}(\text{OTf})_2/\text{NEt}_3/\text{MeCN}$ at a temperature of $-10\text{ }^\circ\text{C}$, with a reaction time of 60 min, the molar ratio of the reagents $\text{PhCCH}:\text{Sn}(\text{OTf})_2:\text{RCOR}':\text{NEt}_3:\text{MeCN}$ equal to 1,5:0,75:1,5:0,75:1,5 the maximum yield of the target product was observed. The results are shown in the table.

Synthesized acetylene alcohols	Yields of product, %	
	$\text{ZnEt}_2/\text{Ti}(\text{O}^i\text{Pr})_4/\text{PhMe}$	$\text{Sn}(\text{OTf})_2/\text{NEt}_3/\text{MeCN}$
I	84	86
II	72	84
III	77	80
IV	89	92
V	83	85
VI	86	90
VII	71	76
VIII	67	73
IX	62	67
X	53	58

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NOVEL COMPOSITE SUPPORT FOR CoMoS HYDROTREATING CATALYST BASED ON MWCNTs GROWN ON γ -Al₂O₃ BY CVD

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Hydrotreating (HDT) processes are largely carried out over sulfided CoMo catalysts supported on alumina, which has good thermal, mechanical and textural properties. However, the main drawback of alumina is strong interaction with the active components, which hinders the complete sulfidation of supported metals and decreases the number of active sites. Recently, in the preparation of CoMoS hydrotreating catalysts attention has shifted towards carbon supports. However, carbon supports have significant disadvantages, such as low bulk density and low crushing strength, and in the case of activated carbon, the presence of micropores, which limits their use for preparation of commercial HDT catalysts. Thus, the development of a composite support with improved physicochemical properties combining a high surface area with the mechanical strength of alumina is an urgent task to obtain effective HDT catalysts. Multi-walled carbon nanotubes (MWCNTs) attract a great attention as a catalyst support due to high specific surface area, low acidity, relatively large pore size, and almost complete absence of micropores. In this work, a comparative study of the influence of various supports (γ -Al₂O₃, MWCNT and composite support MWCNT- γ -Al₂O₃) on the properties of CoMoS HDT catalysts is carried out. The main idea is to combine the advantages of alumina and carbon in one support by preparing Al₂O₃-MWCNTs composite.

The γ -Al₂O₃ support was prepared by extrusion of boehmite paste with subsequent drying and calcination of obtained extrudates. MWCNT and MWCNT- γ -Al₂O₃ composite support were synthesized by CVD of ethylene decomposition over the bimetallic Fe-Co catalysts at 680°C. For CoMo/MWCNT catalyst preparation the functionalized MWCNT containing surface carboxylic groups (2.4 groups per 1 nm²) were used. CoMo/ γ -Al₂O₃, CoMo/MWCNT and CoMo/MWCNT- γ -Al₂O₃ catalysts were prepared by incipient wetness impregnation of the supports with aqueous solution containing Co and Mo precursors and citric acid. The catalysts contained about 12.0 wt% of Mo and 3.2 wt% of Co. The catalysts in sulfide form were studied by N₂ physisorption, XPS and HRTEM. The catalysts were tested in dibenzothiophene (DBT) hydrodesulfurization (HDS) in fixed-bed reactor under the following conditions: t = 270°C, P = 3.5 MPa, LHSV 20 h⁻¹, H₂/feed = 500 nm³/m³.

Figure 1 shows HRTEM data for sulfide CoMo/ γ -Al₂O₃, CoMo/MWCNT and CoMo/MWCNT- γ -Al₂O₃ samples. For each catalyst the unsulfided species of active component are not observed. Active phase is uniformly distributed over γ -Al₂O₃ surface in CoMo/ γ -Al₂O₃ catalyst. For CoMo/MWCNT the presence of active phase both inside and outside the nanotube channels is observed. This particle distribution is characteristic of oxidized MWCNTs, since in this case their internal and external surfaces are hydrophilic. In the case of CoMo/MWCNT- γ -Al₂O₃, a uniform distribution of active phase both over the surface of alumina and on the outer surface of MWCNTs is observed. According to HRTEM, the average stacking number for CoMo/ γ -Al₂O₃, CoMo/MWCNT and CoMo/MWCNT- γ -Al₂O₃ samples is 1.6, 1.7 and 1.3, correspondingly. The average slab length is 2.8 nm for CoMo/Al₂O₃ and CoMo/MWCNT- γ -Al₂O₃ samples and 3.0 nm for CoMo/MWCNT.

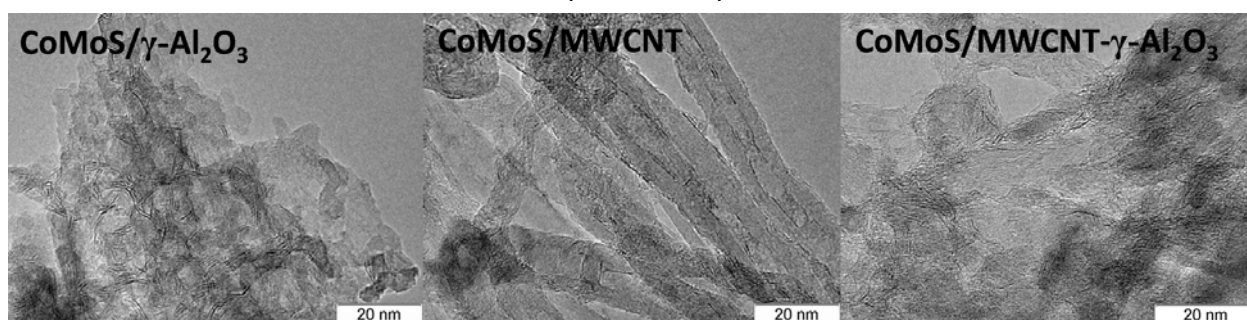


Figure 1. TEM micrographs of CoMoS samples based on γ -Al₂O₃, MWCNT and MWCNT- γ -Al₂O₃.

The formation of active CoMoS phase on the surface of supports was confirmed by XPS. For both catalysts Mo3d spectra contain an intensive peak with binding energy of 229±0.1 eV and Co2p spectra contain an intensive peak with binding energy of 779.0±0.1 eV. The results of catalysts testing in hydrotreating of model feedstock (Table 1) show that CoMoS/MWCNT- γ -Al₂O₃ catalyst has higher activity in HDS of DBT. Thus, the data obtained clearly point to the fact that the combination of advantages of alumina and MWCNT in one support is a perspective approach for improving HDT catalysts.

Table 1. HDS activity of CoMoS/ γ -Al₂O₃, CoMoS/MWCNT and CoMoS/MWCNT- γ -Al₂O₃ catalysts.

Sample	DBT* conversion, %
CoMoS/ γ -Al ₂ O ₃	46.9
CoMoS/MWCNT	44.7
CoMoS/MWCNT- γ -Al ₂ O ₃	61.5

DBT* Model feedstock - Undecane + DBT

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CATALYTIC CONVERSION OF HYDROCARBONS USING OXYGEN-SELECTIVE MICROTUBULAR MEMBRANES FOR HYDROGEN PRODUCTION

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Currently, hydrogen energetics plays an important role in human's lives due to the global reduction of resources [1]. The use of hydrogen for the production and storage of energy is very promising, being that this element is widely distributed on the earth. Hydrogen fuel can be used, for example, for solid oxide fuel cells, which are an efficient and environmentally friendly source of energy [2]. One of the important things in modern hydrogen energetics is studying the ceramic perovskite-type membranes with mixed ion-electronic conductivity. They have 100% oxygen selectivity and are easily integrated into high-temperature processes, that allows using them in the membrane catalytic oxidation reactors [3].

The study is devoted to the research of catalytic conversion processes on microtubular oxygen-permeable $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8-x}\text{Fe}_{0.2}\text{Mo}_x\text{O}_{3-z}$ (BSCFMx) membranes using direct AC heating technique.



Figure 1. Microtubular membrane reactor for hydrocarbons conversion

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CATALYTIC HYDROPROCESSING OF ORGANIC MATTER OF SAPROPELS IN VALUABLE CHEMICAL PRODUCTS



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The direction of involvement of biorenewable resources including low-rank coals (lignites, brown coal, shale oil, peat) in order to obtain bio-oil and other fine chemicals is intensively developing worldwide [1]. One of the promising areas for the use of this type of raw material is hydroprocessing with the production of liquid organic substances (hydroliquefaction). However, the high content of oxygen, nitrogen and low fuel efficiency hinder their wide application. To solve these problems, modern catalysts and selection of conditions for the hydroliquefaction are necessary. To intensify depolymerization, cracking, hydrogenolysis, hydrogenation and deoxygenation, catalysts based on oxides, sulfides and chlorides of groups VIII, VI and IV metals are introduced. Among low-rank coals, lake sapropel deposits are also of interest [1]. A large number of sapropel deposits are in the middle zone of Europe and Asia, in the American continent, Canada, Lithuania, Latvia, Ukraine and Republic of Belarus. In the Russian Federation, which takes one of the leading places in the world (225 billion m³), the main deposits are located in the central part of Russia and also in the territory of Western Siberia and Far East. Sapropel is a centuries-old bottom deposit that was formed from dead aquatic vegetation and debris of living organisms, plankton and humus particles under fresh and sea water, with an organic matter (OM) content of 15–90 wt.%. The specific microflora enriches them with biologically active substances, particularly, carotins, chlorophyll, xanthophylls, sterols, organic acids, alcohols, enzyme-like substances, amino acids, and group B vitamins, C, E. Based on the ratio of H/C and O/C, according to the Van Crevelen diagram, sapropels are located between lignites and peat and can be attributed to type I (sapropelic) and type II (planktonic) kerogen, which is promising from the point of view of producing liquid hydrocarbons. Thus, sapropel can be used directly in the process of hydroliquefaction or after the stage of preliminary extraction of O- and N-containing valuable biologically active components, which in addition increases the H/C index and facilitates further OM hydrotransformation [2].

In this paper hydroliquefaction sapropels was carried out on a laboratory system at 180-475°C and 6 MPa of H₂ pressure. Sapropels differing in the content of organic matter and the ratio of biogenic atoms were chosen for the study. Hydrogen donor (decalin D, ethanol (including supercritical conditions) Et) and non-H-donor solvents (anthracene oil AO) which are known as

effective for materials derived from coal were selected. The following catalysts were synthesized: $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$, $\text{CoMo/Al}_2\text{O}_3$, and $\text{FeNi/Al}_2\text{O}_3$. In addition, carbon-mineral supports obtained by sapropel carbonization were used. To study the composition of the products, gas chromatography was used coupled with mass spectrometer (Agilent Technologies 6890/5973N) was employed. ^{13}C NMR spectra were recorded on a Bruker AC-200P NMR spectrometer.

A study of the hydroliquefaction temperature effect showed that the maximum OM sapropels conversion to D and AO was reached at 450°C and amounted about 80 wt.%. The catalyst ($\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$) addition to the system results in high conversion at lower temperatures. The introduction of hydrogen contributes to a deeper course of reactions with breaking bonds of C-C and C-N (O, S) and leads to a decrease in the molecular weight of sapropel oil by more than 2.5 times. The GC-MS method found that the main components of sapropel oil are phenol, methyl derivatives of phenol homologues, naphthalene, mono- and dimethylsubstituted naphthalene, anthracene. Nitrogen-containing compounds are presented as quinoline.

Regarding the role of the catalytic composition on the hydroliquefaction of sapropels in decalin in the temperature range $350\text{-}475^\circ\text{C}$ it was found that the maximum yield of sapropel oil (56 wt% in OM) is achieved for the $\text{CoMo/Al}_2\text{O}_3$ catalyst at 400°C . At higher temperatures, an increase in OM conversion is observed, however, the yield of liquid products decreases as a result of secondary decomposition processes with the release of gaseous products.

When elucidating the influence of the nature of sapropels on the yield and composition of sapropel oil (Et, 200°C), it has been shown that maximum conversion (64 wt.%) is achieved for samples in which OM is represented mainly by protein residues. For "plant" sapropels, this result is 12 wt.% lower. A study of the composition of sapropel oil found that with an increase in the proportion of the protein component, the amount of oxygen-containing compounds decreases (by 18 wt.%), and the proportion of hydrocarbons increases by more than 50 wt.%. Thus, under the conditions of catalytic hydro-processing of sapropel organic matter, high conversion is achieved at a lower temperature, and varying the solvent, catalyst composition, and sapropel nature make it possible to control the conversion depth and composition of the resulting organic substances.

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JOINT HYDROTREATING OF DIESEL FRACTION WITH GASOLINE**Krivtsova N.I., Kotkova E.P.***National Research Tomsk Polytechnic University, Tomsk, Russia**E-mail: krivtcovani@mail.ru*

Currently in the field of oil general trend is to increase the consumption of motor fuels, the crude oil consumption is reduced. Oil quality deteriorates, it is more sour and heavy on the composition of each year [1]. However, the requirements for motor fuels, stricter every year. This poses the problem of researchers to improve technology of secondary processes. The most large-capacity process is hydrotreating of diesel fuel.

Today this process is given special attention. To improve the efficiency of the results hydrotreating today research is being conducted to develop new formulations of the mixing process of raw materials [2]. To feed hydrotreating a middle fraction was added the lighter fractions, the products of thermal processes, oil and vegetable oil [3].

In laboratory conditions, an experiment was conducted to study the effect of the composition of the feedstock on the degree of hydrotreatment. The experiment was conducted on a facility designed to study processes occurring under conditions of high pressure in a flow mode. The installation includes three blocks: block distribution and hydrogen feedstock, a reaction unit, a separation of the product.

The diesel fraction with a total sulfur content of 0.699% was used as raw material weight. and diesel fraction mixture (95, 85 and 75 vol.%) with the light gasoline fraction (5, 15 and 25 vol.%), respectively.

It was established experimentally that the optimum parameters of the process are hydrotreatment of diesel fuel the following process conditions: $T = 340\text{ }^{\circ}\text{C}$, $\text{H}_2/\text{feedstock} = 350/1$, $P = 3,5\text{MPa}$, $\text{OSPS} = 2\text{ h}^{-1}$. Raising the temperature above $340\text{ }^{\circ}\text{C}$ has no significant impact on the composition and degree of hydrogenation of sulfur removal. When the feed space velocity (OSPS) 2 h^{-1} observed best degree of hydrotreatment.

When added to diesel fuel sulfur content of gasoline fraction and hydrogenate aromatic hydrocarbons is markedly reduced, and the proportion of saturated hydrocarbons increased. Results for hydrotreating a mixture of diesel and gasoline fractions given in Table 1.

Table 1 - The results of hydrotreating a mixture of diesel and gasoline fractions ($T = 340\text{ }^{\circ}\text{C}$, $\text{H}_2/\text{feed} = 350/1$, $P = 3,5\text{ MPa}$, $\text{OSPS} = 2\text{ h}^{-1}$).

Mixture of fractions	The content in the initial mixture,% wt.			The content in the hydrogenate,% wt.			The degree of hydrotreatment %
	sulfur	Saturated hydrocarbons	Aromatic hydrocarbons	sulfur	Saturated hydrocarbons	Aromatic hydrocarbons	
100% DF	0,699	58,38	31,53	0,061	59,31	26,39	91,3
95% DF + 5% GF	0,674			0,049			92,5
85% DF + 15% GF	0,668	64,44	26,34	0,045	67,01	22,23	93,3
75% DF + 25% GF	0,621			0,042			93,3

The best results were obtained by hydrotreating when added to diesel fraction is about 5% gasoline fraction. The total sulfur content in this case is reduced from 0.061 to 0.049 wt%. Further dilution of the gasoline fraction (up to 25 vol.%) does not significantly increase the degree of hydrotreatment. The degree of sulfur removal increases by 2% during hydrotreating of mixed raw materials in comparison with hydrotreating only diesel fraction. The content of aromatic hydrocarbons increases by 4.11% wt.

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OPTIMIZATION OF A SEMIREGENERATIVE CATALYTIC REFORMING OF NAPHTHA WITH THE MATHEMATICAL MODELLING METHOD USING

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Polymetallic highly stable reforming catalysts, specially designed for operation under low and medium pressure and ensuring a high yield with a given octane number over the entire working period play the key role in catalytic reforming process optimization. The non-stationary process of naphtha hydrocarbons conversion on the surface of a Pt-catalyst is performed as system of material and heat balances:

$$\left\{ \begin{array}{l} G_c \frac{\partial C_i}{\partial Z} + G_c \frac{\partial C_i}{\partial V} = \sum_{j=1}^m a_j \cdot r_j \\ G_c \frac{\partial T}{\partial V} + G_c \frac{\partial T}{\partial Z} = \frac{1}{\rho \cdot C_p^{mix}} \sum_{j=1}^m a_j \cdot r_j \cdot \left(\frac{RT}{P} \right) \cdot \Delta H_j \end{array} \right. \quad \begin{array}{l} \text{The initial conditions:} \\ \text{at } z = 0, C_i = 0, T = 0; \\ \text{at } V = 0, T = T_0, C_i = C_{i0}; \end{array}$$

where G_c is a raw material flow rate, m^3/s ; C_i is a concentration of i th component, mol/m^3 ; Z is a volume of raw material processed from the moment when the fresh catalyst (new catalyst, no regenerations were done) was loaded, m^3 ; V is a catalyst volume in the reactors, m^3 ; a_j is a catalyst's activity; r_j is a reaction's rate, $mol/m^3 \cdot s$; i is a component's number in a mixture; j is a reaction's number due to formalized scheme accepted; T is a temperature, K ; ρ is a density, mol/m^3 ; C_p^{mix} is a heat capacity of mixture, $kJ/mol \cdot K$; ΔH is j th reaction heat, kJ/mol ; R is the gas constant, $8,314 \text{ MPa} \cdot l/mol \cdot K$; P is a pressure, MPa .

The model allows to consider the catalyst activity changes during its working period. There are current and optimal activity. The first is determined by the catalyst operating conditions, the second corresponds to maximum selectivity and is determined by the equilibrium conditions of the reactions of coke formation - hydrogenation of compaction intermediate products. The choice of the optimal operating mode helps to maintain optimal activity and depends on many factors: technological conditions, raw material composition, type of catalyst. A single efficiency criterion that determines the coke formation rate and selectivity for a given technological mode is calculated by the equation:

$$\Delta = \frac{\sum_{i=1}^n [A_{cur}^i - A_{opt}^i]}{\Delta_{max}}$$

PP-19

where Δ – criteria of effectiveness; A_{cur}^i – current catalyst activity; A_{opt}^i – optimal catalyst activity; Δ_{max} – maximum deviation between current and optimal catalyst activity.

A comparative analysis of two different reforming catalysts loaded on the same semi-regenerative reforming unit was carried out with mathematical model using (Table 1, 2).

Table 1. The catalyst potential evaluation in the last working cycle (R-98)

The number of experiment	Activity		Yield, % mass.		Criteria of effectiveness, Δ
	Current	Optimal	Current	Optimal	
1	0,76	0,86	81,64	83,97	0,71
2	0,78	0,84	81,69	84,50	0,43
3	0,80	0,81	81,44	85,10	0,29
4	0,81	0,82	81,66	83,32	0,07
5	0,81	0,83	81,97	84,96	0,14
6	0,79	0,85	82,12	85,10	0,43
7	0,81	0,90	82,52	84,77	0,64
8	0,82	0,89	81,93	84,87	0,50

Table 2. The catalyst potential evaluation (RB-33U/RB-44U grade Sh) in the second working cycle

The number of experiment	Activity		Yield, % mass.		Criteria of effectiveness, Δ
	Current	Optimal	Current	Optimal	
1	1,05	1,21	91,14	90,16	1,00
2	1,17	1,20	89,68	89,43	0,19
3	1,20	1,22	89,87	89,76	0,13
4	1,20	1,23	89,99	89,78	0,19
5	1,18	1,23	90,25	89,94	0,31
6	1,16	1,20	90,20	89,91	0,25
7	1,19	1,24	90,64	90,25	0,31
8	1,02	1,16	90,54	89,66	0,88

Improving of the catalytic naphtha reforming by conducting the process under conditions of optimal catalyst activity allows the reformate yield increasing by 2–3 % mass. In fact, exceeding the process selectivity with the current activity compared with the optimal allows to judge the effective operation of the catalyst.

MONO- AND BIMETALLIC CATALYSTS BASED ON HYPER-CROSSLINKED POLYSTYRENE FOR HYDROGENATION OF BIOMASS-DERIVED LEVULINIC ACID

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At present the search of new sources of energy is of high importance due to the limited sources of fossil fuels. 2-Methyltetrahydrofuran (2-MTHF) is one of the key biomass-derived compounds, which can be used as a fuel additive [1]. 2-MTHF can be synthesized via direct processing of levulinic acid (LA), which in turn can be obtained from cellulose-containing biomass including wastes such as corn stalks, flax shive, wood wastes, etc. However, synthesis of 2-MTHF from gamma-valerolactone (GVL) as an intermediate is preferable (Fig. 1) [1, 2].

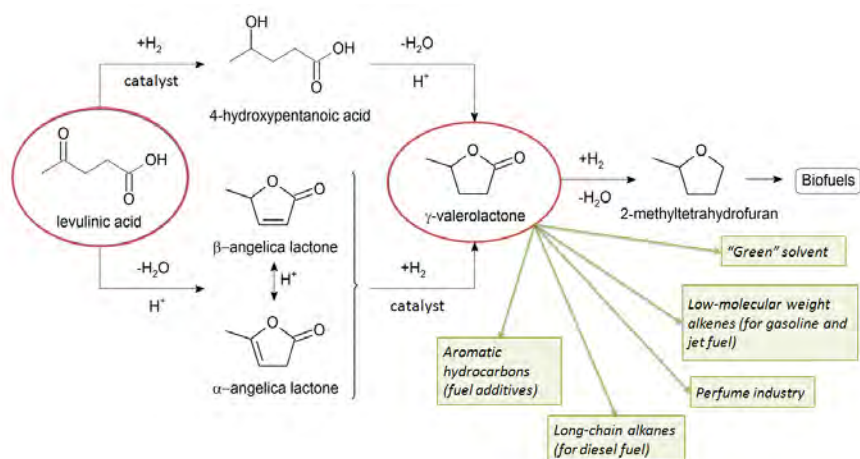


Fig. 1. Scheme of LA obtaining and possible ways of LA conversion to GVL.

There are numerous homo- and heterogeneous catalysts of LA transformation to GVL [3]. Heterogeneous catalysts are preferable due to the possibility of easy separation from the reaction mixture. 5%-Ru/C, 10%-Pd/C and Ni Raney are the most widely used catalysts of GVL synthesis [4, 5]. However, in order to achieve high conversion of LA and selectivity to GVL, the addition of co-catalyst or the increase of reaction temperature are necessary [6]. Besides, the key factor influencing the behavior of Ru-containing catalysts of LA hydrogenation is the size and dispersity of Ru nanoparticles [7]. In this work we propose to use polymer-stabilized Ru-containing nanoparticles as a catalyst of selective hydrogenation of LA.

Series of catalysts was synthesized at variation of Ru loading (3 wt.% or 5 wt.%) and HPS type (HPS bearing amino-groups (MN100) or non-functionalized HPS (MN270)). Moreover, bimetallic Ru-Co and Ru-Fe catalysts were synthesized. Before the reaction, the catalysts were activated in hydrogen flow at 300°C for 2 h. Hydrogenation of LA was carried out in Parr Series 5000 Multiple

Reactor System in aqueous medium at a stirring rate of 1500 rpm, at variation of reaction temperature (80-150°C), hydrogen pressure (1-4 MPa) and LA-to-catalyst ratio (50-200 g/g). Samples of reaction mixture were analyzed via HPLC.

While testing Ru/HPS catalysts, it was found that activity of 3%-Ru/MN270 is lower than activity of analogous catalyst based on MN100. The increase of Ru loading in the case of Ru/MN270 did not allow exceeding the LA conversion achieved for 5%-Ru/C. However, the replacement of MN270 to MN100 for the samples with Ru loading of 5 wt.% led to noticeable increase of LA conversion to >99 %. By the XPS and TEM methods it was shown that high activity of 5%-Ru/MN100 can be attributed to the formation of small nanoparticles (about 1-2 nm in diameter) of RuO₂ on the catalyst surface. For the most active HPS-based catalyst (5%-Ru/MN100), main kinetic parameters (apparent activation energy, reaction orders) were calculated and formal kinetic modeling was carried out for deeper understanding of the observed kinetic behavior.

Amongst bimetallic catalysts Ru-Co, which allowed nearly twofold increase of LA conversion, in comparison with monometallic ruthenium-containing sample, was found to be most promising.

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FURFURYL ALCOHOL AS ONE OF THE PRODUCTS OF LIGNOCELLULOSIC BIOMASS HYDROTREATMENT

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The increasing interest in biomass as a source of chemicals and energy has recently arisen due to the limited fossil fuel resources and the demand for new clean chemical processes. The research on the development of alternative liquid transport fuels has considerably increased in recent years influenced by the implementation of legislation and directives on alternative energy. To achieve these aims in an ethical, environmental and economical manner the use of lignocellulosic biomass or agri-waste for the production of second-generation biofuels is proposed. Chemicals derived from biomass have recently attracted considerable interest [1]. The production of biofuels from hemicellulose requires acid hydrolysis to open the biomass structure giving large quantities of xylose [2]. The synthesis of furfural (FF) as a by-product of this biofuel production process has developed an additional important research area. Furfural is one of the key derivatives which can be obtained from renewable biomass for the production of different important fine chemicals [3]. Selective hydrogenation of furfural has attracted much attention to the production of furfuryl alcohol (FA), methyl furan, tetrahydrofurfuryl alcohol, and others. Furfuryl alcohol is widely used in the chemical industry, mainly for the production of special resins, polymers, and coatings on their basis, which is resistant to acids, alkalies, and various solvents. In addition, furfuryl alcohol is employed as a diluent for epoxy resins and as a solvent for phenol-formaldehyde resins and poorly soluble pigments. In organic synthesis, furfuryl alcohol is a feedstock for the production of tetrahydrofurfuryl alcohol and 2,3-dihydropyran and an intermediate in the synthesis of lysine, vitamin C, various lubricants and plasticizers. There are two ways of producing furfuryl alcohol: through hydrogenation of furfural, gas-phase hydrogenation and liquid phase hydrogenation. In industry, furfuryl alcohol is obtained by catalytic hydrogenation of furfural in a liquid or vapor phase. The liquid-phase process is carried out with copper chromite systems as the catalysts. The main disadvantage of copper-chromite catalysts is their toxicity caused by the presence of chromium oxides, which allows considering such catalysts as environmental pollutants [1].

By varying the conditions of furfural hydrogenation (pressure, temperature, etc.), it is possible to regulate the selectivity to one or another product. In this paper, we want to demonstrate the use of hypercrosslinked polystyrene (HPS) as a stabilizer. HPS is the class of cross-linked polymers is characterized by unique topology and unusual properties. HPS consists of nanosized rigid micro-

and meso-cavities. This material can act as a nanostructured matrix, which governs particles growth [4]. The nanoparticles of catalytically active metals such as Ru, Pt, Pd were successfully stabilized in the pores of the HPS matrix and showed high catalytic activity in the selective hydrogenation reactions. In addition, HPS is commercially available and produced on an industrial scale (PUROLATE International Ltd). Pd and Ru-containing nanoparticles stabilized by HPS have been synthesized with different precursors and studied as catalysts in the FF hydrogenation to FA. The formation of metal nanoparticles depends on the nature of the precursor.

This research is devoted to the hydrogenation of FF to FA with Pd-containing catalysts stabilized by hypercrosslinked polystyrene (HPS). FF is one of the major ingredients of bio-oil produced by biomass pyrolysis, while FA is a source of value-added chemicals, thus, creating an effective path from biomass to important compounds. Different metal precursors were used for the synthesis of the catalysts. The nature of the precursor influences the size of metal nanoparticles and their catalytic properties.

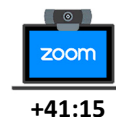
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INVESTIGATION THE INFLUENCE OF ADDITION THE HEAVY N-PARAFFINS ON THE EFFECTIVENESS OF DEPRESSANT ADDITIVE ACTION



+41:15

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Despite the growing interest in alternative fuels, in particular biodiesel and greendiesel, traditional diesel fuel remains the most consumed oil product – global diesel consumption in the period from 2010 to 2017 increased by 1.5 % [1]. However, unsatisfactory low-temperature properties significantly limit the use of this fuel in the wintertime, as well as in the northern and Arctic territories. A rational way to improve the low-temperature properties of diesel fuels is to use depressant additives. At the same time, a significant difficulty, in the use of depressant additives, is the influence of the diesel fuel composition on the effectiveness of the additive, which in some cases can completely neutralize the effect of the additive.

Previously, the authors hypothesized about the qualitative influence of the diesel fuels group composition on the effectiveness of low-temperature additives [2], according to which depressant additives are most effective in relation to the low-temperature properties of diesel fuels, characterized by high content of heavy n-paraffins.

The consequence of this hypothesis is the possibility of increasing the effectiveness of depressant additives by adding a small amount of heavy n-paraffins to diesel fuel. Thus, the object of this work is to study the effect of adding heavy n-paraffins to diesel fuel, on the effectiveness of the depressant additive.

A straight-run diesel fuel sample (DF), obtained from one of the oil refineries of the Russian Federation (density at 15 °C – 835.5 kg/m³, boiling range – 134-348 °C), was used as an research object in this work. N-paraffins were extracted from heavy vacuum gasoil (density at 15 °C – 896.5 kg/m³), according to the method presented in [3]. A depressant additive was used in a ratio of 0.26 ml per 100 ml of diesel fuel. Cloud point (CP) was determined according to the method presented in [4]; cold filter plugging point (CFPP) was determined according to the method presented in [5]; pour point (PP) was determined according to the method presented in [6]. The results of determining the low temperature properties of DF and mixture of DF with a depressant additive (DF + Ad) are presented in Table 1.

Table 1 – Low temperature properties of DF and DF + Ad

Sample	CP, °C	CFPP, °C	PP, °C
DF	-4	-5	-16
DF + Ad	-5	-25	-42

As can be seen from the data presented in Table 1, the using additive effectively improves the low-temperature properties of DF – CFPP by 20 °C, PP by 26 °C.

Then, heavy n-paraffins (P) were added to DF in the amount of 1.00 % wt., 0.50 % wt., 0.25 % wt., 0.10 % wt., it is mixtures of DF + P; mixtures with the additive DF + P + Ad were also prepared. The results of determination mixtures CFPP are presented in Table 2.

Table 2 – CFPP of DF + P and DF + P + Ad mixtures

Characteristic	DF + 1.00% P	DF + 1.00% P + Ad	DF + 0.50% P	DF + 0.50% P + Ad
CFPP, °C	-3	-13	-4	-21
Characteristic	DF + 0.25% P	DF + 0.25% P + Ad	DF + 0.10% P	DF + 0.10% P + Ad
CFPP, °C	-4	-28	-5	-31

As can be seen from the data presented in Table 2, the addition of heavy n-paraffins, solidifying at positive temperatures, into DF worsens CFPP of mixtures. At the same time, the addition of heavy n-paraffins into the DF + Ad mixture in small amounts can increase the effectiveness of the additive in relation to CFPP (adding of 0.25 % wt. P by 3 °C; adding of 0.10 % wt. P by 6 °C). The observed effect is explained by the mechanism of depressant additives action – heavy n-paraffins function as primary crystallization centers on the surface of which the depressant additive is adsorbed, thereby preventing the growing of crystals, which ultimately leads to an improvement of CFPP.

Thus, the results of the studies allow us to conclude that the addition of heavy n-paraffins in small amounts allow increase the effectiveness of depressant additive to CFPP of diesel fuels.

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Acknowledgements

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DEVELOPING OF MULTISCALE APPROACH TO HPC-SIMULATION OF MULTIPHASE FLUID FLOWS

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The proposed work is devoted to the development of multiscale approaches [1-3] for modeling multiphase flows of liquid and gaseous hydrocarbons in plants for the processing of organic fuels. One of the important stages of such processing is the purification of crude oil or natural gas from various kinds of contaminants (metal particles, solid organic compounds, etc.). To model the cleaning processes, we proposed multilevel mathematical models combining macroscopic and microscopic descriptions of the multiphase fluid flows in the channel of the treatment system. This work deals with the purification of natural gas by passing it through a porous material. The general mathematical model of the flow of a contaminated gas mixture consists of two main components. The first component is related to the macroscopic scale of the treatment system and includes modified quasigasdynamic (QGD) equations [4-5] for a gas mixture, supplemented by convection-diffusion equations for particle concentrations of solid impurities. The second component of the model describes the processes in the boundary layers and is based on the equations of molecular dynamics (MD) [6]. The aim of the work was a physically justified implementation of the conjugation of the components of the model.

On a macroscopic scale, a model for calculating the non-isothermal flow of a multiphase weakly compressible fluid through a porous medium, which is an analog of the QGD system of equations [4-5], written in hyperbolic form [7-8], was used. Conservative requirements make it necessary to take into account the multicomponent composition of fluids in the model. Conservation laws in the proposed formulation of the model are performed component by component and for each phase. The mass balance equation includes a regularizing term and a second-order time derivative with small parameters that have the meaning of minimum reference scales in space and time. The equation is approximated by a three-level explicit difference scheme with a second order of approximation in time and space and with a rather mild stability condition. The model includes one total energy conservation equation, modified by analogy with the QGD equations and approximated by an explicit scheme. Phase densities as well as viscosities depend on the multicomponent composition. The phase equilibrium constants are indicated for all components

that must be condensed. The model takes into account gravitational and capillary forces, includes strongly nonlinear functions of relative phase permeability.

An explicit type algorithm was developed for the numerical implementation of the macroscopic model. The verification of a pure macroscopic model (without convection-diffusion equations and without MD) was carried out using a wide range of test predictions of hydrocarbon recovery, contaminant infiltration into the soil, flows with phase transitions in technological facilities. Physically correct results were obtained; good agreement with the results of other authors [9–10] was achieved. High parallelization efficiency was demonstrated on CPU cores and on GPUs of a hybrid supercomputer.

On a microscopic scale, the molecular dynamics [6] method was used as a model. The evolution of the studied system of microparticles is described by Newton's equations. MD shows the interaction of particles with surfaces bounding the medium, including penetration into pores, processes in the pores themselves and in their boundary layers. To integrate the equations, the Verlet scheme was used, that allows statistically correctly reproducing the behavior of particles of a medium over a long period of time.

The preliminary numerical experiments made it possible to determine the matching parameters of the model components and confirmed the possibility of its application to the selected class of problems. The presented model is planned to be expanded in the future to the case of multicomponent flows containing solid, liquid, and gaseous phases.

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DECOMPOSITION OF LIGHT HYDROCARBON TO HYDROGEN ON A FIBERGLASS CATALYST

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Currently, most remote oil fields burn associated petroleum gas (APG) in flares. More than 100 million tons of CO₂ are formed in the world when APG is burned. One promising method for utilizing associated petroleum gas is catalytic decomposition. This method is an environmentally friendly and less energy-intensive way to produce hydrogen and carbon nanofibres. The catalytic decomposition of APG proceeds in one stage; it does not have CO and CO₂ impurities; therefore, it does not require additional purification steps.

The use of catalysts can reduce the process temperature to 450-700 °C [1]. A glass-fiber catalyst was used on which nickel oxide was applied as an active component [2]. Glass-fiber was chosen as a carrier, which has an original geometric structure, high mechanical strength, and flexibility, which allows creating various forms of the catalyst with improved heat and mass transfer [3]. The high-silica glass-fiber fabric (GFF) KT-11-TO (produced by Stekloplastik Co., Zelenograd, Russia), containing ~ 95 % SiO₂ and 4 % Al₂O₃, was used as the primary GFC support. The GFF was impregnated by the water solution of silica sol (type K-1, produced by NPO IREA, Moscow, Russia) and nickel acetate. After impregnation and drying, the GFC was thermally treated by heating from ambient temperature up to 500 °C. Silica addition was needed to create the intermediate layer of secondary porous support in order to improve the strength of bonding between NiO and GFF surface and to develop the specific surface area for better accessibility of the supported NiO by gaseous reactants.

Gases were used: APG, vol.% (CH₄ - 85%, C₃H₈ - 11%, C₄H₁₀ - 3%, C₂H₆ - 1%, H₂S <0.003%) and pure methane (CH₄ - 99.999%) in the process of catalytic decomposition. The catalytic decomposition of hydrocarbons was carried out in a flow catalytic installation BTRS Jn (Autoclave Engineers, USA) in a tubular reactor. The composition of the gaseous reaction products was measured using a gas chromatograph (Chromos, Russia). The temperature in the reactor was 550–600 °C, pressure - 1–2 bar. The reaction was carried out before catalyst deactivation.

Table shows the results of calculating the hydrogen production rate of hydrogen obtained during catalytic decomposition.

PP-24

T, °C	CH ₄		APG	
	Hydrogen production rate, l/min·g _{cat}	Reaction time, min	Hydrogen production rate, l/min·g _{cat}	Reaction time, min
Pressure: 1 bar				
550	0,75	180	0,92	180
600	1.0	140	1,1	180
Pressure: 2 bar				
550	0,75	312	0,57	192*
600	1,1	234	0,81	282*

* reaction was not carried out until the catalyst was completely deactivated

It was determined that with increasing temperature of the process of catalytic decomposition of the initial hydrocarbon on a glass-fiber catalyst the specific rate of hydrogen formation increases. At the same time, with increasing temperature catalyst lifetime decreases, regardless of the initial hydrocarbon used. With an increase in pressure from 1 to 2 bar a significant increase in the catalyst lifetime occurs regardless of the initial hydrocarbon used. It was found that during the catalytic decomposition of APG the rate of hydrogen formation decreases by 16% at 550 ° C and by 29% at 600 ° C with an increase in pressure from 1 to 2 bar.

Thus, the use of glass-fiber catalysts with low nickel content may be promising for catalytic decomposition of hydrocarbons with formation of hydrogen without carbon emissions to atmosphere. In case of APG processing on the base of the proposed approach it is possible to use the produced hydrogen for primary hydroprocessing of the produced oil to decrease its sulfur content and viscosity before transportation. The co-produced nano-fibrous carbon may be used as a sorbent to prevent the pollution of environment by hydrocarbons.

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MATHEMATICAL MODELING AND EXPERIMENTAL STUDIES OF HYDROGEN COMBUSTION IN MICROTUBULAR SOLID OXIDE FUEL CELLS

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Recently, active efforts have been made to develop catalytic membrane reactors (CMR) in which separation of atmospheric oxygen with the help of oxygen-permeable (OP) membranes and catalytic conversion of hydrocarbons are combined in one reactor, which allows to significantly decrease in the prime cost of syngas [1]. In addition, OP membranes can also be used to produce pure oxygen for efficient fuel combustion in power engineering and as cathodes for solid oxide fuel cells (SOFC) [2]. The SOFC electrochemical generators are capable to convert the fuel chemical energy directly to the electricity. In these processes hydrogen can be used as fuel that plays a keyrole in many processes including the hydroprocessing in oil refining.

The microtubular (MT) SOFC have the cells with outer diameter less than 5 mm. Due to their high porosity and small size, MT SOFCs have high impact resistance and resistance to thermal shock, which allow them to be used in devices where a high starting speed is required. In this study the technology of MT SOFCs manufacturing (Fig. 1) and experimental technique are presented.

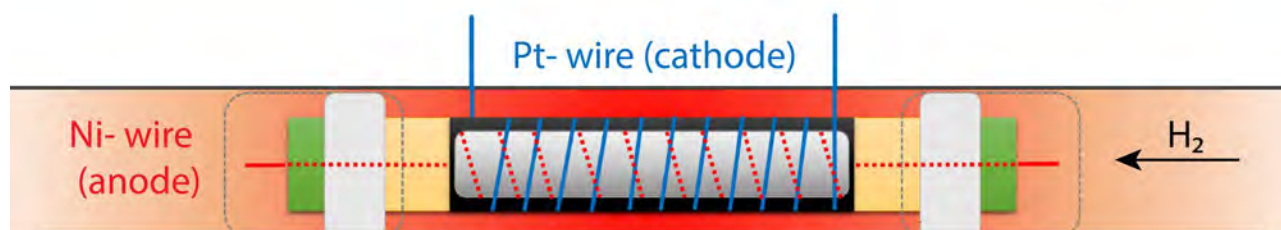


Fig. 1. The reactor scheme for the MT SOFC VI-characteristics measuring.

Also it was built the mathematical model describing the electric current generation during burning of hydrogen fuel in MT SOFCs. The model describes the chemical reactions (1, 2), diffusion and heat transfer processes.



The kinetic parameters for the reactions (1, 2) were determined during the model verification that allowed to achieve the best agreement between experimental and model data. Fig. 2 shows the current density depending on the process temperature in the range 600-850 °C, and the model describes the experimental data with a good accuracy.

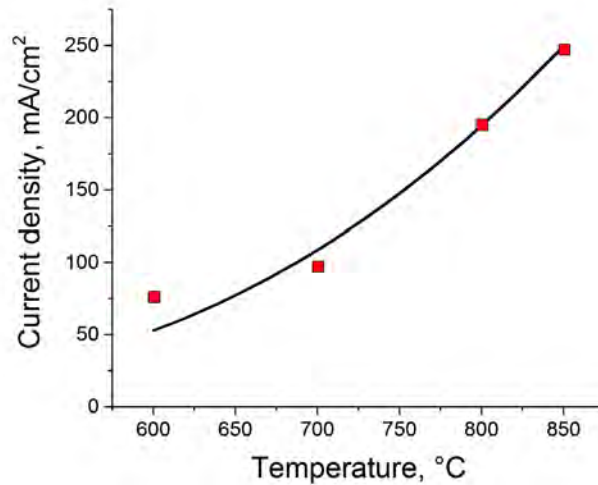


Fig. 2. The current density in model (black curve) and experiments (red dots).

So the model was applied for the process geometrical and technological parameters variation to detect the ones that give the best performance. The study opens the way to improving the process of hydrogen combustion reaction energy conversion to the electricity in MT SOFCs.

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MODELING OF HYDROGEN PRODUCTION BY DIESEL REFORMING AT Rh/Ce_{0.75}Zr_{0.25}O_{2-δ}-η-Al₂O₃/FeCrAl WIRE MESH HONEYCOMB CATALYTIC MODULE

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The study was dedicated to the mathematical modeling of the catalytic autothermal reforming (ATR) of diesel fuel – effective method for hydrogen production. The structured wire mesh Rh/Ce_{0.75}Zr_{0.25}O_{2-δ}-η-Al₂O₃/FeCrAl catalyst (Fig.1) was tested in pilot scale reactor and showed high efficiency in studied diesel autothermal reaction conditions.

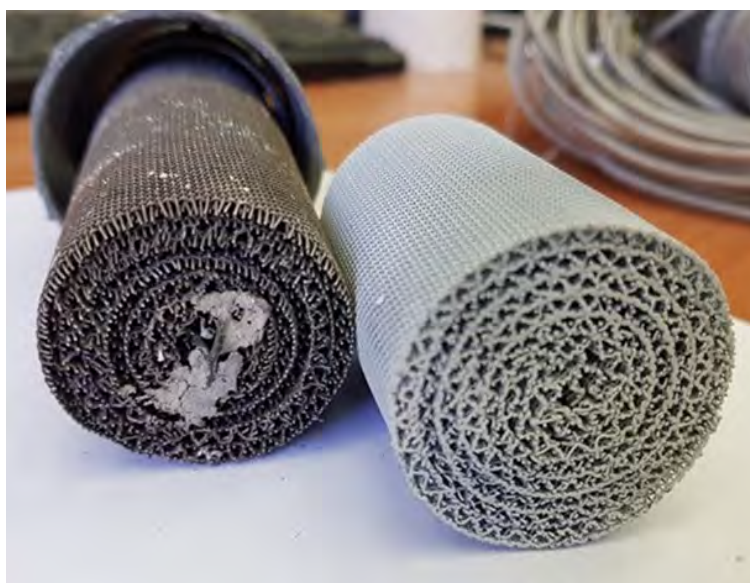


Fig.1. Appearance of the experimental wire-mesh cartridges: freshly prepared before Rh deposition (at the right) and after experiments (at the left).

The process simulation was carried out by commercial software COMSOL Multiphysics in 2D axisymmetric geometry. The catalyst module was simulated as homogeneous porous medium. Reaction model included oxidation and steam reforming of hexadecane, water-gas shift reaction, CO methanation, CO oxidation and hydrogen oxidation. Fitting the experimental results including product distribution and temperature profile allowed to define the kinetic parameters corresponding to the best fit.

Examples of modeling results are presented in Fig.2 and Table 1.

The model and experimental values are rather close, in spite of some minor quantitative misfits the model reflects the general process regularities concerned with catalyst length and mixture composition.

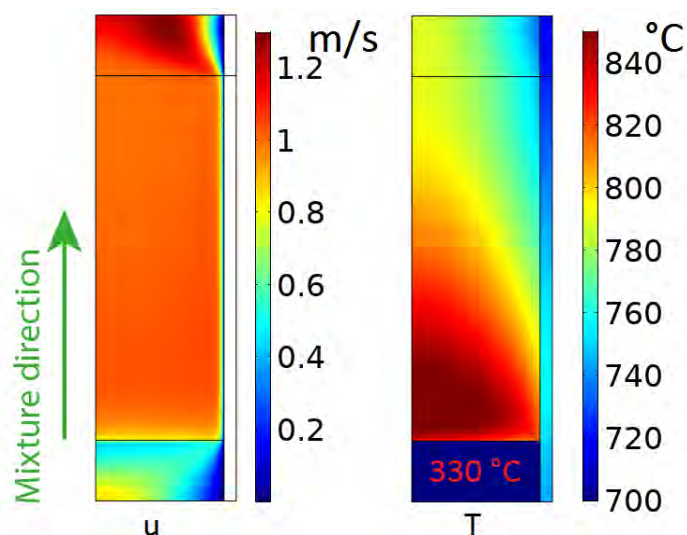


Fig. 2. Calculated gas velocity (a) and temperature distribution (b) in the catalytic module.

Table 1. Outlet model and experimental concentrations (vol. %)

	Experiments				Model			
	CO	CO ₂	H ₂	CH ₄	CO	CO ₂	H ₂	CH ₄
Exp. 1	9.4	14.4	29.6	0.22	10	11.4	29.7	0.26
Exp. 2	10.9	12.6	27.9	0.16	9.2	11.3	24	0.11
Exp. 3	10.5	13.1	31.2	0.21	9.3	12	30	0.35
Exp. 4	10.4	12.9	28	0.2	8.5	11.8	24	0.15

In general, the suggested simple quasi-homogeneous model describes experimental results (module temperature and outlet gas composition) with a good accuracy and could be used for process optimization and up-scaling.

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HYTHANE PRODUCTION VIA LOW-TEMPERATURE STEAM REFORMING OF NATURAL GAS

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Methane-hydrogen mixtures also known as hythane (a pre-prepared mixture of natural gas with 20% hydrogen) have a number of advantages comparing with conventional fuels: reduction in the total toxicity of emissions by 1.5-2 times, a relatively low cost, the absence of harmful impurities, a high hydrogen content, which ensures complete combustion of fuel in the absence of carbon deposits and environmental friendliness. One of the most promising areas is gas turbine installations in idle modes, where the turbine power is not fully used and it is possible to use diluted mixtures with hydrogen-initiating additives as fuels. The scheme for converting an engine to hydrogen-containing fuel was considered by car manufacturers in the USA, Canada, and China, but did not receive wide practical application due to the need to produce hydrogen, its intermediate storage and transportation to a gas station. In addition, the inability to quickly change the composition of the methane-hydrogen mixture does not allow to effectively organize the working process of the turbine. Therefore, it is reasonable to switch to using not hydrogen gas as additives to natural gas, but methane-hydrogen mixtures obtained from pipeline natural gas.

In this work, the thermodynamic aspects and the main approaches to the design of the catalysts and the technological implementation of the catalytic steam reforming of natural gas into methane-hydrogen mixtures with a hydrogen concentration of 20-27 vol.% are considered. The properties of industrial Ni-containing catalysts for steam reforming and methanation of carbon oxides are compared with the suggested Ni/Ce_{0.75}Zr_{0.25}O₂ and Ni-MgO-Al₂O₃ catalysts. It was shown that 1) Catalysts x% Ni/Ce_{0.75}Zr_{0.25}O₂ (x ≈ 5, 9, 12, 15) prepared by incipient wetness impregnation using an aqueous glycolic solution of nickel nitrate have high activity. This preparation method is a simple and effective. 2) An increase in the amount of supported nickel on the support increases the activity of the catalyst in the steam reforming reaction. 3) The most active catalyst of the series is a catalyst with a nickel content of 15.9 wt.%. This catalyst has a higher catalytic activity than the industrial nickel catalyst NIAP-07-05, containing 40 wt.% Ni.

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ZEOLITES AS A TOOL FOR INTENSIFICATION OF MASS TRANSFER ON THE SURFACE OF A COBALT FISCHER–TROPSCH SYNTHESIS CATALYST



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Low-temperature Fischer–Tropsch synthesis (FTS) over cobalt catalysts is an alternative source of environmentally friendly components of motor fuels. The technologies implemented in industry are aimed at obtaining high-molecular-weight hydrocarbons for their subsequent hydrocracking. In this case, FTS is carried out at low feed gas flow rate and low conversions in order to avoid overheating, since the reaction of CO and H₂ is strongly exothermic. The problem of heat removal can be solved by introducing a heat-conducting additive into the catalyst [1], but the problem of mass transfer remains since the high-molecular-weight products of FTS fill the catalyst surface. In industrial technology, this problem is solved by periodic treatment in a stream of hydrogen. However, another solution is also possible i.e. the intensification of mass exchange *in situ* due to cracking ability of zeolites [2]. Zeolites are widely used in industrial processes, mainly related to their activity in cracking and isomerization reactions. Such processes, as a rule, are carried out at high pressures and temperatures in a large excess of hydrogen [3].

The aim of this work is to study possible transformations of hydrocarbons over zeolite-containing Co catalysts under typical low-temperature FTS conditions implying 170–260 °C range and the presence of water — main byproduct of FTS.

In the present work, the conversion of a liquid hydrocarbons mixture (HC) obtained from CO and H₂ was studied over catalysts based on zeolite HY, HB and HZSM-5 ([Co] = 20 wt.%). 20%Co/Al₂O₃ was used as reference sample. All catalytic systems were activated in hydrogen at 400°C. The reaction was carried out in a stream of inert gas or hydrogen at 0.1 MPa and 170–260°C. HC + H₂O were applied at a rate of (1 + 1) ml/hour.

The introduction of hydrogen instead of inert as a carrier gas led to higher conversion into gaseous products with keeping however the same trend of decreasing in the range HZSM-5 > HBeta > HY ≈ Ref (Fig. 1a). The composition of gaseous products formed over all catalysts in hydrogen flow changed mainly due to an increase in the selectivity of methane (Fig. 1b). A shift from inert to hydrogen carrier gas leads to lower average molecular weight of the liquid hydrocarbons mixture (Fig. 2).

Two distinct areas can be identified in temperature dependencies of reaction parameters, namely 170–210°C and 220–260°C. The former area is characterized by hydrogenolysis and hydrogenation

at cobalt centers as main reactions; while the latter area is characterized by strong contribution from acidic centers. Methane and n-paraffins are the main products of transformations in the 170–210°C area, while iso-paraffins and light products of cracking are typical for the 220–260°C area. The distribution of products in both gaseous and liquid phase is determined mostly by the properties of a zeolite. It is very important observation that the introduction of HBeta zeolite leads to methanation suppression even in presence of water, which is determined different HBeta properties in competitive adsorption of water and hydrocarbons.

The results of this work suggest that zeolites can be instrumental in controlling composition of the products of Fischer–Tropsch synthesis produced over hybrid catalysts due to intensification of mass transfer.

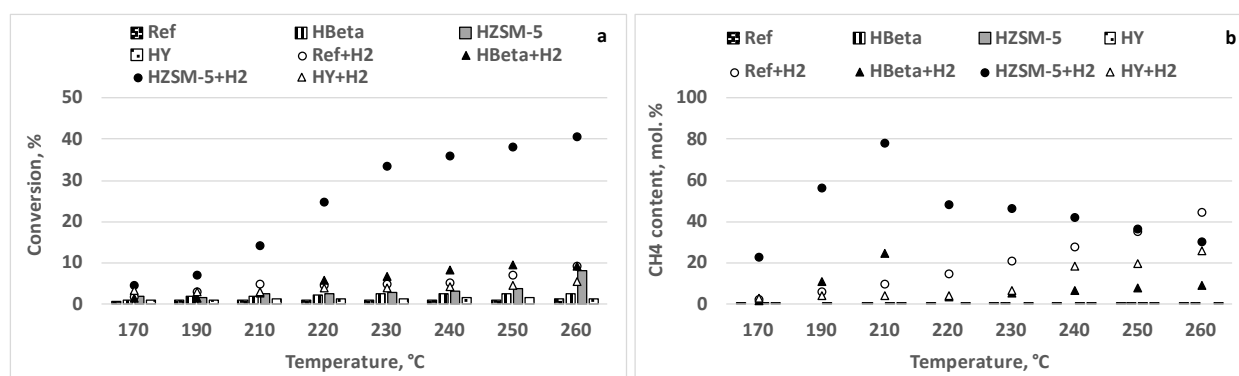


Fig. 1. Effect of zeolite type in the catalyst on conversion of liquid hydrocarbons mixture into gaseous products (a) and CH₄ content in them (b).

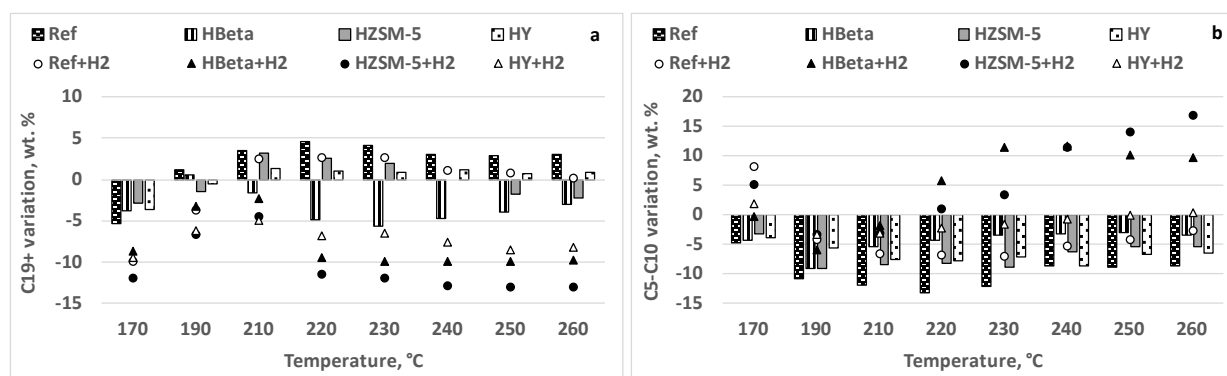


Fig. 2. Effect of zeolite type in the catalyst on the change in content of hydrocarbon C₁₉₊ (a) and C₅–C₁₀ (b) in liquid hydrocarbons mixture during contact with the catalyst.

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NOBLE METAL-CONTAINING NANOPARTICLES STABILIZED IN HYPERCROSSLINKED POLYSTYRENE AS EFFECTIVE CATALYSTS OF AROMATIC RING HYDROGENATION

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This study is devoted to the investigation of catalytic behavior of noble metals (Pd, Pt, Ru) stabilized in the aromatic polymeric network in liquid-phase hydrogenation of arenes. Catalytic systems were synthesized by the impregnation of metal compounds dissolved in suitable solvents in the polymeric matrix of hypercrosslinked polystyrene of MN100 type. Before the experiments, all the catalytic systems were reduced in hydrogen flow at 300°C. Catalytic testing was carried out in a liquid-phase using hexane or dodecane as solvents at elevated hydrogen pressure. Benzene, aniline, and naphthalene were used as hydrogenation substrates.

Both the initial polymer and synthesized catalytic systems (before and after catalytic experiments) were characterized by diffuse reflectance infrared spectroscopy, X-ray photoelectron spectroscopy, and thermogravimetry. The composition of the reaction mixture was analyzed by GC and GC-MS.

During the investigation, 1%-Pt/MN100 and 1%-Ru/MN100 were shown to allow carrying out the selective liquid-phase hydrogenation of benzene to cyclohexane in hexane solution and also in pure benzene. It is noteworthy that the isomerization of cyclohexane to methyl cyclopentane under chosen reaction conditions in the presence of the above catalysts was not observed.

1%-Pt/MN100 was found to allow carrying out the process of liquid-phase hydrogenation of naphthalene with the selectivity to tetralin higher than 98%. In the hydrogenation of aniline to cyclohexylamine in hexane solution, the maximum selectivity of 94% toward cyclohexylamine was observed while using 1%-Ru/MN100. Moreover, the transformation of metal salts in the polymeric environment (MN100) was studied during the synthesis of each catalyst; reduction process; after the first catalytic run, and also after the second consecutive run. For 1%-Pt/MN100 and 1%-Pd/MN100, it was demonstrated that metal precursors were not completely converted to metallic particles during both the reduction procedure and the first catalytic experiment (Fig. 1). Nevertheless, the high stability of the optimal catalytic system for each studied reaction was shown.

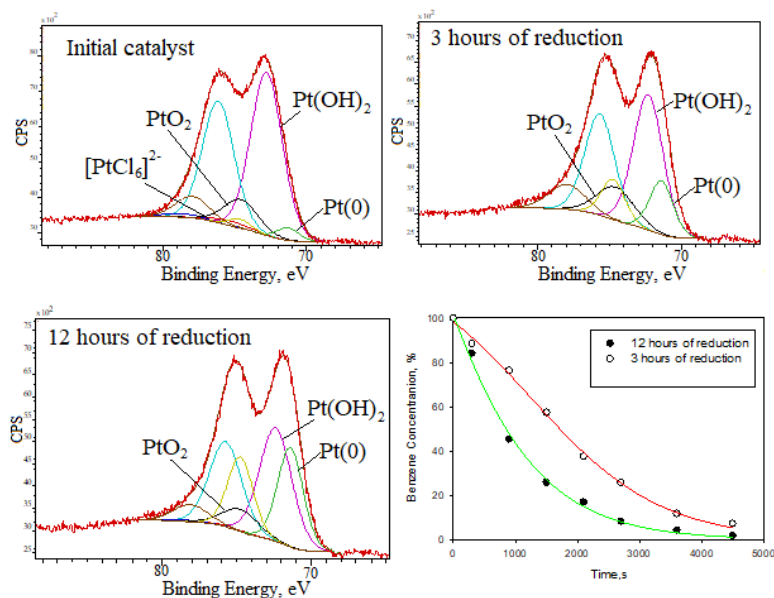


Fig. 1. Chemical states of platinum on the surface of Pt/MN100 before and after reduction with H_2 (300°C) and their influence on liquid-phase benzene hydrogenation

Thus, it can be concluded that the studied catalytic systems allowed carrying out the reaction of liquid-phase hydrogenation of aromatic rings with high selectivity. It was shown that during the first catalytic experiments the additional transformation of catalytic systems took place including partial hydrogenation of aromatic rings of the polymeric supports. At the same time, the used polymeric matrices prevented the complete reduction of metal salts.

Acknowledgments

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LIGNIN AND MODEL SUBSTANCE CATALYTIC HYDROGENOLYSIS

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The particular interest to the lignin due to the fact that in the last decade renewable raw material (biomass or its components) is considered as an alternative to fuel in the oil delivery [1, 2]. Interest in biofuels is associated with the search for new areas of energy and the rational use of resources and reducing waste. Among the products obtained during hydroprocessing of lignin-containing raw materials fuel aromatic and cyclic hydrocarbon (benzene, toluene, and cyclohexane), as well as phenolic compounds are the most promising. The latter can be used as additives to conventional fuels and fuels derived from biomass. Moreover, a number of cyclic and aromatic hydrocarbons may also be used in various fields of fine chemicals production as solvents and reagents. Furfuryl alcohol obtained by using catalysts based on aluminum oxide may also be used as an alternative source of energy [3, 4]. The aim of this work was to study the conditions of catalytic processing of lignin-containing raw materials by hydrogenolysis. The object of the study was sawdust softwood obtained from sawmill of Sandovsky district of Tver region of Russia. The following catalysts were used: commercial 5% Pd / C and synthesized 5% Pt/Al₂O₃. Due to the complex lignin composition anisole as one of the major lignin monomers was chosen as a model compound for the preliminary experiments to determine possible products of lignin-containing material hydrogenolysis.

Hydroprocessing of 30 mL of anisole was carried out for 4 hours in Parr Series 5000 Multiple Reactor System reactor-cell equipped with a magnetic stirrer in the presence of 0.1 g of the catalyst at a temperature of 250 °C and hydrogen pressure 1.0 MPa. The hydrotreatment process was conducted at constant stirring (1700 rpm) to eliminate the influence of external diffusion. Then hydrogenolysis of the sawdust was carried out. The process was carried out for 4 hours in the reactor in a hydrogen atmosphere under the following conditions: substrate weight – 1.0 g, catalyst weight – 0.1 g, temperature – 250 °C, hydrogen partial pressure – 1 MPa, solvent volume – 30 mL. The following polar solvents are used: 2-propanol, water, and ethanol. Substrate conversion was calculated at the end of the reaction basing on the difference between the initial mass of the substrate and the dry weight of the residue. During both processes, liquid phase samples were taken every 30 minutes. The analysis of the samples was performed using GC-2010 chromatograph and GCMS-QP2010S mass spectrometer (SHIMADZU, Japan). The analysis duration was 25 minutes with the following conditions: initial column temperature of 150 °C was

maintained for 5 min, and then the temperature was increased up to 250 °C with the heating rate 5°K/min.

It was found that the use of Pt-containing catalyst based on alumina in both processes of anisole and lignin-containing feedstock conversion allowed obtaining phenolic compounds whereas in the presence of the commercial Pd/C the major products were cycloalkanes. Moreover, the investigation of the solvent influence on sawdust processing was carried out in the presence of the commercial catalyst Pd/C (Sigma-Aldrich, USA). With Pd/C catalyst the substrate conversion values are 45% in a water medium, 50% in propanol-2 and 37% in ethanol. Depending on the desirable products propanol-2 was chosen as the solvent showing high substrate conversion and product yield.

The comparison of the catalytic action of synthesized systems in sawdust hydroprocessing in propanol-2 medium showed that platinum group metals supported on alumina are the most promising in the one-step process. The use of the catalysts based on alumina resulted in the formation of the following products: phenol, cresol, furfuryl alcohol.

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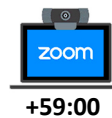
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DOUBLE PROMOTION EFFECT ON HDS CoNiMo/Al₂O₃ CATALYSTS APPLIED IN THE HYDRODESULFURIZATION OF DIBENZOTHIOPHENE



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There is a global demand for clean fuels and, consequently, to develop highly active hydrotreatment catalysts to achieve ultra-low sulfur in fuels (15 ppm S for diesel). Improvements in catalyst formulation like a third metal or organic additives may prevent promoter migration and increase the MoS₂ crystallites dispersion [1]. The double cobalt and nickel promotion resulted in synergetic improvement of the CoNiMo/ γ -Al₂O₃ catalyst performance [2]. Such good performance is provided by tri-metallic Ni-Co-Mo sites more reactive than those on bi-metallic Co(Ni)-Mo-S counterparts. Despite better catalytic properties of CoNiMo catalysts, the preparation method needs to be optimized to hinder Ni segregation as low active (Co/Ni)₉S₈ phases, limiting the formation of Ni-Co-Mo sites. As the trimetallic site formation has been known to be the key to high catalytic activities in deep HDS of fuels [2], we explore in this work four different compositions in CoNiMo/ γ -Al₂O₃ sulfides that have been prepared by the co-impregnation method.

Our results show that the co-impregnation method gives preference toward Co to form a bimetallic Co-Mo precursor that maintains cobalt in bimetallic structures like β -CoMoO₄. We found better textural properties and smaller particle sizes in trimetallic CoNiMo catalysts of high cobalt and low Ni content. Therefore, low nickel content enhances the catalytic performance due to an improved metal dispersion of the mixed Co-Ni-Mo-S than the isolated CoMoS active sites. Those optimized CoNiMo/Al₂O₃ catalysts exhibited higher hds rates than bimetallic/commercial CoMo/Al₂O₃ materials. Fig. 1a shows the diffuse reflectance UV-vis spectra of catalysts with different Co/Co+Ni molar ratio. The visible region showed a plateau (from 545 nm to 630 nm) related to β -CoMoO₄, where the Mo⁶⁺ presents tetrahedral coordination and Co²⁺ stills in octahedral coordination. This plateau has overlapped signals, with the contribution of tetrahedral Ni species (NiAl₂O₄ spinels), in which the primary signal is located at 635 nm. NiAl₂O₄ spinels usually are related to inactive nickel compounds. Fig. 1b shows a representative micrograph of MoS₂ particles; statistical analysis of MoS₂ slabs indicated smaller length and similar stacking height of MoS₂ slabs at high cobalt content. Then, we obtained higher MoS₂ dispersion of the Co_{0.95}Ni_{0.05}Mo/Al₂O₃ catalyst with an average slab length of 2.5 nm. On the other hand, at high Ni content, the Co_{0.65}Ni_{0.35}Mo/Al₂O₃ material exhibited low dispersion with a larger slab size of 3.7 nm. In Fig. 1c, all catalysts present a type-4 isotherm. The isotherm of Co_{0.95}Ni_{0.05}Mo/Al₂O₃ catalyst exhibited the maximum hysteresis loop and slope values. Therefore, in general, as the cobalt content of the catalysts increases, the textural properties increases.

Figure 1d shows the catalytic activity of trimetallic catalysts in the reaction of hydrodesulfurization of dibenzothiophene. The catalytic performance was compared with a bimetallic lab-synthesized CoMoS/Al₂O₃ and an industrial CoMoS/Al₂O₃ catalyst. All five synthesized catalysts exhibited higher activity than industrial CoMo/Al₂O₃ material. We observed low activity of Co_{0.75}Ni_{0.25}Mo and Co_{0.65}Ni_{0.35}Mo that can be explained either as a moderate dispersion of nickel in MoS₂ nanostructure or by the formation of segregated nickel species like NiAl₂O₄ structures. The increased activity was explained in terms of a co-electronic promotion induced in Mo atoms by the presence of Co and Ni atoms in the edge of MoS₂ slabs. Our theoretical DFT results showed that Co and Ni atoms modify Mo local coordination to promote Mo atoms' electronic participation at the metallic edges of trimetallic sulfides, increasing their reactivity.

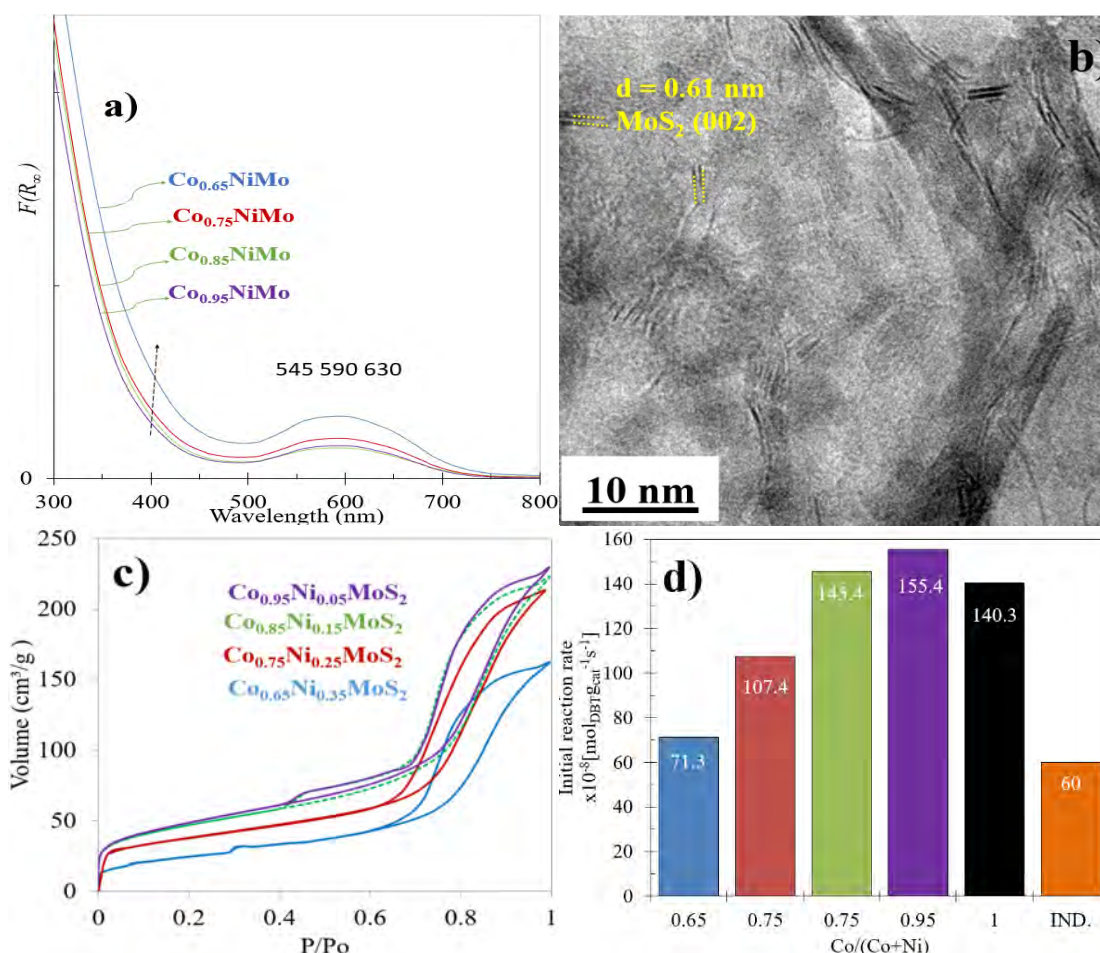


Fig. 1. a) UV-Vis spectra, (b) TEM micrograph, (c) Isotherms, (d) Initial reaction rate.

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NiMoW CATALYSTS SUPPORTED ON MgO-Al₂O₃ MIXED OXIDES FOR THE HYDRODESULFURIZATION OF DIBENZOTHIOPHENE

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There is a global demand for clean fuels and, consequently, developing highly active HDS catalysts to achieve ultra-low sulfur in fuels required by world environmental regulations to move toward a sustainable future. Experimental and theoretical studies on the trimetallic NiMoW base catalysts have shown improved catalytic properties than bimetallic ones [1]. Great activities exhibited by trimetallic NiMoW systems were attributed to the mixed Mo_{1-x}W_xS₂ sulfide phases [2, 3]. Recently, NiMoW sulfides supported on Mg-Al binary oxides were reported as a catalyst for a reaction like higher alcohol synthesis in carbon monoxide catalytic hydrogenation. In that report, a synergetic effect from tungsten doping MoS₂ slabs was suggested to increase the active phase formation [4]. Herein, we present an approach to obtain new NiMoW/MgO-Al₂O₃ catalysts. We explore tungsten's influence in the catalytic properties for the HDS of DBT comparing NiMoW/MgO-Al₂O₃ and NiMo/MgO-Al₂O₃ sulfide catalysts. Additionally, we complemented our experimental results incorporating the Density Functional Theory (DFT) to explain the synergic effect when the molybdenum is substituted isomorphically for tungsten to obtain Mo_{1-x}W_xS₂ structures with a different W atom distribution on the hexagonal MoS₂ slab.

The MgO-Al₂O_{3-x} catalytic supports were synthesized by precipitation method, and they were labeled as MgAl-x with $x = \text{Al}/(\text{Al} + \text{Mg}) = 0, 0.20, 0.25, 0.33, \text{ and } 1.0$. The initial reaction rate in the HDS of DBT for bimetallic and trimetallic catalysts is shown in Fig. 1a. In general trimetallic catalyst exhibited higher HDS activity than bimetallic materials. The improved activity was showed at $x=0.20$.

The developed NiMoW/MgAl-0.20 and NiMoW/MgAl-1 catalysts displayed a higher HDS rate than the industrial catalyst. Our study indicated that, in most cases, the activity increases with the introduction of W in the MoS₂ network. Particularly the reaction rate increases for the NiMoW/MgAl-0 (46%), NiMoW/MgAl-0.20 (72.2%) and NiMoW/MgAl-1 (31.4%) catalysts. Thus the increased activity was explained in terms of a co-electronic promotion induced in Mo atoms by W atoms in the MoS₂ nanostructure. The activity results for the NiMo MgO based catalysts resembled a typical volcano curve centered at the NiMo/MgAl-0.25 catalysts. In the NiMoW series, we found better catalytic performance at $x=0.20$ than other MgO-based catalysts that correspond with better mesopore distribution. In Fig. 1b, the XRD patterns show NiMoO₄/NiWO₄ species' formation in NiMoMgAl-0.20 and WO₃ in NiMoMgAl-0 catalysts. Those species could exhibit a weak interaction with alkaline support like MgO or mixed oxides of hydrotalcites [4]; thus, tuning the Al content in MgO influenced the active-metals-support interaction, as exhibited in our XRD and UV-Vis data.

Fig. 1c shows the two Mo_{1-x}W_xS₂ structures with different W atom distribution on the hexagonal MoS₂ network that were optimized. The first structure exhibits W atoms decorating the hexagonal borders

of a MoS₂ network; in the second structure, the W atoms resulted in a mixed distribution in the entire MoS₂ network. Fig. 1d depicts the total density of states (DOS) for the two Mo_{1-x}W_xS₂ structures. The two curves are noticeably different, which is a clear indication of how W atoms give better electronic promotion to Mo atoms in the structural variation with W mixed distribution (this W mixed distribution displays higher DOS values near the Fermi level) than the other one structural variation. In general, high values over the Fermi level correspond to an improvement in the electronic properties and frequently are correlated to an enhancement in reactivity [5].

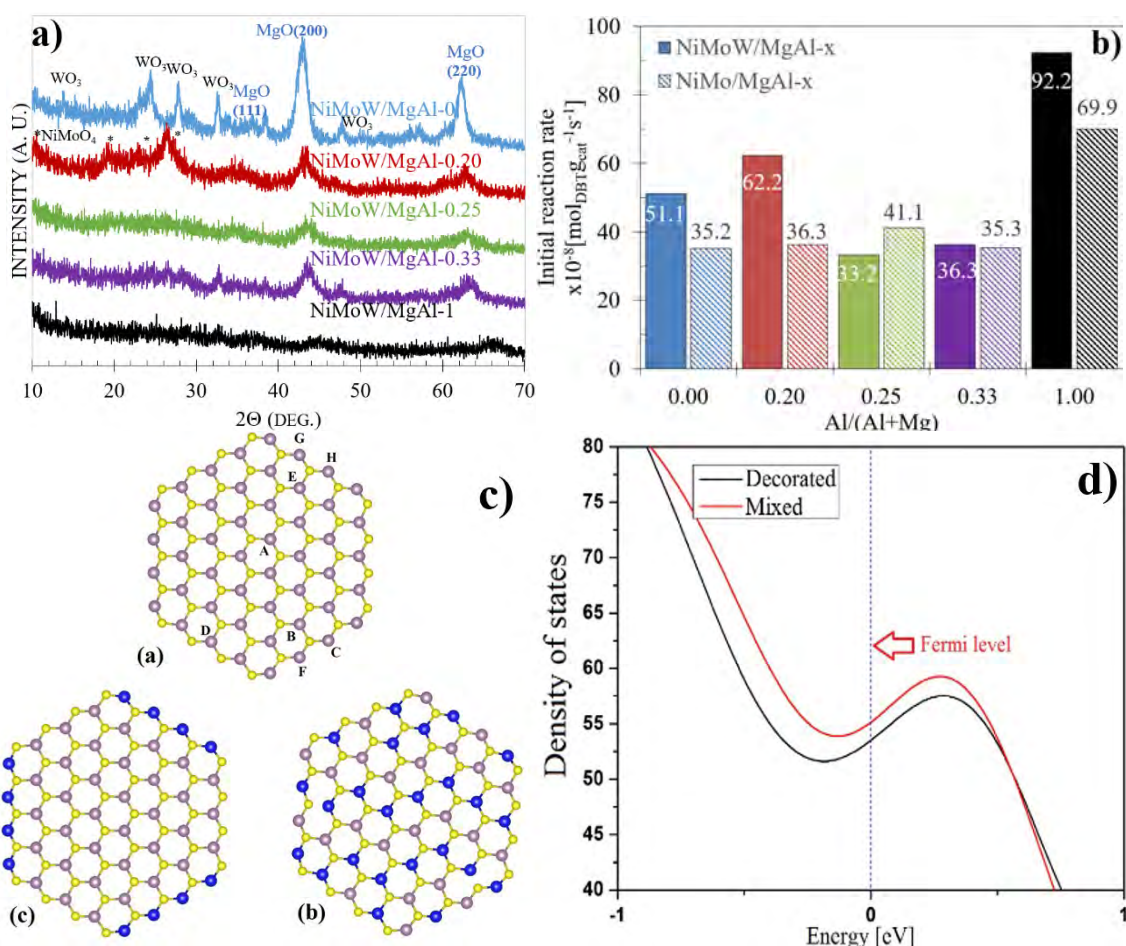


Fig. 1. a) XRD patterns, (b) Initial reaction rate, (c) Mo_{1-x}W_xS₂ structures, (d) DOS near Fermi level.

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INVESTIGATION OF CATALYTIC CRACKING PROCESSES OF PROPANE AND POLYPROPYLENE USING GADOLINIUM MOLYBDATES AND TUNGSTATES $Gd_2(MO_4)_3$ (M=Mo, W)

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Currently, the solid materials with multifunctional properties are of great scientific and practical interest. For example, these include complex oxide compounds of transition d-and f-elements. A special place in this group is occupied by complex oxides of rare earth elements (REE) that have unoccupied 4f-orbitals. They have unique chemical properties and can be used to create highly efficient catalysts and catalytic systems [1]. REE-based catalysts are widely used in the chemical and petrochemical industry, in thermo-catalytic processes of oil and gas processing, in detoxifying transport emissions, and for cleaning the environment from industrial waste [2].

To obtain catalysts, the estimated amount of the aqueous solution of gadolinium nitrate was added to the aqueous solution of sodium molybdate or tungstate. The resulting solution was mixed for 1 hour at temperature of 30-40 °C. The precipitate of gadolinium tungstate dihydrate $Gd_2(WO_4)_3 \cdot 2H_2O$ or gadolinium molybdenum dihydrate $Gd_2(MoO_4)_3 \cdot 2H_2O$ was filtered and dried at temperature of 60 °C for 8 hours. Then the resulting precipitate was calcined at temperature of 800 °C for 5 hours. After removing the crystallohydrate water, powders of tungstate and gadolinium molybdate were obtained.

The study of powders of synthesized materials was carried out using x-ray phase analysis and Raman spectroscopy (Figure 1).

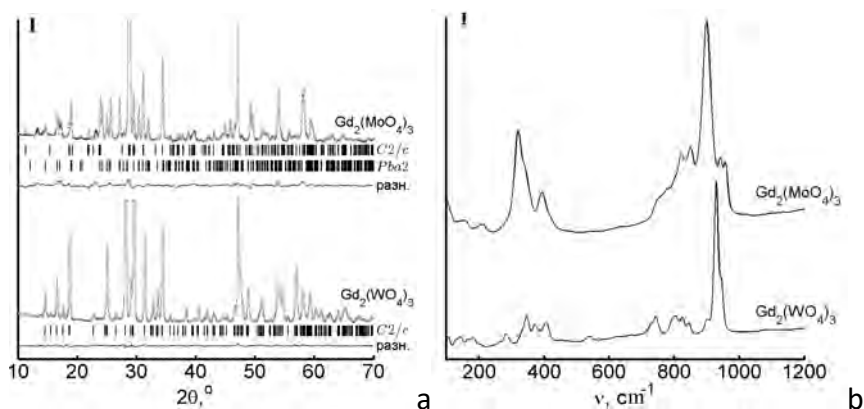


Fig. 1. X-ray diffraction patterns (a) and Raman scattering spectra (b) of crystalline structures of gadolinium molybdate and tungstate

Simultaneous presence of monoclinic and rhombic structures was found for tungstate and gadolinium molybdate. The surface of the materials was mesoporous with pore sizes from 30 nm to 50 nm.

Testing of catalysts was carried out in the processes of cracking propane and polypropylene at temperatures of 500 °C and 550 °C (figure 2) in order to obtain propylene and ethylene.

The using of catalysts in all cases increased the selectivity of the thermo-catalytic process in comparison with non-catalytic cracking. The most interesting results were obtained when gadolinium molybdenum was used for cracking polypropylene. The selectivity of the process for propylene was 97.2 %. For gadolinium tungstate with similar structural properties, the selectivity for propylene was 68.0 %.

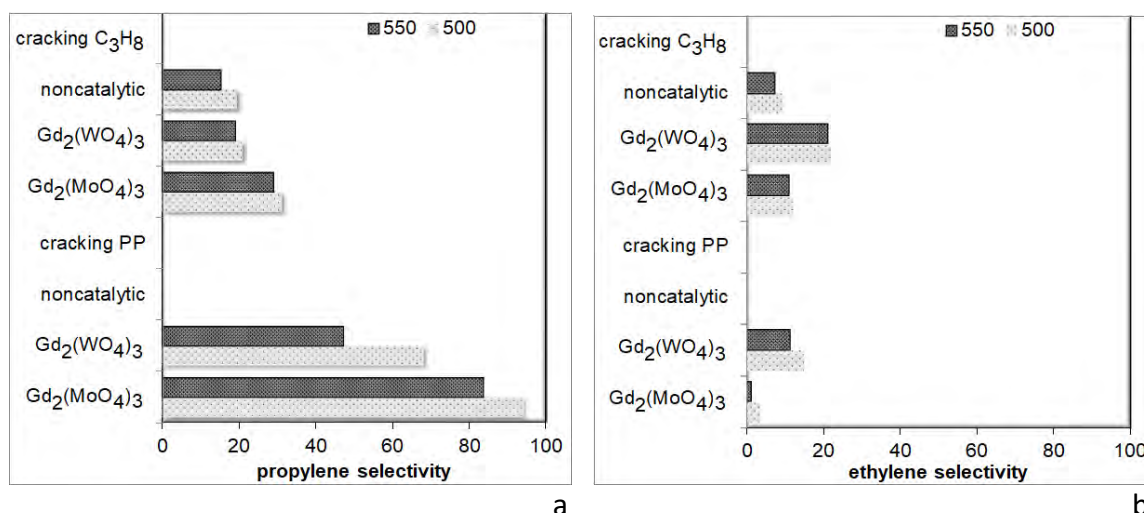


Fig. 2. Dependence of selectivity of catalytic and non-catalytic cracking of propane and polypropylene for propylene (a) and ethylene (b) production

The selectivity of catalytic cracking of propane in the production of propylene and ethylene in comparison with non-catalytic cracking increased slightly.

Thus the synthesized materials based on tungstate and molybdate gadolinium can be used as highly selective catalysts in the cracking of polypropylene for the processing of plastic waste.

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THE REVIEW OF RECENT FISCHER TROPSCH CATALYSTS: A GUIDE TO UNDERSTAND THE EFFECT OF CATALYST STRUCTURE ON THE CATALYST ACTIVITY

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Metallosilicates offer high activity and tuneable molecular sieving property[1] and have been applied in Fischer-Tropsch synthesis with cobalt as the active catalyst not yet with iron[2][3]. We prepared a series of iron-metallosilicate catalysts by a novel sol-gel method. Ce, Zr, V and Ti were the metal precursor supports, which were characterized by SEM, BET and XPS. Also, bulk iron is used to compare the impact of metallosilicate supports. Catalysts were activated at 350°C, 4 bar for 4 hours. The reaction takes place at 20 bar with gradually increased temperature from 200°C to 350°C for 90 hours, and H₂/CO molar ratio of 2. The synthesis method produces a more homogeneous structure with tailored physico-chemical properties: particle size and pore size distribution [4][5]. We achieved the highest surface area for Fe/Ti/SiO₂ and Fe/Zr/ SiO₂ with 228 and 335 m²/g respectively. Fe/V/ SiO₂ and Fe/Ce/ SiO₂ agglomerates were larger than those of Fe/Ti/SiO₂ and Fe/Zr/ SiO₂, which accounts for the lower surface area, but the porous structure was preserved. Bulk iron had the lowest surface area (0.16 m²/g). CO conversion increased with temperature and reached 68 % and 52 % for the Ce-silicate and Zr-silicate supports, respectively at 350 ° C and 20 bar and produce 7 g of liquid product. The bulk iron converted less at most 1% of CO.

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JOINT HYDROTRANSFORMATION OF A MIXTURE OF STRAIGHT-RUN GASOLINE AND TOLUENE ON A COMPOSITE ZEOLITE CONTAINING CATALYST

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The development of processes for producing high-octane gasolines with a low content of aromatic hydrocarbons is an actual problem for the petrochemical and oil refining industries. Earlier, we showed the possibility of isomerization-disproportionate processing of straight-run gasoline (SRG) into high-octane gasolines by contacting it with composite catalysts of the type Co (Ni)/H-zeolite/SO²⁻₄-ZrO₂ at atmospheric pressure, 160–200°C, WHSV=2 h⁻¹, H₂/CH = 2 - 3 [1, 2].

Considering the possible content of aromatic hydrocarbons in SRG, the purpose of this report is to study their influence on the noted conversion of SRG.

This report presents the results of hydrotransformation of toluene and its mixture with SRG on a synthesized composite catalytic system, the components of which are sulfated zirconia and cobalt-modified decationized zeolite HZSM-5 (composition of the catalyst: 0.4% Co/HZSM-5/ SO²⁻₄ (2.0%) ZrO₂ - catalyst M - 11).

The conversion of SRG, toluene, and their mixture was studied in a flow-type laboratory catalytic unit equipped with a quartz reactor under the conditions noted above.

The results of the studies (table 1) showed that the developed catalyst under the conditions of isomerization-syncretization processing of SRG have a high hydrogenating activity with respect to toluene.

Table 1. The conversion of toluene on M-11. T = 180°C; H₂/C₇H₈ = 3; WHSV = 2 h⁻¹

T, min.	Conversion of C ₇ H ₈ , %	Distribution of reaction products, % wt			
		C ₅	MCP*	CH*	MCH*
30	59.2	5.4	30.6	7.1	16.1
60	58.2	1.8	17.5	0.9	48.0

*MCP - methylcyclopentane; CH - cyclohexane; MCH - methylcyclohexane

As can be seen from the data in table 1, the contacting of toluene with the catalyst M - 11 leads to the formation of alicyclic molecules. Moreover, the change in the yields of MCH and CH change antipatically: with a decrease in the yield of CH, the output of the MCH increases. Consequently, the hydrotransformation of toluene on the M-11 catalyst proceeds in a series-parallel fashion for the formation of its conversion products.

As can be seen from the data in table 2, the distribution of hydrocarbons in the initial SRG and in the products of its conversion change significantly. From these data it can be seen that C₈₊ is

converted to low molecular weight C₅ - C₇ isocomponents without the formation of undesirable gaseous alkanes.

Table 2. The conversion of straight-run gasoline on the catalyst M-11. $\tau = 30$ min; CH/H₂ = 1:3; WHSV = 2.5h⁻¹, T = 180°C.

Hydrocarbon composition, % wt	C ₄₊	iC ₅	C ₅	iC ₆	C ₆	iC ₇	C ₇	C ₈₊
Initial	2	4.2	4.4	6.5	5.3	21	5.6	51
After the reaction	1.4	10.2	13	16.6	17.8	20.2	10.7	10.1

In the table 3 presents the results of joint hydrotransformation of a mixture of SRG and toluene (1:1 mass). From a comparison of the data of table 3 with the data of tables 1 and 2, it follows that the components of the mixture are mutually activated and this leads to an increase in the conversions: toluene by 11.0%, and C₈₊ paraffins of SRG by more than 25.0%.

Table 3. The conversion of the mixture of SRG : toluene=1:1 (mass) on M-11 at 180°C. H₂/CH = 3; WHSV = 2h⁻¹.

τ , min	Hydrocarbon composition, % wt										
	C ₄₋	i-C ₅	C ₅	i-C ₆	C ₆	MCP	i-C ₇	C ₇	MCH	C ₈₊	T
0*	1.0	2.1	2.2	3.2	2.7	0	10.5	2.8	0	23.6	51.9
15	8.1	8.0	6.2	10.5	5.9	22.6	13.2	-	14.5	5.6	5.4
30	9.1	8.9	6.9	11.4	6.6	21.7	12.0	-	6.0	5.4	12.0
60	11.4	12.8	10.2	14.4	7.1	13.7	14.3	-	-	5.1	11

* Initial reactant

Consequently, as a result of the joint conversion of toluene with straight-run gasoline, an interaction occurs between the components of the mixture. An assumption was made about the formation of bimolecular intermediates with the participation of toluene and components of SRG, and the mechanism of their formation corresponds to the mechanism of syncretizational conversion of gaseous and liquid paraffins [3].

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JOINT CONVERSION OF STRAIGHT-RUN GASOLINE AND PROPANE-BUTANE FRACTION ON ZEOLITE CONTAINING COMPOSITE CATALYSTS

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Earlier, on the examples of joint conversion of C_6H_{14} or C_7H_{16} and C_4H_{10} on composite catalytic systems consisting of H-zeolites and anion-modified ZrO_2 , the formation of $C_5 - C_6$ paraffins of various structures was shown as a result of their isomerization-disproportionation conversion [1, 2]. Based on these data, this work is devoted to solving the problem of increasing the resource of environmentally friendly components of high-octane gasolines - branched $C_5 - C_6$ alkanes in fuel by co-processing the propane-butane fraction (PBF) of associated petroleum gas with straight-run gasoline (SRG).

The study of the joint conversion of SRG with PBF was carried out on synthesized composite catalysts (CC), the components of which are H-zeolite (MOR or ZSM-5) and SO_4^{2-}/ZrO_2 (SZ).

The composition of the synthesized catalysts : M-11: HZSM-5/Co(0.4%)/ ZrO_2 (10%)/ SO_4^{2-} (2%); M-12: HZSM-5/Co(0.4%)/ ZrO_2 (10%)/ SO_4^{2-} (6%); M – 2: HM(17)/Co(0.4%)/ ZrO_2 (10%)/ SO_4^{2-} (2%).

The experiments were carried out at atmospheric pressure in a flow catalytic setting under the following conditions: temperature 160-200 $^{\circ}C$, WHSV-2-3 h^{-1} ; $H_2/CH = 2-4$. The composition of the feedstoc: $C_2 - 5.0\%$; $C_3 - 17.8\%$; i- $C_4 - 9.9\%$; $C_4 - 15\%$; i- $C_5 - 4.3\%$; $C_5 - 4.2\%$, i- $C_6-3.0\%$, n- $C_6 -2.0\%$, i- $C_7- 9.4\%$, n- $C_7-2.5\%$, $C_{8+}- 27.7$.

In the marked conditions, PBF, unlike SRG [3], does not undergo noticeable changes. On the other hand, in the temperature range 160-200 $^{\circ}C$, the mixture of SRG and PBF is intensively involved in the process of their joint conversion.

As shown in the table the composition of the PBF: SRG mixture undergoes a change upon contact with CC. The conversion products are C_5-C_6 paraffins of a predominantly branched structure. With increasing temperature, the conversion of C_4- increases from 46.3 to 67%, and the conversion of $C_8 +$ decreases from 63.2 to 33.7%. At 180 $^{\circ}C$, up to 63.5% of gaseous C_4- and 55.5% of liquid $C_8 +$ alkanes are involved in the joint processing of SRG and PBF (1:1 wt), which makes it possible to increase the content of C_5-C_6 in the catalysate by 21.4%, which consist of 80% of branched alkanes.

The effect of H_2 on the conversion of PBF: SRG mixture was studied. It was found that the increasing of H_2 /hydrocarbon ratio from 2 to 4 leads to an increase in the conversion of C_4- alkanes from 63.5% to 90% and an increase in the target products.

PP-36

Table. Conversion of PBF: SRG (1:1 mass) mixture on composite catalysts.

$T=180^{\circ}\text{C}$, $\text{WHSV} = 2.5\text{ h}^{-1}$; $\text{GHSV} = 500\text{ h}^{-1}$; $\nu_{\text{H}_2}= 20\text{ml/min}$.

Catalyst	Conversion, %		Accumulation,%	
	C ₄₋	C ₈₊	$\sum(\text{C}_5\text{-C}_6)$	$\sum(\text{C}_7\text{-C}_7)$
M-2	75.0	41.0	25.2	23.2
M-12	40.0	21.0	16.6	1.7
M-11	63,5	55,4	21.4	23.3

On the basis of the analysis of the conversion products of the SRG: PBF mixture on composite catalysts, it was suggested that, in contrast to the individual components, the CC have activity in the formation of a bimolecular intermediate in the participation of gaseous C₄₋ and liquid C₈₊ alkanes under conditions of their low-temperature processing (160-200^oC). The involvement of C₄₋ and C₈₊ alkanes in the reaction of formation and isomerization of these intermediates on KK depends on the composition of the anion-modified ZrO₂ component, and the subsequent cleavage of these intermediates depends on the nature of the zeolite and its modification with a transition element.

Results of conducted research allow to suggest the possibility of producing modern high-octane gasolines by involving straight-run gasolines and gaseous alkanes in the low-temperature process of isomerization-disproportionation conversion on composite catalytic systems.

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STUDY OF ZEOLITE SORBENTS SYNTHESIZED BASED ON LOCAL KAOLIN**Yunusov M.P.¹, Nasullaev Kh.A.^{1,2}, Djalalova Sh.B.¹, Gulomov Sh.T.¹, Sultanov A.P.¹**¹*UzKFITI, Tashkent, Uzbekistan*²*National University of Uzbekistan named after M.Ulugbek, Tashkent, Uzbekistan**E-mail: kh.a.nasullaev@gmail.com*

This paper discusses the technology of synthesis and the properties of zeolite sorbent NaA on the basis of kaolin, the mineral composition of which includes a significant amount of hydromica and quartz. Synthesis of zeolite sorbent samples in granules, without a binder, was produced by the developed technology. The crystallization time of the reaction mixture formed into granules was 5 hours at 93°C. The obtained sorbent samples were studied by X-ray phase analysis in a powder on a DRON-3 instrument using Cu K α -filtered radiation with subsequent identification of the crystalline zeolite phase using data on interplanar spacings.

Determination of the sorption capacity was produced by static conditions for samples, pre-heat-treated at least for 4 hours at 500°C. The method of synthesis using a mixture of plasticizers (pectin + carbamide-formaldehyde resin) also allows to get a sorbent with a good sorption capacity for water vapor. However, there was a slight decrease in the sorption capacity after the 17th adsorption-thermal desorption cycle, which may indicate the beginning of sintering; for this reason, the use of the specified plasticizer mixture requires further refinement.

By the method of X-ray phase analysis, no tangible differences for the initial and spent in the 17-20 cycles adsorption-thermal desorption of the samples could not be found, except for a very slight change. It was shown that samples of type A zeolite adsorbent obtained on the basis of enriched primary Angren kaolin containing a significant amount of hydromica and quartz, in comparison with foreign analogues, have a comparable sorption capacity for water vapor. The most complete desorption of water, without the use of a gas propellant, is achieved during the holding time of the final temperature at least 4 hours for the analytical sample mass (0.5 - 1.0 g).

In the process of thermal desorption of ammonia at 400°C, slightly acidic centers with $pK_a \leq 3.8$ appear on the surface of the zeolite sorbent in the ammonium form, but in general the surface of the sorbent is close to neutral.

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OPTIMIZATION OF THE SYNTHESIS TECHNOLOGY OF HIGHLY DISPERSED ALUMINUM HYDROXIDE USING VARIOUS REAGENTS

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Having regard to the rather large need of industrial enterprises of Uzbekistan for adsorbents for drying various process gases, this work is devoted to the development of a technology for producing an aluminium oxide adsorbent-desiccant from a by-product of polyethylene production at Shurtan Gas Chemical Complex (hereinafter referred to as AOAD). It is known from our previous AOAD studies that its porous structure does not meet the main criteria of adsorbent-desiccants; therefore, we will consider options for the maximum extraction of aluminum from AOAD spherical granules in the form of various salts, followed by precipitation of aluminum hydroxide, extrusion molding and its conversion into highly dispersed γ -Al₂O₃.

To optimize the technology, two samples AHO-Na-S-1 and AHO-N-1 were selected as the closest in phase composition, texture and strength characteristics as precursors of active aluminium oxide. Various factors have been studied.

From the analysis of the literature it follows that often attempts to form a developed porous structure of aluminum oxide based on a precursor — aluminum hydroxide with recommended morphology and a developed specific surface and microporous texture — lead to a deterioration of the physical-mechanical characteristics and a decrease in the specific surface of the finished alumina adsorbent. In turn, changes in the conditions for the synthesis of aluminum hydroxide and treatments aimed at improving its physical-mechanical characteristics (increase in coefficient and strength, bulk density, specific surface, pore volume) lead to catastrophic changes in morphology and porous structure, which makes such an adsorbent less active and unstable during operation. In the preparation of adsorbents from various precursors, as a rule, it is necessary to specially select technological equipment for the corresponding modifications of aluminum hydroxide. In particular, when aluminum trihydroxides are used as a source material, rapid heating in a gas pipe for 5-30 minutes or heat treatment with a liquid metal coolant for 1-10 minutes [1] is preferred, according to [2], thermochemical activation is carried out at a temperature of 400- 800 ° C for a few seconds followed by rapid cooling of the material. For the implementation of thermochemical

activation of the Institute of Catalysis, SB RAS named after G.K.Boreskova developed a centrifugal flash reactor of the drum type (CEFLAR™) [3].

Considering these factors, we have found a compromise type for the preparation of an adsorbent that is potentially resistant to the effect of trickle moisture and has good sorption characteristics due to the formation of a bidisperse porous structure by mixing in a certain proportion aluminum hydroxides with different morphology.

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MATHEMATICAL MODELING OF KINETICS OF GASOLINE CATALYTIC REFORMING

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The process of catalytic reforming of gasoline is one of the main processes for oil refineries in Russia. The purpose is to increase the octane number (OC) of gasoline, by completely converting naphthenic and partial - paraffinic to aromatic hydrocarbons with high octane numbers, as well as the production of individual aromatic hydrocarbons, raw materials for petrochemicals. From environmental requirements for commercial gasolines, the content of aromatic hydrocarbons and benzene separately is limited and should not exceed 35 and 1% vol. Therefore, there is a restriction on the introduction of reformat (reforming product) in the composition of commercial gasoline. A potential area for finding a solution to the problem is the reactor unit for catalytic reforming of gasoline, namely, the development of a detailed kinetic model of the process that describes the basic laws of chemical transformations. When considering the kinetic component of the process, difficulties arise with its description. This is primarily due to the large number of raw material components, which may exceed 1000 individual hydrocarbons. They resort to the grouping of components according to their hydrocarbon class and the number of carbon atoms in the structure of the molecule [1]. When developing a kinetic model of the process of catalytic reforming of gasoline, the use of adiabatic reactors with an endothermic effect is taken into account. The temperature difference can reach up to 80°C in the first reactor. Such a decrease in temperature strongly affects the rates of chemical reactions. An adequate description of the temperature dependence of the rates of the chemical reaction is necessary. The molar flow rate of the reaction mixture is formed from the molar flow rates of the components. It is necessary to take into account changes in the number of moles of the reaction mixture [2,3]. Mathematical model of the kinetics of gasoline catalytic reforming has the form:

$$\frac{dy_i}{d\tau} = \sum_{j=1}^J v_{ij} w_j, i = 1, \dots, I; y_i(0) = y_i^0;$$

$$\frac{dT}{d\tau} = - \frac{\sum_{i=1}^n \frac{dy_i}{d\tau} \cdot \Delta H_i(T)}{\sum_{i=1}^n y_i \cdot C_{pi}(T)}; \quad T(0) = T^0;$$

$$\frac{dQ}{d\tau} = \sum_{i=1}^I \frac{dy_i}{d\tau}; \quad Q(0) = Q^0;$$

$$w_j = k_j \cdot \prod_{i=1}^I \left(\frac{y_i}{Q}\right)^{\alpha_{ij}} - k_{-j} \cdot \prod_{i=1}^I \left(\frac{y_i}{Q}\right)^{\beta_{ij}};$$

$$\Delta H_i(T) = \Delta H_{298} + \int_{298}^T C_{pi}(T) dT;$$

$$C_{pi}(T) = a_i + b_i T + c_i T^2 + d_i T^3 + e_i T^4;$$

τ – contact time, kg catalyst; v_{ij} – matrix stoichiometric coefficients; J – number of stages; y_i – concentration of substances, mol/L; I – number of substances; w_j – rate j-th stage, 1/min; k_j, k_{-j} – constant velocity stage (reduced), 1 / min; T – temperature, K; α_j^i – negative elements v_{ij} ; β_j^i – positive elements v_{ij} ; k_j^0, k_{-j}^0 – preexponential factors, 1/min; H_i - enthalpy, j/mol; C_{pi} - heat capacity, J/(mol*K); Q - changing the number of moles in the reaction mixture (mol / min).

In the developed kinetic model, the individual components are combined into 38 groups, among which the following classes are present: normal paraffins (nP_i), iso paraffins (iP_i), five-membered naphthenes (ACP_i), six-membered naphthenes (ACH_i) and aromatic hydrocarbons (A_i), where i – the number of carbon atoms in the structure of the molecule. Based on the available industrial compositions of raw materials and products obtained by gas chromatography, adjusted flow rates, and according to the accepted grouping principle, group compositions of raw materials and products at the input and output of the reactor cascade were calculated. The thermodynamic parameters of the group components were calculated by considering the possible limits of change and determining the degree of influence of the concentration profile parameters of the components through a detailed kinetic model. An indicator of the adequacy proposed model, as well as the calculated parameters in the absence of intermediate values of the concentrations of the components of the mixture, is that the composition of the product at the outlet of the last reactor and the temperature differences in all reactors in the cascade are close to industrial data. It is justified by the direct dependence of temperature on the composition of the reaction mixture.

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MULTI-CRITERIAL OPTIMIZATION OF A HETEROGENEOUS CATALYTIC REACTION

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When developing kinetic models, the use of kinetic equations within the framework of the law of mass action is possible for homogeneous reactions [1]. In the study of heterogeneous reactions, it is necessary to use more complex kinetic equations in the form of Langmuir-Hinshelwood dependencies or regularities based on the law of acting surfaces. Such equations are given in the scientific literature in the development of kinetic models, for example, reactions of alkylation of benzene with ethylene or dehydrogenation of ethylbenzene [2].

The reaction of dehydrogenation of ethanol to ethyl acetate is a reaction from the field of "green chemistry", since bioethanol is used as a raw material. The target reaction product, ethyl acetate, is used as a solvent in the manufacture of paints and varnishes. This reaction has a high conversion and selectivity when using copper-zinc-chromium catalysts [2]. The gas phase reaction on the metal complex catalyst is a heterogeneous reaction.

The mathematical description of the kinetics of the heterogeneous reaction on the catalyst surface has the form (1)

$$\frac{dy_i}{d\tau} = \sum_{j=1}^J v_{ij} w_j, i = 1, \dots, I; \quad w_j = k_j \cdot \prod_{i=1}^I (y_i)^{|\alpha_{ij}|} \prod_{i=1}^I (\theta_i)^{|\alpha_{ij}|} - k_{-j} \cdot \prod_{i=1}^I (y_i)^{\beta_{ij}} \prod_{i=1}^I (\theta_i)^{\beta_{ij}}; \quad (1)$$

$$\theta^* = 1 - \sum_{i=1}^I \theta_i; \quad \theta_i = \frac{b_i * y_i}{1 + \sum_{i=1}^I b_i * y_i}$$

τ – contact time, kg catalyst; v_{ij} – matrix stoichiometric coefficients; J – number of stages; y_i – concentration of substances, mol/L; I – number of substances; w_j – rate j-th stage, 1/min; k_j, k_{-j} – constant velocity stage (reduced), 1 / min; α_{ij} – negative elements v_{ij} ; β_{ij} – positive elements v_{ij} ; θ_i – fraction of the catalyst surface occupied by the i-th component; θ^* – free fraction of the surface of the catalyst at any time; b_i – adsorption coefficient of the i-th substance.

Based on the developed kinetic model of a complex catalytic reaction, optimization of the reaction conditions is possible [3].

To optimize the conditions for the chemical reaction of the dehydrogenation of ethanol to ethyl acetate, the following criteria can be used.

1) The yield of the target product, depending on temperature and pressure:

$$R_1(T, P) = y_{prod}(T, P) \rightarrow \max. \quad (2)$$

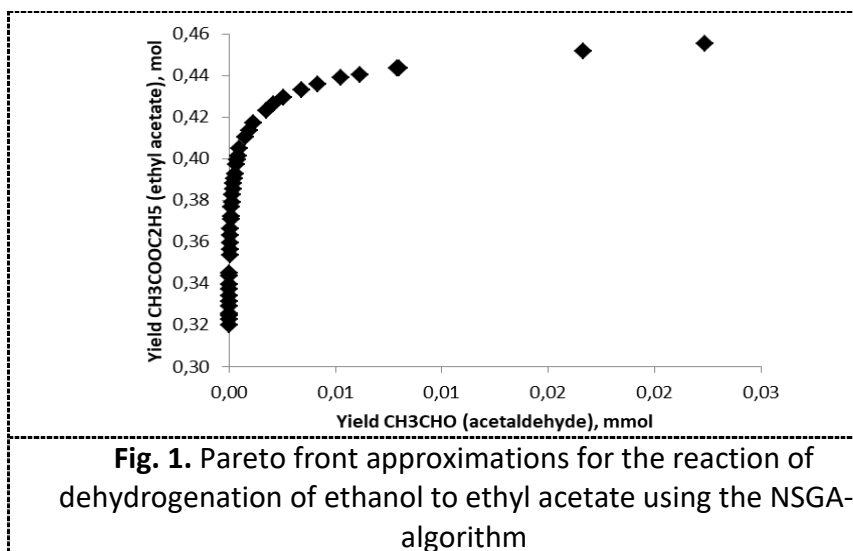
The target product in this reaction is ethyl acetate.

2) The output of the by-product, depending on temperature and pressure:

$$R_2(T, P) = y_{by-prod}(T, P) \rightarrow \min. \quad (3)$$

A side product in this reaction is acetaldehyde.

The solution of the multicriteria optimization problem for the heterogeneous catalytic reaction of ethanol dehydrogenation to ethyl acetate was carried out for optimization criteria: yield of the target product and yield of the by-product. The results of computational experiments are presented in Fig. 1.



The obtained approximations of the front and Pareto sets for the dehydrogenation of ethanol into ethyl acetate allow the user to choose the reaction conditions based on a comparison of the approximations of the Pareto sets for the corresponding objective functions (2), (3) (Fig. 1). In the case when it is necessary to achieve the maximum yield of the target product (the target product is very valuable) or the minimum by-product, you can use the corresponding values of the approximation of the set and Pareto front [3].

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PUT INTO INDUSTRIAL PRODUCTION DIFFICULTIES OF NOVEL EFFECTIVE HYDRODESULFURIZATION-CATALYSTS IN RUSSIAN FEDERATION

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Currently the extensive researches were executed in order to optimize supports properties, active phase chemical and weight composition and main technological parameters of initial components conversion into active six-sided MoS₂ groups, which are decorated by CoS₂ molecules, involving sulfurization stages of catalyst oxide forms. Despite the identical principle properties of modern domestic and import catalysts, the operational efficiency of the latter one is much higher, therefore in Russian Federation the Hydrodesulphurization (HDS) processes organization at refinery plants is carried out with foreign catalysts (approximately 80%). Thus the possible reason of the described fact due to microstructure difference of Al₂O₃-supports derived from different genesis hydrate alumina initial materials, and import substitution difficulties using available in RF hydrate alumina materials base, are extensively discussed.

Due to the complex and time-consuming technology for obtaining modern catalysts and supports, our country has a problem with a large share of catalysts imports that are used at refineries, specifically the share of domestic production is almost two times lower than imports.

For effective the catalytic process flow, it is desirable to develop the number of active centers, dispersion of active phases, and transport access of organic molecules to them. The implementation of the last two conditions is achieved by using a support that allows reducing the content of active components to an optimal minimum due to the thin-layer distribution of Mo (W) - Ni(Co) metals and the necessary porous structure formation that would completely eliminate or minimize diffusion inhibition during reagents transferring to the active centers of the catalyst.

The complexity of choosing aluminum hydroxide as a raw material for multi-tonnage production of the support, in addition to the demand to obtain the specified high structural characteristics, depends on its binding properties and formability. To increase the geometric contact surface of liquid hydrocarbons with the catalyst surface, different forms of single granules were produced as follows: spheres, cylinders, rings, extrudates of complex shape with low bulk density.

Nowadays, in accordance with the import substitution program, the new generation of domestic competitive HDS catalysts production demanding is being raised in the oil industry. The terms of development are the domestic industrial hydroxide-aluminum raw materials use for the catalyst support base production.

On the Department of Chemical Technology and Processing of Utilities of the St. Petersburg Mining University, an optimal formulation of the support was developed, with a complicated profile form extrudates (three-or four-lobe, diameter equals 1.59 mm). In this case, there is an effect of catalyst the geometric surface area increasing the with a minimum strength properties loss.

However, on this step it is desirable to carry out more in-depth research involving all technological methods of transforming these types of aluminum hydroxide into anhydrous porous systems and determine their potential competitiveness and the ability to act as supports of new HDS catalysts with improved textural and acid-base properties.

This work was complete as a part of the state assignments “Development of the scientific foundations of innovative technologies for the processing of heavy hydrocarbon feedstocks into environmentally friendly motor fuels and new carbon materials with controlled macro- and microstructural organization of the mesophase”. Studies were conducted with the involvement of the laboratory base of the Center for collective use of Saint-Petersburg Mining University.



CONTENT

VIRTUAL PARTICIPATIONS (abstract publication)

THE USE OF CHROMATOGRAPHY-MASS SPECTROMETRY IN THE STUDY OF THE HYDROCARBON COMPOSITION OF DIESEL FUELS

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Diesel fuel compositions are complex chemical systems consisting of hydrocarbons of different homology groups. Since the chemical composition of diesel fuels is complex, there may be intermolecular interactions due to different polarities of hydrocarbons of various nature and additives, which, in turn, influence properties and performance characteristics. [1]. The aim of this work was to identify the hydrocarbon composition of diesel fuels using the chromatography-mass spectrometric method of analysis.

Using the chromatography-mass spectrometric method of analysis the group hydrocarbon compositions of diesel fractions have been determined. The effects of hydrocarbons on the physicochemical and operational properties of the fractions were analyzed and compared with the requirements of the standard for diesel fuels [2]. The hydrocarbon composition of diesel fractions was determined by chromatography-mass spectrometry using Agilent 7890B (GC) – Agilent Q-TOF 7200 (MS) instrument and DB-5MS (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm). Analysis conditions: temperature of the evaporator: 300 °C; temperature program: initial temperature: 50° C, heating: 5 °C/min to 150 °C, then 3 °C/min to 310 °C, and holding at 310 °C for 20 min. The velocity of the carrier gas (helium) is 0.9 ml/min. The volume of the added sample is 0.5 μl (Helium is used as a solvent).

In order to identify the components, the authors used the NIST 14 Mass Spectral Library and studied in detail the mass spectrum of fragment and molecular ions using reference books on mass spectrometry, previously analyzed by a laboratory of rock extracts and oils, as well as standards. Concentrations of the components were determined using the appropriate commercially available standards (C10-C40 alkane series, tetracosane-d50, deuterated naphthalene, n-hexyl benzene, phenanthrene, benzpyrene).

The molecular-mass distribution of normal paraffin hydrocarbons (Fig. 1) was considered in detail, as well as their relationship with the low-temperature properties of the fractions.

VP-1

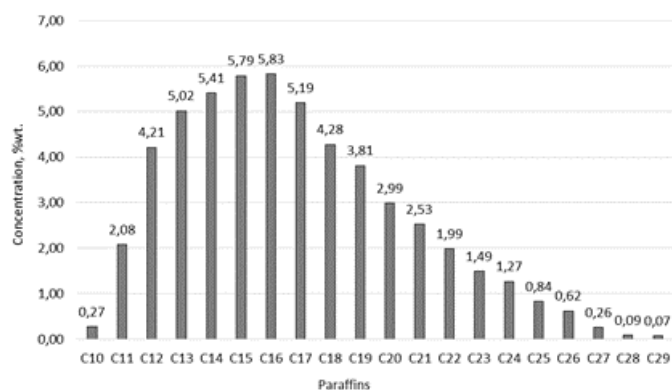


Fig. 1. Molecular-weight distribution of the n-Paraffins in the straight-run diesel fraction (C9, C10 etc. – the number of carbon atoms in the chain of n-alkane)
The aromatic compounds were analyzed in the two-dimensional chromatography method (Fig. 2).

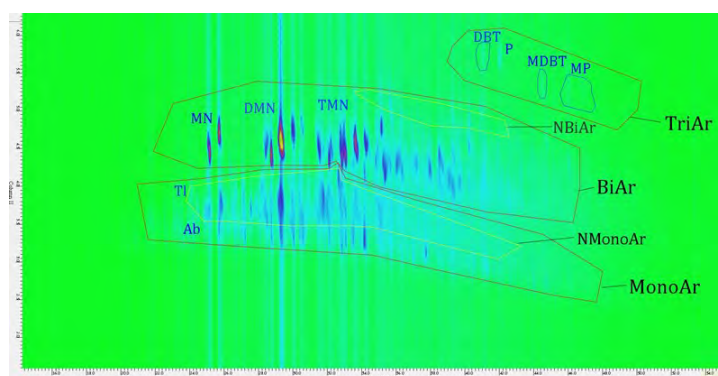


Fig. 3. Analysis of the aromatic compounds distribution in the straight-run diesel fraction (2D chromatogram) (MonoAr – monoaromatic hydrocarbons, NMonoAr – naphtho-monoaromatic hydrocarbons, BiAr – biaromatic hydrocarbons, NBiAr – biaromatic hydrocarbons, TriAr – triaromatic hydrocarbons, DBT – dibenzothiophenes, MDBT – methyl-dibenzothiophenes, P – phenanthrene, MP – methylphenanthrenes, MN – methylnaphthalenes, DMN – dimethylnaphthalenes, TMN – trimethylnaphthalenes, TI – alkyltetralin series, Ab – alkylbenzenes).

Based on the chromatographic-mass spectrometric analysis of samples of diesel fractions, the mass content of various hydrocarbons included in their composition was determined and the hydrocarbon composition was determined. The characteristic structures of mono-, bi- and tri-aromatic compounds have been identified. The reproducibility of the results calculated from parallel determinations did not exceed 5%. That allows you to use this method in the study of the hydrocarbon composition of raw materials and products of various oil refining processes.

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HEAVY FEEDSTOCK HYDROPROCESSING FOR MARINE FUELS PRODUCTION

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Depletion of traditional deposits of “light” crudes goes hand in hand with an increase in the production of heavy, highly viscous oils and natural bitumen [1]. Such feeds processing is unprofitable without hydrocracking and so includes some stage of pretreating, usually kind of hydrotreating, allowing to decrease sulfur, nitrogen and metal content before the main hydrocracking stage [2].

Hydrotreating of heavy feeds is an even more important process within the context of the tightening of the International Marine Organization (IMO) requirements for sulfur content in marine fuels (>0.5 %wt and 0.1% wt depend on area) [3].

While hydrotreating of heavy feeds is important and relevant it is as well a task requiring specific approaches: optimized process flowchart, additional equipment, and, most of all, fit-to-purpose catalysts.

Macroporous catalysts seem to be the best fitting to process such feeds as atmospheric bottoms, while their large pores provide access to active sites during catalyst cycle length. The second factor guaranteed the maximal profit is the choice of the correct catalyst. Inert filter material should collect mechanical impurities, but without a fast increase of reactor pressure drop. Hydrodemetallation catalyst should have maximal metal adsorption capacity and moderate hydrotreating activity. Finally, the main catalyst bed should be loaded with a hydrotreating catalyst, optimized for heavy feed processing.

The catalyst pack, containing 5 % vol. of high-porous cellular material, 45 % vol. of macro-mesoporous zeolite-containing NiCoMo hydrodemetallation catalyst and 45 % vol. of NiMoW-catalyst, was suggested for hydroprocessing of atmospheric residue.

Straight-run atmospheric residue, containing 1.058 wt. % of sulfur, 16.3 ppm Ni and 25.7 ppm V, was processed on the laboratory-scale unit at hydrogen pressure 15 MPa, the reaction temperature in the range of 360-420 °C, Liquid hourly space velocity in the range of 0.3-0.5 h⁻¹, and hydrogen/feed ration in range of 1500-2000 NI/l.

Sulfur and metal content in process products shown in Fig.1

VP-2

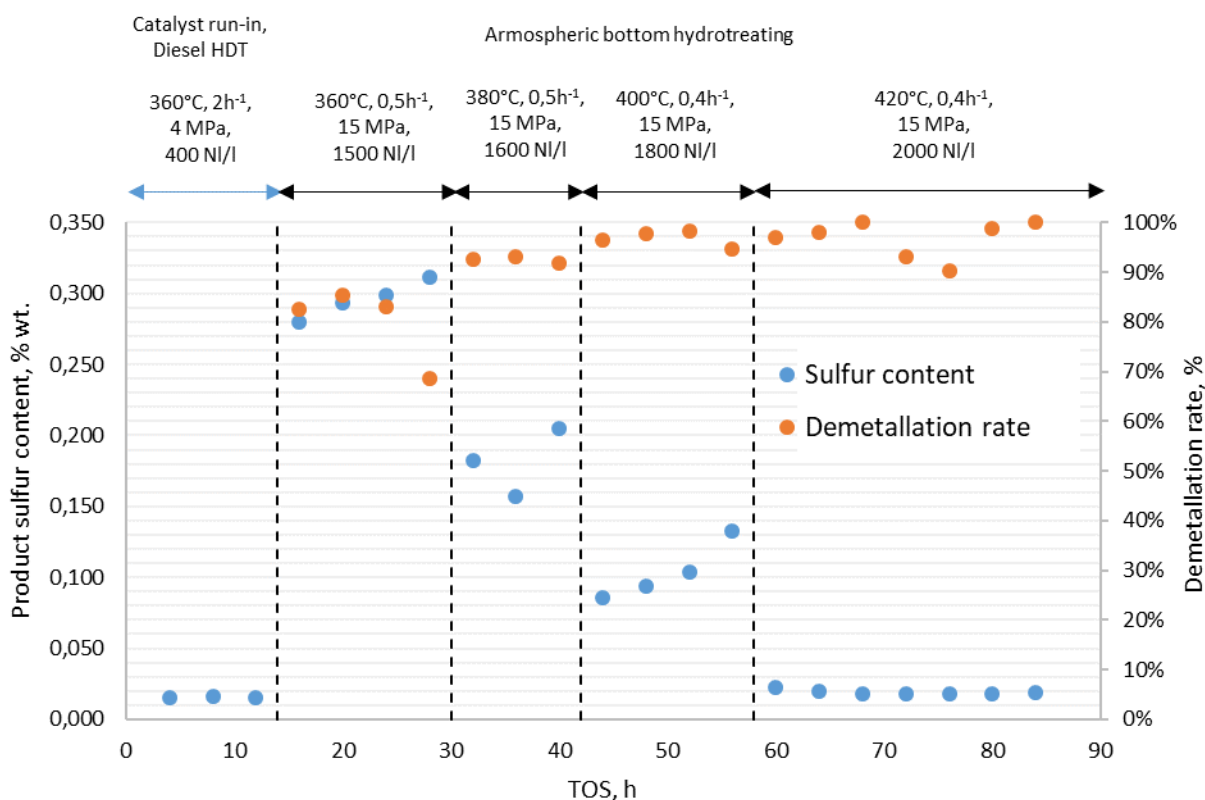


Fig.1 Results of atmospheric residue hydroprocessing over the proposed catalyst pack

As the catalytic experiment had shown, the proposed catalyst pack demonstrated sufficient activity in hydrotreating of atmospheric residue. The obtaining of products with a sulfur content of less than 0.10 and 0.05% wt., which is necessary for the production of modern marine fuels, is possible at temperatures above 400 °C. Lower processing temperatures allows obtaining pretreat feed for hydrocracking units.

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REGENERATION OF LD-145 CATALYST BY SUPERCRITICAL FLUID EXTRACTION**Khazipov M.R., Pastushenko I.L., Galimova A.T., Sagdeev A.A., Kiryukhin V.G., Pletnev A.S.***Nizhnekamsk Institute of Chemical Technology (branch) Federal State Budgetary Educational Establishment of Higher Education, KNITU, Nizhnekamsk, Russia**E-mail: 2351092@mail.ru*

Modern innovative scientific and technological areas are associated with technologies that use media without phase separation in the absence of a capillary effect, which leads to an increase in the ability to penetrate into structures of a porous nature. This creates obvious prospects in solving the problems of the regeneration of heterogeneous catalysts. The innovativeness of the issue is determined by the solubility of deactivating compounds. The disadvantages of the currently used gas-air and steam-air methods for the regeneration of catalysts, especially in terms of high temperature conditions, on the one hand lead to high resource and energy costs, and on the other, to changes in the composition and structure of the catalysts. The search for new methods of catalyst regeneration is caused by an increase in technical, economic and environmental requirements, as well as requirements for the quality of petrochemical products.

This work is devoted to assessing the appropriateness of using the method of supercritical fluid extraction (SCFE) in solving the problem of regeneration of the selective hydrogenation catalyst LD-145 used at PJSC "Nizhnekamskneftekhim" in the process of producing benzene from pyrolysis gasoline.

Chromatographic analysis showed that the classes of substances such as alkanes, naphthenes and alkylbenzenes that contribute to the formation of coke are present in the composition of the LD-145 catalyst deactivating compounds.

For a qualitative assessment of the catalyst regeneration process, samples were selected reflecting the greatest representativeness in the matter of changing the mass of the catalyst [1]: sample No. 1 - deactivated catalyst (spent) LD-145; sample No. 2 - the LD-145 catalyst regenerated by pure SK-CO₂ at T = 473 K and P = 20 MPa; sample No. 3 - catalyst LD-145, regenerated SK-CO₂ + hexane 2% at T = 473 K and P = 20 MPa; sample No. 4 - catalyst LD-145, regenerated SK-CO₂ + ethanol 2% at T = 473 K and P = 20 MPa; sample No. 5 - catalyst LD-145, fresh in oxide form. Texture characteristics were determined for the studied catalyst samples. Samples No. 2, 3, 4, which underwent regeneration by the SCFE method, restored the specific area almost to the initial level of oxide sample No. 5, which indirectly confirms the removal of coke from the catalyst surface.

VP-3

The activity of the catalyst samples was evaluated by accelerating the reactions of hydrogenation of naphthalene (Naft) and hydrodesulfurization of dibenzothiophene (DBT) [2], the results are presented in table 1. The highest hydrogenating ability of naphthalene was achieved for the sample regenerated by SC-CO₂ modified with hexane (sample No. 3).

Thus, it was found that regeneration by the SCFE method allows one to increase the catalytic activity of the LD-145 catalyst, which was to be utilized after six industrial regeneration cycles. It has been revealed that both hydrogenating and hydrodesulfurizing properties of the catalyst are subject to reduction.

Table 1. Catalytic Test Results

Sample	ISPS (h-1)	Molar flow (mol / h)		Conversion%		$k_{HDS} \times 10^4$ (molg ⁻¹ h ⁻¹)	$k_{HYD} \times 10^4$ (molg ⁻¹ h ⁻¹)
		DBT	Naft.	DBT	Naft.		
1	30	0.0004	0.0022	30	12	4.9	9.7
	50	0.0007	0.0037	16	7		
2	30	0.0004	0.0018	57	16	10.6	10,2
	50	0.0006	0.0030	42	9		
3	30	0.0004	0.0018	44	21	6.8	13.4
	50	0.0006	0.0030	28	12		
4	30	0.0004	0.0018	57	18	11.1	10.7
5	30	0.0006	0.0030	76	32	17.1	23.5

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HYDROTHERMAL SYNTHESIS OF FLUORINATED TITANIA FOR PHOTOCATALYTIC APPLICATIONS

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Nanocrystalline titanium dioxide and titania-based materials are widely used as photocatalysts for the remediation of environmental pollutants, including water treatment and air purification, as well as components of photoelectrochemical devices that convert the sun's energy [1]. Solar energy conversion efficiency depends on several factors, among which the charge carrier lifetime, the particle size and the specific surface area of the photocatalyst are the key factors [2]. The specific adsorption of various ions on the TiO₂ surface, as well as TiO₂ doping with various elements, also plays an important role in modifying its photocatalytic activity [3].

Several recent studies have shown that the increase of the photocatalytic activity of titanium dioxide is possible due to crystal engineering [4]. In particular, the formation of the crystalline anatase of a predetermined habitus of particles occurs during the synthesis of titanium dioxide in a fluoride-containing media [5]. Under such conditions, a single phase anatase is formed, wherein the fluoride ions are preferably adsorbed on the {0 0 1} facets, thereby inhibiting their growth and promoting growth along (0 1 0) and (1 0 0) directions, forming sheet-like microcrystals [6]. These experimental data are in good agreement with the surface energy estimations of anatase facets {0 0 1} and {1 0 1}, demonstrating that the adsorption of fluoride ions on {0 0 1} surfaces is energetically more favorable than the adsorption on {1 0 1} surfaces [5]. Actually, fluorination has multiple effects on the surface chemistry of TiO₂, and the other possible reasons for enhanced photocatalytic activity of fluorinated titania are connected with the increase in specific surface area, adsorption activity and changes in the mechanisms of photodegradation [7]. The use of titanyl sulfate, which is stable and very cheap, as a precursor, does not produce titanium dioxide with a high photocatalytic activity, due to strong adsorption of sulfate anions on the surface of titanium dioxide, which adversely affects the activity of the photocatalyst [8].

Our goals include development new facile method for producing titanium dioxide with high photocatalytic activity, based on hydrothermal treatment of suspensions of hydrated titanium dioxide amorphous gels in a solution of ammonium fluoride. The study of the crystal violet dye photodegradation showed that all the titanium dioxide samples have significant photocatalytic activity. In some cases, the photodecomposition reaction rate constant in the presence of titanium dioxide powders obtained by us greatly exceeded a similar value for the industrial photocatalyst

Evonik Aeroxide® TiO₂ P25. Was investigated the dependence of crystal violet concentration on the duration of irradiation of the solution in the presence of three different samples of nanocrystalline titanium dioxide: industrial photocatalyst, a sample synthesized at 200 °C in 1 M NH₄F solution, and a sample synthesized at 200 °C in distilled water. Thus we summarize that the method of synthesis we have proposed, consisting of hydrothermal treatment of the hydrated titanium dioxide in the presence of ammonium fluoride results in the formation of titanium dioxide, characterized by a high photocatalytic activity, comparable to commercial photocatalysts. The nanocrystalline titania was analyzed by X-ray powder diffraction, N₂ adsorption isotherms, SEM.

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HYDROTREATMENT OF FURFURAL AS BIO-OIL MODEL COMPOUND OVER Ru-CATALYSTS SUPPORTED ON MESOPOROUS MATERIALS

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One of the most promising sources for biofuel production is the lignocellulosic biomass, namely, wood wastes of nonfood crops industry. Bio-oil obtained from biomass by fast pyrolysis technology can not be directly used as transportation fuel because of complicate composition and high oxygen and water content. Bio-oil mainly contains water and hundreds of oxygen-containing, organic compounds formed during thermal decomposition of biomass biopolymers – cellulose (30–40 wt%), hemicelluloses (20–30 wt%) and lignin (20–25 wt%) [1]. The main compounds produced by fast pyrolysis of cellulose and hemicelluloses are levoglucosan, hydroxyacetaldehyde, hydroxyacetone, furfural, 5-hydroxymethylfurfural, acetic acid, glycol aldehyde, and anhydrosugars. The distribution of compounds directly depends on the type of a biomass and on the conditions of fast pyrolysis [2]. A promising technology to improve the quality of bio-oil is catalytic hydrotreatment (hydrodeoxygenation, HDO), during which oxygen is removed from bio-oil composition in the form of water. Furfural as one of the main products formed after fast pyrolysis of cellulose/hemicellulose part of biomass is frequently used as a model compound in studies of bio-oil hydrodeoxygenation processes.

The HDO of furfural was investigated over Ru-containing catalysts based on mesoporous zirconium, aluminium and titanium silicates using water as the solvent. Water is used as the second component of model system, since it is initially contained in a significant amount in bio-oil (up to 40 wt%) and is also formed during hydrotreating reactions. Mesoporous aluminosilicate (Al-HMS), zirconium silicate (m-ZrO₂-SiO₂) and titanium silicate (Ti-MCM-41) were synthesized. Then the supported Ru-catalysts were prepared by an impregnation method from RuCl₃-containing solution, characterized with NH₃-TPD, TEM, XPS, N₂ adsorption–desorption methods (Table) and tested in the furfural HDO reaction in an autoclave.

The main products formed in the HDO of furfural were tetrahydrofurfuryl alcohol (THFA), cyclopentanol, methyltetrahydrofuran/tetrahydrofuran (MeTHF+THF), mono- and diatomic C₄–C₅ alcohols of varied structure (1,2-pentanediol, 1,5-pentanediol, 2-pentanol, n-pentanol, and n-butanol), and condensation products contained several furan/tetrahydrofuran rings (fig.) [3].

Table. Physicochemical characteristics of catalysts

Catalyst	S_{BET} , (m^2/g)	Total number of acid sites, ($\mu\text{mol}/\text{g NH}_3$)	$d_n(\text{Ru})$, nm
Ru/Al-HMS	599	326	1.9
Ru/m-ZrO ₂ -SiO ₂	614	424	3.5
Ru/Ti-MCM-41	828	409	2.1

$d_n(\text{Ru})$ – number average diameter carried out from TEM images

Si/Al ratio in Al-HMS=10, Si/Zr ratio in m-ZrO₂-SiO₂=1.3, Si/Ti ratio in Ti-MCM-41=10

The activity of Ru-containing catalysts in hydrotreatment of furfural in aqueous solution decreases in the following order: Ru/Al-HMS ~ Ru/Ti-MCM-41 > Ru/m-ZrO₂-SiO₂, and the distribution of reaction products depends on the nature of support material. The main product of the HDO of furfural over Ru/Al-HMS catalyst was cyclopentanol (47%), over Ru/Ti-MCM-41 – pentanediols (45%) with quantitative conversion of the substrate in both cases. The main product of the HDO of furfural over Ru/m-ZrO₂-SiO₂ catalyst was tetrahydrofurfuryl alcohol with 84% selectivity and 86% conversion.

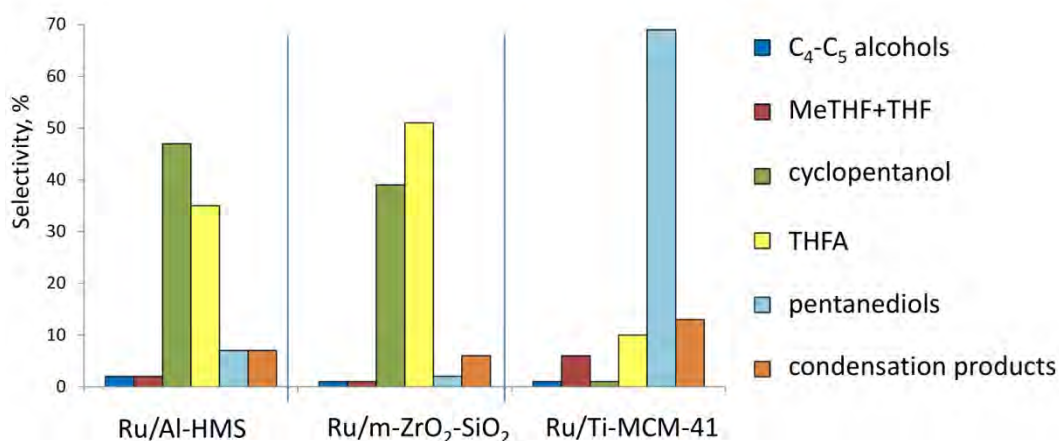


Fig. Liquid phase hydrotreatment of furfural. Conditions: 0.1 g of catalyst (2 wt%Ru), 0.25 g of furfural, 1 g of H₂O, $p(\text{H}_2)=5\text{MPa}$, 200°C, 2 h

The synthesized Ru-containing catalysts based on mesoporous zirconium, aluminium and titanium silicates are highly active in the hydrotreatment of bio-oil components, which are formed during fast pyrolysis of cellulosic/hemicellulosic fragments of biomass, in the presence of a large amount of water under fairly mild conditions – 200°C and hydrogen pressure of 5 MPa.

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CONTENT

	OPENING	
	PLENARY LECTURES	5
	PL-1 Schwieger W. HIERARCHICAL ZEOLITES IN PROCESSING OF HYDROCARBONS	7
	PL-2 Rana M.S. RECENT ADVANCES IN RESIDUE HYDROPROCESSING	8
	PL-3 Lemonidou A.A. INTENSIFICATION OF STEAM REFORMING FOR HYDROGEN PRODUCTION	10
	KEYNOTE LECTURES	13
	KL-1 Bezergianni S. CATALYTIC HYDROPROCESSING: AN EFFECTIVE MODE FOR DIRECT FUELS DECARBONIZATION	15
	KL-2 Thybaut J. SIMULATING COMPLEX MIXTURES CONVERSION FROM FIRST PRINCIPLES	16
	KL-3 <u>Danilevich V., Nadeina K., Stolyarova E., Klimov O., Noskov A.</u> ALUMINUM OXIDES AS SUPPORTS FOR HYDROTREATING CATALYSTS	17
	ORAL PRESENTATIONS	19
	OP-1 Nadeina K.A., Danilevich V.V., Kazakov M.O., Romanova T.S., Gabrienko A.A., Pakharukova V.A., Danilova I.G., Nikolaeva O.A., Gerasimov E.Yu., Kondrashev D.O., Kleimenov A.V., Klimov O.V., Noskov A.S. INFLUENCE OF Si DOPING TO HYDROTREATING CATALYSTS OF FCC FEED PRETREATMENT	21

	OP-2 Glišić S.B. , Prokić-Vidojević D., Orlović A.M. INFLUENCE OF THE TRANSITION METAL AND CATALYST DRYING PROCEDURE ON THE CATALYTIC PERFORMANCE OF Re/Pd, Co/Mo AND COMMERCIAL CATALYSTS SUPPORTED ON HEXAGONAL MESOPOROUS SILICAS DOPED WITH TI-IONS DURING THE HDS OF DIBENZOTHIOPHENE AND 4,6-DIMETHYLDIBENZOTHIOPHENE	23
	OP-3 Kazakov M.O. , Revyakin M.E., Nadeina K.A., Vatutina Yu.V., Kondrashev D.O., Golovachev V.A., Kleimenov A.V., Vedernikov O.S., Klimov O.V., Noskov A.S. TUNING METAL-ACID PROPERTIES OF ZEOLITE HYDROCRACKING CATALYSTS BY SUPPORTING NiMo WITH IMPREGNATION SOLUTIONS OF DIFFERENT COMPOSITION	25
	OP-4 Shkurenok V.A. , Yablokova S.S., Smolikov M.D., Kir'yanov D.I., Belyi A.S., Kondrashev D.O., Kleimenov A.V. NEW DIRECTION IN THE HYDROPROCESSING OF GASOLINE FRACTIONS: INTEGRATION OF C₅-C₆ AND C₇-PARAFFIN HYDROCARBONS ISOMERIZATION PROCESSES.....	27
	OP-5 Yashnik S.A. , Ismailov E.G., Ismagilov Z.R. EFFECT OF BENTONITE ADDITION ON PROPERTIES OF NANOSTRUCTURED PtPd-ZEOLITE HYDRODESULFURIZATION CATALYST	29
	OP-6 Devers E. , Lesage C., Legens C., Briois V. NEW METHODOLOGY COUPLING RAMAN AND XAS FOR THE SPECIATION OF ADDITIVATED Mo-BASED HDS CATALYSTS AND CHARACTERIZATION BY QUICK-XAS OPERANDO OF THEIR LIQUID SULFIDATION	31
	OP-7 Dagonikou V. , Bezergianni S., Karonis D. AN ALTERNATIVE APPROACH FOR LCO UPGRADING	33
	OP-8 Pacheco-Jiménez H.O. , Santes V., Sotelo-Boyás R., Santolalla-Vargas C.E., Gonzalez-Alatrisme J.E. HYBRID DIESEL PRODUCTION VIA CATALYTIC CO-HYDROPROCESSING OF BLENDS GASOIL-WASTE COOKING OIL	35
	OP-9 Alvarez-Majmutov A. , Badoga S., Xing T., Chen J. PRODUCING LOW CARBON FUELS BY CO-HYDROCRACKING HTL BIOCRUDE WITH VACUUM GAS OIL	36
	OP-10 Quintana-Gamboa S., Richards-Figueroa Z., Torres-Otañez G., Fuentes-Moyado S., Díaz de León J.N. NiMoS NANOCUBES FOR HYDRODESULFURIZATION OF LIGHT HYDROCARBONS.....	38

OP-11

Saiko A.V., Potapenko O.V., Nadeina K.A., Porotikova O.V., Sorokina T.P.,
Doronin V.P., Kazakov M.O., Klimov O.V., Kondrashev D.O.³, Kleimenov A.V.³, Noskov A.S.

INFLUENCE OF NITROGEN CONTAINING COMPOUNDS OF DIFFERENT NATURE IN HYDROTREATED VGO ON PRODUCT COMPOSITION OF FCC PROCESS FOR LIGHT OLEFINS PRODUCTION..... 40

OP-12

Xuanjun Ai, Xiujuan Chi, Donge Wang, Zhjian Tian, Qi Shi, Jihui Wang

DETERMINATION OF VARIOUS CHEMICAL STRUCTURES IN BASE OIL USING MULTIDIMENSIONAL NMR SPECTROSCOPY 42

OP-13

Vatutina Yu.V., Kazakov M.O., Nadeina K.A., Budukva S.V.,
Gerasimov E.Yu., Klimov O.V., Noskov A.S.

IS IT POSSIBLE TO REACTIVATE HYDROTREATING CATALYST POISONED BY Si? 44

OP-14

Danilova I.G., Dik P.P., Gabrienko A.A., Sorokina T.P., Paukshtis E.A., Kazakov M.O.,
Doronin V.P., Kondrashev D.O., Golovachev V.A., Kleimenov A.V., Vedernikov O.S.,
Klimov O.V., Noskov A.S.

THE INFLUENCE OF FRAMEWORK AND EXTRAFramework ALUMINIUM SPECIES IN FAUJASITE ZEOLITES ON VGO HYDROCRACKING OVER NiMo/USY CATALYSTS 46

OP-15

Tregubenko V.Yu., Vinichenko N.V., Vagapova M.N., Veretelnikov K.V., Belyi A.S.

NEW NAPHTHA-REFORMING Pt/Al₂O₃ CATALYSTS WITH Mo OR In 48

OP-16

Shamanaev I., Suvorova A., Gerasimov E., Pakharukova V., Bukhtiyarova G.

COMPARATIVE STUDY OF Ni-PHOSPHIDE CATALYSTS SUPPORTED ON GRANULATED AL₂O₃ IN HYDROTREATING OF STRAIGHT RUN GAS OIL 50

OP-17

Belopukhov E.A., Smolikov M.D., Kir'yanov D.I., Shkurenok V.A.,
Belyi A.S., Kondrashev D.O., Kleimenov A.V.

REFORMING CATALYST FOR PRODUCING OF A LOW AROMATICS GASOLINE COMPONENT 52

OP-18

Golubev I.S., Dik P.P., Kazakov M.O., Pereyma V.Yu., Klimov O.V., Kondrashev D.O.,
Golovachev V.A., Vedernikov O.S., Kleimenov A.V., Noskov A.S.

NiW/Y-ASA-Al₂O₃ CATALYSTS FOR SECOND STAGE HYDROCRACKING: INFLUENCE OF Si/Al RATIO IN ZEOLITE 54

OP-19

Belinskaya N.S., Ivanchina E.D., Ivashkina E.N., Vymyatnin E.K., Mauzhigunova E.N.

DEVELOPMENT OF THE APPROACH TO MODELLING OF THE DESTRUCTIVE CATALYTIC HYDROPROCESSES OF ATMOSPHERIC AND VACUUM DISTILLATES CONVERSION 56

OP-20

Karakoulia S.A., Heracleous E., Lappas A.A.

Ni AND Pt CATALYSTS SUPPORTED ON SILICOALUMINOPHOSPHATES FOR n-HEXADECANE HYDROISOMERIZATION 58



OP-21

Kokliukhin A., Nikulshina M., Mozhaev A., Lancelot C., Blanchard P.,
Marinova M., Mentré O., Lamonier C., Nikulshin P.

**EFFECT OF Mo/W RATIO ON THE CATALYTIC PROPERTIES OF ALUMINA SUPPORTED
HYDROTREATING CATALYSTS PREPARED FROM MIXED $\text{SiMo}_n\text{W}_{12-n}$ KEGGIN TYPE
HETEROPOLYACIDS 60**

**OP-22**

Vela F.J., Trueba D., Palos R., Arandes J.M., Gutiérrez A.

**FUELS OBTAINED FROM HYDROCRACKING OF DIFFERENTS BLENDS OF VGO AND
POLYOLEFINIC WASTES 62**

**OP-23**

Pernalete C.G., Ibáñez J., Van Geem K.M., Thybaut J.W.

FROM BULK PROPERTIES TO SINGLE EVENT MICROKINETICS FOR VGO HYDROCRACKING..... 64

**OP-24**

Stepanova L., Belskaya O., Trenikhin M., Leont'eva N., Gulyaeva T., Likholobov V.

**THE EFFECT OF THE SUPPORT PRECURSOR ON THE PROPERTIES OF BIMETALLIC
CATALYSTS Pt-Au/MgAlO_x IN THE PROPANE DEHYDROGENATION 66**

**OP-25**

Margellou A., Rekos K., Fotopoulos A., Triantafyllidis K.

**CATALYTIC HYDROGENOLYSIS OF LIGNIN TOWARDS THE PRODUCTION
OF PHENOLIC BIO-OILS 68**

**OP-26**

Simakova I.L., Warna J., Murzin D.Yu.

**BIODERIVED ANTIKNOCK ADDITIVES: SYNTHESIS OF GAMMA-VALEROLACTONE BY LIQUID-PHASE
LEVULINIC ACID HYDROGENATION OVER VIII GROUP METALS..... 70**

**OP-27**

Zagoruiko A., Mikenin P., Lopatin S.

**DECOMPOSITION OF HYDROGEN SULFIDE INTO ELEMENTS IN THE CYCLIC
CHEMISORPTION-CATALYTIC REGIME 72**

OP-28

Pimerzin Al.A., Glotov A.P., Savinov A.A.

**LINEAR ALKANES HYDROISOMERIZATION OVER COMOS CATALYSTS SUPPORTED
ON MODIFIED ALUMINOSILICATES 74**

**OP-29**

Belskaya O.

**NEW CATALYSTS BASED ON LAYERED DOUBLE HYDROXIDES FOR
THE FURFURAL HYDROGENATION 75**

**OP-30**

Bogomolova T.S., Smirnova M.Yu., Klimov O.V., Noskov A.S.

**CHARACTERIZATION AND HYDROISOMERIZATION PERFORMANCE OF Mg-PROMOTED
Pt/ZSM-23/Al₂O₃ CATALYSTS 77**

	OP-31 Nazarova G. , Ivashkina E., Ivanchina E., Burumbaeva G., Kaliev T., Seitenova G. KINETIC PATTERNS OF VACUUM DISTILLATE CATALYTIC CRACKING ON DIFFERENT CATALYST 79
	OP-32 Vlasova E., Porsin A. , Aleksandrov P., Bukhtiyarova G. CO-PROCESSING OF RAPESEED OIL – STRAIGHT RUN GAS OIL MIXTURE: PECULIARITIES OF ULSD PRODUCTION WITH IMPROVED COLD FLOW PROPERTIES..... 81
	OP-33 Snytnikov P.V. , Rogozhnikov V.N., Badmaev S.D., Potemkin D.I. , Shilov V.A., Ruban N.V., Gorlova A.M., Pechenkin A.A.; Zazhigalov S.V., Belyaev V.D.; Zagoruiko A.N.; Sobyanin V.A. STRUCTURED CATALYSTS FOR HYDROCARBONS AND OXYGENATES MIXTURES CONVERSION TO HYDROGEN-RICH GAS 83
	OP-34 Krivtcova N. , Ivanchina E.D., Kotcova E. MATHEMATICAL MODELING OF THE HYDROTREATING PROCESS USING BI-FUNCTIONAL CATALYSTS 85
	OP-35 Potapenko O.V. , Doronin V.P., Sorokina T.P., Iurtaeva A.S., Plekhova K.S., Lipin P.V., Dmitriev K.I., Porotikova O.V., Kondrashev D.O., Kleimenov A.V. NEW ACHIEVEMENTS OF THE CRACKING CATALYSTS DEVELOPMENT FOR PETROCHEMICAL DIRECTION OF PJSC «GAZPROMNEFT» 87
	OP-36 Naranov E.R. , Sadovnikov A.A., Maximov A.L. A STEPWISE FABRICATION OF MORDENITE FRAMEWORK INVERTED (MFI) NANOSHEETS IN ACCELERATED MODE 89
	OP-37 Romero M.A. , Prieto C. INDUSTRIAL HYDROCRACKING UNITS: NEW R&D CHALLENGES AND OPPORTUNITIES AS A WAY FORWARD TO IMPROVE REFINERY MARGINS..... 91
	OP-38 Glotov A. , Stavitskaya A., Smirnova E., Gushchin P., Vinokurov V., Lvov Y. MESOPOROUS ALUMINOSILICATES BASED ON NATURAL CLAY NANOTUBES FOR HYDROPROCESSING: SYNTHESIS, PROPERTIES, APPLICATION 93
	OP-39 Dimitriadis A. , Bezergianni S., Meletidis G., Kokkalis A., Doufas L. ANIMAL FATS: A PROSPEROUS FEED FOR 2ND GEN BIOFUELS PRODUCTION 95
	OP-40 Ivanchina E., Chuzlov V. , Ivashkina E., Nazarova G., Tyumentsev A. MODELING OF MOTOR GASOLINE COMPONENTS COMPLEX PRODUCTION 97
	OP-41 Stepacheva A.A. , Markova M.E., Gavrilenko A.V., Lugovoy Yu.V., Sulman M.G., Matveeva V.G., Sulman E.M. HIGHLY DISPERSED CATALYSTS FOR OIL HYDROPROCESSING IN SUPERCRITICAL CONDITIONS..... 99



OP-42

Manaenkov O.V., Kislitsa O.V., Ratkevich E.A., **Matveeva V.G.**, Sulman M.G., Sulman E.M.

MAGNETICALLY RECOVERABLE CATALYST BASED ON HYPERCROSSLINKED POLYSTERENE FOR CELLULOSE HYDROCONVERSION INTO GLYCOLS..... 101

OP-43

Malbakhova I.A., Titkov A.I., Matvienko A.A., Popov M.P., Nemudry A.P.

THE DEVELOPMENT OF NICKEL MEMBRANES FOR HYDROGEN PURIFICATION..... 103

POSTER PRESENTATIONS..... 105

PP-1

AlHumaidan F.S., **Rana M.S.**, Bouresli R., Raajasekaran N.

GUARD BED CATALYST: ROLE OF TEXTURAL PROPERTIES AND THEIR CHARACTERIZATION 107

PP-2

Altynov A.A., Bogdanov I.A., Kirgina M.V.

INVESTIGATION OF THE INFLUENCE OF STABLE GAS CONDENSATE ZEOFORMING PROCESS TECHNOLOGICAL PARAMETERS ON THE OBTAINED PRODUCTS CHARACTERISTICS..... 109

PP-3

Baygildin I.G., Vutolkina A.V., Maksimov A.L., Karakhanov E.A.

HYDRODESULFURIZATION OF SULFUR-CONTAINING AROMATIC COMPOUNDS VIA WGSR OVER DISPERSED Ni–Mo SULFIDE CATALYSTS 111

PP-4

Belinskaya N.S., Ivashkina E.N., Afanasyeva D.A., Krivtsova N.I., Vymyatnin E.K., Arkenova S.B., Kaliev T.A.

DEVELOPMENT OF THE FORMALIZED SCHEME OF CHEMICAL CONVERSIONS IN THE PROCESS OF VACUUM GAS OIL HYDROTREATING FOR THE PROCESS MODELLING..... 113

PP-5

Ivanchina E., Ivashkina E., Lutsenko A., Nazarova G., Vymyatnin E., **Belinskaya N.S.**

HYDROCARBONS CONVERSION REGULARITIES OF DIESEL FRACTION WITH ATMOSPHERIC GAS OIL DURING HYDRODEPARAFFINIZATION 115



+01:20

PP-6

Sosnina D.V., Belozertseva N.E., Bogdanov I.A.

INVESTIGATION OF THE SYNTHESIS PARAMETERS INFLUENCE ON THE PRODUCT YIELD AND CHARACTERISTICS OF THE PRODUCED BIODIESEL FUELS..... 117

PP-7

Bogdanov I.A., Martyanova E.I., Altynov A.A.

IMPROVEMENT OF STRAIGHT-RUN DIESEL FUEL LOW-TEMPERATURE PROPERTIES ON THE ZEOLITE CATALYST 119

PP-8

Demikhova N., Artemova M., Glotov A., Tsaplin D., Ivanov E., Vinokurov V.

MICRO-MESOPOROUS Pt-CONTAINING CATALYSTS FOR XYLENES HYDROISOMERIZATION..... 121**PP-9**Dolganov I.M., Dolganova I.O., Solopova A.A., Pasyukova M.A., Bunaev A.A.
Ivanchina E.D., Ivashkina E.N.**INFLUENCE OF FLOW RATE OF LINEAR ALKYL BENZENE IN FILM SULFONATION REACTOR ON CONCENTRATION OF TARGET PRODUCT AND TETRALINES AND SULFONES CONCENTRATION 123****PP-10**

Enikeeva L.V., Faskhutdinov A.G., Arefyev I.A., Enikeev M.R., Gubaydullin I.M.

SIMULATION THE CATALYTIC PROCESS OF ISOMERIZATION REACTION OF PENTANE-HEXANE FRACTION TO MAXIMIZE THE OCTANE NUMBER OF REACTION PRODUCTS..... 125**PP-11**

Enikeeva L.V., Potemkin D.I., Uskov S.I., Snytnikov P.V., Enikeev M.R., Gubaydullin I.M.

GRAVITY SEARCH ALGORITHM FOR DETERMINING THE OPTIMAL KINETIC PARAMETERS OF LOW-TEMPERATURE STEAM CONVERSION OF C₂ + HYDROCARBONS 127**PP-12**

Díaz de León J.N., Huerta-Mata C., Kumar Chowdari R., Infantes-Molina A., Zepeda T., Alonso-Núñez G., Fuentes-Moyado S., Huirache-Acuña R.

TWO STEPS SYNTHESIS OF BULK NiW CATALYSTS FOR 3-METHYL THIOPHENE DESULFURIZATION 129**PP-13**

Glazov N.A., Zagoruiko A.N., Dik P.P.

CONNECTION BETWEEN STRUCTURE ATTRIBUTES AND ANALYTICAL METHODS USED FOR STOCHASTIC RECONSTRUCTION OF VACUUM GASOIL 131**PP-14**

Ziyadullaev O.E., Abdurakhmanova S.S., Samatov S.B., Otamukhamedova G.Q., Tirkasheva S.I., Ikramov A.

SYNTHESIS OF ACETYLENE ALCOHOLS BY CATALYSTS ZnEt₂/Ti(OⁱPr)₄/PhMe AND Sn(OTf)₂/NEt₃/MeCN..... 133**PP-15**

Kazakova M.A., Vatutina Y.V., Kazakov M.O., Klimov O.V., Noskov A.S.

NOVEL COMPOSITE SUPPORT FOR CoMoS HYDROTREATING CATALYST BASED ON MWCNTs GROWN ON γ-Al₂O₃ BY CVD 135**PP-16**

Kovalev I.V., Popov M.P., Bychkov S.F., Malbakhova I.A., Nemudry A.P.

CATALYTIC CONVERSION OF HYDROCARBONS USING OXYGEN-SELECTIVE MICROTUBULAR MEMBRANES FOR HYDROGEN PRODUCTION 137**PP-17**

Krivonos O.I., Terekhova E.N., Belskaya O.B.

CATALYTIC HYDROPROCESSING OF ORGANIC MATTER OF SAPROPELS IN VALUABLE CHEMICAL PRODUCTS 138

PP-18

Krivtsova N.I., Kotkova E.P.

JOINT HYDROTREATING OF DIESEL FRACTION WITH GASOLINE 140

PP-19

Nazarova G.Yu., Ivanchina E.D., Chernyakova E.S., Pchelintseva I.V., Poluboyartsev D.S.

OPTIMIZATION OF A SEMIREGENERATIVE CATALYTIC REFORMING OF NAPHTHA WITH THE MATHEMATICAL MODELLING METHOD USING 142

PP-20

Nikoshvili L., Grigorev M., Abusuek D., Mikhailov S., Matveeva V., Sulman E.

MONO- AND BIMETALLIC CATALYSTS BASED ON HYPER-CROSSLINKED POLYSTYRENE FOR HYDROGENATION OF BIOMASS-DERIVED LEVULINIC ACID..... 144

PP-21

Salnikova K.E., Sulman M.G., Mikhailov S.P., Bykov A.V., Matveeva V.G.

FURFURYL ALCOHOL AS ONE OF THE PRODUCTS OF LIGNOCELLULOSIC BIOMASS HYDROTREATMENT 146

PP-22

Orlova A.M., Bogdanov I.A., Kirgina M.V.

INVESTIGATION THE INFLUENCE OF ADDITION THE HEAVY N-PARAFFINS ON THE EFFECTIVENESS OF DEPRESSANT ADDITIVE ACTION 148

PP-23

Podryga V., Polyakov S., Trapeznikova M., Churbanova N.

DEVELOPING OF MULTISCALE APPROACH TO HPC-SIMULATION OF MULTIPHASE FLUID FLOWS 150

PP-24

Popov M.V., Zagoruiko A.N., Brester A.E., Lopatin S.A.

DECOMPOSITION OF LIGHT HYDROCARBON TO HYDROGEN ON A FIBERGLASS CATALYST 152

PP-25

Zazhigalov S., Popov M., Belotserkovskiy V., Nemudry A., Zagoruiko A.

MATHEMATICAL MODELING AND EXPERIMENTAL STUDIES OF HYDROGEN COMBUSTION IN MICROTUBULAR SOLID OXIDE FUEL CELLS 154

PP-26

Zazhigalov S.V., Rogozhnikov V.N., Snytnikov P.V., Potemkin D.I., Simonov P.A., Shilov V.A., Ruban N.V., Kulikov A.V., Sobyenin V.A., Zagoruiko A.N.

MODELING OF HYDROGEN PRODUCTION BY DIESEL REFORMING AT Rh/Ce_{0.75}Zr_{0.25}O_{2-δ}-η-Al₂O₃/FECRAL WIRE MESH HONEYCOMB CATALYTIC MODULE 156

PP-27

Potemkin D.I., Uskov S.I., Gorlova A.M., Zagoruiko A.N.,

Fedorova Z.A., Snytnikov P.V., Kirillov V.A., Sobyenin V.A.

HYTHANE PRODUCTION VIA LOW-TEMPERATURE STEAM REFORMING OF NATURAL GAS..... 158



PP-28

Sineva L.V., Nalivaiko (Gorokhova) E.O., Gryaznov K.O., Mordkovich V.Z.

ZEOLITES AS A TOOL FOR INTENSIFICATION OF MASS TRANSFER ON THE SURFACE OF A COBALT FISCHER–TROPSCH SYNTHESIS CATALYST..... 159

PP-29

Stepacheva A.A., Bykov A., Demidenko G., Nikoshvili L., Bakhvalova E., Dobryanskaya A., Matveeva V., Sulman M.

NOBLE METAL-CONTAINING NANOPARTICLES STABILIZED IN HYPERCROSSLINKED POLYSTYRENE AS EFFECTIVE CATALYSTS OF AROMATIC RING HYDROGENATION.....161



PP-30

Stepacheva A.A., Shimanskaya E., Molchanov V., Sulman A., Sulman E., Sulman M.

LIGNIN AND MODEL SUBSTANCE CATALYTIC HYDROGENOLYSIS 163



PP-31

Pérez-Cabrera L., Antúnez-García J., Díaz de León J.N., Suresh C., Zepeda T.A., Fuentes-Moyado S., Alonso-Núñez G.

DOUBLE PROMOTION EFFECT ON HDS CoNiMo/Al₂O₃ CATALYSTS APPLIED IN THE HYDRODESULFURIZATION OF DIBENZOTHIOPHENE..... 165



PP-32

Pérez-Cabrera L., Antúnez-García J., Díaz de León J.N., Galván D.H., Zepeda T.A., Alonso-Núñez G., Fuentes-Moyado S.

NiMoW CATALYSTS SUPPORTED ON MgO-Al₂O₃ MIXED OXIDES FOR THE HYDRODESULFURIZATION OF DIBENZOTHIOPHENE..... 167

PP-33

Cherednichenko A.G., Markova E.B., Akhmedova L.S., Kovtun S.O., Serov Ju.M.

INVESTIGATION OF CATALYTIC CRACKING PROCESSES OF PROPANE AND POLYPROPYLENE USING GADOLINIUM MOLYBDATES AND TUNGSTATES Gd₂(MO₄)₃ (M=Mo, W). 169

PP-34

Eran N.T., Galli F., Pirola C, Mazzoni F, Patience G.S.

THE REVIEW OF RECENT FISCHER TROPSCH CATALYSTS: A GUIDE TO UNDERSTAND THE EFFECT OF CATALYST STRUCTURE ON THE CATALYST ACTIVITY 171

PP-35

Mamedova M.T., Abasov S.I., Agaeva S.V., Isaeva E.S., Imanova A.A., Zarbaliev R.R., Khudiev A.T.

JOINT HYDROTRANSFORMATION OF A MIXTURE OF STRAIGHT-RUN GASOLINE AND TOLUENE ON A COMPOSITE ZEOLITE CONTAINING CATALYST.....172

PP-36

Mamedova M.T., Abasov S.I., Agaeva S.B., Iskenderova A.A., Nasibova A.R., Nasirova F.M., Chalabova K.S.

JOINT CONVERSION OF STRAIGHT-RUN GASOLINE AND PROPANE-BUTANE FRACTION ON ZEOLITE CONTAINING COMPOSITE CATALYSTS.....174

PP-37

Yunusov M.P., Nasullaev Kh.A., Djalalova Sh.B., Gulomov Sh.T., Sultanov A.P.

STUDY OF ZEOLITE SORBENTS SYNTHESIZED BASED ON LOCAL KAOLIN..... 176

PP-38	
Yunusov M.P., Nasullaev Kh.A. , Gulomov Sh.T., Turdieva D.P., Abduraxmanova I.S., Rahimjanov B.B.	
OPTIMIZATION OF THE SYNTHESIS TECHNOLOGY OF HIGHLY DISPERSED ALUMINUM HYDROXIDE USING VARIOUS REAGENTS	177
PP-39	
Gubaydullin I.M. , Koledina K.F., Zaynullin R.Z., Koledin S.N.	
MATHEMATICAL MODELING OF KINETICS OF GASOLINE CATALYTIC REFORMING	179
PP-40	
Koledina K.F., Gubaydullin I.M. , Koledin S.N.	
MULTI-CRITERIAL OPTIMIZATION OF A HETEROGENEOUS CATALYTIC REACTION	181
PP-41	
Kondrasheva N.K. , Konoplin R.R., Kondrashev D.O., Parfenova L.V., Shaidulina A.A.	
PUT INTO INDUSTRIAL PRODUCTION DIFFICULTIES OF NOVEL EFFECTIVE HYDRODESULFURIZATION-CATALYSTS IN RUSSIAN FEDERATION	183
VIRTUAL PRESENTATIONS (abstract publication)	185
VP-1	
Frantsina E.V. , Grinko A.A., Maylin M.V., Berdnikova A.A., Mashnich V.S.	
THE USE OF CHROMATOGRAPHY-MASS SPECTROMETRY IN THE STUDY OF THE HYDROCARBON COMPOSITION OF DIESEL FUELS	187
VP-2	
Boldushevskii R. , Iusovskii A., Guseva A., Nikulshin P., Shmelkova O., Chernysheva E., Kapustin V.	
HEAVY FEEDSTOCK HYDROPROCESSING FOR MARINE FUELS PRODUCTION	189
VP-3	
Khazipov M.R. , Pastushenko I.L., Galimova A.T., Sagdeev A.A., Kiryukhin V.G., Pletnev A.S.	
REGENERATION OF LD-145 CATALYST BY SUPERCRITICAL FLUID EXTRACTION	191
VP-4	
Sadovnikov A.A. , Naranov E.R., Maximov A.L.	
HYDROTHERMAL SYNTHESIS OF FLUORINATED TITANIA FOR PHOTOCATALYTIC APPLICATIONS	193
VP-5	
Roldugina E.A. , Shayakhmetov N.N., Maximov A.L., Karakhanov E.A.	
HYDROTREATMENT OF FURFURAL AS BIO-OIL MODEL COMPOUND OVER Ru-CATALYSTS SUPPORTED ON MESOPOROUS MATERIALS	195
List of participants	197
Content	202



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