Synchrotron Radiation Techniques for Catalysts and Functional Materials

October 31 – November 3, 2022

Novosibirsk, Russia

ABSTRACTS

Federal Research Center Boreskov Institute of Catalysis
Synchrotron Radiation Facility SKIF
Budker Institute of Nuclear Physics of SB RAS
Novosibirsk State University

International Conference
«Synchrotron Radiation Techniques for Catalysts and Functional Materials»

October 31 – November 3, 2022
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ABSTRACTS

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Сборник включает тезисы пленарных, устных и стендовых докладов.
Основные темы научной программы конференции:
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- Theoretical and applied aspects of experimental techniques utilizing synchrotron radiation
- Structure-driven design of catalysts and functional materials based on synchrotron diagnostics
- Synchrotron radiation for structural biology
- Development of instrumentation for synchrotron beamlines
- New data processing algorithms, artificial intelligence and machine learning in bulk data analysis
- Update on the status and scientific program of the Synchrotron Radiation Facility SKIF

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Plenary Lectures

PL-1 ÷ PL-7

PL-1

The Status of the Implementation of the Synchrotron Radiation Facility "SKIF"

Bukhtiyarov V.I.[1], Levichev E.B.[2]
1 – Boreskov Institute of Catalysis, Novosibirsk, Russia
2 – Synchrotron Radiation Facility SKIF, Novosibirsk, Russia
e.b.levichev@srf-skif.ru

Synchrotron Radiation Facility SKIF is a new large-scale research infrastructure project currently underway in the Science City Koltsovo, 15 km apart from Novosibirsk. The 3 GeV electron storage ring designed by specialists from the Budker Institute of Nuclear Physics SB RAS will provide the record low emittance of 75 pm·rad by the date of scheduled commissioning in December, 2024.

The SRF SKIF will become a national-level multidisciplinary research and innovative centre. Key directions of the scientific program to be deployed at the SRF SKIF will encompass biomedicine, green technologies in chemistry and energetics, advanced engineering materials and mechanical engineering technologies.

The aerial view of the construction site as of summer 2022 is shown in Fig. 1. More than 30 specialized buildings with advanced engineering infrastructure will appear within several months.

Fig. 1. Construction site of the Synchrotron Radiation Facility SKIF (as of summer 2022).

The present contribution gives a concise survey on technological parameters of the project, current status of the project implementation, and potential scientific impact of the facility. More information on the SRF SKIF project may be found elsewhere [1].

Acknowledgement: The work was supported by the Russian Ministry of Science and Higher Education of the Russian Federation within the Budget project for the Synchrotron Radiation Facility SKIF, Boreskov Institute of Catalysis SB RAS.

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PL-2

Online Precise Analysis of X-Ray Spectral Data Powered by Machine Learning Algorithms

Guda A.A.
The Smart Materials Research Institute, Southern Federal University, Rostov-on-Don, Russia
guda@sfedu.ru

The history of X-ray absorption spectroscopy goes back in 1913 when first absorption edge was measured by Maurice de Broglie. Further development of experimental techniques was supported by theoretical models of the EXAFS (1970s) and XANES (1990s). Independent research groups have developed instruments and approaches to analyze different energy intervals of spectra: pre-edge, near-edge and extended regions. Due to many nuances, it is still nontrivial for nonspectroscopists performing quantitative analysis of their data.

Machine learning (ML) algorithms offer a possibility to combine knowledge of experts and create a valuable tool for quantitative analysis of spectral data that can be applied by chemists and physicists in their research. In the talk we will start from a brief literature review of the remarkable case studies including classification of the coordination motifs and structural refinement. Both supervised and unsupervised approaches will be discussed along with popular machine learning algorithms: ridge regression, decision trees, convolutional neural network, autoencoder, and others. We will highlight an integral part of every supervised machine learning algorithm, the cross-validation procedure, that is important for uncertainties estimation.

The second part of the talk will be devoted to our experience in practical applications of ML to the real experimental data. We will answer the questions “Why linear combination fit is outdated?”, “How fingerprint analysis should be performed”, “When chemical intuition is needed to perform structural refinement of distances and angles?”. Machine learning is not a black box and requires careful tuning. Adaptive sampling helps to improve the quality of machine learning approximation while keeping the training set size small enough. Compared to Neural networks the Radial basis functions or Extra Trees algorithms may further help to reduce the number of calculations for supervised learning. The training set should be extended with mixtures if the experimental spectrum may contain a superposition of signal from several inequivalent sites. XANES calculations still contain systematic errors and reducing the dimensionality of the spectra helps to perform a calibration and improve predictive quality. For this purpose, the descriptors of the spectra are introduced in the analysis.

We foresee the further development of the ML analysis in combining several energy intervals of spectra (pre-edge, XANES, EXAFS for the K-edge along with $L_{2,3}$ edges of the same element) and other spectroscopic local probes (EPR, NMR, Mossbauer). Our group aims in developing the user-friendly online tools where users can upload their data and receive a chemically relevant answer. Such cloud platforms will join worldwide efforts of theoreticians

who create high-quality datasets for supervised learning and experimentalists who provide high-quality experimental references and operando data for the analysis.

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PL-3

Advanced Synchrotron-Based Techniques Shedding Light on Properties of Morphologically Complex Functional Materials

Kiskinova M.
Elettra Sincrotrone Trieste, Area Science Park, 34149 Trieste, Italy
maya.kiskinova@elettra.eu

The trend of modern nano-technology to invent new materials with improved structural, chemical, electric, magnetic and optical properties has endorsed the implementation of appropriate scattering, imaging and spectroscopic techniques, based on photon-matter interactions, for exploring their structure, dynamics and function at proper spatial, temporal and energy scales. Thanks to the brightness, tunability, polarization and time structure of the synchrotron light these techniques have become state-of-the art shedding light on the exotic properties of thin films, strongly correlated electron materials, nano-sized and 2D materials and relevant surface and interfacial phenomena which are the key for selecting the best to be used in (i) electronic and sensor devices with broad applications fields, where from spintronics to quantum information triggering and switching magnetic moments in thin films is a crucial step; (ii) catalysis, the core of chemical industry, fuel and energy production, devices for energy conversion and storage, etc. Ongoing developments are pushing the lateral and temporal resolution and implementation of variable set-ups for allowing for in-situ measurements under realistic operational conditions. The most recent achievements thanks to the use of synchrotron light will be illustrated by selected results from studies at Elettra of technologically relevant materials following the effects of chemical ambient, temperature, electromagnetic fields and radiation. The examples will include free-standing nanostructures, 'real' 2D devices, thin films and magnetic dynamics, catalysis and key functional constituents in electrochemical devices, emphasizing the potential of X-ray and photoelectron microscopes and coherent diffraction imaging approaches. Ongoing efforts and recent achievements in developing in-operando microscopy set-ups will be outlined.

PL-4

Application of In Situ X-Ray Diffraction to Study Oxide and Metal Oxide Catalyst

Bulavchenko O.A.
Boreskov Institute of Catalysis, Novosibirsk, Russia
obulavchenko@catalysis.ru

X-ray diffraction is a useful tool to characterize catalysts. First of all, the technique discriminates between amorphous and crystalline material. For crystalline materials, it allows for the determination of the phase composition, structural and microstructural characteristics such as atomic structure, crystallite size, and strains. The development of new technologies requires the deep understanding of the processes occurring at all stages of synthesis of catalyst and operation. Modern in situ methods for the analysis of materials make it possible to monitor the state of the catalyst under different non ambient conditions. It is useful for applied science since it can probe functional materials under conditions very close to their operation in reactor.

The application of *in situ* XRD may help with characterization of the active catalyst, activation/deactivation behavior of the catalyst, characterization of catalyst precursor materials, investigation of some catalyst preparation steps, study the catalyst in the reaction medium (e.g. oxidation, reduction, decomposition reactions). *In situ* diffraction has been used to follow the evolution of phases and their crystalline size, the formation of both stable phases and intermediate compounds during reaction, analyze the presence of point and planar defects, the formation of nanostructured states or the superstructural ordering, monitor fast processes and kinetics of chemical reactions. Due to the various methodological possibilities of XRD, it is possible to characterize in detail the structural changes at the atomic level occurring under the influence of the environment and temperature. In the context of *in situ* X-ray diffraction applications, the following examples are discussed: study of preparation, activation steps for Mn-Ce-Zr oxide, Mn-Al catalysts for environment application, activation process of Ni-Cu catalyst for bio oil upgrading, *operando* study of Mn-Zr catalyst.

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PL-5

Functional Cagelike Metallasesquioxanes: (Supra)molecular Design in the Focus of X-ray Diffraction Studies

Bilyachenko A.N.[1,2]
1 – INEOS RAS, Moscow, Russia
2 – RUDN University, Moscow, Russia
bilyachenko@ineos.ac.ru

Cagelike sil-[1] and germsesquioxanes [2] are objects of research of many scientific teams worldwide. Kaleidoscopic variety of sesquioxane ($REO_{1.5}$, E = Si or Ge) ligands – from monomeric to condensed polycyclic – provides a wide number of metallacomplexes, including polynuclear heterometallic ones. Additional opportunities metallasesquioxane design is due to easiness of application of additional organic (N,N-, P,P-, N,O-, O,O-) ligands (Fig. 1) [3]. Metallasesquioxanes' functionalities include important catalytic [4], magnetic [5], and photophysical [6] properties. Presentation will discuss recent results of our group in design of cagelike metallasesquioxanes as well as their homogeneous catalytic activities, magnetic (spin glass and SMM) effects and temperature sensing.

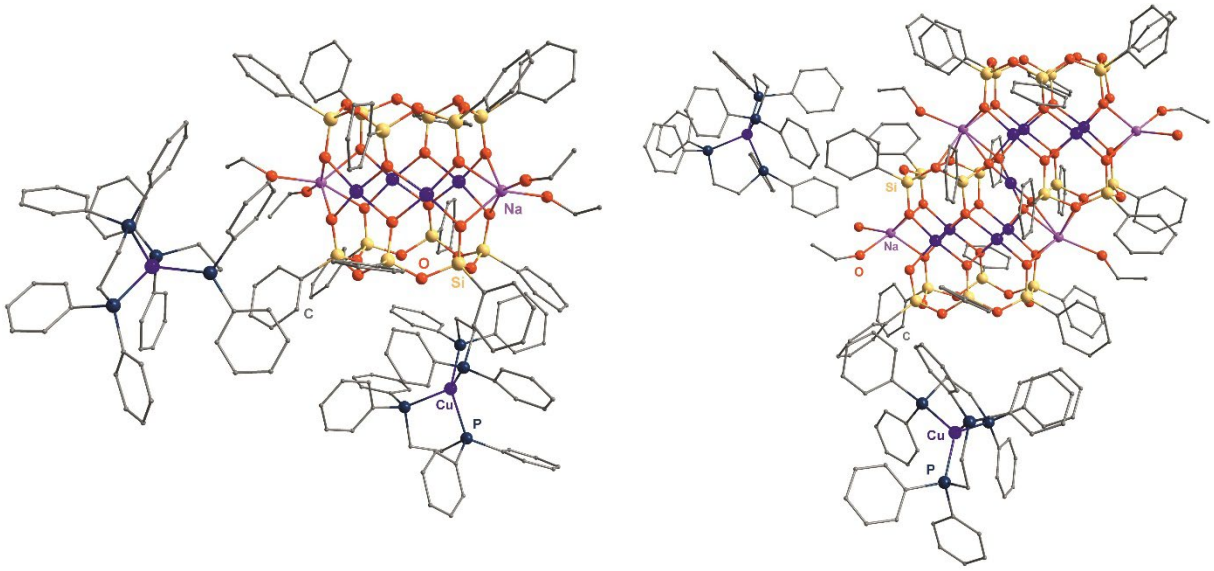

Fig. 1. Examples of CuNa-silsesquioxane complexes with dppe ligands

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PL-6

Modern Applications of Synchrotron Soft X-Ray Spectroscopy to Functional Organic Thin Films

Zharnikov M.
Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany
Michael.Zharnikov@pci.uni-heidelberg.de

Functional organic thin films, including self-assembling monolayers, are of primary importance for applications in such frontier areas of modern technology as organic electronics and photovoltaics, molecular electronics, bioengineering, nanofabrication, etc. Rational design and application of these films rely to a large extent on information about their parameters and properties, which can be readily gained by synchrotron soft X-ray spectroscopy, taking advantage of tunable photon energy and high energy resolution. In my talk, I will give you representative examples of using such techniques as X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and resonant Auger electron spectroscopy (RAES) to address specific problems in context of both fundamental research and particular applications. The related subjects include extension of the chemical shift concept in XPS, design of novel dipolar monomolecular films, fabrication of binary molecular films, charge-transfer dynamics in molecular systems, thermal stability of self-assembling monolayers, soft-matter nanofabrication, application of functional molecular films in organic electronics and photovoltaics, molecular electronics, etc..

PL-7

Probing the Surface of Steels During Friction with Synchrotron X-Ray Microbeam

Bataev I.A.
Novosibirsk State Technical University, Novosibirsk, Russia
i.bataev@copr.nstu.ru

Characterization of structure of materials in the process of friction and wear is one of the common tasks of tribology and materials science. As a rule, destructive characterization techniques, such as light or scanning electron microscopy, are used for this purpose. The information obtained using microscopy characterizes the state of the sample at a certain moment of friction, and it is not possible to draw indisputable conclusions about the previous or subsequent structural states. It should also be noted the high laboriousness of conducting studies of this type which is related to long procedure of specimens' preparation.

In our works [1-5], we have proposed an approach to characterize the structure of materials during friction using *operando* synchrotron X-ray diffraction. For this, a special setup was developed by our group that allows analyzing the surface layer of the material under study in a moment after it has been subjected to friction (Fig. 1). Data on the state of the material can be accumulated for a specified time and such parameters of the microstructure as the size of coherent scattering regions, lattice microdistortions, dislocation density, type of dislocations (edge or screw), etc. can be estimated.

The setup can be used to analyze various materials. This report presents the results of a study of various steels. The details of materials characterization results can be found in studies [1-3].

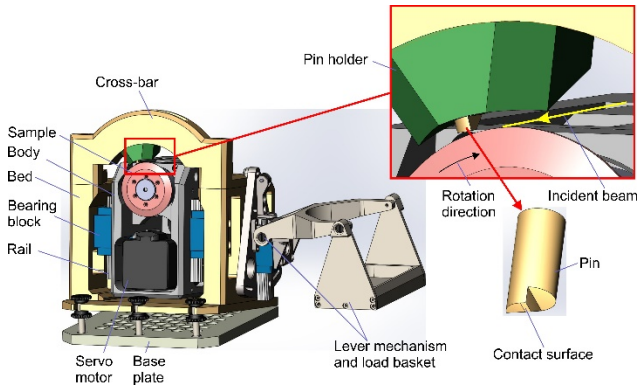

Fig. 1. Friction tester intended for synchrotron beamlines

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Oral Presentations

OP-1 ÷ OP-25

OP-1

Evolution of Active Sites of Ru-Catalysts during Hydrogenation of Oxygen Containing Substances

Naranov E.[1], Sadovnikov A.[1], Arapova O.[1], Bugaev A.[2], Usoltsev O.[2]

1 – Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prospekt, bld. 29, 119991, Moscow, Russia

2 – The Smart Materials Research Institute, Southern Federal University, Sladkova Street 178/24, Rostov-on-Don 344090, Russia

naranov@ips.ac.ru

The catalytic systems based on Ru have several limitations including high-energy requirements for the preparation of catalyst, which usually higher than that required for the HDO process [1,2]. The harsh reduction conditions, necessity of environmentally polluting organic solvents, increase in cost owing to the use of expensive catalyst precursors involving multistep processes are among them [3–5]. These limitations prevent the effective application of such catalysts for industrial scale. There are some studies demonstrating the prevailing catalytic activity of partially oxidized Ru catalysts compared to reduced ones [3,4,6]. On the contrary, Liu and co-workers showed that oxidized $Ru/WO_x/ZrO_2$ was inactive during the HDO process of guaiacol [7]. There is still some controversy related to the oxidation state of Ru in the catalytically active phase regarding the nature of relationship of RuO_2 with the porous supports and the associated HDO activity in the conversion of bio-oil substances. To address these shortcomings, the current study investigated the HDO of oxygen containing substances such as guaiacol and diphenyl ether over different types of catalysts to reveal the effect of the textural and acidic properties of the supports on the catalytic behavior. Ruthenium was selected as the catalytic metal being deposited on different porous support. The starting phase of Ru-catalyst was RuO_2, which was *in situ* converted into the active state avoiding *ex-situ* reduction or pre-treatment which is often reported for Ru-based catalysts for HDO. In addition to the extensive physico-chemical and catalytic characterization the evolution of the atomic and electronic structure of ruthenium was followed by *operando* X-ray absorption spectroscopy (XAS).

The *operando* XAS and *in situ* DRIFT spectroscopy analyses of the RuO_2 based catalysts during guaiacol hydrogenation revealed that reaction initiates simulteniously with the formation of ruthenium hydrous oxide. It was shown that RuO_2 catalysts demostrated better catalytic activity compared to the reduced catalysts due to the formation of ruthenium hydrous oxide phase. For the first time our team revealed the $RuO_2 \rightarrow$ ruthenium hydrous oxide phase transformation by *operando* XAS method. In addition, we proposed an effective

way to observe the state of Ru during catalytic process under high hydrogen pressure. As the result, the mechanism of ruthenium hydrous oxide formation was proposed.

The work was financially supported by the Russian Science Foundation (project № 22-79-10294).

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OP-2

Application of PDF and EXAFS Methods for Structural Analysis of Rh-Doped CeO_2 Catalysts

Kardash T.Yu.[1], Fedorova E.A.[2], Kibis L.S.[1], Pollastri S.[3], Stonkus O.A.[1], Slavinskaya E.M.[1], Boronin A.I.[1]

1 – Boreskov Institute of Catalysis, Novosibirsk, Russia

2 – Leibniz Institute for Catalysis, Rostock, Germany

3 – Elettra-Sincrotrone Trieste, Italy

kardash@catalysis.ru

Recently, single-atom catalysts have been proposed as highly-active catalytic systems that allow maximizing the catalytic efficiency of the expensive active component through its atomic dispersion on supports. Maximum dispersion of the active component in Me/CeO_2 systems can be achieved, when active component is dispersed within the CeO_2 lattice. As a result, very effective species are formed, including ionic single sites and MeOx clusters [1-2]. In this work, we studied the Rh-doped CeO_2 catalysts prepared by coprecipitation method.

Our structural insights are based in the combination of EXAFS and Pair Distribution function (PDF) methods. PDF enables direct measurements of interatomic distances of RhOx clusters and propose a structural model. The refinement of structural model was based on Rh-K EXAFS spectra. The obtained results were confirmed by XPS and TEM data.

XAS spectra were collected at the ELETTRA Synchrotron (Trieste, Italy) at XAFS beamline. The measurements were recorded at the Rh K-edge (23220 eV) at room temperature in transmission mode. The background removal and extraction of the EXAFS oscillatory part from the experimental spectra and EXAFS modeling were performed in Athena and Artemis software [3]. The diffraction data for PDF were obtained using synchrotron radiation at ID22 beamline at ESRF, Grenoble, France. X-ray scattering data were obtained using a Perkin Elmer disordered silicon detector and a wavelength of λ = 0.177005 Å. The normalized scattering curves S(Q) and PDF curves were calculated using the PDFgetX3 program [4]. The VESTA software was used to build local structure model of rhodium in the catalyst [5].

For $Rh\text{-}CeO_2$ catalysts, the formation of exclusively ionic highly dispersed forms of Rh^{3+} was observed by XPS. The XRD and Raman spectroscopy data indicate the bulk incorporation of Rh^{3+} into the CeO_2 lattice, where Rh^{3+} replaces the Ce^{4+} positions. In this case, an increase in the amount of rhodium in the catalyst leads to an increase in the amount of microstrain in the lattice.

According to XANES data, there is a difference between spectra for catalysts and the spectrum of Rh_2O_3. This difference was associated with the formation of highly dispersed Rh species. The most significant change was observed for the 1% sample, which is associated with the formation of Rh single sites, which are embedded in the CeO_2 lattice. This observation was confirmed by TEM data with EDX mapping. An increase in the rhodium content in the sample

leads to the formation of additional RhOx clusters, which makes the XANES spectra close to Rh_2O_3 oxide.

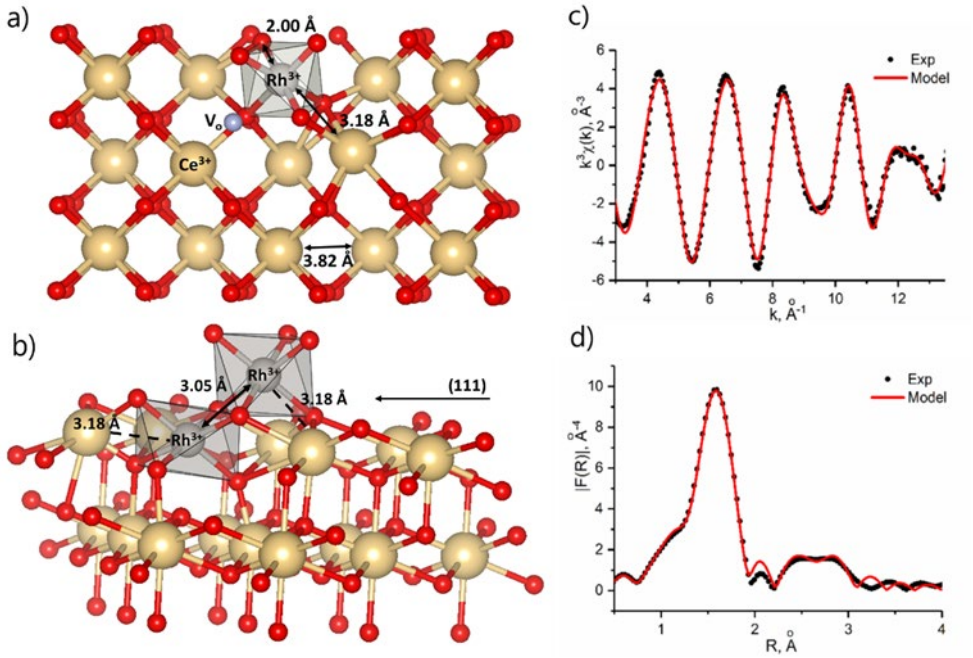

Fig. 1. Local structure of (a) Rh-SA and (b) RhO_x cluster on CeO_2. Comparison of experimental (dots) k^3-waited oscillation parts (c) χ(k) of Rh K-edge EXAFS and (d) their FT magnitudes corresponding theoretical curve (solid red) of the 5Rh-CeO_2 sample

Using XAS and PDF data, it was shown that adjacent single rhodium sites form RhO_x clusters with a local environment close to Rh_2O_3 and $CeRh_2O_5$ oxides. Due to the formation of a defective environment in the CeO_2 lattice, single and cluster forms of rhodium exhibit activity in the CO oxidation reaction at temperatures below 100°C (LTO-CO), while rhodium clusters and Rh single atoms demonstrate similar activity.

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OP-3

Local Atomic Structure of Borate Glasses Based on X-Ray Absorption Spectroscopy

Sukharina G.B.[1], Ermakova A.M.[1], Avakyan L.A.[1], Alekseev R.O.[2], Shakhgildyn G.Yu.[2], Savinkov V.I.[2], Romanov N.A.[2], Veligzhanin A.A.[3], Bugaev L.A.[1], Sigaev V.N.[2]

1 – Southern Federal University, Rostov-on-Don, Russia

2 – Mendeleev University and Chemical Technology, Moscow, Russia

3 – National Research Centre "Kurchatov Institute", Moscow, Russia

gbsukharina@sfedu.ru

Recently, great attention was focused on borate glasses considered as the promising materials for optical instrumentation, electrotechnics, biomedicine and other industries [1]. The research of the borate glass structure will make it possible to determine its effect on the optical properties of the material and to develop a composition with the required refractive index and density.

In the presented work the borate glasses of composition La_2O_3-Nb_2O_5-B_2O_3 (LNB) with the same concentration of lanthanum oxide (22.5%), but with different contents of niobium oxide (from 5% to 30%) and boron oxide (from 72.5% to 47.5%) were synthesised and then characterized by X-ray absorption spectroscopy.

The experimental La L_3-XANES spectra in LNB glasses were measured at "Kurchatov Synchrotron Center" on beamline "Structural materials science" [2]. For interpretation of the obtained experimental data we performed computer modelling of La L_3 -XANES in LNB glasses by full potential finite difference method (FDMNES) [3]. The quantitative analysis of XANES was done using the multi-dimensional interpolation spectra as a function of structural parameters (interatomic distances R_{La-O} and bond-angles O-La-O) [4]. By this approach the refinement of 3D local structure of LNB glasses carried out. Model of the La local structure for LNB_30 sample in which La is surrounded by 10 oxygen atoms gave the best agreement with the experimental data (see Figure 1). Interatomic distances obtained are presented in Table 1.

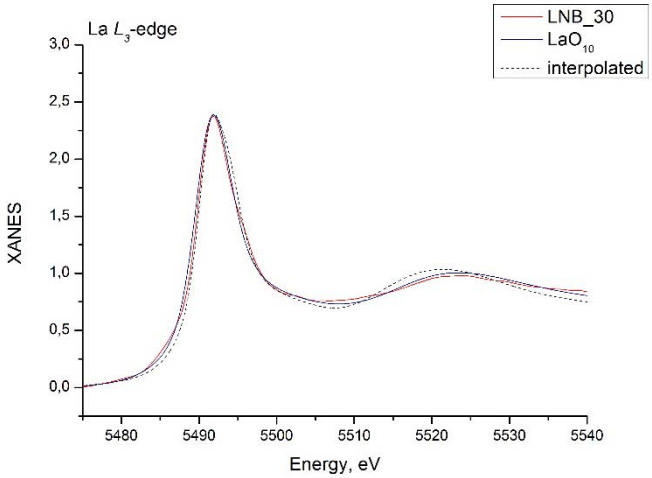

Fig.1 Comparison of the experimental (solid red line) , interpolated (dash black line) and calculated (solid black line) La L_3-XANES in LNB_30 glass for optimal structural parameters.

Table 1. Measured interatomic distances ($R_{La\text{-}O}$, Å) in LNB glasses.

	XANES	EXAFS
LNB_30	2.47 ± 0.01	2.46 ± 0.01
LNB_20	2.46 ± 0.01	2.45 ± 0.01
LNB_5	2.45 ± 0.01	2.43 ± 0.01

Within our study both the interatomic distances and the bond angles for all considered LNB glass samples were determined. Thus, the studies performed demonstrate the unique possibilities of the approach used in this work to determine the local atomic structure of materials without long-range order and allow one to efficiently establish the relationship between structure and properties for materials of this type.

Acknowledgement: This work was supported by the Russian Science Foundation, grant No.22-12-00106.

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OP-4

Single-Atom Catalysts for Oxidative Methane Conversion to Acetic Acid: Catalyst Study by Spectroscopic Analysis Methods

Batova T.I.[1], Khramov E.V.[2], Obukhova T.K.[1], Kolesnichenko N.V.[1]
1 – A.V.Topchiev Institute of Petrochemical Synthesis, RAS, Moscow, Russia
2 – National Research Center «Kurchatov Institute», Moscow, Russia
batova.ti@ips.ac.ru

One-stage processing of methane into acetic acid (according to reactions involving carbon oxides and oxygen) is very economically attractive, since it is a very effective way to monetize natural gas (the cost of production increases by 7-10 times), and the new process can be easily integrated into operating industrial schemes for the gas feedstock processing (synthesis gas and/or hydrogen production). The recent appearance of a fundamentally new class of heterogeneous catalysts, with single atom active metal sites (SAC – single-atom catalysts) possessing unique catalytic properties and capable of activating a strong methane molecule even at low temperatures and selectively converting it, indicates the potential for the development of highly efficient catalysts of such type for reactions of direct methane conversion. Such systems have recently appeared, and now they are of great prospects to increase the catalytic efficiency of heterogeneous catalysts by reducing the active site size [1-4]. The appearance in recent years of a new generation instrumental equipment, with a high resolution, which makes it possible to determine the structure of catalysts at the atomic level (in particular, by methods using synchrotron radiation), creates the necessary scientific basis for a full-fledged fundamental study of the SACs and fruitful work on their creation [1, 5].

We have developed integrated approach to the synthesis of single atom rhodium zeolite catalysts (Rh_1-SAC) for the reaction of oxidative methane carbonylation to produce oxygenates (methanol and acetic acid) using an original technique [6, 7]. This approach includes primary "fixing" of active metal atoms in a polymer matrix due to chemical interaction of a rhodium precursor with a nitrogen-containing polymer with the subsequent transfer of the obtained isolated rhodium centers from the polymer base to the zeolite surface. The subsequent pyrolytic destruction of the polymer allows to fix single rhodium centers on the zeolite surface. With this method of SAC synthesis, the "network" of single active metal centers on the zeolite surface is actually set by the chemical structure of the initial polymer matrix, which makes it possible to obtain highly efficient catalytic systems with spatially isolated active metal sites fixed on a zeolite support.

Using XAS spectroscopy, all rhodium was found to be as single atom metal sites in the zeolite structure, which contributes to the acetic acid formation. In addition, the spatial arrangement and structure of single atom metal sites play an important role. For the first time, using the XPS method, an increase in the proportion of rhodium atoms being at the zeolite channel intersections was stated to promote the formation of acetic acid. According to DFT calculations combined with EXAFS simulations, rhodium anchored at the zeolite channel

intersections was shown to coordinate with four zeolite oxygen atoms and one hydroxyl group and be the dominant catalytic compound in the acetic acid formation. In addition, the synergism between strong Brönsted acid zeolite sites and single atom rhodium ones during formation of acetic acid was established. Not only the strong acid site concentration but also their proximity to the rhodium sites play the crucial role.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 21-73-20042.

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OP-5

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

Bukhtiyarov A.V.[1,2], Prosvirin I.P.[1], Panafidin M.A.[1,2], Fedorov A.Yu.[1], Klyushin A.Yu.[3], Knop-Gericke A.[3], Zubavichus Y.V.[1,2], Bukhtiyarov V.I.[1]

1 – Synchrotron radiation facility SKIF, Boreskov Institute of Catalysis, Kol'tsovo, Russia

2 – Boreskov Institute of Catalysis, Novosibirsk, Russia

3 – Fritz-Haber-Institute der Max Planck Society, Berlin, Germany

avb@catalysis.ru

The ability of bimetallic supported catalysts to overperform their monometallic counterparts has induced a great deal of interest to these systems within scientific community. However, despite a large number of investigations of various bimetallic catalysts published in the last decade, the structure of catalytic active sites therein is still under debate. The reason for that is the proneness of bimetallic particles to transformations under the influence of temperature and reaction mixture. PdAu system is among the most studied ones due to its enhanced catalytic properties for a number of reactions, such as vinyl acetate synthesis, low temperature CO oxidation, NO reduction and others. However, the structure of catalytic active sites remains elusive since the actual ratio of the metals on the surface of a working catalyst is not determined unambiguously by the amount of initially introduced metals, but is also strongly affected by the calcination temperature. Moreover, a redistribution of the metals in the particle can occur directly during the course of a catalytic reaction, under the influence of temperature and reaction mixture. To address the problem, *operando* studies have to be performed. In our recently published papers [1, 2], the model bimetallic PdAu/HOPG catalysts have been investigated towards the CO oxidation reaction using a combination of NAP XPS and MS techniques. The samples have shown an onset of catalytic activity at temperatures above 150°C. CO adsorption on the bimetallic nanoparticles under reaction conditions has been shown to induce segregation that manifested itself as an enrichment of the surface with Pd. It has been shown that heating of the sample under reaction conditions above 150°C gives rise to the decomposition of the Pd–CO state due to the CO desorption immediately followed by oxidation and simultaneous Pd–Au alloy formation on the surface. Thus, it was clearly demonstrated that it is exactly the alloyed surface that is responsible for the CO oxidation. This conclusion is in line with the Goodman's mechanism which suggests that gold atoms are responsible for the CO adsorption, whereas contiguous Pd sites are responsible for the O2 dissociation and a further spillover of O_{ads} to Au and/or to isolated Pd sites followed by the oxidation of activated adsorbed CO. However, according to this mechanism, CO oxidation should occur at relatively low temperatures when weak interaction between CO and Au can provide an appropriate concentration of adsorbed CO molecules. But significant surface segregation of Pd atoms induced by CO adsorption can destroy the alloy structure and inhibit the metal surface completely thus effectively

deactivating the catalysts. We suggested that such a situation was indeed realized for the samples studied in [1]. In that case, the mechanism of the CO oxidation reaction could switch to that typical of monometallic Pd nanoparticles due to a prominent shortage of Au atoms on the topmost surface layer. In a full agreement with this consideration the Pd-Au/HOPG catalysts were inactive towards the CO oxidation in the low-temperature mode, the activity ignited only at temperatures above 150°C. Finally, it was suggested that the use of bimetallic model Pd-Au/HOPG samples with a lower Pd/Au ratio would lead to increased activity below 150°C.

In the presented work [3], we have compared the results obtained in the previously published paper [1] with ones obtained for the Pd-Au/HOPG model bimetallic catalyst with a lower Pd/Au ratio on the particles surface. The key goal of this investigation was to find a correlation between the catalytic activity of those model catalysts towards the CO oxidation reaction and the Au/Pd atomic ratio on the surface of bimetallic particles. A systematic elucidation of electronic properties of the elements in bimetallic PdAg particles and their depth profiles as well as their transformation induced by the reaction environment of CO oxidation was performed using a combination of NAP XPS and MS techniques for different reaction conditions and initial Pd/Au ratios.

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

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OP-6

XPS and NEXAFS Study of the Interaction of Carbon Materials with Alkali Metals for Electrochemical Applications

Fedoseeva Yu.V.[1], Shlyakhova E.V.[1], Vorfolomeeva A.A.[1], Stolyarova S.G.[1], Makarova A.A.[2], Smirnov D.A.[3], Bulusheva L.G.[1], Okotrub A.V.[1]

1 – Nikolaev Institute of Inorganic Chemistry SB RAS, 3 Acad. Lavrentiev Ave., 630090 Novosibirsk, Russia

2 – Physical Chemistry, Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany

3 – Institut für Festkörper- und Materialphysik, Technische Universität Dresden, 01062 Dresden, Germany

fedoseeva@niic.nsc.ru

Carbon nanomaterials due to their unique structure, high chemical stability and electrical conductivity are promising electrode materials for various electrochemical devices, such as lithium-ion batteries, sodium-ion batteries, supercapacitors, hybrid lithium-ion supercapacitors etc. In this work, to gain insight into the effect of the interaction of lithium and sodium with carbon nanomaterials and chemically modified carbon nanomaterials, we used in situ X-ray photoelectron spectroscopy (XPS) and near-edge X-ray adsorption fine structure (NEXAFS) experiments. Carbon nanotubes, graphites, porous carbon nanomaterials modified with nitrogen and bromine have been studied. The deposition of alkali metals was carried out in an ultra-high vacuum simultaneously on the surface of samples. The changes in the composition and electronic structure of carbon nanomaterials after their interaction with alkali metals have been detected by XPS and NEXAFS. High temperature annealing or air exposing were applied to the lithiated or sodiated samples in order to remove intercalated or adsorbed alkali metals.

Quantum chemical modeling of the carbon nanostructures with alkali metals was used to interpret the experimental XPS and NEXAFS data and reveal the features in the electronic structure of chemically modified carbon samples after interaction with lithium and sodium. Electrochemical testing of the nitrogen-doped carbon materials and brominated nitrogen-doped carbon materials in lithium and sodium-ion batteries showed the high electrochemical performance and good stability of the working electrodes.

This finding can help to understand the processes occurring in chemically modified carbon electrodes and to develop advanced materials for efficient lithium-ion batteries.

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OP-7

Evolution of the Experimental Capabilities of the "XSA" and "Belok" Beamlines of the Kurchatov Synchrotron Radiation Source for Single Crystals X-Ray Diffraction Analysis of Molecules with Various Complexity

Lazarenko V.A., Dorovskii P.V., Svetogorov R.D.
NRC "Kurchatov institute", Moscow, Russia
Vladimir.a.lazarenko@gmail.com

At the moment, single-crystal diffraction remains the most popular and widespread method for solving different structures of varying complexity for tasks of coordination chemistry and biology. The use of a synchrotron radiation source for carrying out experiments of this type makes it possible to achieve high resolution and quality of the data obtained in the shortest possible time. And, of course, the use of the synchrotrons makes it possible to expand the obtained experimental data through the use of additional X-ray methods

Research in structural chemistry and biology is part of the vast amount of scientific research in the modern world. Despite the daily increase in demand for solving problems of coordination chemistry and, accordingly, work with small molecules, the number of synchrotron beamlines for single-crystal diffraction on small molecules in the world is quite small, which makes each of them a unique scientific instrument.

To make it easier for Russian users and provide an additional opportunity for foreign users to access this type of synchrotron beamline and to quickly collect high-resolution diffraction data from a wide range of samples, one of the installations of the Kurchatov synchrotron radiation source was optimized for working with crystalline samples in mass flow measurements, which allowed it to become a device that has no analogues in Russia for conducting this type of experiment [1]. Raytracing of the XSA station was carried out and a noticeable increase in the photon flux on the sample was shown in comparison with the Belok station, where the hight-throutput single-crystal small-molecular crystallography experiments had previously been started [2].For now, "Belok/XSA" beamline allows to investigate the structures of single crystals of simple organic compounds (with a cell in the region of 5-10 angstroms) and up to complex macromolecular complexes (with a cell of up to 100-200 angstroms). Theoretically calculated photon flux on the sample for an aperture of 400 × 400 μm, in confirmation of the values obtained from the ionization chambers, amounted to N(λ)=~6〖·10〗^11 photons/s.

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OP-8

Supramolecular Materials for DNA Trap and Storage: How to Analyse with Machine Leaning

Aliev T.A.[1], Timralieva A.A.[1], Shilovskikh V.V.[2], Skorb E.V.[1]
1 – ITMO University, St. Petersburg, Russia
2 – Immanuel Kant Baltic Federal University, Kaliningrad, Russia
aliev@infochemistry.ru

DNA can be used in different areas such as bioanalysis, diagnostics, biosensing [1-3]. Specific conditions are required to store DNA without its destruction. A great challenge is to neutralize negative charge of DNA to upload it into the capsules. Another question that is still open is DNA release. Mostly all the proposed capsules require heat treatment, moisture increase or the presence of complementary DNA.

We perform a novel approach to use supramolecular materials such as melamine cyanurate as the capsules. Melamine cyanurate (M-C) is widely known self-assembly of melamine and cyanuric acid bind by three hydrogen bonding. The rosette-like layers are also bind by π- πstacking. Organic molecules can become nucleation centre for M-C crystal growth. We proposed that fluorophore-labelled single strand DNA can be incorporated into M-C structure according to above mentioned. We perform a specifically designed reaction-diffusion system to see the dynamics of crystal growth and add magnesium cations to neutralize DNA negative charge. Obtained crystalline capsules have highly different morphology than M-C crystals. Magnesium ions promote DNA behaviour as a nucleation centre, and DNA luminescence is focused into the centre of capsules.

The design of reaction-diffusion system complicates the differentiation of samples with different magnesium concentration by eye. All of them have almost similar luminescence distribution. We used convolution neural networks (CNN) combined with transfer learning method to predict magnesium ions concentration. The prediction accuracy is 96% (Figure 1).

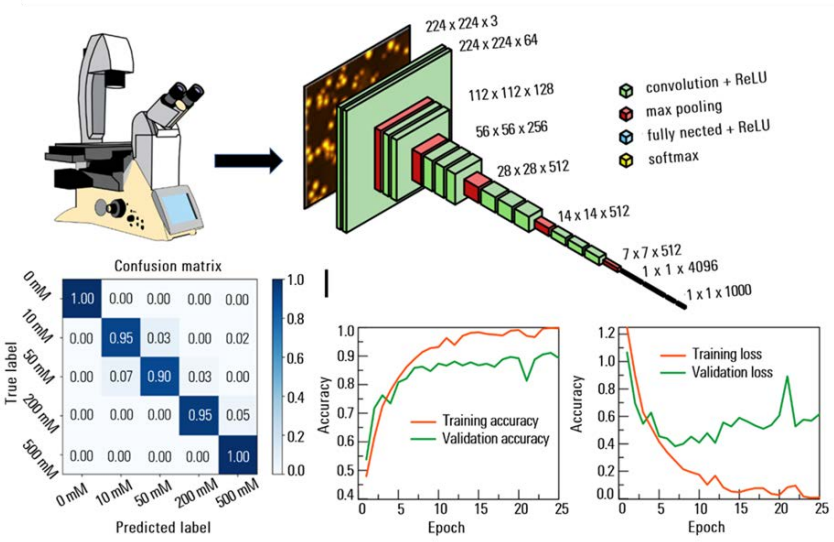

Fig. 1. CNN VGG16 architecture and prediction results

OP-8

We coded a program to automatically predict concentration and get statistical data from the samples. One question that stays open is the change of structure according to magnesium ions concentration. We suppose that reflex bind with interplanar space should increase with the increase of ions concentration. We suppose to use SAXS/WAX method to analyze it.

Acknowledgement: The work was carried out with the support of the Ministry of Science and Higher Education of the Russian Federation (agreement № 075-15-2021-1349).

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OP-9

ARPES Synchrotron Study of Localized Charge Carriers in HTSC YBCO Cuprates

Titova S.G.[1], Shkvarin A.S.[2], Lukoyanov A.V.[2], Pryanichnikov S.V.[1], Chumakov R.G.[3], Lebedev A.M.[3]

1 – Institute of Metallurgy, RAS Urals Branch, Ekaterinburg, Russia

2 – Institute of Metal Physics, RAS Urals Branch, Ekaterinburg, Russia

3- National Research Center "Kurchatov Institute", Moscow, Russia

sgtitova@mail.ru

For high-superconducting YBCO cuprates the height of CuO_5 pyramids has a minimum at temperature between ~150 *K* and ~250 *K.* According to band structure calculations [1] the short Cu-O bond length corresponds to an emergence of electronic states peak at ~ 0.4 eV below Fermi level due to localized charge carriers [1]. By means ARPES for $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{6.8}$ single crystal we have found an experimental evidence for this feature in band structure.

The measurements were performed using PHOIBOS225 hemispherical analyzer mounted on the NanoPES beamline in the Kurchatov synchrotron radiation source. The spectra were measured at 20 K and at higher temperature using 34.6 and 90.2 eV photon energy. Used excitation energy corresponds to the point of about 0.05 and 0.26 $k_{\perp}/k_{\Gamma\text{-}Z}$ in the $k_{\perp}$ (G-Z) direction, respectively. The results are shown in Fig. 1

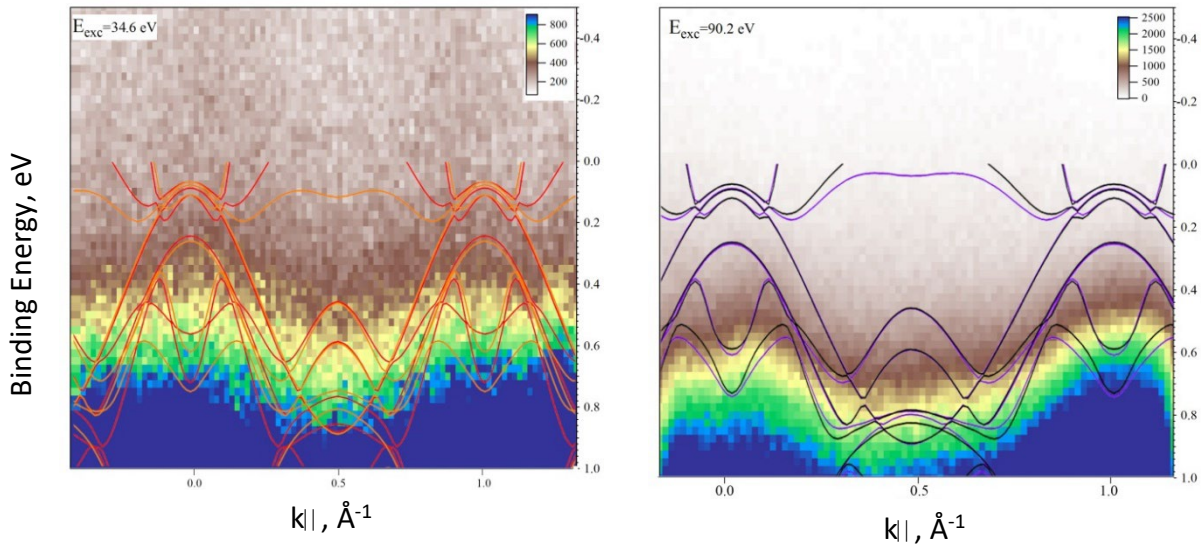

Fig. 1. ARPES for $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{6.8}$ single crystal at 20 K with 34.6 eV (left) and 90.2 eV (right) photon energy.

The experimental data are in a good agreement with calculations and confirm charge carrier localization at compression of the CuO_5 pyramids in the crystal structure.

Acknowledgement: This work was performed within theme No 122013100200-2 (Institute of Metallurgy, RAS Urals Branch).

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OP-10

Application of Synchrotron Radiation for In Situ XRD Investigation of Hydrogen Desorption from Composites Based on Hydrides and Nanomaterials

Kudiiarov V.N., Kurdyumov N.E., Elman R.R., Pushilina N.S.
Tomsk Polytechnic University, Tomsk, Russia
kudiyarov@tpu.ru

Magnesium hydride is considered one of the most promising hydrogen storage materials, although it nevertheless has some problems, such as the high value of the activation energy of hydrogen desorption. To solve this problem, some scientists have proposed adding nanomaterials, in particular metal-organic frameworks or carbon nanotubes, to magnesium hydride. Currently, a detailed understanding of the mechanisms of obtaining composites based on magnesium hydride and nanomaterials is lacking, as is our understanding of the effect of additives on the activation energy and temperature of hydrogen desorption depending on the parameters of the composite synthesis. In addition, the data obtained at various values of milling parameters are very different, and in some works the effect of nanomaterials on the hydrogen properties of magnesium hydride was not confirmed at all. Thus, it is important to determine the effect of nanomaterials additives on the properties of hydrogen storage of magnesium hydride under various milling parameters. This work is devoted to the application of synchrotron radiation for In Situ XRD investigation of hydrogen desorption from composites based on hydrides and nanomaterials. In situ X-ray diffraction measurements of the process of thermo-stimulated decay of magnesium hydrides were carried out at the station "Precision diffractometry» at Siberian Synchrotron and Terahertz Radiation Center of the Budker Institute of Nuclear Physics. Measurements were performed using SR from the VEPP-3 storage ring.

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OP-11

Efficiency of the SR Scattering for the Study of the Coupling of the Antiferrodistortive Oxygen Modes in Perovskites

Vakhrushev S.B.[1], Petroukhno K.A.[1,2], Filimonov A.V.[1,3]
1 – Ioffe Institute, St.Petersburg, Russia
2 – Peter the Great St.Petersburg Polytechnic University, St.Petersburg, Russia
3 – Alferov University, St.Petersburg, Russia
s.vakhrushev@mail.ioffe.ru

Many perovskite-like crystals undergo antiferrodistortive (AFD) phase transitions related to the condensation of the soft modes SM at the Brillouin zone (BZ) boundaries. These SMs are associated with the parallel (M_3) or anti-parallel (R_{25}) rotation of the oxygen octahedra. Mode softening should result in the critical growth of the diffuse scattering intensity at M or R points of the BZ. However in the case of the X-ray scattering at around M-points instead of the Lorentzian-shaped peak centred at the M-point temperature dependent DS scattering with the maximum shifted to one side of the M-point and minimum to the other side is observed. Such asymmetric scattering was never reported for the neutron scattering.

We have studied the critical behaviour in the vicinity of M-point of the BZ in several perovskite-like crystals including Zr-rich PbZr1-xTixO3 (PZT) [1,2]solid solutions with x<0.06 and $PbMg_{1/3}Nb_{2/3}O_3$- $PbSc_{1/2}Nb_{1/2}O_3$ (PMN-PSN) using high-resolution X-ray (synchrotron radiation) inelastic scattering (IXS) and diffuse scattering techniques. Lattice dynamics of the pure $PbSc_{1/2}Nb_{1/2}O_3$ was studied using inelastic neutron scattering [3]. The observed phenomena in terms of coupling between the AFD M3 mode and the transverse acoustic phonons. We demonstrated that the effect is easily observed in the case of the X-ray scattering, but surprisingly is strongly suppressed for the neutron scattering. The details of the developed model will be discussed.

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OP-12

Analysis of Total X-Ray Scattering Data at Studying Nanostructure of γ-Al_2O_3

Pakharukova V.P.[1,2], Yatsenko D.A.[1,2], Gerasimov E.Yu.[1,2], Tsybulya S.V.[1,2]
1 – Boreskov Institute of Catalysis, Novosibirsk, Russia
2 – Novosibirsk State University, Novosibirsk, Russia
verapakh@catalysis.ru

Among all the oxide materials used in the catalysis, nanocrystalline metastable aluminas (γ-, η-, χ- Al_2O_3) seem to be the most employed as catalysts and catalyst supports. However, details of their structure are still under discussion and investigation. Structure solving is strongly complicated by high dispersion and defectiveness of the metastable aluminas. As a rule, the crystal structure of all the forms is described as defective spinel structure. However, none of the proposed crystallographic models is suitable for structure refinement, for example, by the Rietveld analysis. The crystallographic models do not describe the characteristic features of powder X-ray diffraction (XRD) patterns such as anisotropic broadening of the Bragg peaks with equivalent hkl indices and pronounced diffuse scattering. At the same time, these features are the criteria for differentiating the metastable Al_2O_3 phases at XRD phase analysis. The current studies move toward analysis of a real structure of the nanocrystalline Al_2O_3 phases. The concept of classification of Al_2O_3 forms on the base of their nanostructure features was proposed [1]. The particles of the various Al_2O_3 polymorphs were suggested to differ in the prevailing planar defects, the shape and stacking of crystalline blocks. A simulation of XRD patterns for 1D disordered crystals allowed one to suggest planar defects typical for different Al_2O_3 phases. However, models of 1D disordered crystals did not allow one to describe XRD profiles completely. The development of the method of direct calculating XRD patterns from model nanoparticles with use of the Debye scattering equation (DSE) [2] allows us to continue studying the nanostructure of Al_2O_3 oxides. Generation of 3D models of nanostructured particles with a certain habit and stacking of primary crystalline blocks and direct calculation of corresponding XRD profiles makes it possible to analyze diffraction effects related to specific planar defects and stacking faults.

In this work, commercially available γ-Al_2O_3 powders used for catalyst production were studied with regard to their nanostructure. A deep analysis of high-resolution transmission electron microscopy (HRTEM) data as well as total X-ray scattering data, including both Bragg peaks and defect-related diffuse scattering, was performed. The atomistic models of 3D nanostructured γ-Al_2O_3 nanoparticles were constructed and validated by the Debye function analysis (DFA) and atomic pair distribution function (PDF) analysis. The experimental X-ray scattering data for the PDF analysis were obtained using synchrotron radiation. The original DIANNA program [3] was used for developing atomistic models of nanostructured particles and their verification by the DFA and PDF methods.

It was revealed that in γ-Al_2O_3 particles the specific planar defects disturb the cation sublattice and keep anion sublattice intact. The fragmentation of cation sublattice leads to

separation of nanometer-sized crystalline blocks by partially coherent interfaces. The planar defects lying on {100} and {111} crystallographic planes determine the shape of primary crystalline blocks. The proposed models of 3D nanostructured γ-Al_2O_3 particles are in agreement with the HRTEM data on structural organization of particles and PDF data on the atomic arrangement [3].

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OP-13

In Situ Time-Resolved XAS Study of Core@Shell Pd@PdO Structures

Usoltsev O.A.[1], Skorynina A.A.[1], Bugaev A.L.[1,2], Kozyr E.G.[1], Pnevskaya A.Yu.[1], Stoian D.[3], Pellegrini R.[4], van Bokhoven J.A.[5,6], Soldatov A.V.[1]

1 – Southern Federal University, Rostov-on-Don, Russia

2 – The Southern Scientific Centre of The Russian Academy of Sciences, Rostov-on-Don, Russia

3 – ESRF, Grenoble, France

4 – Chimet S.p.A., Arezzo, Italy

5 – ETH Zurich, Zurich, Switzerland

6 – Paul Sherrer Institute, Villigen, Switzerland

alinaskorynina@gmail.com

Supported palladium nanoparticles (Pd NPs) are extensively used in important catalytic reactions such as oxidation of alcohols or methane combustion. It is known that presence of oxygen in the reaction results in the formation of palladium oxide phase which affects the catalytic activity of the material. Here, we investigate the type of oxide phase, the rate of the phase formation and decomposition and the stability of surface and bulk oxides for differently sized supported Pd NPs by in situ X-ray absorption spectroscopy (XAS).

The experiments were performed at the BM31 beamline of the ESRF using commercial Pd catalysts provided by Chimet S.p.A. ($Pd@Al_2O_3$ with NP size of 3 nm, and Pd@P4VP with NPs size of 1 nm, and Pd microparticles). The treatment procedure included alternate switching of hydrogen and oxygen streams at various temperatures (50, 100, 150, 180, 220, 260, 300, 400 °C). XAS spectra were collected every 10 s and were analysed in both XANES and EXAFS region providing the evolution of Pd oxidation state and changes in the local structure from 12-coordinated metallic Pd to 4-coordinated surrounding in Pd oxide.

XAS spectra were processed in Python 3.7 using self-written procedures for data alignment, normalization, PyFitIt [1] and pyMCR libraries for principal component analysis and multivariate curve resolution analysis [2] of XANES spectra, and Larch library [3] for EXAFS fitting.

The experimental data were complemented by theoretical simulations of the oxidation process over ns timescales using ReaxFF potentials [4, 5]. Molecular dynamics simulations with were performed and visualized in AMS v.2021.1 software. The fcc-like cuboctahedron particle of 561 Pd atoms was placed in cubic box with a = 10 nm and surrounded by 1000 oxygen molecules. The simulations were run at constant temperature with Nosé-Hoover thermostats (damping constant 100 fs). The total simulation time was set to 1 ns, with the integration time of 0.25 fs.

The following results were obtained:

i. Surface palladium oxides are formed immediately upon exposure to molecular oxygen in the temperature interval 50 – 400 °C.

ii. Core-shell structures with metallic core and 4-coordinated palladium oxide shell are formed.

iii. Above 200 °C palladium oxide phase extends from surface to bulk resulting in the formation of full palladium oxide particles.

iv. Particles with smaller size demonstrate higher degree of oxidation due to higher surface-to-bulk ratio.

v. Both surface and bulk oxides are easily reduced in hydrogen at all studies temperatures.

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OP-14

Microfluidic Technologies for Adsorption-Based Industrial Water Remediation

Rajput P., Bugaev A.L., Skorynina A.A., Soldatov A.V.
The Smart Materials Research Institute, Southern Federal University, Sladkova 174/28, 344090 Rostov-on-Don, Russia
priyadarshanirajput22@gmail.com

Removal of heavy metals (HMs) from wastewater is a major issue and development of a novel and eco-friendly approach to remediate polluted water is urgently required. Therefore, this work was aimed to combine modern laboratory and synchrotron analytical techniques, various porous materials and microfluidic technologies to optimize the HMs sorption from model and real industrial wastewater.

Sorbent materials were prepared as mechanical mixtures of activated carbons, zeolites and MOFs in different ratios. The sorbents were filled inside the microtubes connected to an automated microfluidic system with the controlled flow rate. The filtered water was analyzed by atomic absorption spectrometry (AAS) and conductivity measurements (both online and offline). Both AAS and conductivity data showed that a bigger fraction of zeolite-Y gave worse performance for Pb. Bigger fraction of coconut charcoal performed worse for Ni while for UiO-66 MOF it was vice-versa. For Zn, coconut charcoal showed significant performance, and for Cu and Cd, charcoal performed better than MOF. All mixtures performed well for Pb.

The spatial distribution of HMs in the used filters were determined by X-ray fluorescence (XRF), which showed higher concentration of ions at the edges of the filters, explained by the different flow rate due to the friction from the tube walls. XANES data collected at Kurchatov Institute indicated Pb^{2+} as the most abundant species in the used filters (Fig. 1).

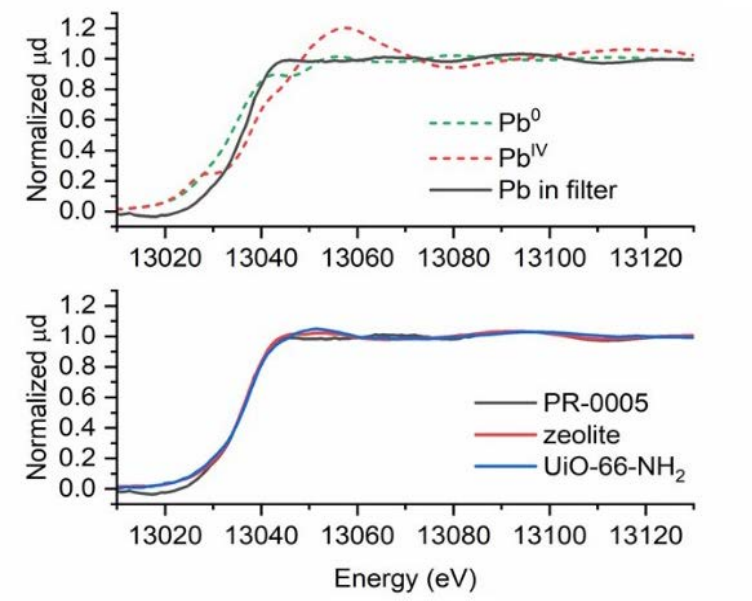

Fig. 1. Pb L_3-edge XANES data for used filters and reference samples

The obtained results allowed us to estimate the performance of filtration towards different HMs as the function of filter composition. Conductivity was proved as an efficient approach for fast online analysis of the filtration quality. Low-cost microfluidic setup worked successfully for water filtration. X-ray based techniques, namely XANES and XRF provided the oxidation state of Pb, as a most abundant HM in the industrial wastewater used, and, respectively, the special distribution of the adsorbed ions in the used filters, which is important for optimizing the filter composition and geometry for practical applications. The future plans are to upgrade the microfluidic system for scalable and parallel testing of filtration quality depending on the filter composition and shape, column geometry, pH, flow rate, etc.

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OP-15

XPS Profiling of Iron Oxide Nanocoatings on the Surface of Porous Alumina Obtained by the Air Oxidation of Magnetron Deposited Iron Films

Valeev R.G., Beltiukov A.N.
Udmurt Federal Research Center of UB RAS, Izhevsk, Russia
rishatvaleev@udman.ru

Due to different magnetic effects in Iron Oxide films such as spin-polarization of electrons in magnetite (Fe_3O_4), magnetoelectric properties in hematite (Fe_2O_3) and antiferromanetic properties of wustite (FeO) they have potential application in spintronics, magnetoelectricity and high density memory devices [1,2]. Moreover, we suppose Iron Oxide coatings obtained on hexagonal oriented porous media can show chirality of magnetic structure. It should be noted that the manifestation of properties mentioned above strongly connected to the thickness of coatings, their electronic and local atomic structure.

In this work for obtaining of Iron Oxide coatings on the surface of porous alumina we propose magnetron deposition technique of Iron followed by thermal annealing in oxygen atmosphere. Porous alumina templates were obtained by anodization process of aluminum foil. The aim of this work was to get closer to the understanding the mechanism of formation of Iron Oxide by XPS profiling in binding to SEM image of cross section and reveal the chemical state of Iron Oxide in the surface, film volume and interface near the porous alumina surface.

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OP-16

Resonant Inelastic X-Ray Scattering

Polyutov S.P.[1], Kimberg V.[1,2], Odelius M.[3], Ignatova N.Yu.[1], Krasnov P.O.[1], Föhlisch A.[4], Gel'mukhanov F.[1,2]

1 – Siberian Federal University, Krasnoyarsk, Russia
2 — Royal Institute of Technology, Stockholm, Sweden
3 – Stockholm University, Stockholm, Sweden
4 – University of Potsdam, Potsdam, Germany
polyutov@mail.ru

Scattering of photons, electrons, and neutrons is utilized in many experimental probes for investigation of the structure of matter and of dynamical processes. We focus here on two spectroscopic techniques, initially enabled by the appearance of x-ray synchrotron radiation light sources. We refer to resonant inelastic x-ray scattering (RIXS) and resonant Auger scattering (RAS) [1-6]. Presently two contemporary sources of polarized intense x-ray radiation are in use. The first category is third-generation synchrotron radiation sources with the storage rings optimized for the use of undulator radiation, while the second category is x-ray free-electron lasers (XFELs) [1-6]. XFELs are in turn subdivided into XFELs based on self-amplified spontaneous emission (SASE), seeded-XFELs in which an external laser is used to initiate the emission process and self-seeded XFELs [1]. Elemental selectivity of X-ray spectroscopy, greatly simplifying the spectrum (compared to optical and ultraviolet spectroscopy), gives detailed information about the local electronic structure in complex systems since, conceptually, an atom projected contribution to the electronic states can be determined. This makes RIXS unique tool in studies of local structure of disordered system like liquids.

In our talk, the most important achievements in investigations of coupled electron-nuclear dynamics in free molecules and structural aspects in studies of liquids and solids are outlined. A special attention will be paid to such a feature of RIXS as unique opportunity to study matter not only in static but also in dynamics using technique of variable scattering duration [1]. The concept of the scattering time varied by the detuning from X-ray absorption resonance allows us to study the electronic-vibrational dynamics and ultrafast dissociation in real time with a femtosecond time resolution [1, 2] without using pump-probe methods with short (femtosecond) x-ray pulses. There is yet another powerful method for studying ultrafast dynamics, namely, core-hole clock technique [4, 7]. This method is used to study the charge-transfer dynamics at interfaces and surfaces with the lifetime of the core hole as an internal reference clock to follow the charge-transfer process. One of the main numerical methods used in our simulations of RIXS and RAS spectra and dynamics is the time-dependent wave packet technique. The advantages of this method relative to the time-independent approach are most pronounced in the case of dissociative states. The developed theory with the corresponding software allowed us to investigate intra- and intermolecular interactions

faraway from equilibrium and to extract from the experimental RIXS data potential energy surfaces [1]. Recently we achieved an experimental realization of the Einstein-Bohr recoiling double-slit gedanken experiment by using RAS from molecular oxygen in an electron-ion coincidence arrangement [1]. Our results are fully compatible with quantum mechanical complementarity. Not so long ago resonant X-ray spectroscopy started to be used for the solution of such a fundamental problem as structure of liquids. Unlike the gaseous and crystalline media, a liquid is more difficult object of study due to its inherent disorder and the fluctuations of the local structure. Therefore, the use of complementary physical methods (to conventional small-angle X-ray and neutron scattering) is necessary to obtain a consistent picture of liquids. Recently we successfully applied the X-ray absorption and RIXS to get insight in the local structure of such important liquids as water, methanol and acetic acid [1]. Coherence of RIXS process and related momentum conservation law [1] allowed to extract from the experimental data the band structure, the dispersion laws of phonons and magnetic excitations as well as parameters of electron-phonon interaction of solids. Due to increase of resolving power of RIXS we evidence significant progress in RIXS studies of magnetic properties and collective excitations in high-temperature superconductors [1, 3, 6].

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OP-17

Single Crystal X-Ray Diffraction at High Pressures: Equipment, X-Ray Source and Other Aspects

Zakharov B.A.
Boreskov Institute of Catalysis, Novosibirsk, Russia
Novosibirsk State University, Novosibirsk, Russia
b.zakharov@yahoo.com

High pressures can influence the structure of different materials leading to a number of interesting phenomena like phase transitions, changes in conductivity, amorphisation *etc*. Pressures can also be used for chemical synthesis and often lead to formation of previously unknown solvates and clathrates. In order to understand all these phenomena one needs to know exact structure changes caused by high pressure. X-ray diffraction with diamond anvil cells (DACs) is widely used to determine crystal structures for most organic, inorganic and biological crystalline samples. The quality of diffraction data is critically important for obtaining reliable information on atomic coordinates and intermolecular distances. Therefore all types of high-pressure studies require rigorous experimental planning and careful choice of equipment, data collection and data treatment strategy since the crystal is not “free” but located in confined environment in hydrostatic liquid inside DAC with certain construction with limited opening windows for X-ray probe. A lot of questions can arise on planning the experiment: which pressure transmitting media to choose? how fast the pressure should be increased? Is not it better to perform all the experiments at synchrotron rather than at lab source if I have this opportunity? Which SR generation device to choose? which factors should be taken into account on data collection and reduction? This list of issues is quite far from being complete. The aim of my contribution is to give a brief overview of the most interesting and useful generally arising questions and try to answer them. I would also like to highlight the importance of considering some “hidden” factors like choice of pressure transmitting media, pressure variation protocol and diffraction equipment while planning and performing the diffraction measurements to obtain the most reliable results of high-pressure experiment.

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OP-18

X-Ray Scanning Photoemission Microscopy (SPEM) as a Tool for Studying the Morphology of the Layered Transition Metal Dichalcogenides

Merentsov A.I., Shkvarin A.S., Titov A.N.
M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, Ekaterinburg, Russia
Alexander.Merentsov@urfu.ru

Solid solutions based on layered transition metal dichalcogenides TCh_2 (T – 3,4d-transition metal, Ch = S, Se, Te) are promising material for use as a cathode in lithium batteries. Preliminary study of the electronic structure of $Cr_xTi_{1-x}Se_2$ single crystals using X-ray photoelectron spectroscopy revealed two Se 3d peaks typical for $TiSe_2$ and $CrSe_2$ [1]. This unusual structure of the Se 3d core-level spectrum allowed to propose the existence of the structural fragments (SFs) of the different composition and electronic structure within the single crystal. To study the electronic structure of these fragments we used the X-ray scanning photoemission microscopy (SPEM) technique, which allow to obtain 100×100 μm images at areas corresponding to different core-level spectra. To study the morphology and electronic structure of the $Cr_xTi_{1-x}Se_2$ and $Cr_xTi_{1-x}S_2$ single crystals, we used Scanning PhotoElectron Microscope located on the ESCA Microscopy beamline at the Elettra synchrotron facility (Trieste, Italy). SPEM measurements were carried out using photon energy of 651 eV (the total energy resolution of 200 meV) and microspot size of 120 nm. The photoelectrons were collected and analyzed with a SPECS-PHOIBOS Class 100 hemispherical analyzer equipped with a 48-channel electron detector. In the SPEM the X-ray beam is focused on the sample by a Fresnel Zone-Plate focusing optic and the chemical images are acquired by collecting core level photoelectrons emitted within the relevant kinetic energy window while raster scanning the specimen with respect to the microprobe [2]. The 48 channels electron detector allows to highlight in the image the lateral distribution of the different chemical states and to remove the topographic contributions. At each scanned position the corresponding 48 points XPS spectrum defined by the selected window energy is stored. We found that the chemical bonding within the SFs in $Cr_xTi_{1-x}Se_2$ and $Cr_xTi_{1-x}S_2$ depends on the type of chalcogen atom: $CrSe_2$-based and $TiSe_2$-based SFs are formed in selenides, and solid solutions $Cr_xTi_{1-x+y}S_2$ with different Ti stoichiometry are formed in sulfides [3]. The formation of SFs was also observed in $V_xTi_{1-x}Se_2$ using angular-resolved X-ray photoelectron spectroscopy (ARPES) complemented with atomic force microscopy (AFM) data [4].

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OP-19

XPS and NEXAFS Analysis of Interface Structure of Fe/SiO_2 Heterogeneous Materials Prepared by Surfactant-Assisted Wet Ball Milling

Syugaev A.V.[1], Maratkanova A.N.[1], Yazovskikh K.[1], Makarova A.A.[2]
1 – Physical-Technical Institute UdmFRC UB RAS, Izhevsk, Russia
2 – Institute of Chemistry and Biochemistry FU Berlin, Berlin, Germany
k.yazovskikh@bk.ru

The fabrication of electromagnetic interference shielding materials is of crucial importance for various applications, such as protection of biological objects from electromagnetic radiation or providing long-term and proper performance of electronic equipment in communication devices. Specific properties and low cost of Fe-based materials could make them promising electromagnetic wave absorbers, but their inherently weak magnetocrystalline anisotropy and attenuated permeability limit their applications over a wide frequency range. The study considers silica- and surfactant-assisted wet ball milling of carbonyl iron powder as a simple way to produce plate-like silica-modified iron particles with a high aspect ratio. As compared to particles of spherical or stone-like shape, plate-like iron particles provide improved characteristics, i.e. higher permeability arisen from the shape-dependent Snoek's law and substantial suppression of the eddy current effect [1]. Reducing eddy current losses can be also reached by using iron particles which are as fine as skin depth (~1 μm and less) and insulator-isolated, and desired surface anisotropy being provided due to modified electronic state of atoms in the surface layer [2].

The samples were prepared by co-milling of carbonyl iron and 20 vol. % silica glass powders in *n*-heptane and *n*-heptane with added surfactants (stearic acid (SA) or perfluoro-*n*-nonanoic (PFNA) acid) at 800 rpm for 24 h. The mass ball-to-powder ratio was 20:1. Fig. 1 shows SEM images for the particles formed under milling (1) and the insoluble precipitate of SiO_2 particles (2) remained after the dissolution of (1) in concentrated hydrochloric acid. As seen, the as-milled Fe particles and SiO_2 precipitates are similar in their morphology.

The study gives the insight into the processes in surfaces/interfaces of the iron particles under their silica- and surfactant-assisted wet ball milling. The structure of the as-formed interface has been analyzed by means of X-ray photoelectron and Near-edge X-ray absorption fine structure spectroscopies. The XPS and NEXAFS spectra were acquired at the Russian-German dipole beamline (RGBL Dipole) at the BESSY II, HZB Berlin GmbH. Figure 2 shows schematically the structure of interfaces in the samples studied. Under milling, silica glass is finely powdered and its mechanical rubbing into ductile iron particles induces chemical transformations at interfaces between iron and silica followed by the formation of various products. Surfactants are then adsorbed on silica-enriched particle surfaces. In the case of SA, the surfactant is attached through the hydrogen bonds between the carboxyl and silanol groups of the outermost hydrated layer, whereas PFNA is adsorbed through carboxylates formed with iron atoms in the outer silicate layer.

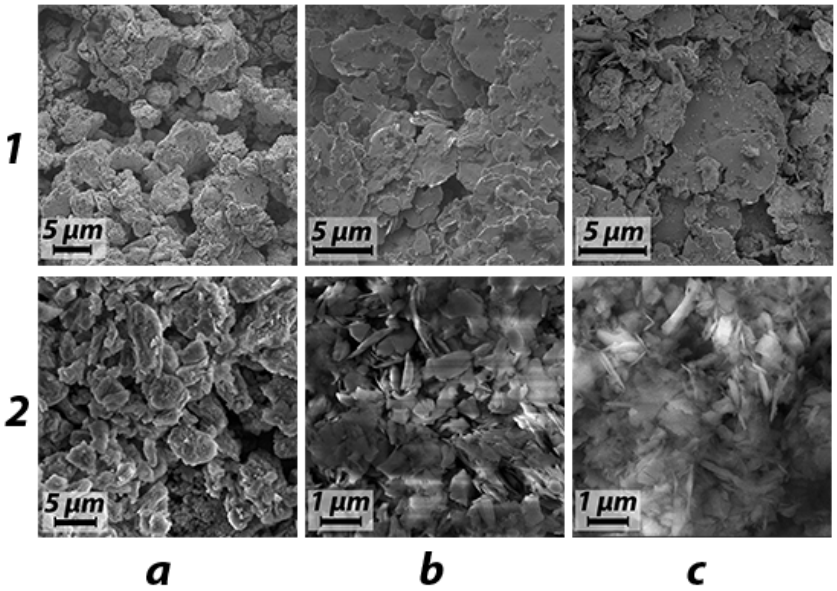

Fig. 1. SEM images of (1) particles formed under co-milling of carbonyl iron and silica glass powders in n-heptane (a) and n-heptane with added SA (b) and PFNA (c); (2) SiO_2 precipitates

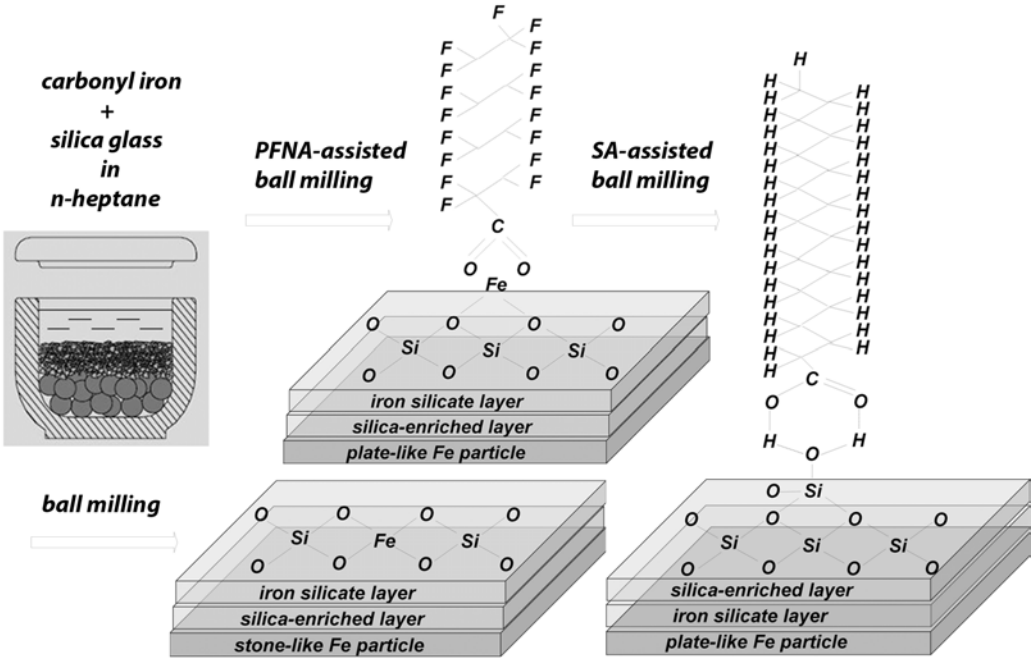

Fig. 2. Schematics of the interface structure

The angle-dependent NEXAFS analysis has shown that the surface layer composition is not critical in the arrangement of the tails of adsorbed surfactant molecules, which are predominantly oriented up-right relative to the plane of mostly planar-arranged particles.

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OP-20

X-ray Resonant Reflectometry as a Multifunctional Synchrotron Method for Studying Magnetic Nanofilms

Suturin S.M., Dvortsova P.A., Korovin A.M.
Solid State Physics Dept., Ioffe Institute, St. Petersburg, Russia
suturin@mail.ioffe.ru

Abstract — X-ray resonant magnetic reflectometry is a synchrotron based non-destructive method of investigation of electronic and magnetic depth profiles in nanoscale multilayers. The choice of x-ray photon energy close to the absorption edges makes the method selective to oxidation state, crystallographic environment and magnetization of individual chemical elements. The enhanced technique dealing with acquisition and modelling of the angle-energy maps of resonant reflectance is discussed in the present contribution.

I. Introduction

The synchrotron method of x-ray resonant reflectometry is based on measuring reflectance of epitaxial multilayer heterostructures as a function of incident angle and photon energy. The measurements are carried out across the absorption edges of individual chemical elements, which makes the method highly sensitive to the oxidation state, crystallographic environment and magnetic state of the involved atoms. The method can be effectively used to perform a non-destructive depth-resolved element-selective structural, chemical and magnetic analysis of functional multilayer heterostructures for nanoelectronics and spintronics. Despite the many benefits of the described technique, currently there exist not so many works dedicated to resonant X-ray reflectometry due to the difficulties in accurate determination of the optical constants near the absorption edges. The existing software packages used to simulate reflectometry data [1], [2], [3] assume that the optical constants at the used photon energies are known. The often-used approach is to extract the imaginary part from the separate X-ray absorption measurements and to derive the real part using the Kramers-Kronig transformation. This approach is not very accurate since the absorption spectra are often measured with distortions. Moreover, the spectral shape of the optical constants in the studied heterostructure may differ from those of the reference material due to the variation of crystallographic environment, stoichiometry, oxidation state and magnetic state.

II. Discussion

In the present contribution we describe a synchrotron-based approach to the study of thin iron oxide magnetic films. In this study we measure and model 2D reflectivity maps describing the dependance of x-ray reflectance on the incident angle, photon energy, photon helicity and external magnetic field. A high-end software has been developed to perform the on-the-fly analysis, simulation and fitting of the resonant reflectance maps. The developed software uses the differential evolution algorithm with calculations carried out on the GPU to fit reflectance maps.

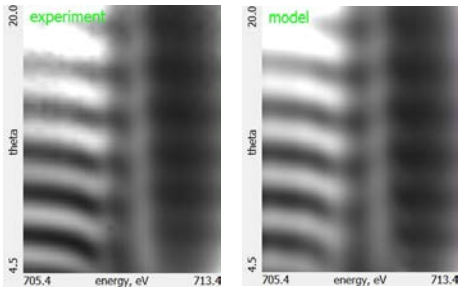

Fig. 1. Resonant reflectance maps in YIG (111) film measured experimentally (left) and modelled (right).

The modeling can be performed by using the initially known shapes of the optical constants or by blind-fitting the optical constants spectral shapes with an automatic fulfillment of the Kramers-Kronig relations [4]. In the latter approach a very good agreement between the experimental and modeled reflectance maps can be achieved (Fig. 1). The proposed technique is supposed to become an effective tool to non-destructively investigations of the depth profiles of important physical properties within nanoscale epitaxial heterostructures involved in fabrication of novel electronic / spintronic devices.

Acknowledgement: The study was funded by Russian Science Foundation (project 22-22-00763).

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OP-21

Study of co-Crystals of L-Ascorbic Acid with Amino Acids by X-Ray Diffraction Analysis in a Wide Range of Temperatures and Pressures

Arkhipov S.G.[1,2], Kolybalov D.S.[2], Boldyreva E.V.[1,2]
1 – Boreskov Institute of Catalysis, Novosibirsk, Russia
2 – Novosibirsk State University, Novosibirsk, Russia
arksergey@gmail.com

Molecular crystals formed by small molecular compounds can be divided into the following groups: solvates, molecular salts, co-crystals and ionic co-crystals. The term "salt" includes molecular crystals of the A^+B^- type, during the formation of which H^+ is transferred from B molecule to the molecule A. If there is no transfer of a proton and a compound AB is formed, this compound is called "co-crystal". However, the molecules that build the co-crystal structure can have a partial effective charge. External influences, such as low temperature and high pressures, affect both the value of the effective partial charge and the geometry of the molecules that build the molecular crystal [1]. This work presents the results of studying a L-ascorbic acid L-serine cocrystal by single crystal X-ray diffraction in the temperature range from 300K to 100K (with a step of 25K) and pressures from 1 atmosphere to 5.2 GPa (with a step of approximately 0.5 GPa), as well as for L-ascorbic acid sarcosine cocrystal in the wide temperature range. For each structure, the partial effective charges were calculated and the relationship between the partial effective change of the L-ascorbic acid molecule and the conformation changes of this molecule was analysed.

Acknowledgement: This work was supported by the Russian Presidential Research Grant (grant 075-15-2022-607); the work was carried out jointly by Boreskov Institute of Catalysis (project AAAA-A21-121011390011-4) and Novosibirsk State University (project Priority 2030). The equipment of MDEST laboratory at NSU was used for in-house diffraction experiments.

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OP-22

X-Ray Microtomography for in Situ Study of Evolution of Liquid Hydrocarbons in the Pore Structure of Catalyst

Mordkovich V.Z., Sineva L.V., Asalieva E.Yu.
Technological Institute for Superhard and Novel Carbon Materials, Troitsk, Moscow, Russia
mordkovich@tisnum.ru

Fischer–Tropsch synthesis is a catalytic process of synthesis gas conversion into liquid hydrocarbons The process is relevant for the applied material and, even more, for environmental research, as it is particularly important for the biofuel production, city garbage utilization and natural gas monetization into alternative clean synthetic fuel. The ability of composite catalyst to remove the released heat is provided not only by its thermal conductivity, but also by availability of meso- and macropores [1], which provide intensified mass transfer and lower diffusion limitations. Mass transfer is essential for the process [2, 3]: notwithstanding that the reactants exist in the gas phase, catalyst pores are filled with liquid products.

Normally efficiency of reaction is evaluated indirectly by real-time material balance and temperature-programmed sorption/desorption technique after reaction is over. There is no technique for in situ insight into intragrain/intrapore processes, which serve a genuine drive for catalytic efficiency.

Preliminary µCT images of a used catalyst show that features with characteristic size more than 5 µm can be clearly distinguished and that debris can be seen. It is expected that upon filling with a liquid, contrast of a pore should change and it must be possible to investigate origination and diffusion of hydrocarbons.

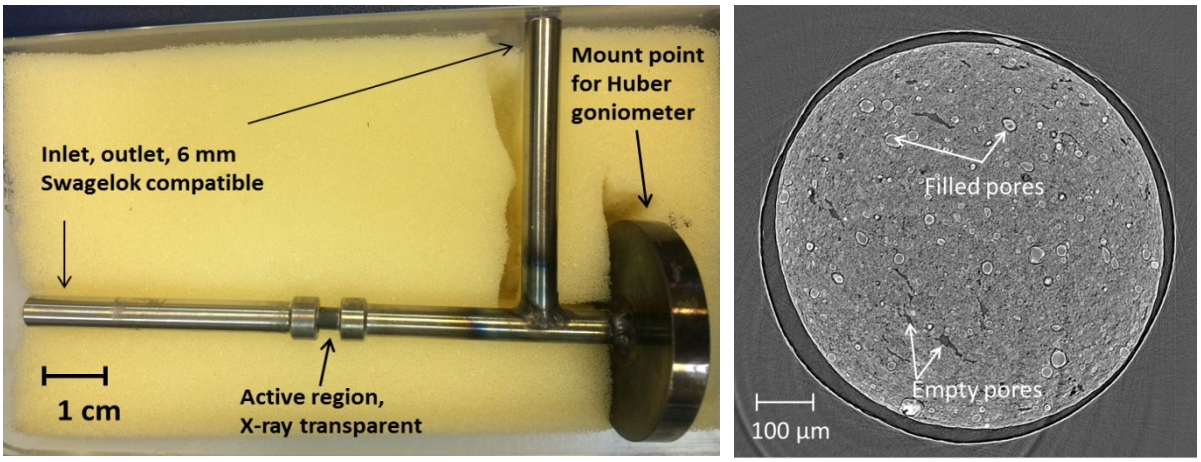

Fig. 1. CT compatible reaction cell (left panel). Reconstructed image of catalyst in the cell (right panel)

Ultra-fast, absorption-based X-ray microtomography (µCT) is required to perform time lapse studies of the evolution of liquid hydrocarbons in the pore structure of catalyst. One would need the X-ray beam with mean energy of ~17 keV, relative energy bandwidth of 2-3%, homogeneous intensity distribution at the sample with the field of view of ~ 2×2 mm^2. Experimental station must be equipped with a rapid CT stage. It is important that the number

of photons at sample must be sufficient to acquire 3000 projections in 2–3 minutes, which demands flux density of about 1012 photons/sec/mm^2.

Measurements are to be organized as follows: catalyst is loaded in the reaction cell and is activated in a stream of pure hydrogen for one hour (total amount of gas ~10 ml) at T=400° C. Then the operator switches the gas stream to the $CO+H_2$ mixture and reduces temperature to 180° C. Reaction begins at this point and continues for about 16 hours and CT snapshots of catalyst are acquired every 10–15 minutes over the entire duration of the chemical reaction.

We have developed a specific container made of a single crystal diamond, which allows maintaining reaction conditions and compatible with tomographic imaging — see Fig. 1. This container has inlet and outlet to enable gas flow. It is integrated by means of flexible high quality PTFE gas pipes in a sealed gas supply system, which start with gas cylinder and ends with a bag collecting reaction waste. Heating is provided by means of hot-air blower device(s) with programmable settings. Samples are small cylindrically shaped rods with diameter of <2 mm and length <5 mm; they can be loaded in the container after it is disconnected from the gas pipes.

We have done preliminary experiments in frame of ESRF collaboration program and showed that both pore system and liquid flow can be detected successfully — see Fig. 2. We believe that application of more advanced synchrotron facilities may bring quite exciting results revealing mechanisms of flow-and-diffusion control in heterogeneous catalysis.

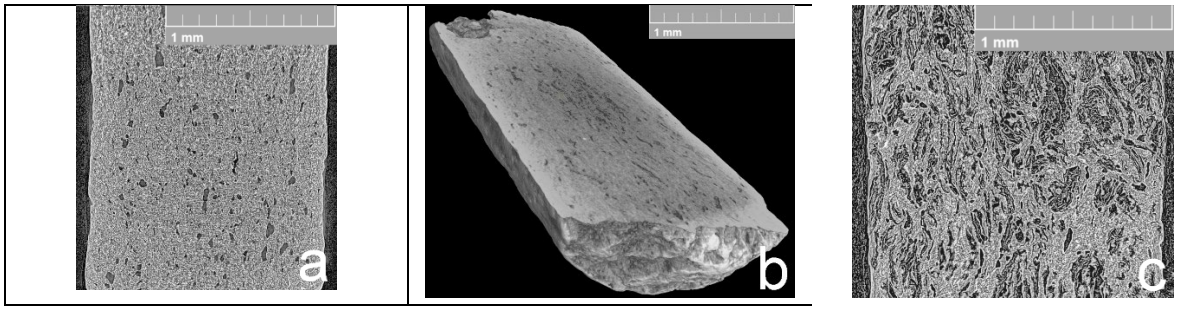

Fig. 2. µCT visualization of catalyst pellets of CoAl and CoG catalysts after our work [5]: CoAl cross-section (a);3D visualization of a halved pellet at the example of CoAl (b); CoG cross-section (c)

Acknowledgement: The authors thank S. Gasilov for help in preliminary experiments.

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OP-23

Radiation-Resistant Luminescent Diamond Composites for Imaging High Power X-Ray Beams

Kuznetsov S.V.[1], Sedov V.S.[1], Drobysheva A.R.[1], Martyanov A.K.[1], Batygov S.Ch.[1], Ermakova Yu.A.[1], Alexandrov A.A.[1], Rezaeva A.D.[1], Voronov V.V.[1], Tiazhelov I.A.[1], Tarala V.A.[2], Vakalov D.S.[2], Boldyrev K.N.[3]

1 – Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia

2 – Scientific and Laboratory Complex Clean Room, North Caucasus Federal University, Stavropol, Russia

3 – Institute of Spectroscopy of the Russian Academy of Sciences, Troitsk, Moscow, Russia

kouznetzovsv@gmail.com

An increase in the output power of synchrotrons and X-ray free-electron lasers dictates the need to develop efficient X-ray luminescent screens and scintillators that would have long-term stability when exposed to high-energy beams. The currently used bulk crystalline materials, although they exhibit rather intense X-ray luminescence, have low thermal conductivity and, therefore, have a high tendency to degradation under the influence of powerful X-ray radiation. The new developed material for X-ray luminescence screen is composite based on poly- and single-crystal diamond with embedded nanoparticles of oxides and fluorides [1].

Techniques for the synthesis of submicron particles of yttrium-aluminium-garnet doped with cerium and strontium fluoride doped with europium have been developed. The compositions of the powders showing the highest values of the intensity of photo- and X-ray luminescence have been determined. The effect of annealing in hydrogen and methane-hydrogen plasma at temperatures of 600-950 ^{o}C without overgrowing them with diamonds on the structural-phase and luminescent characteristics of particles has been recognized.

Polycrystalline diamond composite films and membranes with a thickness of 500 nm to 10 μm with embedded synthesized nanoparticles have been manufactured in according to optimal modes of diamond synthesis in microwave plasma.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-13-00401.

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OP-24

Functional Materials Spectromicroscopy in the Ultra-Soft X-Ray Region of Synchrotron Radiation

Turishchev S.Yu., Parinova E.V.
Voronezh State University, Voronezh, Russia
tsu@phys.vsu.ru

X-ray and electron spectroscopy and microscopy techniques are known as power tools for modern functional materials fundamental properties deep understanding. These atomic and electronic structure investigations techniques combine high surfaces and achievable interfaces sensitivity with local atomic surrounding specificity. In their turn phase composition and evolution with physical and chemical nature of the objects under study can be revealed by direct experiments analysis. Scientific core advantages mentioned above of the ultrasoft X-rays range spectroscopy measurements are resulted from the wavelengths comparable in general with actual sizes of single or discrete morphology elements of structures under study.

Shift to real microscopic scale is really demanded for such experiments allowing to study atomic and electronic structure directly from low-dimensional surface areas and their characteristic elements making traditional approaches really micro-scale sensitive. PhotoEmission Electron Microscopy (PEEM) technique is one of the best example for this subject area of research combining microscopic imaging possibilities with local atomic structure and chemical state sensitivity at 'one run experiments'.

Examples of this technique applications will be presented characterizing high resolution experiments that can be conducted in frameworks of direct joint microscopy and spectroscopy approaches applied for several types of functional nanostructural materials. The surface (or achievable interfaces) sensitivity at micro-scale plays the crucial role for the deep understanding and searching for the prospective applications of modern nanomaterials and structures on their basis from well-known silicon-based systems to molecule- or cell-based hybrid nature-like objects. The best energy and/or lateral resolution that can be achieved experimentally with the use of synchrotron radiation plays extremely important role in scientifically correct understanding of different kind of structures nature.

Acknowledgement: The work is supported by the RSF (19-72-20180) and RFBR (21-53-12042) in parts of studied materials choice. The work is supported by the Ministry of Science and Higher Education of Russian Federation under Agreement No. 075-15-2021-1351 in part of PEEM for materials diagnostics.

OP-25

The Interpretation of XANES and EXAFS Signal for Cu-Sites in Cu-Exchanged Zeolites via Molecular Dynamics and Machine Learning Approaches

Pankin I.A.[1], Paolucci C.[2], Soldatov A.V.[1]

1 – The Smart Materials Research Institute, Southern Federal University, Rostov-on-Don, 344090 Russia

2 – Department of Chemical Engineering, University of Virginia, Virginia 22903, United States

pankin@sfedu.ru

Cu-exchanged zeolites have been shown as a very promising catalysts for wide range of redox reactions (e.g. NH_3-assisted deNOx and MTM) because of their superior hydrothermal stability, redox capability, and coordinative flexibility. Among variety of different zeolite topologies Cu-exchanged chabazite (also known as SSZ-13) can be considered as a model system due it's structure simplicity and many experimental and theoretical studies available in the literature [1]. Based on the analysis of experimental XAS data it has been recently shown that both activation conditions [2] as well as Cu and Al loadings [3] have a great impact on the formation of different Cu-sites in Cu-CHA catalysts.

The direct mapping of structural parameters based on XANES is not straightforward due to the presence of different contributions into the averaged experimental signal, steaming from variety of Cu-oxo sites that might be formed after the activation. Moreover, most of the Cu sites geometries possess several local minima. In this work we have performed XANES and EXAFS analysis using the structural dataset extracted from AIMD simulations earlier reported in [4]. XANES simulations has been performed in full-potential mode using FDMNES code, while EXAFS simulations were performed using Feff8.6 code and Larch-based scripts.

The obtained MD-averaged theoretical XANES and EXAFS curves were compared with experimental data collected on O_2-activated Cu-CHA characterized by majority of the isolated "1Al" and paired "2Al" docking sites (typical for Cu-CHA with high and low Si:Al ratios, respectively). For "2Al" case the system roughly can be described by the single redox inactive bare Cu^{2+} ions equilibrated in square planar geometry in proximity of paired Al sites in 6MR. It was shown that for correct description of experimental XANES for "2Al" case two competitive adsorption channels should be considered. Similar approach has been previously employed for highly symmetric square planar tetra-amino complexes $Cu^{2+}(NH_3)_4$ [5].

For "1Al" case the variety of different dimeric structures and redox active ZCuOH monomer (which may serve as a precursor for MTM active sites formation [6] were considered, following the same computational strategy as reported in [4] for UV-vis multi-scale simulations. The analysis of MD-averaged theoretical XANES demonstrate sharp differences for the models with 3-fold and 4-fold coordinated Cu ions (see Fig. 1a). Moreover, the qualitative examination along with the bond-length distributions in the proximity of absorbing Cu ions (see Fig 1c,d) demonstrates that the shape of theoretical XANES mostly governed by the Cu-O distances in the first coordination shell, while Cu-Cu spacing has low impact on the intensity distribution and energy localization of the features A, B and C.

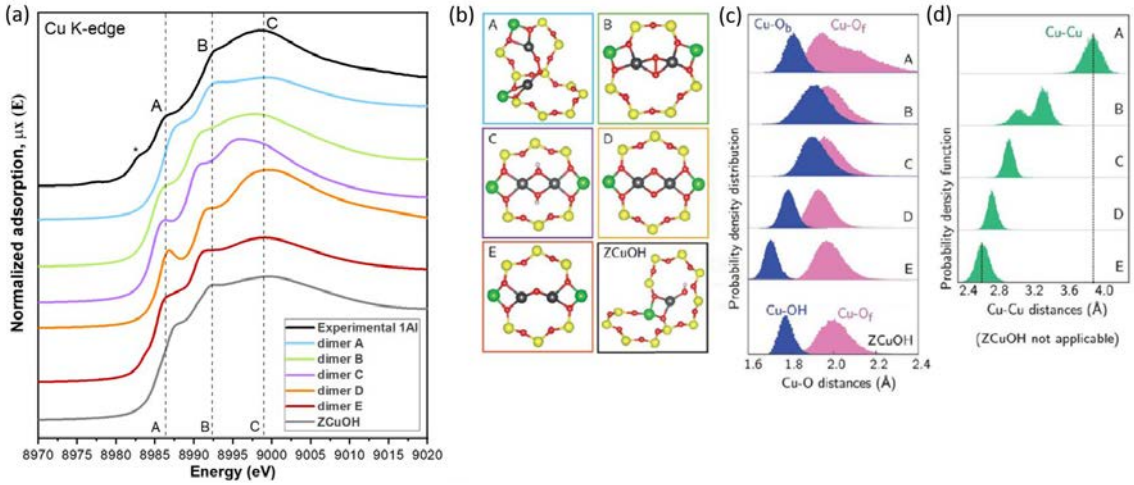

Fig. 1. (a) Comparison of experimental Cu K-edge XANES collected for O_2-activated Cu-CHA characterized by majority of 1Al isolated sites in comparison with MD-averaged theoretical XANES curves computed for the structures shown in (b) panel. (c) and (d) represent histograms of Cu-O and Cu-Cu bond lengths extracted from entire MD trajectories (adopted from [4]).

On the next step the dataframe composed by the set of structural parameters in the local environment of Cu ions and integral XANES intensity in the different ranges of the spectra (employed as a simple XANES descriptor) has been subjected for ML-based analysis. The ML-model was constructed based on Extra-trees and SVR Sklearn algorithms. Then the subset of structural parameters was divided into different parts and ML model was learned to predict the spectral descriptors. ML-assisted analysis demonstrated that more distant atoms (e.g Al and Cu) have relatively strong impact on the simulated XANES signal, thus assuming more complicated dependence between experimentally observed XANES features intensity and their energy localization and Cu local environment.

Finally, for “1Al” case the linear combination fit analysis of both XANES and EXAFS parts based on the MD-averaged “theoretical references” demonstrated that overall contributions from 4-fold coordinated species might be as high as 40-50%. This result is reconsidering the previous findings reported in liturature, which assume exclusively the formation of 3-fold coordinated Cu-complexes in the O_2-activated Cu-CHA catalyst with low Si:Al ratio.

Acknowledgement: This work was supported by the RSF project (№ 21-73-00309).

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Poster Presentations

PP-1 ÷ PP-37

PP-1

XAFS Study of Local Atomic Structure of High Refraction Index Glasses

Alekseev R.O.[1], Avakyan L.A.[2], Shakhgildyan G.Yu.[1], Savinkov V.I.[1], Veligzhanin A.A.[3], Bugaev L.A.[2], Sigaev V.N.[1]

1 – Mendeleev University of Chemical Technology, Moscow, Russia

2 – Southern Federal University, Rostov-on-Don, Russia

3 – National Research Centre "Kurchatov Institute", Moscow, Russia

alexeev-roma@mail.ru

Local structure of high refraction index glasses in the La_2O_3–Nb_2O_5–B_2O_3 (LNB) system were investigated by X-ray absorption (XANES and EXAFS) spectroscopy. The refraction index of studied glasses (up to 1.98) is determined by the Nb_2O_5 content, which was varied from 5 to 30 mol%. Content of Nb_2O_5 more than 30 mol% leads to glass crystallization, therefore the structure of such samples was not studied. It was found that niobium atoms retain its octahedral coordination at an average Nb–O distance of 1.87 Å. In the region of the second coordination shell other Nb atoms can be found at an average distance of 3.73 Å. This corresponds to the connection of niobium octahedra “by corners” with the average number of octahedra 1.2. The large value of the coordination number of lanthanum atoms (up to 10) indicates on the similarity of its local structure to the local structure of LaB_3O_6 and $LaNb_3O_9$ crystals, but with a higher degree of disorder which is inherent for glasses [1].

The obtained information on the local atomic structure of LNB glasses is important for the development of new optical glasses with a high refractive index to design optical devices such as digital cameras, optical lithography and advanced AR devices [2, 3].

Acknowledgement: The reported study was funded by RFBR, project number 20-33-90270.

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PP-2

Near-Field Phase-Contrast Imaging Using a Secondary SR Source

Kohn V.G.[1], Argunova T.S.[2]
1 – National Research Centre "Kurchatov Institute", Moscow, Russia
2 – Ioffe Institute RAS, St. Petersburg, Russia
argunova@mail.ioffe.ru

The third generation synchrotron radiation (SR) sources provide a powerful tool for studying microstructures by means of in-line phase contrast imaging [1]. This technique allows immediate and fast visualization of any electron density variation inside the material. A thickness variation of a few microns, for instance associated with a pore within the material, involves a very small variation of absorption, but can be associated with a phase shift sufficient for detection. The real size of a micro-pore correlates with the image size only on a very short distance behind the sample. For that, the near-field condition has to be fulfilled; namely, $2r_1 << D$, where $r_1 = (\lambda z)^{1/2}$ is the radius of the first Fresnel zone for the wavelength λ and D is the transverse pore size. Towards the far-field region, where $2r_1 >> D$, the fringe pattern arises, and the object size is visible only in the modulation of the fringes.

Quantitative information from image data can be obtained by solving the inverse problem. The goal is the phase of the transmission function of the object, which is proportional to the total electron density along the beam path. It can be determined, for example, using computer simulations. In the pioneer work by Snigirev *et al*. [1], the first variant of the theory of phase-contrast imaging was also presented. Later, many papers and review articles described the theory, for example [2, 3].

It follows from the theory that the properties of the image depend on the effective distance $Z = z_0 z_1 / z_t$, where z_0 is the distance from the sample to the SR source, z_1 is the distance from the sample to the detector, and $z_t = z_0 + z_1$. In a standard SR phase-contrast imaging setup (Fig.1,*a*) the following relation is fulfilled: $z_0 >> z_1$. Therefore, Z is very close to z_1. In such a scheme, the projection of the source size is much smaller than the source size itself, which allows the use of the source with relatively large size. A small value of Z is achieved using a small value of z_1.

However, there is another possibility to obtain a small value of Z and implement the near-field regime. We can realize the inverse relationship $z_0 << z_1$. This case is shown in Fig. 1,*b*. In such a case, the experimental image corresponds to the near-field condition, but the image size will be much larger than the object size. At the same time, the projection of the source size also increases, as shown in the figure. The high resolution can be attained only when the transverse source size is smaller than the object size.

A secondary source is required to implement such a scheme with SR source, which, for example, can be created utilizing a compound refractive lens (CRL), first proposed by Snigirev

et al. [4]. Figure 1,*c* presents an outline of the setup based on such a scheme. Analytical theory of imaging and focusing by CRL was first developed by Kohn [5–7].

We performed the computer simulations choosing a cylindrical micropipe (MP) with a diameter of 2 μm as a model object. MP was located in a SiC crystal. We show the images of the MP calculated at different distances. The intensity ratio at the detector to the intensity in front of the CRL is discussed. The properties of the image recorded using such a scheme are analysed and compared to those of the image recorded using the standard set up. Finally, we show that one can achieve stronger coherence by focusing the beam by the CRL. Consequently, one can implement the secondary-source setup in light sources with a relatively large angular size.

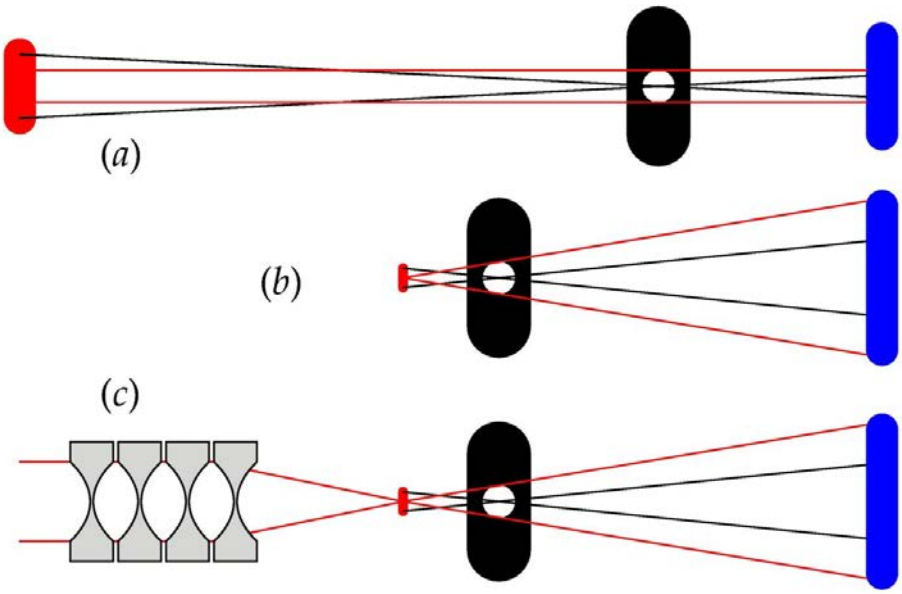

Fig. 1. Experimental schemes considered in this communication. See text for details.

Acknowledgement: V.G. Kohn (conceptualization, software, computer simulations) acknowledges Russian Foundation for Basic Research (RFBR), grant 19-29-12043mk. T.S. Argunova (experimental investigation) acknowledges RFBR, grant 19-29-12041mk, and Ministry of Science and Higher Education of the Russian Federation (Project 075-15-2021-1349).

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PP-3

Local Atomic Structure of Iron Dopants in Hydroxyapatite from Hybride DFT Calculations and Fe K-XANES

Paramonova E.V.[1], Avakyan L.A.[2], Tolchina D.B.[2], Bystrov V.S.[1]

1 – Institute of Mathematical Problems of Biology, branch of Keldysh Institute of Applied Mathematics, RAS, Pushchino, Moscow, Russia

2 – Southern Federal University, Rostov-on-Don, Russia

laavakyan@sfedu.ru

Hydroxylapatite (HAp = $Ca_5(PO_4)_3OH$) is known as a main mineral component of bones. The innate bio-compatibility of HAp ceramics is promising for numerous medical applications [1]. The Fe-HAp (Fe doped HAp) presents magnetic properties and can be used in magnetic hyperthermia, MRI diagnostics, as a part of grug delivery systems. However, the reported Fe-HAp materials [2-4] show insuperior magnetic properties – the magnetization is lower than that expected from iron content. In order to improve the Fe-HAp material and to find optimal synthesis conditions the knowledge about atomic structure and iron oxidation state are required.

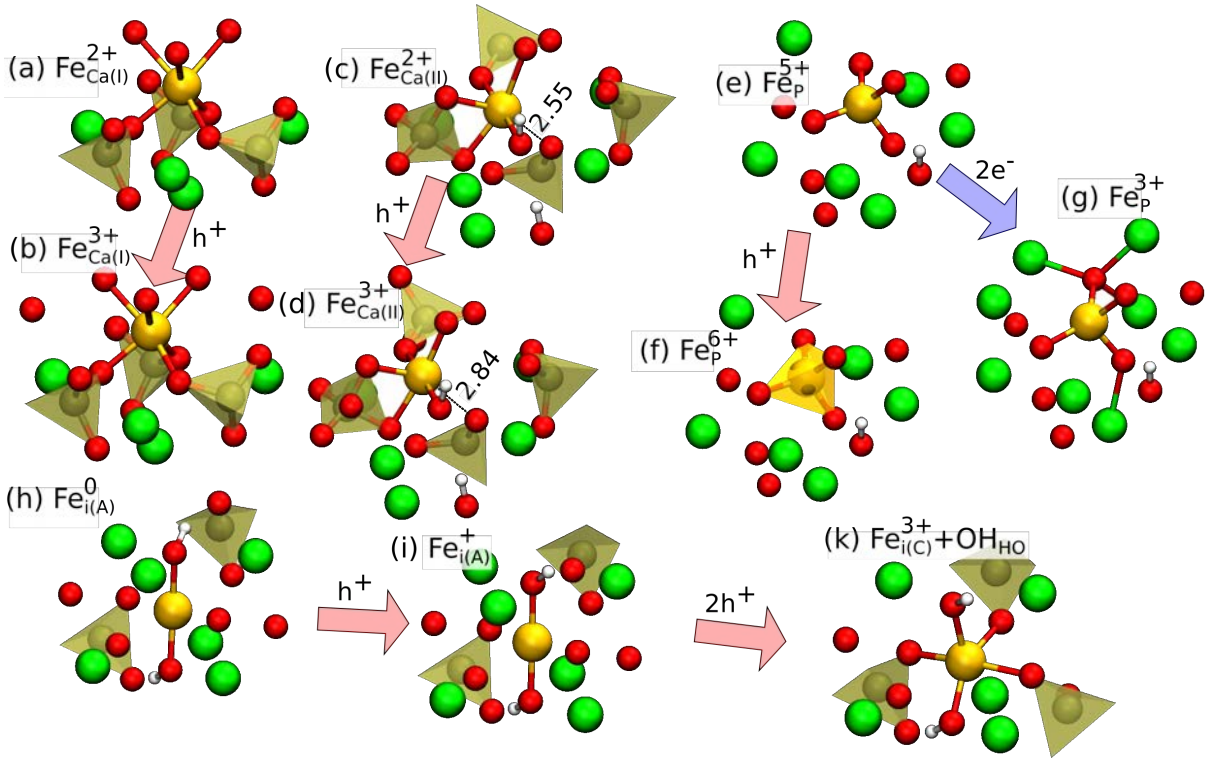

Fig. 1. Illustration of local atomic structure of iron for some of the possible Fe-HAp configurations.

In this study we applied the state of the art density functional theory (DFT) methods [5] to determine the atomic and electronic structure of iron dopants in HAp material [6]. Figure 1 illustrates some of the obtained structures, which differ by iron charge state and position: interstitial (i) site or cation substitution (Ca(I), Ca(II) or P). We also calculated the Fe K-XANES

spectra and compared them with the experimental data available in the literature. The comparison show that some of the iron-oxide groups replace the phosphate groups in HAp (Figure 1e-g), which result in the low-spin iron species. This opens the room for improvement of the magnetic properties by domination of high-spin iron configurations, i.e. $Fe_{Ca(I)}^{3+}$ (Figure 1b) and $Fe_{i(C)}^{3+}$ (Figure 1k).

Acknowledgement: This work was supported by the Russian Science Foundation, grant 21-12-00251.

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Nanomaterials 11 (2021) 2978

PP-4

Room-Temperature Ferromagnetism of Few-Layer Nanographene Clusters in Carbon Nano- and Micro-Spheres

Avakyan L.A.[1], Srabionyan V.V.[1], Tolchina D.B.[1], Kozakov A.T.[2], Nikolskiy A.V.[2], Emelyanov A.V.[3], Sysakyan N.S.[4], Gyulasaryan H.[4], Manukyan A.S.[4], Bugaev L.A.[1]

1 – Faculty of Physics, Southern Federal University, Rostov-on-Don, Russia

2 – Institute of Physics, Southern Federal University, Rostov-on-Don, Russia

3 – National Research Center "Kurchatov Institute", Moscow, Russia

4 – Institute for Physical Research, National Academy of Sciences of Armenia, Ashtarak, Armenia

laavakyan@sfedu.ru

Ferromagnetism of compounds containing only p- and s-electrons is a very rapidly developing branch of science [1]. Recently, many experimental and theoretical works have appeared, indicating that the features of the electronic structure of carbon can lead to the appearance of ferromagnetic correlations, persisting up to high temperatures [2]. It was shown in [3] that if some carbon atoms in a graphene sheet are replaced by trivalent atoms (for example, B, N, Al) then a sufficiently large magnetic moment can occur in such a systems. According to [4], the magnetic moment can also be formed in a pure carbon structure if sp^2- and sp^3-hybridized carbon atoms are presented as the atoms of different valency.

In this work, we study the magnetic characteristics of three nitrogen-containing carbon samples at room temperature (RT), which were obtained by solid-phase pyrolysis of phthalonitrile PN = $C_6H_4(CN)_2$ at a temperature of 700°C, a duration of 30 min, and various pressures (*p*) in an autoclave. With the aim to vary the nitrogen atomic states in the synthesized samples, different pressures were considered: 0.01 bar (sample PN_0), 0.5 bar (sample PN_0.5), 1 bar, 3 bar, *etc*. TEM study of samples showed the presence of nanographene clusters in carbon nano- and micro-spheres. Analysis of X-ray photoelectron spectra (XPS) of the samples showed the variation of concentration of nitrogen in the samples. The decomposition of the C 1s-XPS spectra into the components of different carbon fractions enabled to determine the dependence of sp^2/sp^3 ratio (planar/spatial) of carbon bonds [4] in the samples upon the conditions of their synthesis.

The local atomic structure of carbon and nitrogen atoms was probed using C and N K-edge NEXAFS spectra. Panel a of Figure 1 shows the experimental N K-edge NEXAFS of the sample, while panel b presentes the theoretical spectra, obtained using simple atomic models, based on a few atoms clusters, with some of them shown on the right figure part. The comparison of experimental and theoretical spectra shows that features A and B are originated from pyridinic and pyrrolic nitrogen atoms. The feature C emerges only whan oxygen atoms are introduced in the vicinity of nitrogen.

The consideration of C K-edge NEXAFS shows the presence of both sp^2 and sp^3 hybridized carbon atoms. This allows it conclude that RT ferromagnetism in the studied samples arises as

a result of the coexistence of two mechanisms associated both with the presence of trivalent N ions and with the presence of variously hybridized carbon atoms.

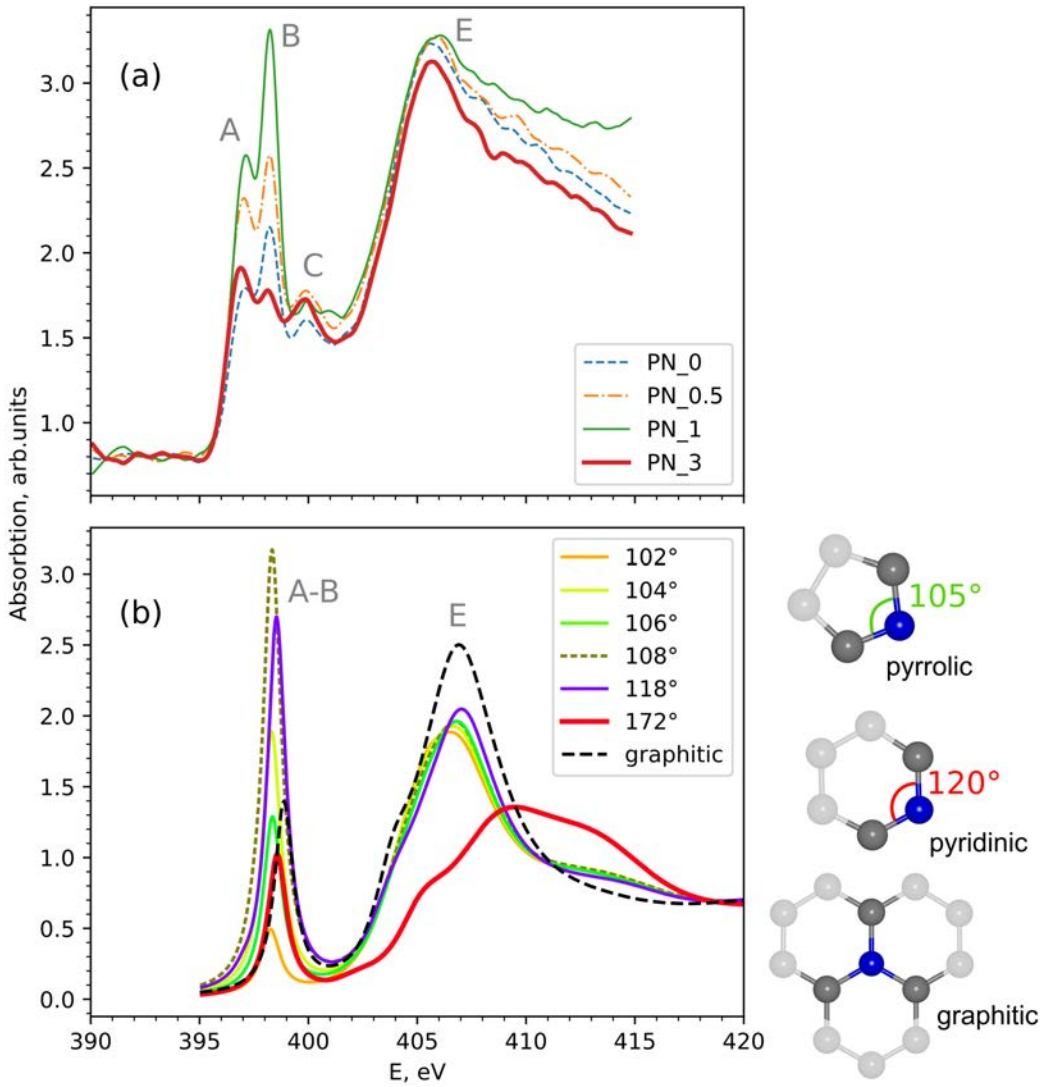

Fig. 1. (a) Experimental N K-NEXAFS spectra of the samples obtained at different pressures (0.01 – 3 bar); (b) theoretical N K-NEXAFS spectra.

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PP-5

The Influence of Experimental Setup on Ferroelectric Phase Transition of Glycinium Phosphite

Bogdanov N.E.[1,2], Zakharov B.A.[1,2], Boldyreva E.V.[1,2]
1 – Boreskov Institute of Catalysis, Novosibirsk, Russia
2 – Novosibirsk State University, Novosibirsk, Russia
bogdanovne@catalysis.ru

Glycinium phosphite (GPI) is the thoroughly studied crystalline compounds with ferroelectric properties. It has a phase transition at 225 K what has been confirmed in the literature by a wide range of different methods. To characterize the structural changes during the phase transition, two separated series of experiments were carried out using synchrotron radiation at the Swiss-Norwegian BM01A line of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and also by a similar experiment with a laboratory STOE IPDS X-ray diffractometer. The obtained data sets reveal the influence of X-ray source been used: synchrotron experiment show an abnormal non-linear increase in volume on cooling whereas laboratory data confirm the overall structure compression (Fig. 1). We link the resulting difference to a radiation damage accumulated during consecutive data collections, thus, the structure expansion as the result of beam radiation partially compensate by the compression of the structure upon cooling so the total change in volume remains positive [1].

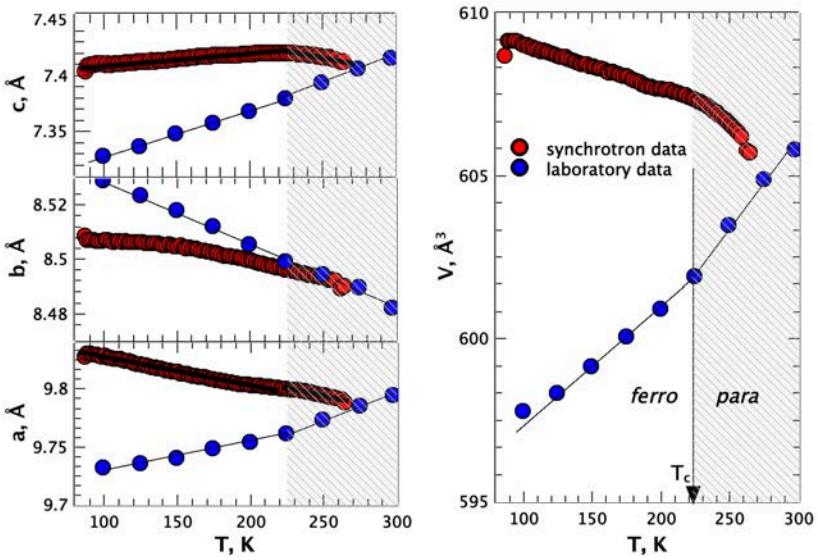

Fig. 1. The unit cell parameters and volume vs. temperature from the synchrotron and laboratory data, the error bars are smaller than the symbols. Shaded zone indicates the temperature domain for the paraelectric phase.

The effect of the radiation damage of GPI affect the temperature dependence of the lattice constants and static disorder of the entire molecular structure, however, it does not prevent the temperature induced ferroelectric phase transition. Thus, the radiation damage

may therefore be considered not only as a negative effect, but also as a tool for fine-tune crystal structure and potentially reveal new properties [2].

Acknowledgement: The laboratory experiments were carried out using the equipment of the laboratory "Molecular design and ecologically safe technologies" (NSU). The authors acknowledge support by the Ministry of Science and Higher Education of Russia and Boreskov Institute of Catalysis (governmental order AAAA-A21-121011390011-4) and Novosibirsk State University.

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PP-6

High-Pressure Phases of R-(3)-Quinuclidinol

Sharaya S.S.[1,2], Ivanova A.G.[3], Smirnova E.S. [3], Zakharov B.A.[1,2]
1 – Boreskov Institute of Catalysis, Novosibirsk, Russia
2 – Novosibirsk State University, Novosibirsk, Russia
3 – Federal Scientific Research Center "Crystallography and photonics", Moscow, Russia
s.sharaya@g.nsu.ru

R-(3)-quinuclidinol is a promising low molecular weight organic ferroelectric. The study of the structure under high pressure conditions can provide additional information about intermolecular interactions, and therefore about the nature of the physical properties of the crystal. The aim of this work is to study the structure of R-(3)-quinuclidinol by single-crystal X-ray diffraction and Raman spectroscopy under high pressure conditions.

For the first time, the structure of the crystals of R-(3)-quinuclidinol was described by Rousselin Y. and Clavel A. [1]. The quinuclidinol molecules in the structure form chains along the polarization axis connected by hydrogen bonds.

In this study, the diffraction experiment was carried out on a modern Rigaku XtaLAB Synergy-DW laboratory X-ray source with an increase in pressure from 0 to 3.2 GPa. By changing the cell parameters, it was possible to calculate a tensor of compressibility coefficients. Up to 0.3-0.6 GPa, the axis of polarization remains the least deformable direction, after that it becomes the most deformable. The crystal structures were determined at each point. Additionally, changes in the length of hydrogen bonds between quinuclidinol molecules were described.

Raman spectra of R-(3)-quinuclidinol were collected on a Horiba Jobin-Yvon HR800 spectrometer with a pressure change from 0 to 6 GPa. When comparing the spectra at different pressures, special attention is paid to the change in the frequencies of lattice vibrations, as the most highly variable and associated with intermolecular interactions.

Acknowledgement: The work was supported by the Ministry of Science and Higher Education of the Russian Federation jointly by the Boreskov Institute of Catalysis (project AAAA-A21-121011390011-4) and under the “Priority 2030” program in cooperation with Novosibirsk State University.

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PP-7

Synchrotron Radiation Technology Station as a Training Stand for novice SR Users

Goldenberg B.G.[1,2], Gusev I.S.[2], Zubavichus Y.V.[1,3]
1 – Synchrotron Radiation Facility SKIF, Boreskov Institute of Catalysis, Koltsovo, Russia
2 – Budker Institute of Nuclear Physics, Novosibirsk, Russia
3 – Boreskov Institute of Catalysis, Novosibirsk, Russia
b.g.goldenberg@sfr-skif.ru

A unique project is underway in Novosibirsk state to create a scientific facility Siberian Ring Photon Source (SKIFF). The education of human resources that will realize the investigative capacity is major challenge. We are presenting the special synchrotron radiation technological station for practical training university students and novice SR users in synchrotron research techniques. This article describes the design of station, realized research methods and plan for upgrading of this facility.

Acknowledgement: The work was done at the shared research centre SSTRC on the basis of the "VEPP-4 - VEPP-2000" complex at BINP SB RAS, with financial support by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2022-263).

PP-8

Influence of Synthesis Method on the Phase Composition, Structure, and Catalytic Activity of Strontium Titanium Oxides

Gorkusha A.S.[1,2], Pavlova S.N.[2], Gerasimov E.Yu.[2], Nartova A.V.[2], Cherepanova S.V.[2], Tsybulya S.V.[1,2]

1 – Novosibirsk State University, Novosibirsk, Russia

2 – Boreskov Institute of Catalysis, Novosibirsk, Russia

Deepforesttt922@gmail.com

Layered perovskite Sr_2TiO_4 attracts attention as a promising catalyst for the oxidative condensation of methane. It is known that the activity of these catalysts depends to a large extent on the method of preparation, which determines their phase composition, real structure, and surface composition.

Within the framework of this work, a series of Sr-Ti-O samples synthesized using the stage of mechanochemical activation, citrate and polymer methods were studied. The phase composition of Sr-Ti-O samples was established using X-ray diffraction, including synchrotron radiation. The content of the Sr_2TiO_4 phase, close to 100%, is achieved in the case of samples synthesized from strontium carbonates using the stage of mechanochemical activation, as well as using the polymer method. It is shown that the differences in the catalytic activity of the samples in the reaction of oxidative condensation of methane are not explained only by their phase composition, but correlate with the surface composition (presence of Sr-containing phases on the surface). High-resolution electron microscopy for a number of Sr_2TiO_4 samples revealed multiple planar defects in the form of a violation of the periodicity in the alternation of layers, leading to a violation of the stoichiometry of this phase and enrichment of the surface with strontium.

The diffraction patterns of Sr_2TiO_4 in the presence of layer alternation defects are simulated. The calculated results are compared with experimental data. An original technique for estimating the concentration of planar defects for A_2BO_4 systems with a layered perovskite structure is proposed.

PP-9

MOCVD and Sputtered Tin Oxides Thin Films Atomic and Electronic Structure by Synchrotron Studies

Chuvenkova O.A.[1], Turishchev S.Yu.[1], Kakuliia I.S.[1], Ryabtsev S.V.[1], Kurganskii S.I.[1], Manyakin M.D.[1], Parinova E.V.[1], Pelagina A.K.[1], Sivakov V.[2]

1 – Voronezh State University, Voronezh, Russia

2 – Leibniz Institute of Photonic Technologies, Jena, Germany

kakuliia@phys.vsu.ru

Tin oxides are promising materials for production of new electronic devices, such as resistive gas sensors with enhanced characteristics: miniaturization and low energy consumption are achieved by advanced technologies aimed at creating active thin nanolayers. Comprehensive studies of morphology, local atomic and electronic structure using electron microscopy, synchrotron X-ray absorption near edge structure (XANES), X-ray photoelectron spectroscopy (XPS) methods in combination with calculations and modelling from the first principles are necessary to predict the properties of the obtained objects based on the Sn-O system in modern technologies.

Tin layers with a thickness of ~ 30 nm obtained by two methods were studied: magnetron sputtering (MR) and metal organic chemical vapor deposition (MOCVD). In the case of the magnetron sputtering method, the samples were obtained in argon plasma and in argon-oxygen media at a pressure of 10^{-3}Torr and 10^{-4}Torr, respectively, at direct current. Tin was used as a target. The resulting tin films were then annealed in air at temperatures from 180 to 750 ° C. In the case of the MOCVD method, tert-butoxide of tetravalent tin Sn(OtBu) (IV) was used as a precursor, the pressure in the reactor was 10^{-5} Torr. The substrate temperature was 650 ° C. In both methods, films were deposited on silicon substrates.

A comprehensive and comparative study of the obtained structures showed that the MOCVD method produced films of predominantly tin dioxide SnO_{2-x} tetragonal modification. Multiphase films containing metastable phases of tin monoxide and orthorhombic tin dioxide were obtained by magnetron sputtering. High-temperature (750 ° C) annealing in air of films obtained by magnetron sputtering leads to the formation of orthorhombic and tetragonal modifications of tin dioxide. For the formation of films similar to those obtained using the MOCVD method, the magnetron sputtering method requires additional changes in technological modes. Thus, the production of MR layers provides a wide range of phases during the formation of a granular film, which indicates flexibility in the properties of the structures formed. At the same time, the MOCVD approach demonstrated the possibility of forming a stable low-dimensional granular SnO_{2-x} film with the possible formation of "core-shell" nanogranules, where the core has a composition different from SnO_{2-x}. All approaches are considered as possible and promising for the functionalization of developed surfaces.

Acknowledgement: The work is supported by RFBR (21-53-12042). The work is supported by the Ministry of Science and Higher Education of Russian Federation under Agreement No. 075-15-2021-1351 in part synchrotron diagnostics methodology.

PP-10

Local Structural Features and Microscopic Dynamics of Nickel Melt: Experimental Investigation and Molecular Dynamics Simulation

Khusnutdinoff R.M.[1,2], Khairullina R.R.[1], Mokshin A.V.[1,2], Suslov A.A.[2], Lad'yanov V.I.[2]
1 – Department of Physics, Kazan Federal University, Kazan, Russia
2 – Udmurt Federal Research Center,
Ural Branch of Russian Academy of Sciences, Izhevsk, Russia
khrm@mail.ru

The paper presents the results of a study of local structural features and transport properties of an equilibrium and supercooled nickel melt. Comprehensive studies of the corresponding physical properties of the nickel melt were carried out using large-scale numerical calculations, X-ray diffraction analysis, and viscometry experiments. A good agreement between the results of X-ray diffraction analysis for an equilibrium nickel melt and the simulation results and experimental data on neutron diffraction was found. It has been established that in liquid nickel the contribution of pair entropy to the excess configurational entropy is ~60% in the high-temperature region and ~80% near and below the melting temperature. A good agreement was found between our experimental results on viscometry and other known experimental data as well as the simulation results for the transport characteristics (self-diffusion coefficients and viscosity) of the nickel melt in a wide temperature range. It is shown that the simulation results and experimental data are correctly reproduced by the modified Stokes-Einstein relation obtained in the framework of the Rosenfeld scaling transformations.

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PP-11

Selection of Chymosin Crystallization Conditions. Solution and Refinement of the 3D Chymosin Structure

Kolybalov D.S.[1,2], Dusenova S.E.[2,3], Arkhipov S.G.[1,2,3], Shevtsov M.B.[4], Borschevsky, V.I.[4], Shcherbakov D.N.[5]

1 – SRF "SKIF", Koltsovo, Russia

2 – Novosibirsk State University, Novosibirsk, Russia

3 – Boreskov Institute of Catalysis, Novosibirsk, Russia

4 – Moscow Institute of Physics and Technology, Dolgoprudny, Russia

5 – State Research Center of Virology and Biotechnology VECTOR, Rospotrebnadzor, Koltsovo, Russia

d.kolybalov@g.nsu.ru

Chymosin – it is aspartic protease, which produced in the stomachs of mammals. It cleaves κ-casein, led to coagulating the milk, which lets better milk protein absorption. This enzyme is used for the cheese manufacture. Justesen et al. (2009) suggested the extended use of chymosin in the preparation of pharmaceutical proteins. [1]

In this work, maral, elk and tupai chymosins were obtained and purified by State Research Center of Virology and Biotechnology VECTOR (Koltsovo, Russia) employees. With the Center for Research on Molecular Mechanisms of Aging and Age-Related Diseases (MIPT, Moscow, Russia) equipment chymosins were concentrated to 7.5 mg/mL, 7.0 mg/mL and 10.2 mg/mL respectively. Suitable for single crystal X-ray diffraction (SCXRD) crystals maral and elk were obtained with crystallization robot Formulator NT8 and PACT premier™ standard screening kit. Collection of diffraction data was performed on ID30A-3 beamline ESRF, Grenoble, France with a remote procedure. Obtained data were indexed and integrated in XDS software [2]. After that, a structure solution by molecular replacement in Phenix software package [3] was performed. The initial model was predicted by the AlfaFold2 neural network [4].

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PP-12

Transformations of Fe in Graphene Nanoflakes under Oxidation Treatment

Krot A.D., Savilov S.V., Kalmykov S.N.
Lomonosov Moscow State University, Moscow, Russia
Anna.d.krot@gmail.com

Recently, an increased interest was shown to carbon nanostructures derived from graphene since they can exhibit excellent electronic and magnetic properties [1]. Doped graphene nanostructures are promising materials for spintronics, catalysis applications [2, 3] as well as an electrode material in supercapacitors [4].

In this work, graphene nanoflakes (GNFs) were synthetized as described in [5]. The synthesis resulted in the intercalation of ppb concentrations of Fe from template material into graphene nanostructure. However, investigation of such extremely low concentrations of metal atoms is restricted since there are few methods with a sufficient detection limit that could provide valuable information about Fe speciation in the structure. Fe-GNFs samples were treated with nitric acid and studied using x-ray absorption spectroscopy (XAS), which is one of the most powerful tools for determination of element's valence state and local surrounding in low concentrated, amorphous materials. Using the unique capabilities of the Rossendorf Beamline (BM20) of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) [6], reliable information about Fe local environment during the oxidation process was obtained, which previously could not be achieved.

According to XANES (X-Ray absorption Near edge Structure) and EXAFS (Extended X-Ray Absorption Fine Structure) data, single-atoms of Fe intercalate into the structure of GNFs during synthesis and stabilize between the layers. At the first step of oxidation with nitric acid, only structural changes in Fe local environment occur, without affecting its oxidation state. Oxidation of intercalated Fe begins after prolongated treatment with nitric acid followed by the substantial restructuring of the GNFs structure. At the end of the reaction, according to spectral data, Fe^{3+} is predominantly coordinated to oxygen-containing functional groups at the edges and defects of graphene planes, while a part of Fe remains stabilized as single-atom Fe^{0}. Results obtained reveal that the system of graphene layers in GNF structure possess an extremely high affinity to iron single-atoms and provide their «extraction» from the template with further encapsulation in the material. Moreover, they are highly stable in few-layered graphene structure and cannot be fully oxidized even by long acid treatment that provides the partial decay of the GNF structure. These effects can discover the features of graphene and carbon nanotubes behaviour when they are applied as components of modern devices.

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PP-13

Generation of Twisted Waves on SKIF

Bogdanov O.V.[1,2], Kazinski P.O.[1], Lazarenko G.Yu.[1]
1 – Physics Faculty, Tomsk State University, Tomsk 634050, Russia
2 – Tomsk Polytechnic University, Tomsk 634050, Russia
laz@phys.tsu.ru

The vortex waves are called the electromagnetic waves with a helical phase front characterized by the phase dependence of the form $e^{il\varphi}$, where l is the projection of the orbital angular momentum (OAM) and φ is the azimuthal angle [1,2]. The amplitude of the electromagnetic field of the vortex wave vanishes on the axis of its propagation. The notion of twisted waves is generalized to the nonparaxial regime [3] where the photons constituting such an electromagnetic wave possess the projection of the total angular momentum m and the helicity s. In the paraxial regime, the twisted photons constituting a vortex wave carry the projection of OAM l=m−s [3]. Note that the pure sources of twisted photons already found their applications in microscopy, in development of optical tweezers, in telecommunication and quantum cryptography, and in studying rotational degrees of freedom of quantum systems by exciting nondipole transitions [1,2].

The undulator can be used for generation of an intense flux of twisted photons from THz up to X-ray spectral range [3-6]. The undulator radiation obeys the selection rules providing a relation between harmonic numbers and an OAM of twisted photons [4-6]. For example, for a helical undulator the harmonic number n coincides with the total angular momentum projection m [3].

Usually, the chamber where charged particles move in the undulator or the whole undulator are mounted in an ultrahigh vacuum. Nevertheless, there are theoretical and experimental works where the undulators filled with dielectric medium are studied [7,8]. One of the advantages of this design is that such undulators can be turned to radiate the photons with higher energies and narrower spectral bands than the vacuum undulator for a given energy of electrons. Of course, the presence of a medium in the undulator degrades the properties of the electron beam evolving in it but this degradation can be overcome [7,8].

We consider in detail undulator radiation in the dipole regime and the radiation from elliptic wigglers [6]. The selection rules for radiation of twisted photons by such undulators are found. These selection rules generalize the known ones for undulators in a vacuum [3,5]. We investigate the influence of the anomalous Doppler effect on the properties of radiated twisted photons. In the case of a medium with plasma permittivity, the lower undulator harmonics do not form. As a result, in such undulators, the main contribution to radiation coming from the lowest allowed harmonic possesses a nonzero projection of OAM in the paraxial regime. As examples, we describe the radiation of twisted photons produced by electron and proton beams in the undulators filled with helium in the ultraviolet and X-ray spectral ranges. Moreover, we consider the production of X-ray twisted photons with l=2 by

the electron beam propagating in the undulator filled with xenon. The parameters are chosen so as to be achievable at the present experimental facilities.

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PP-14

Electronic Structure of Graphene-Caped Iron and Cobalt Silicides

Lobanova E.Yu.[1], Grebenyuk G.S.[2], Mikhailenko E.K.[3,4]
1 – ITMO University, Saint Petersburg, Russia
2 – Ioffe Institute, Saint Petersburg, Russia
3 – Konstantinov Nuclear Physics Institute, National Research Center Kurchatov Institute, Gatchina, Russia
4 – Saint Petersburg State Electrotechnical University LETI, Saint Petersburg, Russia
elobanova@itmo.ru

The large spin relaxation length and weak spin-orbit interaction in graphene open the way for the development of graphene-based spintronic devices. In this regard, materials constructed from graphene, ferromagnetic metals, and their silicides are of particular interest. A potential application of such interfaces is the injection of spin-polarized electrons into graphene. To implement this possibility, a high spin polarization of the material is required. Such a feature is possessed, for example, by silicides of transition metals—cobalt and iron. A promising approach to the synthesis of such hybrid materials is the intercalation process. Intercalation involves the introduction of atoms of the desired substances under graphene. The aim of the work was a systematic study of the elemental and phase composition, electronic structure of the graphene-based materials produced by intercalation of cobalt, iron, and silicon under graphene grown on Ni(111) and SiC(0001) substrates.

All experiments were carried out using the equipment of the Russian-German beamline at Helmholtz-Zentrum Berlin (BESSY II). The samples were studied using low energy electron diffraction (LEED) and photoelectron spectroscopy (PES). Intercalation of iron, cobalt, and silicon was performed by thermal deposition of thin films of these materials on the surface of samples with subsequent annealing at various temperatures. The amount of deposited material was controlled using quartz microbalance. All experiments were done *in situ* under ultrahigh vacuum conditions (P ~10^{-10} Torr).

It is shown that at 400 °C, intercalation of the graphene on Ni(111) by cobalt occurs in a wide coverage range. Graphene is strongly bonded to the top layer of cobalt atoms. Subsequent intercalation of the system with silicon leads to the formation of an ordered Co_3Si surface phase with the (√3 × √3) R30° structure, as well as Co_2Si silicide and a Co-Si solid solution. The introduction of silicon under graphene leads to a sharp decrease in the interaction of carbon atoms with the substrate, which causes the formation of quasi-freestanding graphene on the surface.

Intercalation of the graphene on SiC(0001) by cobalt or iron occurs when metal films are deposited on samples heated to temperatures of 400 - 500~°C. Subsequent intercalation of silicon and the formation of metal silicides leads to the formation of quasi-freestanding bilayer graphene on the surface of the system due to the transformation of the buffer layer of carbon atoms into the second graphene layer.

These conclusions were confirmed by calculations carried out in the frame of density functional theory (DFT). Figures 1 and 2 depict general schemes of the intercalation synthesis of metal and silicide films under graphene on Ni(111) and SiC(0001), correspondingly, and the changes in the electronic structure of graphene.

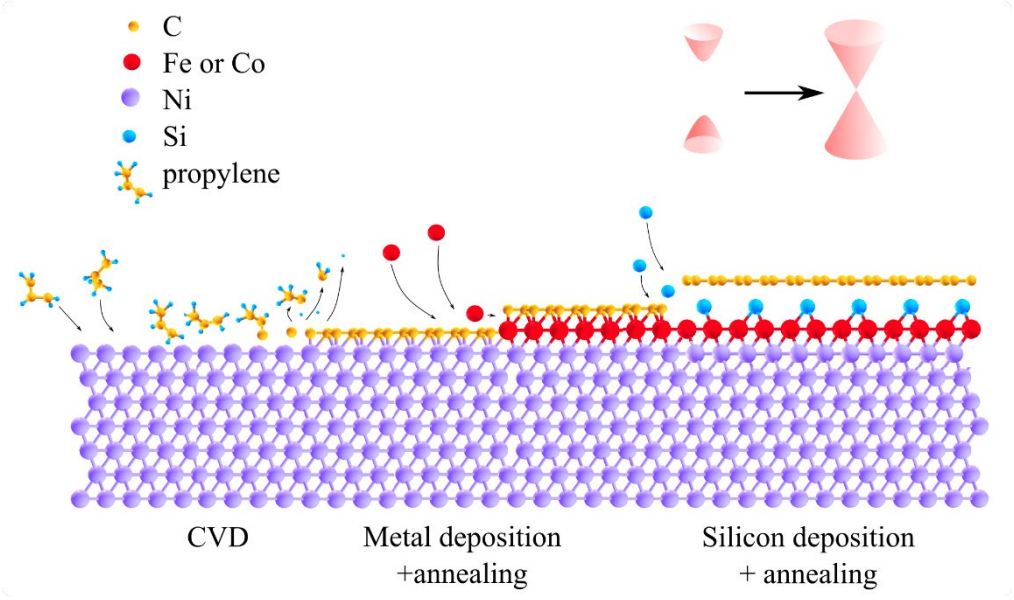

Fig. 1. General scheme of intercalation of graphene on nickel with iron, cobalt, silicon atoms. The top picture schematically shows the transition of the electronic structure of graphene to a quasi-freestanding state.

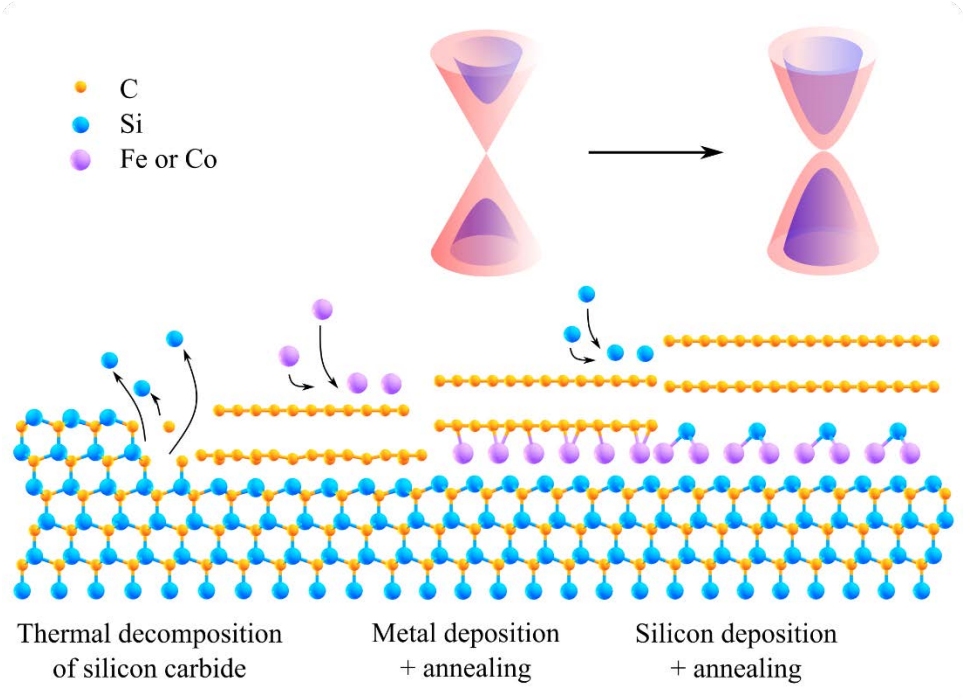

Fig. 2. General scheme of intercalation of graphene on silicon carbide by iron, cobalt, silicon atoms.

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PP-15

Substituting Steel for a Polymer in a Jar for Ball Milling Does Matter

Losev E.A.[1,2], Arkhipov S.G.[1,2], Kolybalov D.S.[2,3], Mineev A.M.[1,2], Ogienko A.G.[2,4], Boldyreva E.V.[1,2], Boldyrev V.V.[2,5]

1 – Boreskov Institute of Catalysis, Novosibirsk, Russia

2 – Novosibirsk State University, Novosibirsk, Russia

3 – SRF-SKIF, Novosibirsk, Russia

4 – LLC "SP IIC", Novosibirsk, Russia

5 – Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia

losev.88@mail.ru

Synchrotron radiation facilities give to researchers a unique chance to investigate various fast processes that cannot be explored in most laboratories. Another benefit of using the synchrotron radiation is the ability to study processes in situ without disturbing a reaction which allows, in particular, to detect unstable intermediate products and trace full reaction path. This is specifically important from mechanochemical reactions that are difficult to study properly in laboratory conditions. Usually, in situ diffraction studies of mechanochemical transformations at synchrotrons use plastic milling jars in place of steel. This is done to reduce the absorption of radiation by the walls and to increase the signal to noise ratio. However, it is only recently that researchers started to pay attention to the influence of the jar material on the investigated process itself [1,2]. In our study we show that the transformation rate can vary significantly depending on the material of the jars, using as an example the polymorphic transformation of β-glycine to α-form. Using ex situ analysis, we here compare the transformation rates using steel and common plastics such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), and polyethylene terephthalate glycol (PETG). Additionally, we describe an approach to easy manufacturing the plastic jars on desire using 3D-printing.

Fig. 1. The steel jar of a vibrational mill (NARVA Vibrator DDRGM9458, 50 Hz) and the 3D-printed polymer inserts for it (from left to right: PLA, PETG and ABS), as well as a steel ball (9.5 mm diameter, 3.5 g)

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PP-16

Electronic Structure of $Cu_{0.5}ZrSe_2$

Shkvarin A.S., Merentsov A.I., Postnikov M.S., Titov A.N.
M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, Ekaterinburg, Russia
shkvarin@imp.uran.ru

The last studies in the field of multiferroics have generated a huge scientific interest in the materials, in which ferroelectric order occurs simultaneously with magnetic order. An increase in the ordering temperature and an increase in the correlation between the electrical and magnetic systems would make these materials promising for practical applications. The crystal structure of material under our interest, $CuCrSe_2$, is similar to delafossite structure ($CuCrO_2$) and can be described as a lattice consisting of CrX_2 layers (X = S, Se) intercalated with copper. In this case, in contrast to delafossite, where copper is distributed over octahedral positions of the interlayer space, in $CuCrX_2$ copper occupies tetrahedral sites in the interlayer space, shifted from the middle of the interlayer gap. Thus, there is no center of symmetry in the $CuCrX_2$ lattice and it is prone to ferroelectric ordering. The magnetic subsystem is formed by layers of chromium atoms arranged in a triangular lattice. The magnetic interaction between chromium atoms within the layer is strong, while the interaction between chromium layers is weak. The problem, however, is that the transition temperature is quite low - about 50 K for $CuCrSe_2$. It seems that the temperature of the effect can be increased by substitution in the Cr sublattice. However, all the previous attempts carried out in this direction led to the loss of the most valuable feature - the non-centrosymmetricity of the lattice. The reason for this is the redistribution of the Cu atoms from tetrahedral sites to octahedral ones situated in the center of the symmetry of the unit cell. We found that, in $CuZrSe_2$, copper is distributed over the tetrahedral sites, as well as in $CuCrX_2$, with the difference that at room temperature in $CuZrSe_2$ copper atoms are distributed uniformly over both sets of tetrahedral sites.

Previously we are investigating the electronic structure of Cu_xZrSe_2 system with low ($x \leq 0.3$) cooper concentration[1]. In current work we are enhance this study by data obtained on SUES beam line of Elettra synchrotron for $Cu_{0.5}ZrSe_2$ sample. X-ray photoemission spectra of Se 3d, Zr 3d and Cu 2p core levels were obtained, together with valence band spectra and Cu $L_{2,3}$ and Zr $M_{2,3}$ x-ray absorption spectra. Cu $L_{2,3}$ spectrum $Cu_{0.5}ZrSe_2$ differs significantly from the spectra of copper in the Cu_xTiSe_2 system, where it occupies only octa positions. This confirms that the copper atoms precisely occupy the tetra positions. The valence band spectra and core level spectra demonstrate a changing in form and energy positions, which in turn also confirms a tetra-coordination of cooper atoms in $Cu_{0.5}ZrSe_2$.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-13-00361.

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PP-17

In Situ Synchrotron XRD Study of Mixed Rare-Earth Nickelates

Mishchenko D.D.[1], Arapova M.V.[2], Vinokurov Z.S.[1], Shmakov A.N.[1]
1 – SRF "SKIF" BIC SB RAS, Novosibirsk, Russia
2 – Boreskov Institute of Catalysis, Novosibirsk, Russia
q14999@yandex.ru

Rare-earth (La, Pr, Nd) nickelates are promising materials for intermediate temperature solid oxide fuel cells (IT-SOFC) cathodes. These materials possess high level of mixed oxide-ionic and electronic conductivity (MIEC) in the intermediate temperature range (500-700 °C). This allows oxygen species to undergo the reduction process at the entire surface of MIEC cathode, not only at a triple phase boundary (cathode-electrolyte-air), which in turn lowers polarisation resistance of the cell. Besides, TECs values for these compounds (10-13*10^{-6} K^{-1}) are compatible with the TECs values of state-of-the-art oxide-ion (YSZ, GDC) and proton conducting ($BaCeO_3$, $BaZrO_3$) electrolyte materials [1].

The best values of surface exchange coefficient (*k'*) and oxygen diffusion coefficient (D^*) in the row RE_2NiO_4 (RE = La, Pr, Nd; $R_{La} > R_{Pr} > R_{Nd}$) were reported for $Pr_2NiO_{4+\delta}$. Unfortunately, this compound is unstable in air at T > 600 °C [2]. Since $La_2NiO_{4+\delta}$ has better thermal stability [3] and $Nd_2NiO_{4+\delta}$ reacts less with electrolyte materials [4], it is reasonable to consider partial substitution by La or Nd in $Pr_2NiO_{4+\delta}$ to get improved stability along with high oxygen transport properties. In this work we also considered substitution by Ce. Since Ce^{3+} cations have close ionic radius to La^{3+} cations we could expect an improvement concerning thermal stability. Sometimes a buffer layer based on CeO_2 is used between $Pr_2NiO_{4+\delta}$ and YSZ for better compatibility [5]. Besides, it was reported that Pr cations prone to diffuse into CeO_2 lattice without the deterioration of the cell performance [6]. However, there are very few studies on Ce substitution into $Pr_2NiO_{4+\delta}$.

In this particular study we synthesized $Pr_{2-x}RE_xNiO_{4+\delta}$ (RE = La, Nd; x = 0, 0.5, 1) samples and attempted to synthesize $Pr_{2-x}Ce_xNiO_{4+\delta}$ (x = 0.1, 0.5, 1) samples via Pechini route. The synthesized samples were studied by XRD using a Bruker D8 Advance diffractometer (Germany). For thermal stability evaluation we performed a synchrotron *in situ* XRD study using equipment of the «Precision diffractometry – 2» station at VEPP-3 storage ring (Siberian Synchrotron and Terahertz Radiation Centre, Novosibirsk, Russia) [7]. The samples were heated/cooled in the temperature range of 30-700-30 °C with a rate of 10 °C/min first in He flow (100 SCCM), then in synthetic air flow (80 SCCM He + 20 SCCM O_2). The composition of the gas phase was controlled by a quadruple mass-spectrometer SRS UGA200 (USA).

The study revealed a phase inhomogeneity: the samples consisted of at least 2-3 distinguishable phases with the same structural type (K_2NiF_4, s.g. *Fmmm*) but with slightly different lattice parameters. In addition, the temperatures of the *Fmmm – I4/mmm* phase transition observed for all the phases were slightly different in each case.

Upon heating the $PrNdNiO_{4+\delta}$ sample in He flow, we observed a deterioration of the structure accompanied by release of H_2, CO_2, H_2O gases detected by a mass-spectrometer signal. Interestingly that after feeding the oxygen the structure reverted back to its original state and remained stable when heated again in the He flow.

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PP-18

Structure-Dependent Functional Self-Assemblies Based on a Thiobarbiturate-Barbiturate-Melamine Three-Component System

Moskalenko I.V.[1], Nesterov P.V.[1], Timralieva A.A.[1], Shilovskikh V.V.[1,2], Skorb E.V.[1]
1 – ITMO University, St. Petersburg, Russia
2 – Immanuel Kant Baltic Federal University, Kaliningrad, Russia
i.v.m.rostov.yar@gmail.com

Melamine-based self-assemblies have been the subject of scientific interest for more than several decades due to its unique structural properties and the prospects of the programmable assembly of functional materials. One of the most interesting is melamine barbiturate (M-B) self-assembly material based on a rigid two-dimensional (2D)-network composed of molecules of melamine (M) and barbituric acid (BA) [1]. It can be used in drug delivery systems, photocatalysts, LED systems, antioxidant systems, piezo sensors [2]. On the other hand, the incorporation of extra compounds into M-B can lead to pronounced change of morphology and structure. Closest structural analog of BA is thiobarbituric acid (TBA).

Self-assembly of melamine thiobarbiturate does not go under normal conditions (room temperature). We add thiobarbituric acid to barbituric acid solution in high or low concentrations to determine whether TBA affect the morphology of M-B crystal. In case of low concentrations of TBA, we observe classic M-B crystals with defective twinning growth points. In case of high concentrations of TBA, we observe "hedgehog" crystal shape. Single needle of the “headgedog” has the shape of a hexagonal prism crowned with the head of a triangular pyramid. If we grow the crystal *via* diffusion control, we observe hexagonal crystals (Fig. 1). All crystals show significant luminescence in fluorescent channels (RHOD, FITC, DAPI). The presence of thiobarbituric acid in the structure was confirmed by EDX spectroscopy as sulfur presents.

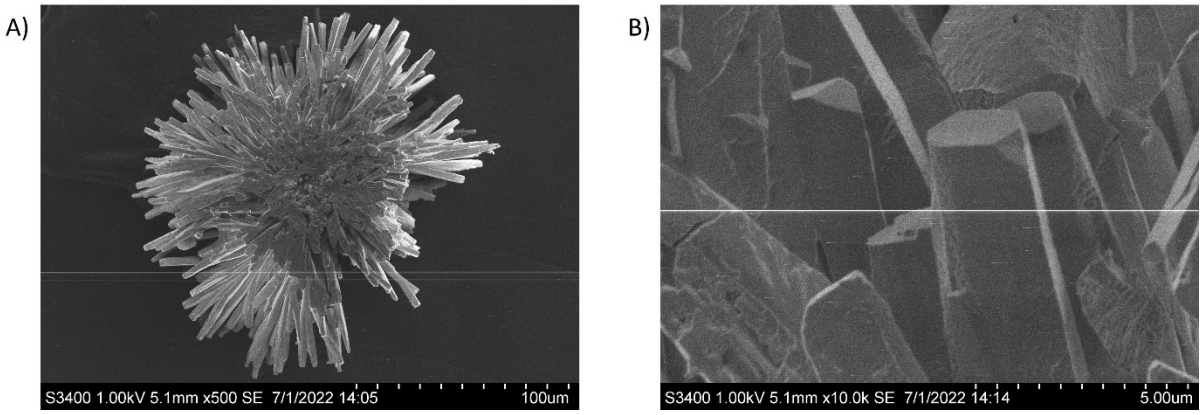

Fig. 1. SEM images of the TBA-BA-M crystal obtained by diffusion control.

X-ray phase analysis shows that the structure of these supramolecular assemblies is the same in comparison to M-B. We calculated Gibbs free energy of formation of self-assembly of melamine thiobarbiturate using DFT. Thiobarbituric acid is less favorable for the formation of a dimer with melamine (ΔG=-28.98 kJ/mol) than barbituric acid (ΔG=-40.9 kJ/mol) as sulfur

atom of TBA does not form hydrogen bonding with M. Thus, arrangement of thiobarbituric acid and melamine in different planes is more favorable (Fig. 2).

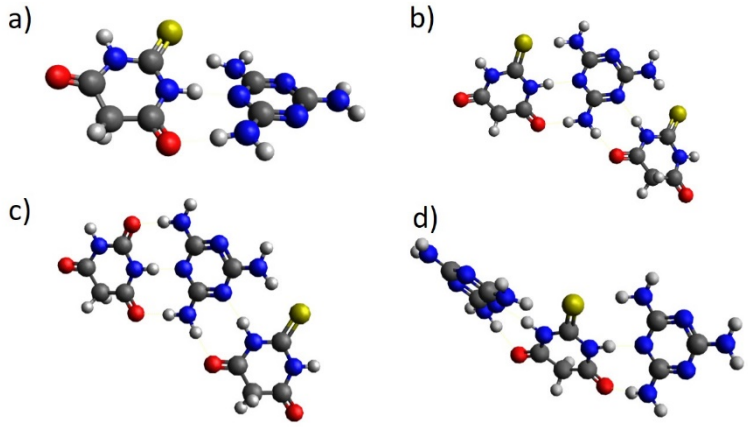

Fig. 2. Optimized structures of TBA-M dimer (a), TBA-M-TBA trimer (b), BA-M-TBA trimer (c), M-TBA-M trimer (d).

Thus, thiobarbituric acid changes the morphology and shape of melamine barbiturate crystals. In this case, the surface area increases that makes this system promising for catalytic systems development.

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PP-19

Identification of Platinum Iodo Complexes in the System Pt(II) – NaI – CH_3I – C_2H_3I – Acetone Using Synchrotron X-Ray Absorption Spectroscopy

Nikitenko D.V.[1], Bugaev A.L.[2], Krasnyakova T.V.[1], Mitchenko S.A.[1]

1 – L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, Donetsk

2 – The Smart Materials Research Institute, Southern Federal University, Rostov-on-Don, Russia

nykytenko.dv@gmail.com

Synchrotron X-ray absorption spectroscopy (XAS) is a widely used method for studying the local geometric and electronic structure of matter. Unlike diffraction methods, XAS can be used to study substances without a long-range order, i.e. amorphous, liquid, gaseous. Another advantage of XAS is its element selectivity with the ability to study systems with a low content of components [1].

The XAS spectrum is a unique and unambiguous characteristic of a substance: each structure has its own position of the absorption edge and a unique spectrum. The XAS spectrum is usually divided into two regions: a near-edge one (X-ray absorption near edge structure, XANES), located within 50-100 eV beyond the absorption edge, and an extended region (extended X-ray absorption fine structure, EXAFS). From EXAFS, it is possible to extract structural parameters such as coordination numbers, interatomic distances and Debye-Waller parameters for the first and several subsequent coordination spheres around a given element. An analysis of the XANES region provides information on the valence state of an atom, symmetry of its environment, ligand type and bond angles [2].

In our work, XAS in combination with ^{1}H, ^{13}C, ^{195}Pt NMR spectroscopy and high-resolution mass spectrometry were used to identify intermediates of a homogeneous catalytic cross-electrophilic coupling reaction in a liquid-phase system Pt(II) – NaI – CH_3I – C_2H_3I – acetone.

The initial state, according to the position of the Pt L_3-edge, corresponds to Pt(II) species. Being dissolved in acetone in presence of NaI, platinum is loosing the Cl-ligands forming bonds with iodide ligands, evidenced by both XANES spectra, which become identical to that of Pt(II) iodide (Fig. 1a), and in FT-EXAFS data, where a clear loss of Pt-Cl contribution at ca. 2 Å (phase-uncorrected) with the growth of Pt-I contribution at ca. 2.5 Å (phase-uncorrected) is observed (Fig. 1b). The decreased intensity of the white line at ca. 11 565 eV indicates smaller electron donation from Pt to ligand for the dissolved sample in comparison with the initial Na_2PtCl_4. After addition of C_2H_3I, a gradual decrease of Pt-I contribution from 4.0 to ca. 3.8 (Fig. 2). This change may indicate the formation of organoplatinum intermediates during the reaction.

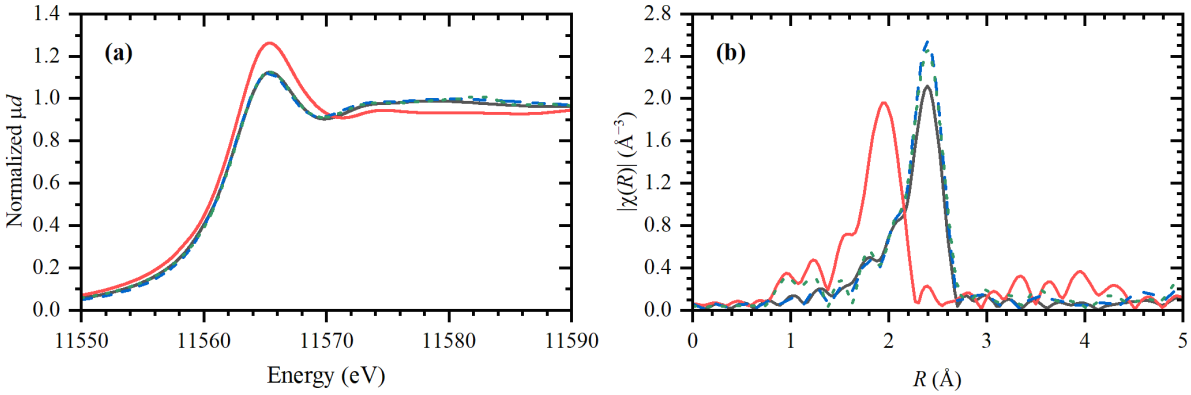

Fig. 1. Experimental Pt L_3-edge XANES (a) and phase-uncorrected FT-EXAFS (b) data for the reference PtI_2 (solid black) and Na_2PtCl_4 in its crystalline form (solid red), after dissolving in acetone with addition of NaI (dashed blue) and addition of NaI and CH_3I (dotted green).

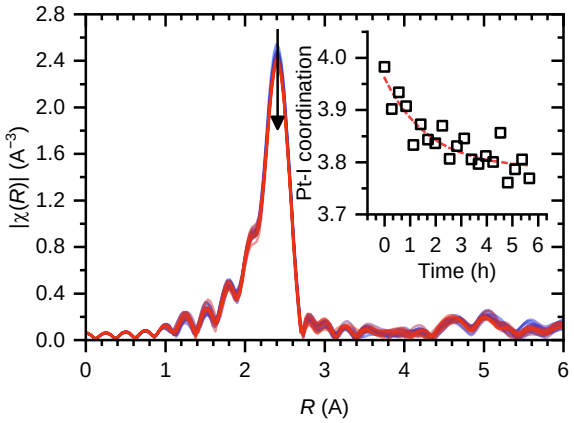

Fig. 2. Evolution of the phase-uncorrected FT-EXAFS data (from blue to red) for Na_2PtCl_4 dissolved in acetone in presence of NaI, CH_3I and C_2H_3I (from blue to red). The inset shows the evolution of Pt-I coordination number from the first-shell EXAFS fitting.

Acknowledgement: A.L. Bugaev acknowledges the President's Grant of Russian Federation for young scientists МК-5853.2021.1.2 for funding XAS investigation.

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PP-20

Theoretical and Experimental IR Investigation of Hydrocarbons Adsorption on Palladium Nanocatalysts

Pnevskaya A.Yu., Usoltsev O.A., Kozyr E.G., Tereshchenko A.A., Skorynina A.A., Bugaev A.L., Soldatov A.V.

The Smart Materials Research Institute, Southern Federal University, Rostov-on-Don, Russia
pnevskaya@sfedu.ru

Nanoparticles have a number of advantages over their bulk counterparts, such as surface area and activity. Palladium catalysts are being extensively used for hydrogenation of unsaturated hydrocarbons (e.g., selective hydrogenation of acetylene traces in ethylene-rich mixtures) [1]; a large number of studies was aimed to get structural insights into the catalytic processes [2-3]. An important step in such reactions is the adsorption of hydrocarbon molecules on the palladium surface, since different adsorption geometries can lead to different reaction products. In this work, we report the combined experimental and theoretical study of the industrial catalysts consisting of 2.6 nm supported palladium nanoparticles (NPs) probed by in situ EXAFS, XANES, X-ray diffraction (XRD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), complemented by DFT calculations.

In situ Pd K-edge XAFS and XRD measurements were performed simultaneously for the Pd/C sample at BM31 beamline of ESRF (Grenoble, France). The sample was loaded inside 2 mm quartz glass capillaries and connected to a remotely controlled gas line. Prior to exposure to hydrocarbons, the samples were activated in 20 mL/min flow of 20% H2/He at 125 °C for 30 min and then purged by He flow. Then, the sample was cooled down to 50 °C and exposed to pure ethylene flow (20 mL/min).

In situ DRIFTS measurements for Pd/Al_2O_3 were performed on Bruker Vertex 70 spectrometer. Measurements were performed in range 5000–400 cm^{-1} with a 1 cm^{-1} resolution, 40 scans, and automatically transformed into absorption units using the Kubelka–Munk function. The powdered sample (12.8 mg) was loaded into a cell enabling to control the temperature and the gas flow. An external gas system equipped with mass flow controllers was used to set the gas flows of Ar, H_2, and C_2H_4 through the cell. The gas mixture flowed either through the cell with the sample, or through a by-pass. Switching was carried out using 3-way valves.

Atomic structures of the adsorbed C_nH_m molecules on palladium (111) and (100) surfaces and their vibrational spectra were obtained using VASP [4]. 5 layer Pd surfaces in (111) and (100) geometries were constructed with initial Pd–Pd distances a = 2.75 Å and then optimized within conjugated gradient algorithm. The cut-off energy for the plane-wave basis set of 500 eV was used. The Monkhorst–Pack method was used to generate k-points 5 × 5 × 1 and 9 × 9 × 1 grids for (111) and (100) surfaces, respectively. The convergence criteria were set to 10^{-6} eV for self-consistent field calculations and 10^{-5} eV for geometry relaxation. The infrared

spectra of the optimized structures with adsorbed hydrocarbon molecules were simulated keeping all palladium atoms fixed, which was checked not to affect the spectra for several selected cases.

In this work, it was shown that adsorbed ethylene dehydrogenates to C_2H_3, C_2H_2 and C_2H and, finally, decomposes into palladium carbide. The combination of in situ XAFS, XRD and DRIFTS data provided not only complementary information, but also facilitated the mutual interpretation of the data from different techniques. This study reveals the evolution pathway of ethylene on industrial Pd-catalyst under atmospheric pressure at moderate temperatures, and provides a conceptual framework for the experimental and theoretical investigation of palladium-based systems.

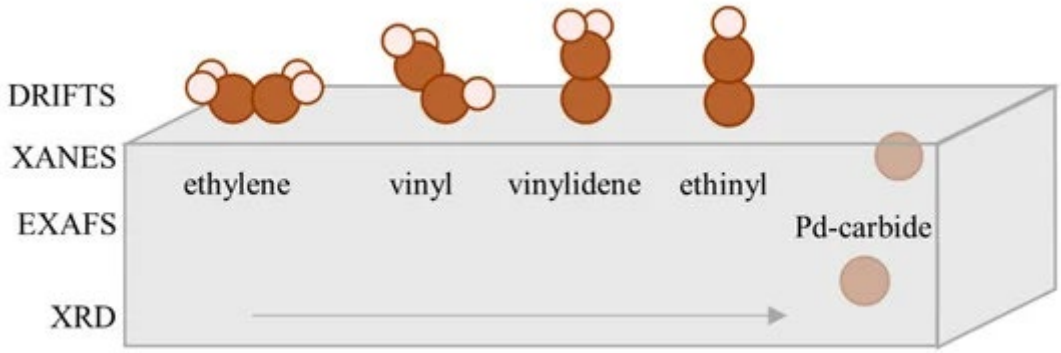

Fig. 1. Ethylene dehydrogenation pathway based on XRD, EXAFS, XANES and DRIFTS data.

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PP-21

Local Chemical Order in Al92Ce8 Metallic Glass

Uporov S.[1], Zubavichus Y.[2], Pryanichnikov S.[1]
1 – Institute of Metallurgy, UrD RAS, Ekaterinburg, Russia
2 – Synchrotron Radiation Facility SKIF, 630559, Koltsovo, Nikolskii pr., 1, Russia
stepian@yandex.ru

For arc-melted $Al_{92}Ce_8$ the comparison of crystalline and amorphous samples is carried out. Amorphous ribbon was obtained by quenching from 1580–1600 K using standard spinning technique at a wheel speed of 32 m/s. Ce L3-edge XANES and EXAFS experiments were performed on was studied using X-ray synchrotron radiation at the Structural Materials Science beamline [1] of the Kurchatov Synchrotron Radiation Center (Moscow, Russia). . X-ray diffraction (XRD) patterns were obtained in the transmission (Debye-Scherrer) geometry using a FujiFilm ImagingPlate 2D detector, λ = 0.68886 Å.

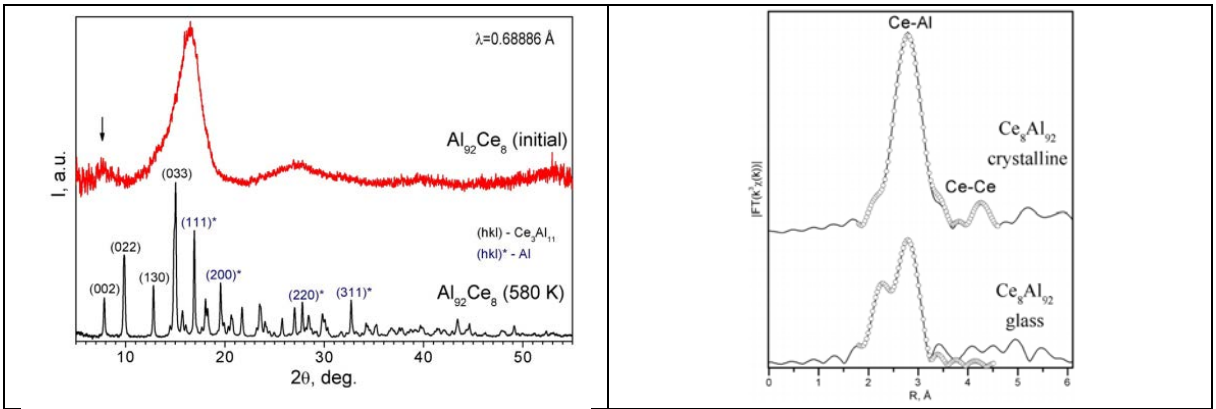

Fig. 1. X-ray diffraction patterns (left) and Fourier transforms of Ce L3-edge EXAFS spectra for Al92Ce8 in the glassy and crystalline samples.

XANES spectroscopy data gives significant fraction of tetravalent cerium 4f 0 (Ce4+) for both amorphous and crystalline states. The local structural parameters for crystalline state such as coordination number N=12.0±1 for Ce-atom and interatomic distance RAl–Ce =3.26 ± 0.02 Å are in excellent agreement with crystallographic data. The best result of the EXAFS fitting procedure for amorphous samples are given by Ce–Al distance that is rather short as compared with one obtained for crystalline samples (RAl–Ce = 3.23 ± 0.02 Å), while the coordination number around cerium is the same. This result contradicts to the prediction of the efficient atomic packing model, which suggests that the coordination number around rare earth atoms is about 17 [2]. Besides, no indication of the Ce atoms presence in the first coordination shell for both condensed phases was found.

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PP-22

Some Basic Aspects of Synchrotron Mössbauer Reflectometry for Depth-Selective Studies of Corrosion Products

Semenov V.G., Panchuk V.V.
St. Petersburg State University, St. Petersburg, Russia
val_sem@mail.ru

Nuclear resonance (Mössbauer) reflectometry, the possibility of which is largely due to the creation of nuclear resonance scattering stations on 3rd and 4th generation synchrotrons, is a unique tool for studying hyperfine interactions reflecting the phase composition, magnetic, and electrical properties of materials containing a Mössbauer isotope. In contrast to conventional Mössbauer spectroscopy sensitive to the (energy domain) hyperfine shift and splitting of nuclear transition nuclear resonance scattering of synchrotron radiation (NRS of SR) shows the effect of hyperfine interactions in form of (time domain) quantum beats. Synchrotron Mossbauer reflectometry **(**SMR) means measuring the time-dependent reflectivity, i.e. taking several time-domain grazing incidence spectra after the coherent excitation of the hyperfine split nuclear sublevels by synchrotron pulse (at t=0) at various angles of grazing incidence Θ and evaluating all these spectra simultaneously in order to determine the depth profile of hyperfine interactions. In other words, the full information is contained in time and angle-dependent 3D spectra. To demonstrate the possibilities of SMR, we present the results of the investigation of the corrosion process in ~20 nm thick ^{57}Fe film deposited by magnetron sputtering on a glass substrate of the “float glass” type. The samples were oxidized in air at various temperatures up to 470° C. The Mössbauer measurements were conducted both in energy and time domains. The depth selective parameters of the iron-containing phases were obtained from the analysis of the time and energy spectra and were well consistent with each other. The proposed approach makes it possible to use Mössbauer reflectometry of synchrotron radiation for depth-selective diagnosis of ultrathin surface layers, multilayer synthetic structures, catalyst surfaces, etc.

PP-23

Photoactivation of Dinitrogen Tetroxide and Carbon Tetrachloride in the Interlayer Space of Fluorinated Graphite Matrices

Semushkina G.I.[1], Fedoseeva Y.V.[1], Makarova A.A.[2], Prosvirin I.P.[3], Pinakov D.V.[1], Chekhova G.N.[1], Okotrub A.V.[1], Bulusheva L.G.[1]

1 – Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia

2 – Physikalische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Berlin, Germany

3 – Boreskov Institute of Catalysis, Novosibirsk, Russia

semushkina.g@niic.nsc.ru

Fluorinated graphites are layered carbon materials possessing a good chemical, mechanical, and thermal stability. Fluorination of graphite using inorganic fluorides at room temperature produces compounds with a composition CF_x, where x is usually bellow 0.5. Due to their layered structure and unique amphoteric redox properties, these compounds can serve as promising carriers of many substances, both donors and acceptors. Of particular research interest are carbon materials as containers for toxic compounds NO_x, SO_2, CCl_4, etc. In addition, the carbon carrier has photocatalytic properties, causing denitrification of NO_x with the formation of non-toxic N_2. The photoionization of NO_x and CCl_4 also attracts attention from the point of view of studying the processes in the Earth's atmosphere under the action of solar radiation, since these compounds play a key role in redox cycles, including contributing to the depletion of the ozone layer.

This work is aimed at an in situ XPS and NEXAFS study of fluorinated graphites with embedded dinitrogen tetroxide and carbon tetrachloride molecules after continuous illumination with a high-intensity polychromatic photon beam (zero-order light from the dipole beamline of the BESSY II synchrotron radiation facility). We investigated two samples of the same matrices composition with embedded N_2O_4 and CCl_4. Density functional theory calculations of a fluorinated graphene fragment are used to interpret experimental data.

In this work, we performed a comprehensive analysis of the functional composition, electronic structure and stability of fluorinated graphite matrices, as well as the photochemical activity of intercalated N_2O_4 and CCl_4 before and after exposure to a zero-order synchrotron beam for up to 420 seconds using in situ XPS and NEXAFS spectroscopy. The introduction of N_2O_4 in the interlayer space of fluorinated graphite matrices causes a number of chemical reactions with the dissociation of N_2O_4 to NO_2 and disproportionation reactions with the formation of NO_3 and NO, followed by denitrification to N_2. It has been found that exposure to a zero-order synchrotron beam leads to defluorination of the fluorinated graphite system with possible removal of carbon and the formation of vacancy defects, regardless of the nature of the intercalate. Photolysis of the NO_x intercalate under the action of synchrotron radiation in the interlayer space of fluorinated graphite matrices leads to the incorporation of nitrogen atoms into the graphite lattice in the form of pyrrole-like nitrogen atoms and the formation of at least two states of chlorine Cl-C and organochlorine for CCl_4.

PP-24

Physicochemical Properties of Three-Component Ionogels Based on Ionic Liquid, Na-Bentonite/Halloysite, and Microcrystalline Cellulose

Shibaeva V.D.
Institute of Chemistry of Solutions. G.A. Krestov Russian Academy of Sciences, Ivanovo, Russia
vds@isc-ras.ru

Currently, more and more attention has been paid to the development of new high-performance materials and technologies that meet the requirements of "green" chemistry. The most notable area of research is the development of high performance nanocomposites containing covalently bonded stable porous structures.

Ionogels based on various ionic liquids and clays, the gel-like state of which is stabilized by polymers, are promising materials in the field of "green" chemistry, as they retain chemical inertness, low vapor pressure, and high ionic conductivity. In addition, an expensive component is diluted with a much cheaper and more common one, without compromising its unique properties, which will reduce its cost while increasing efficiency [1].

As a result of interaction with clays, ionic liquids change their fluidity, temperature range of the liquid state, and thermal stability. The physicochemical properties of such ionogels depend on the interaction of the ionic liquid with the porous spaces of the clay.

Ionic liquids also have good potential for creating new polymeric materials, as they act as very effective solvents for natural polymers such as cellulose. We chose 1-butyl-3-methylimidazolium acetate as the object of research, since this liquid has not only low vapor pressure, high ionic activity, but also the ability to dissolve microcrystalline cellulose up to 25 wt.%, due to the breaking of branched networks of hydrogen bonds in polymer.

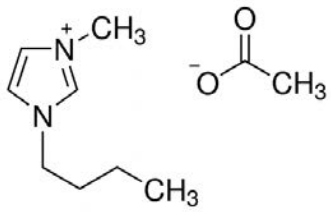

Fig. 1.The structure of the cation and anion of a chemical ionic liquid

As a filler to stabilize the gelation of the ionic liquid/microcrystalline cellulose solution, two clays were used: Na-bentonite and halloysite. Due to the different structure of layered aluminosilicates, we were able to draw conclusions about the effect of the structure of clay minerals on the properties of the ionogels we obtained.

The combination of all three components in one composite makes it possible to obtain a new material that not only has high electrical conductivity, but also exhibits excellent thermal stability, toughness and plasticity.

The properties of the ionogels obtained by us were studied using various methods, such as scanning electron microscopy, X-ray phase analysis, IR spectroscopy, thermogravimetric and rheological studies.

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PP-25

Structure-Dependent Supramolecular Assemblies for Co-Antioxidant Systems

Timralieva A.A.[1], Shilovskikh V.V.[2], Moskalenko I.V.[1], Skorb E.V.[1]
1 – ITMO University, St. Petersburg, Russia
2 – Immanuel Kant Baltic Federal University, Kaliningrad, Russia
timralieva@itmo.ru

Supramolecular assemblies are widely used as functional materials due to their specific properties. Almost all supramolecular assemblies are extremely sensitive to formation conditions and can be specifically designed according to required functions [1]. Melamine barbiturate (MB) self-assembly consists of melamine (M) and barbituric acid (BA) molecules bind by three hydrogen bonding. Layers of M-B linear tapes are also bind by π- π-stacking [2]. Melamine is protonated, and barbituric acid is deprotonated [3]. Thus, this assembly is sensitive to pH changes and reversible.

We observed that M-B crystals show significant luminescence in FITC channel. The schematic structure of M-B shows that there should be no electron transfer in such way. We supposed the presence of radicals in the structure. Electron paramagnetic resonance (EPR) showed that M-B has two radical centres of different nature. One is O-centred radical, second is C-centred radical. Most likely, O-centred radical is hydroperoxyl (HO·) radical. It is likely produced during BA oxidation *via* singlet oxygen. CH· radicals of BA are also produced. Hydroperoxyl radical stay inactive into the structure of M-B. We suppose that hydroperoxyl radical can be activated in the presence of antioxidants. OH· radical involves in the regeneration cycle with antioxidants such as nitroxides, phenols, amines, quinones *via* fast hydrogen atom transfer (HAT). Thus, we perform a novel component of co-antioxidant systems.

Besides, M-B can neutralize HO· radicals and H_2O_2 via also HAT with the CH· radicals produce. However, M-B structure weakly changes in the presence of hydrogen peroxide. We observe several morphological changes and XRD spectra (Figure 1). The reflex intensity (plane 002) that is bind interplanar space increases, and a new little reflex appears. Thus, we suppose to use several methods such as NEXAFS to analyze these changes.

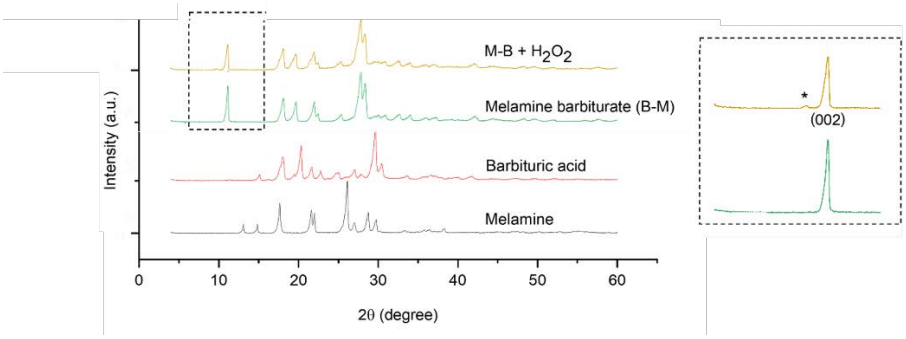

Fig. 1. XRD spectra of M-B and M-B formed in the presence of H_2O_2

Acknowledgement: The work was carried out with the support of the Ministry of Science and Higher Education of the Russian Federation (agreement № 075-15-2021-1349).

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PP-26

Synchrotron Study of the "Mouse Fibroblast Cells – Porous Silicon Nanoparticles" Bio-Nano-Hybrid Structure for Biomedical Applications

Titova S.S.[1], Osminkina L.A.[2], Kakuliia I.S.[1], Parinova E.V.[1], Chuvenkova O.A.[1], Chumakov R.G.[3], Lebedev A.M.[3], Kudryavtsev A.A.[4], Beltiukov A.N.[5], Chukavin A.I.[5], Turishchev S.Yu.[1]

1 – Voronezh State University, Voronezh, Russia

2 – Lomonosov Moscow State University, Moscow, Russia

3 – National Research Center "Kurchatov Institute", Moscow, Russia

4 – Institute of Cell Biophysics of the Russian Academy of Sciences, Pushchino, Russia

5 – Udmurt Federal Research Center of the Ural Branch of the Russian Academy of Sciences, Izhevsk, Russia

titova@phys.vsu.ru

Bio-nano-hybrid materials can be obtained by combining inorganic nanostructures with biological objects. Porous silicon nanoparticles (PSi NPs) have a number of specific, unusual biological properties. These properties make it possible to combine PSi NPs with organic mammalian celluls. Such bio-nano-hybrid structures have a huge research interest in the scientific community. High–precision diagnostics of such materials and structures is an important part of their effective application, including in theranostics and biomedicine. Changes in the physicochemical state of the surface, which largely determines the properties of PSi NPs when integrated with the biological structure, are extremely relevant for study. The synchrotron XANES (X-ray Absorption Near Edge Structure) allows obtaining information about the physicochemical state, composition, structure, atomic and electronic structure of not only nanoscale objects, but also biohybrid nanostructures, which are characterized by an extremely developed surface.

An aqueous suspension of porous silicon nanoparticles was used as a material integrated into cells. The suspension was obtained by grinding porous silicon films (electrochemical etched Si) in the ball mill Fritsch Pulverisette 7. The organic part of the biohybrid structure for this work were 3T3 NIH cell cultures (mouse fibroblasts) grown on the gold surface for three days. As a result of the integration of PSi NPs into 3T3 NIH cells, a hybrid sample was obtained, the incubation time of silicon nanoparticles was 72 hours. XANES spectra were registered for $L_{2,3}$ – edge of silicon atoms or K – edge of oxygen atoms. NanoPES beamline of the Kurchatov synchrotron radiation center (NRC "Kurchatov Institute") was used.

The results of experimental synchrotron studies of the electronic structure and composition of the biohybrid structure "mouse fibroblasts - silicon nanoparticles" by XANES spectroscopy together with scanning electron microscopy data allow us to conclude that nanoparticles combined with biological objects are subject to changes in the composition, structure and physico-chemical state of the surface. In its turn this should allow precision variation of the nanoparticles impact to mammalian cells by integration.

Acknowledgement: This work was supported by the Russian Science Foundation (project 19-72-20180). The work is additionally supported by the Ministry of Science and Higher Education of Russian Federation under Agreement No. 075-15-2021-1351 in part synchrotron diagnostics methodology.

PP-27

The Influence of Mill Jar Material on a Mechanochemical Reaction. A Case Study of the 'Nicotinamide – Adipic Acid System'

Tumanov I.A.[1,2], Arkhipov S.G.[1,2], Kolybalov D.S.,[2] Boldyreva E.V.[1,2]
1 – Boreskov Institute of Catalysis, Novosibirsk, Russia
2 – Novosibirsk State University, Novosibirsk, Russia
tumanov@g.nsu.ru

While different mechanochemical methods attracted ample attention in area of organic synthesis, the fact that the reaction took place in a closed container (i.e. milling jar) made it quite difficult, if not impossible, to observe and control the process without interrupting it. The only reliable method to "observe" the reaction would be to halt it at certain time and then to extract and examine the sample by any available techniques. Since a decade, however, time-resolved in situ (TRIS) studies of mechanochemical reactions became possible using a synchrotron radiation source [1]. Even for synchrotron radiation, the milling jar material (usually stainless steel) is substituted with a plastic, which is more transparent to the X-rays, usually polymethylmethacrylate (PMMA). Recently it was shown that the results of mechanical treatment of a sample from the same batch in the same mill and following exactly the same protocol with the only difference being the jar material: steel or different polymers (polylactic acid PLA, Polyethylene terephthalate glycol PET-G, and acrylonitrile butadiene styrene ABS) can differ [2]. This makes it difficult to compare correctly the results of ex situ and in situ mechanochemical experiments, as well as of the in situ experiments performed by different groups. For a case study, a polymorphic transition in a crystalline amino acid, β-polymorph of glycine ($^{+}NH_3$-CH_2-COO^{-}) was studied in [2]. In the present study we extended the comparison to a multi-component system, namely 'nicotinamide – adipic acid' system. The ball-milling of a mixture of these components was studied recently using synchrotron radiation and shown to give several different products depending on the experimental protocol [3]. Our comparative mechanochemical experiments demonstrate that different products are formed, when using different polymers as milling jar material, all of them differing also from the results of the treatment in a stainless steel milling jar.

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PP-28

Machine Learning Application XANES Analysis of Pd Nanocatalysts

Usoltsev O.A.[1], Bugaev A.L.[2], Guda A.A.[1], Guda S.A.[1], Soldatov A.V.[1]

1 – The Smart Materials Research Institute of The Southern Federal University, Rostov-on-Don, Russia

2 – Federal State Budgetary Institution of Science "Federal Research Centre The Southern Scientific Centre of The Russian Academy of Sciences", Rostov-on-Don, Russia

oleg-usol@yandex.ru

Machine learning (ML) algorithms are a promising analytic tool that has found applications in many areas of science. This method has proven itself for tasks with a large number of parameters and is effective for big data processing. At the same time, near edge X-ray absorption spectroscopy (XANES) is a powerful tool widely used to determine the atomic and electronic properties of catalysts. However, XANES analysis has not completed procedure of analysis, since there is no unambiguous method for determining the structural parameters, while the amount of experimental data increases exponentially every day. We offered 2 options for solving this problem. On the one hand, in many cases, the analysis of XANES data requires the construction of theoretical models with a huge number of variable parameters. Application of ML to fit theoretical experimental data opens up new horizons for determining the structural parameters of the investigated substance. We applied the Extra Trees method for the time-resolved XANES spectra of Pd NPs. The evolution of structural parameters was obtained and compared with the method of principal component analysis (PCA) and multivariate parametric interpolation. We constructed a training set based on theoretical XANES spectra calculated in the FDMNES program for Pd NPs with different interatomic distances and in the presence of hydrogen and carbon-containing particles. On the other hand, it is used as an adjunct to extended-region X-ray absorption spectroscopy (EXAFS) analysis. We have labelled over 500 EXAFS spectra using a single-sphere analysis method. Then the Extra trees training was carried out for only XANES spectral regions, using tagged data. This approach made it possible to predict interatomic distances and the Debye - Waller parameter based only on experimental data.

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PP-29

Development Status of the 1-2 Beamline “Structural Diagnostics” at the SRF SKIF

Vinokurov Z.S.[1], Shmakov A.N.[1], Mishchenko D.D.[1], Selyutin A.G.[1], Syrtanov M.S.[2], Denisov V.V.[3], Teresov A.D.[3], Koval N.N.[3]

1 – SRF “SKIF” BIC SB RAS, Novosibirsk, Russia

2 – Tomsk Polytechnic University, Russia

3 - Institute of High Current Electronics, Tomsk, Russia

vinokurovzs@catalysis.ru

We present progress of the development of the new synchrotron beamline optimised for monochromatic *in situ* powder and single-crystal X-ray diffraction first presented in 2020 [1]. Detailed description of the main components of the instrument and development status of each will be presented. In particular, the equipment choices and specifics in terms of the key beam defining components, end-station diffractometers and detectors will be discussed. The expected performance in terms of photon flux, focusing capabilities and techniques will be compared to the performance of similar beamlines at the ESRF-EBS, MAX IV, Sirius and Diamond-II 4th generation light sources. The scope of the future development will be defined.

Acknowledgement: This work was funded within the framework of budget project for Synchrotron radiation facility SKIF, Boreskov Institute of Catalysis.

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PP-30

Synchrotron Radiation Diffraction Analysis Application for a Wear Resistant Functional Coating Microstructure Diagnostics

Vitoshkin I.E., Golyshev A.A.

1 – Khristianovich Institute of Theoretical and Applied Mechanics, Novosibirsk, Russia

ghatu0oosj37@mail.ru

One of the most significant advantages of synchrotron radiation is its high intensity which allows to acquire a signal of the diffraction even for the beams passed through thick (~1 μm) samples. This feature makes synchrotron radiation diffraction analysis (SRDA) a perfect method for the diagnostics of composite coating materials exceeding the conventional transparent electron microscopy (easier sample preparation, larger volume of the material to analyze) and X-ray diffraction (larger volume of the material to analyze, lower time consumption for the process) methods.

Wear resistance of the composite functional coatings directly depends on its microstructure which can be divided into its phase composition and the morphology of these phases. To control the microstructure of such a coating SRDA and scanning electron microscopy were applied in this work. As a coating there were mixtures of Ti-6Al-4V alloy and WC powders in several proportions which were melted by a fiber laser beam on a surface of a Ti-6Al-4V alloy substrate.

Preliminary results (Figure 1) showed that in the initial materials interaction led to the formation of (Ti, W)C. The released W atoms were dissolved in the liquid Ti resulting in the higher β-Ti phase stabilization at the room temperature:

$$\mathrm{WC}_{\mathrm{P\bar{6}m2}} + Ti_L \rightarrow (Ti,W)C_{Fm\bar{3}m} + (Ti,W)_L$$

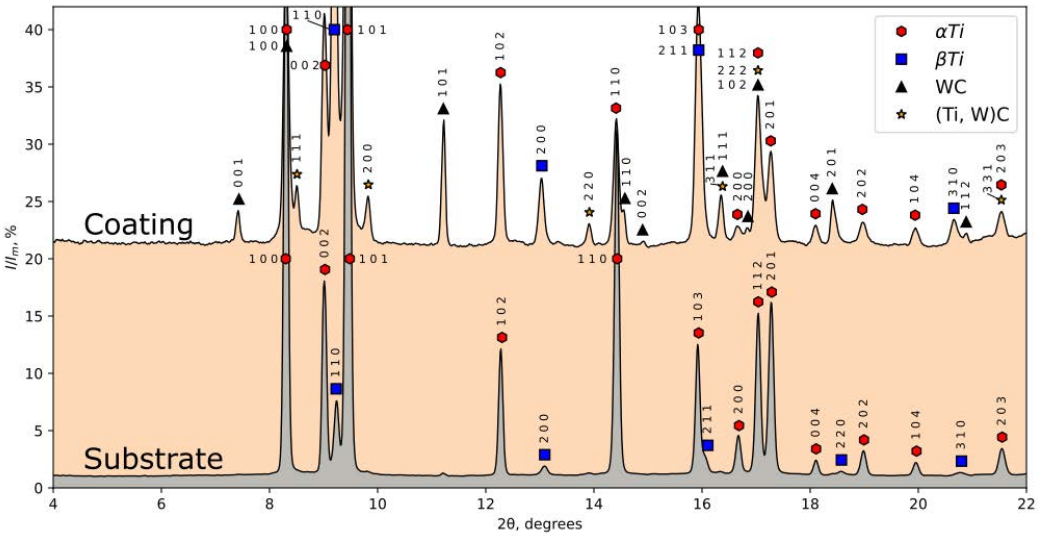

Figure 1 — SRDA patterns of the Ti-6Al4V substrate and the Ti/WC cermet coating

Acknowledgement: In order to notice the contribution, we kindly acknowledge A. Ancharov and INP SB RAS for the provided diffraction data.

PP-31

Mechanochemically Synthesized Biowaste-Derived Carbon Materials Doped with Nano-Sized Transition Metal Oxides as Electrocatalysts for Oxygen Evolution Reaction

Yazovskikh K., Maratkanova A.N., Shakov A.A., Syugaev A.V.
Physical-Technical Institute UdmFRC UB RAS, Izhevsk, Russia
k.yazovskikh@bk.ru

We report on a new type of the mechanochemically synthesized biowaste-based carbon materials doped with nanosized transition metal oxides, which are potentially used as high-performance, low-cost and eco-friendly electrocatalysts for oxygen evolution reaction (OER). By now, low-carbon economy has been the greener way to overcome the environmental challenges of fossil fuel emissions and global energy demands. From this perspective, increasing research efforts are currently applied to develop techniques and devices for energy storage and conversion. For instance, the progress in electrochemical water splitting technologies demands developing advanced OER electrocatalysts with high activity and long-term stability performance. Iridium oxides/hydroxides are now the best OER electrocatalysts to provide low overpotential and high corrosion resistance in acidic media. Nevertheless, poor stability of IrO_2 in alkaline media and natural scarcity of iridium stimulate searching for alternative cheaper materials. Low-cost transition metals (Mn, Co, Ni, Cu) can be used as starting materials for fabricating precious-metals-free electrocatalysts with high electrocatalytic performance [1].

Nowadays, carbon-based nanomaterials, including heteroatom-doped carbon materials and carbon-encapsulated metal/metal oxide nanoparticles, have attracted much interest owing to their remarkable electrocatalytic performance and long-term stability for OER [2]. Thus, the use of biowaste-derived carbon materials has an advantage for fabrication of electrocatalysts due to both their high potential and eco-friendly character. Recently, electrocatalysts containing cobalt nanoparticles evenly embedded in porous carbon networks fabricated via carbonization of a mixture of spent tea leaves and cobalt nitrate have shown the impressive electrocatalytic activity for OER [3].

Sunflower (*Helianthus annuus*) seeds are used as food- and oil crops. To be more specific, in 2020 Russia and Ukraine were the top producers of sunflower seeds making up both 53 % in its global production of ~50 million tonnes [4]. Sunflower seed hull (SSH) left as a by-product in the industrial processing and household using seeds is often just dumped into the environment. Being lignocellulosic biomass, SSH decomposes rather slowly and contains allelopathic compounds toxic to plants [5]. SSH biomass may be potentially used as a fuel, but the inherently low density makes its transportation and storage quite expensive. In this work, we propose a new strategy for the SSH utilization.

The mechanochemical synthesis is a very attractive way to produce the catalysts owing to its simplicity and eco-friendliness [6]. The high catalytic activity of the mechanochemically

synthesized materials arises from nanostructure, significant concentration of defects as well as close interaction between components which is difficult to reach via conventional chemical routes. The mechanochemical synthesis may be used as one-step process or just an intermediate stage in producing bulk catalysts (metal oxides, multi-component systems), supported catalysts (supported metal and metal oxide nanoparticles), composite and hybrid catalytic materials, doped systems, metal-organic frameworks [7].

The samples were prepared by short-term ball milling of SFH and transition metal nitrate to provide the desired fineness of the mixture milled. Also, wet ball milling in surfactant aqueous solution was used to get high surface area in the samples of hull fibers. The temperature of subsequent carbonization was chosen based on the thermal decomposition of lignin and cellulose which are strongly related in the hull structure with the use of thermogravimetric analysis and differential scanning calorimetry. The samples were then thermally air-annealed at the chosen temperature to simultaneously promote SFH carbonization and decomposition of transition metal nitrates into oxides. The electrocatalysts produced were characterized by scanning and transmission electron microscopies, X-ray diffraction analysis, X-ray photoelectron and Raman spectroscopies. The specific surface area of the samples was determined using the Brunauer–Emmett–Teller method. The OER electrocatalytic performance of the samples was tested in both alkaline and acidic environments.

To summarize, a low-cost synthesis route is proposed in this work to successfully fabricate efficient and stable OER electrocatalysts based on biowaste-derived carbon materials doped with transition metal oxide nanoparticles.

Acknowledgement: This study was performed within the scope of the state task of the Ministry of Science and Higher Education of the Russian Federation (no. 121030100003-7), using the equipment of the Center for Shared Usage of the UdmFRC UB RAS supported by the Ministry of Science and Higher Education of the Russian Federation (grant № RFMEFI62119X0035).

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PP-32

Similarity between the Mechanism of the Oxidative Dehydrogenation of Ethylbenzene to Styrene and the Isomerization of n-Alkanes

Mamedova M.T.
Mammadaliyev Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, Khojali pr. 30, Baku, Az1025 Azerbaijan
memmedova-melahet@mail.ru

The production of styrene (St) and the isomerization of n-alkanes are important chemical processes in industry. In this work, an attempt is made to find a relationship between the oxidative dehydrogenation of ethylbenzene (EB) to styrene over aluminum-chromium catalysts and the isomerization of n-alkanes over composite sulfated zirconium catalysts (CC).

It is assumed that both of these reactions proceed in the presence of oxygen. In the first case, this is nucleophilic oxygen - a reagent, and in the second case, it is electrophilic oxygen, which is part of the catalyst. This assumption is based on the following mechanisms of these processes proposed on the basis of experimental data.

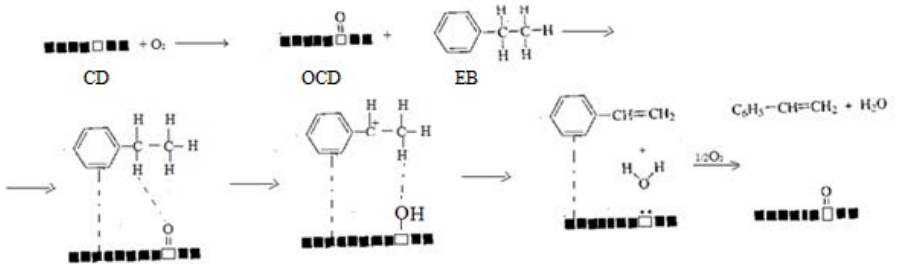
Naturally, the process of oxidative dehydrogenation is accompanied by the formation and accumulations of oxidative carbon deposits (OCD), and as a result, a low-activity catalyst is developed. It is assumed that, in the initial nonstationary stage of the process, St is formed at the Lewis acid centers and OCD formed with the participation of these centers and oxygen. OCD is responsible for the oxidative dehydrogenation of EB. The accumulation of OCD up to a monolayer coating is the beginning of a stable operation of the catalyst. A possible reason for the catalytic activity of OCD may be the geometric correspondence between EB and centers located on the surface of OCD, as a result of which high concentrations of carbon-oxygen centers responsible for the formation of St are created on the surface. Moreover, it is assumed that oxygen from the oxygen-containing groups of the surface is sufficiently reactive to participate in the oxidative dehydrogenation of EB to St. Such a scheme does not imply the formation of any EB intermediates with oxygen. Therefore, the formation of carbon deposits (CD) during direct EB dehydrogenation is similar to CD prior to the formation of OCD.

Thus, we can assume the following scheme for the formation of active sites on CD with the participation of O_2 in the oxidative dehydrogenation of EB to St:

$$2\square + O_2 \rightarrow 2\square = O$$

here □ - carbon defects contained in CD.

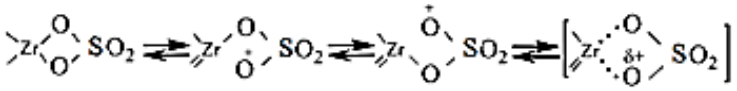
The process proceeds according to the mechanism described below:



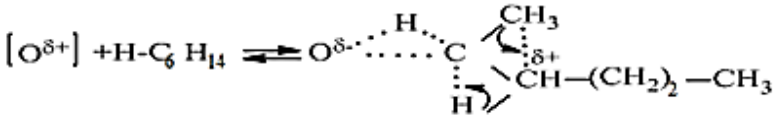
To elucidate the role of oxygen included in a composite catalyst (CC) whose components are sulfated zirconium dioxide and H-zeolite (HZSM-5) in the isomerization of alkanes, the conversion of n-hexane over this catalyst was studied.

The results obtained show that the main product of the process is iso-C_6 alkanes. In this case, both C_1 – C_5 and C_{7+} alkanes are also formed. These data indicate the formation of monomolecular and bimolecular intermediates and their subsequent isomerization or hydrocleavage to the corresponding products.

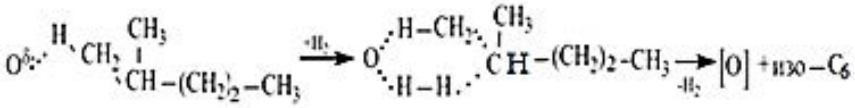
The conversion of hexane on CC can be represented by a multistage scheme: the activation of hexane is associated with interaction with the active sites of CC. Such centers on CC can be Lewis acid centers, which are electrophilic oxygen atoms, which can arise as a result of mobile equilibrium in the SO_4^{2-} - ZrO_2 system:



The interaction of n-C_6H_{14} with such a center leads to the formation of alkoxy groups with an excess of positive charge and their subsequent stabilization through the migration of the methyl group and the transfer of hydride ions, which are characteristic of skeletal izomerization:



The interaction of the resulting monomolecular intermediates with hydrogen molecules promotes the desorption of products according to the scheme:



Hydrogen is able to hydrogenate the C-C bond with the formation of low molecular weight products (β-cleavage), mainly propane, and the contribution of this reaction increases with increasing temperature.

Thus, the proposed schemes of the mechanisms of the oxidative dehydrogenation of ethylbenzene to styrene in the presence of aluminum-chromium catalysts and the isomerization of n-hexane on a composite catalyst containing HZSM-5 zeolite and sulfated zirconia show that both of these processes occur in the presence of oxygen. In the first case, it is free oxygen, the reactant, and in the second case, it is bound oxygen, which is part of the catalyst.

PP-33

Isomerization of Mixtures of n-Alkanes on Modified Zirconium Sulfate Catalysts

Mamedova M.T.
Mammadaliyev Institute of Petrochemical Processes, National Academy of Sciences of Azerbaijan, Khojali pr. 30, Baku, Az1025 Azerbaijan
memmedova-melahet@mail.ru

Modern requirements for high-octane fuel pose the problem of developing new catalysts with high activity and selectivity in the joint conversion and isomerization of aliphatic hydrocarbons - components of straight-run gasolines, gas gasoline, catalytic cracking gases and associated gas.

For the low-temperature isomerization of n-alkanes, their mixture, and gas gasoline - a natural mixture of alkanes, a composite catalyst (CC) Co (0.4%)-HZSM -5 + ZrO_2 (10%) + SO_4^{-2} (2%) + Al_2O_3 was synthesized in this work. The study of the conversion of n-alkanes and natural gasoline on composite catalyst was carried out in a flow type quartz reactor in a hydrogen atmosphere.

The results of the conversion of n-C_4H_{10} on CC are shown in Fig.1. As can be seen from the figure, in the temperature range of 160-200^{0}C n-butane undergoes intense transformations with the formation of i-butane and an equimolar mixture of C_3, C_5 alkanes. As the temperature rises, the selectivity of isobutane formation decreases, while C_3, C_5 alkanes increase. Such a transformation of n-C_4H_{10} can occur due to the primary activation of the formation of the bimolecular intermediate C_8, its isomerization, and subsequent hydrocleavage i.e., forming products are the result of an isomerization-disproportionation process. With an increase in temperature, the yield of C_3, C_5 products increases, which indicates an increase in the disproportionation properties of CC.

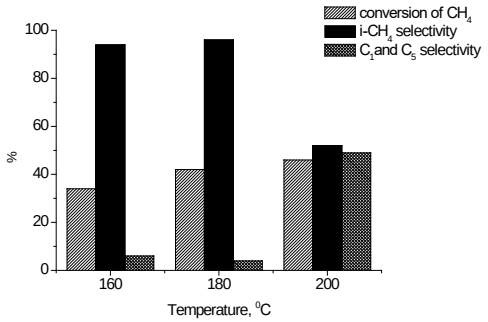


Fig.1. Dependence of catalyst activity on process temperature.
H_2/CH = 3 : 1; t $_{H2\ treatment}$ 350ºC;
WGSH = 350 h^{-1}.

A similar transformation is also observed for the n-hexane, with an increase in the reaction temperature, the conversion of n-hexane, as in the case of n-butane, increases. But the conversion of n-hexane, as a more active alkane, is almost two times higher than that of n-butane. During the conversion of n-hexane, C_1-C_5 alkanes and C_{7+} hydrocarbons are formed. The main product of the process is iso-C_4-C_6 alkanes. These data show the formation of a bimolecular intermediate, as in the case of n-butane, and subsequent isomerization-disproportionation splitting into the corresponding products. As the temperature rises, the yield of isomeric products decreases. As in the case of n-butane, the optimum isomerization temperature is 180°C.

Table 1 presents the results of the study of the joint conversion of n-butane and n-hexane on CC. From the data of table 3 it can be seen that under the influence of n-hexane, the conversion of the less active n-butane increases significantly.

Table1. Conversion of n-C_4H_{10} and n-C_6H_{14} (1:1 mol) on CC. H_2/CH = 3 : 1; $t_{H2\ treatment}$ 350ºC; WGSH = 350 h^{-1}.

Temperature, 0C	Conversion, wt%,		Selectivity, %		
	n-C_4H_{10}	n-C_6H_{14}	C_1-C_3; n-C_5	i-C_4- C_6	C_7
160	18(12)	32(35)	6	64	30
180	60(32)	65(86)	49	73	18
200	88(67)	92(95)	37	59	4

* Individual conversions of n-C_4H_{10} and n-C_6H_{14} are indicated in brackets.

The products of the conversion of the n-butane - n-hexane mixture are C_4-C_6 isoalkanes, C_1-C_3 and n-C_5 by-product hydrocarbons, and higher molecular weight hydrocarbons are also formed than the initial reactants - C_7. The content of n-alkanes in the composition of C_7 does not exceed 5-8%. As noted above, the formation of higher molecular weight hydrocarbons and isomeric alkanes is explained by the preliminary bimolecular formation of intermediates and their subsequent decomposition into iso- and n-alkanes or disproportionation into lower and higher molecular weight hydrocarbons.

The results of studies of the conversion of gas gasoline on CC are presented in table. As can be seen from the data in table 2, the synthesized CC also shows isomerization activity in the conversion of gas gasoline. At the same time, C_{4-}, n-C_6 and C_{7+} components of gas gasoline are converted into iso-C_5-C_6 and n-C_5. In this case, low molecular weight and higher molecular weight components of gas gasoline are involved in the formation of iso-C_5-C_6 and n-C_5 alkanes valuable for the production of gasoline. It is assumed that in this case [C_4- - C_{7+}] bimolecular intermediates are formed between the low-molecular and high-molecular components of gas gasoline and they are converted into iso-C_5 – C_6 and n-C_5.

Table 2. Conversion of gas gasoline on a composite catalyst. H_2/CH = 1 : 3, WGSH= 2h^{-1}.

Temperature, ^{0}C	Composition of raw material, %						
	C_{4-}	iC_5	C_5	iC_6	C_6	iC_7	C_{7+}
	5.5	**25.2**	**19.2**	**18**	**8.4**	**5.4**	**18.3**
	Distribution of products, wt%						
160	2.4	29.7	22.3	21.3	4.6	3.7	16
180	1.0	37.5	26	22.6	2.6	4.5	5.8
200	0.7	28.2	25.1	21	2.8	10	12.2

PP-34

Study of Modified Zirconium Oxide Nanomaterials by XAFS

Kriventsov V.V.
Boreskov Institute of Catalysis, Novosibirsk, Russia
kriven@mail.ru

Currently, mixed oxides having the structure of fluorite of the basic composition ZrO2-x, modified with transition metals, are successfully used to harden ferritic steels used for special applications. For example, this material is suitable for creating a shell of fuel rods of a new generation of fast neutron reactors operating at high temperatures and hard irradiation. The report presents the results of complex examination by XANES/EXAFS methods of the state and local structure of samples of zirconium oxides (modified with yttrium, magnesium, iron) obtained by joint deposition and calcined at various temperatures. XANES/EXAFS spectra (Zr-K, Y-K, Fe-K) of the studied samples were recorded at EXAFS station (SSTRC, Novosibirsk). It was found that from the yttrium side, the XANES spectra of the studied samples are of the same type. It can be assumed that the charge state and the immediate environment of yttrium also practically do not change depending on the composition of the samples. As for zirconium, the XANES spectra have minor differences. Apparently, for zirconium with an unchanged charge state, changes in the immediate oxygen environment are due to the different composition of the samples. It is established that the curves of the radial distribution of atoms (RDFs) obtained from the EXAFS spectra of the studied samples have a number of characteristic features. Only the first Me-O and Me-Me coordination spheres are observed, but the remote coordination spheres (in the region of ~4.1-6.7Å) are practically absent, which indicates significant distortions of the long-range order. The local environment of yttrium is stable when the composition of the samples changes, which may indicate the formation of clusters containing only elements Y and O. The local environment of zirconium depends on the composition and background of the samples, since there are some differences in the RDFs curves. Thus, the peak amplitudes assigned to the Zr-O and Zr-Me coordination spheres are significantly reduced (by more than 30%) for the Y, Mg modified sample compared to those for the Y modified sample, which indicates distortions of the initial fluorite structure. It is shown that the changes in the Zr-O and Zr-Me distances (more than 0.06 Å) are greater than the changes caused by differences in the cell parameters for the compared samples. It was suggested that the presence of Y-O clusters hinders the refinement of structures using a statistical model of a solid solution with a fluorite structure. The lengths of interatomic bonds and the corresponding coordination numbers are calculated. Possible variants of structural models are considered in detail. This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2022-263). The experiments were performed using large-scale research facilities "EXAFS spectroscopy beamline". SR investigations were done at the shared research center SSTRC on the basis of the Novosibirsk VEPP-4-VEPP-2000 complex at BINP SB RAS.

PP-35

Study of Metal-Carbon Nanocomposite Catalysts by XAFS

Kriventsov V.V.
Boreskov Institute of Catalysis, Novosibirsk, Russia
kriven@mail.ru

Presented work is devoted to XAFS study of the state and local structure of the active component of model low-percentage (0.05-1.0%) of modified metal-carbon nanocomposite catalysts containing nano-forms of Pt and Pd. Nowadays low-percentage catalytic nanosystems containing platinoids deposited on various carbon supports are of great interest to researchers because of their practical significance, possibilities for varying catalytic properties and applications for a wide range of processes (conversion of industrial substrates, debenzylation of amines, hydrogenation, etc.), low cost of final products, ease of disposal and recovery of expensive components from spent catalysts. Model samples were prepared from precursors of different nature by varying methods of synthesis and formation of the applied component, recovery and activation modes. XAFS spectra (Pt-L3, Pd-K) of studied samples were recorded at SSTRC, Novosibirsk. The lengths of interatomic distances and the corresponding coordination numbers were calculated. Additionally HRTEM, XPS, XRD, XRF-SR methods were used to study morphology, chemical and phase compositions of the samples. The data obtained by various methods are in good agreement with each other. All possible variants of structural models are considered in detail. Some correlations were found between the structure of the active component and the catalytic properties of the studied samples. The perspectives of the proposed approach for the study of nanocomposite model metal-carbon catalysts containing platinoids are demonstrated. This work was supported by the Ministry of Science and Higher Education of the Russian Federation via the budget project of Boreskov Institute of Catalysis SB RAS. SR investigations were done at the shared research center SSTRC on the basis of the Novosibirsk VEPP-4-VEPP-2000 complex at BINP SB RAS.

PP-36

Study of Platinum Complexes Existing in a Solution of Water by XAFS

Kriventsov V.V.
Boreskov Institute of Catalysis, Novosibirsk, Russia
kriven@mail.ru

This paper presents the results of the investigation of the process of hydrolysis of platinum complexes of different nature existing in a solution of water by XAFS method. It is well-known fact that deposited platinum catalysts, due to their unique properties, are irreplaceable in various industrial oxidation and reduction processes. The variety of catalytic properties is determined by the possibility of varying the dispersion and lability of the state of the active component. It is quite obvious that the development of methods for fine control of Pt dispersion is necessary to study the fundamental relationships between the size, state of the active component nanoparticles, their detailed electronic structure, and the actual properties of the catalyst in a chemical reaction. As a rule, various precursor solutions based on Pt(4+) and Pt(2+) salts are used for the synthesis of platinum catalysts after precipitation to the carrier, the system undergoes various heat treatments. The main factor affecting the dispersion of Pt forms existing in salt solutions is the ongoing hydrolysis process. To implement the research goals, ~0.01-0.1M aqueous solutions of K2PtCl4 and nitrate solutions of Pt(4+) with different ligand arrangements were prepared. XAFS spectra (Pt-L3 edge) of all studied samples were recorded at SSTRC, Novosibirsk. The state and structures of hydrolysis products – polynuclear platinum (2+) hydroxocomplexes (PHC-Pt) were studied. It was shown that during the hydrolysis reaction of [PtCl4]2 - complexes, oligomeric chains containing Pt-O-Pt fragments are formed, in which neighboring Pt atoms are connected by a single O – bridge atom. Aging of solutions containing PHC-Pt for a long time is not accompanied, in contrast to solutions of PHC Pd (2+) and PHC Pt (4+), by the formation of 3D - oxide structures. An increase in the size of PHC-Pt particles is shown as the process of oligomerization of Pt(2+) mononuclear complexes proceeds. It was found that during hydrolysis of Pt(4+) nitrate solutions, Pt(4+) polynuclear hydroxocomplexes were formed. It was established that the nearest environment of Pt in solution is always octahedral, the distortion is caused by replacing the O part with the N part. However, formation and stabilization of various agglomerated Pt-containing forms of different nuclear are possible. It was shown that the nuclearity of various forms and resistance to hydrolysis depend on from the preliminary history of the sample and the nature of O, N-ligands in the coordination sphere platinum in solutions. The lengths of interatomic Pt-O, Pt-N and Pt-Pt bonds and the corresponded coordination numbers are established. All variants of possible structural models are considered. Additionally, all prepared samples of solutions were examined by HRTEM, NMR methods. Data obtained by different methods do not contradict each other. The perspective of the proposed approach for the study of platinum complexes in aqueous solution is shown.
This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2022-263). The experiments were performed using large-scale research facilities "EXAFS spectroscopy beamline". SR investigations were done at the shared research center SSTRC on the basis of the Novosibirsk VEPP-4-VEPP-2000 complex at BINP SB RAS.

PP-37

Study of Model Metal-Carbon Nanocomposites Prepared by Pyrolysis by EXAFS

Kriventsov V.V.[1], Bairamukov V.Yu.[2]
1 – Boreskov Institute of Catalysis, Novosibirsk, Russia
2 – Petersburg Nuclear Physics Institute Named by B.P. Konstantinov of NRC «Kurchatov Institute», Gatchina, Russia
kriven@mail.ru

Technologies of long-term storage of nuclear fuel waste and many other tasks of industry, nuclear medicine, today require the development and creation of new functional materials. Nanocarbon structures (fullerenes, carbon nanotubes and other forms of carbon) are promising. Their properties – heat resistance, electrical conductivity, thermal conductivity, strength – can be enhanced by the introduction of metals. The key principle of isolation of radioactive waste is the presence of several barriers that restrain the spread of radionuclides in the environment. One of the methods of primary immobilization of radioactive waste is the use of metal–carbon nanocomposite matrices. Also, these materials can be used in nuclear medicine – as contrasting agents. There are various traditional ways of creating metal-carbon nanocomposites, that is, introducing atoms of various metals into the carbon matrix. New technology based on pyrolysis (thermal decomposition in an oxygen-free environment) of precursor compounds (precursors) of metal diphthalocyanine molecules and their subsequent pyrolysis was developed. Organometallic compounds are used as precursors. The first experiments were performed on a nanosystem of yttrium metal and carbon. The EXAFS method was used to study samples of new metal-carbon nanocomposites Y/C developed at the Petersburg Nuclear Physics Institute of NRC «Kurchatov Institute» (Gatchina). EXAFS spectra (Y-K edge) of all studied samples were recorded at SSTRC (BINP SB RAS, Novosibirsk). It is established that, depending on the pyrolysis temperature, Y can be stabilized in various forms – in the form of atomically dispersed yttrium, yttrium clusters and nanoparticles. The presence of short strong Y-C bonds that rigidly fix yttrium clusters in the carbon matrix is shown. The EXAFS data are in good agreement with the results of HRTEM, XPS, XRD. This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2022-263). The experiments were performed using large-scale research facilities "EXAFS spectroscopy beamline". SR investigations were done at the shared research center SSTRC on the basis of the Novosibirsk VEPP-4-VEPP-2000 complex at BINP SB RAS.

List of Participants

Akhmadeev Albert
Ural Federal University
Ekaterinburg, Russia
t0lpar@yandex.ru

Alekseev Roman
Mendeleev University of Chemical Technology
Moscow, Russia
alexeev-roma@mail.ru

Alexandrova Daria
Novosibirsk State University
Novosibirsk, Russia
d.aleksandrova@catalysis.ru

Aliev Timur
ITMO University
Saint Petersburg, Russia
aliev@infochemistry.ru

Anikina Anastasiia
Boreskov Institute of Catalysis
Novosibirsk, Russia
anikina@catalysis.ru

Arakcheev Andrei
A.N. Frumkin institute of physical chemistry
and electrochemistry of RAS
Moscow, Russia
andrejus_nm@mail.ru

Argunova Tatiana
Ioffe Institute
Saint Petersburg, Russia
argunova@mail.ioffe.ru

Arkhipov Sergey
Novosibirsk State University
Novosibirsk, Russia
arksergey@gmail.com

Atlaskina Maria
Lobachevsky State University
of Nizhny Novgorod
Nizhniy Novgorod, Russia
atlaskina.m.e@gmail.com

Aydakov Egor
Novosibirsk State University
Novosibirsk, Russia
e.ajdakov@g.nsu.ru

Bataev Ivan
Novosibirsk State Technical University
Novosibirsk, Russia
i.bataev@corp.nstu.ru

Batova Tatiana
A.V. Topchiev Institute
of Petrochemical Synthesis RAS
Moscow, Russia
batova.ti@ips.ac.ru

Belskaya Nadejda
Ioffe Institute
Saint Petersburg, Russia
nbelsk@mail.ioffe.ru

Bikchurina Marina
Budker Institute of Nuclear Physics of SB RAS
Novosibirsk, Russia
knkstdor@gmail.com

Bilyachenko Alexey
A.N. Nesmeyanov Institute
of Organoelement Compounds RAS
Moscow, Russia
xeloff@gmail.com

Bogdanov Nikita
Boreskov Institute of Catalysis
Novosibirsk, Russia
nebo1329@gmail.com

Bugaev Aram
The Smart Materials Research Institute
at the Southern Federal University
Rostov-on-Don, Russia
abugaev@sfedu.ru

Bukhtiyarov Andrey
SRF SKIF Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
avb@catalysis.ru

Bukhtiyarov Valerii
Boreskov Institute of Catalysis
Novosibirsk, Russia
vib@catalysis.ru

Bulavchenko Olga
Boreskov Institute of Catalysis
Novosibirsk, Russia
obulavchenko@catalysis.ru

List of Participants

Bykov Timofey
Budker Institute of Nuclear Physics of SB RAS
Novosibirsk, Russia
T.A.Bykov@inp.nsk.su

Chemakina Irina
University of Tyumen
Tyumen, Russia
irina.s.chemakina@yandex.ru

Danilova Valeria
National Research University
of Electronic Technology
Moscow, Russia
valeriajurgenson@gmail.com

Dobrovolskaia Arina
The Smart Materials Research Institute
at the Southern Federal University
Rostov-on-Don, Russia
arinadobro.volya@gmail.com

Drozhilkin Pavel
Lobachevsky State University
of Nizhny Novgorod
Nizhniy Novgorod, Russia
pddrozhilkin@yandex.ru

Dybtsev Danil
Nikolaev Institute
of Inorganic Chemistry SB RAS Novosibirsk,
Russia
dan@niic.nsc.ru

Dzharkinov Ruslan
Novosibirsk State University
Novosibirsk, Russia
r.dzharkinov@g.nsu.ru

Enikeeva Maria
Ioffe Institute
Saint Petersburg, Russia
odin2tri45678@gmail.com

Emurlaev Kemal
Novosibirsk State Technical University
Novosibirsk, Russia
emurlaev@corp.nstu.ru

Ermakova Alexandra
Southern Federal University
Rostov-on-Don, Russia
ermakova.alexandra.bk@mail.ru

Fedin Vladimir
Nikolaev Institute
of Inorganic Chemistry SB RAS
Novosibirsk, Russia
cluster@niic.nsc.ru

Fedorenko Anastasiya
Nikolaev Institute
of Inorganic Chemistry SB RAS
Novosibirsk, Russia
fedorenko@niic.nsc.ru

Fedoseeva Yuliya
Nikolaev Institute
of Inorganic Chemistry SB RAS
Novosibirsk, Russia
fedoseeva@niic.nsc.ru

Filimonov Alexey
Alferov University
Saint Petersburg, Russia
filalex@inbox.ru

Filippov Artem
Khristianovich Institute
of Theoretical and Applied Mechanics of SB RAS
Novosibirsk, Russia
Filippov@itam.nsc.ru

Fokin Mikhail
Trofimuk Institute
of petroleum Geology and Geophysics SB RAS
Novosibirsk, Russia
fokinmi@ipgg.sbras.ru

Gaydamaka Anna
Boreskov Institute of Catalysis
Novosibirsk, Russia
a.gaidamaka@g.nsu.ru

Goldenberg Boris
SRF SKIF Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
b.g.goldenberg@srf-skif.ru

Golub Fedor
Boreskov Institute of Catalysis
Novosibirsk, Russia
fedorglb@gmail.com

List of Participants

Golubkov Viktor
Institute of Chemistry
and Chemical Technology of SB RAS
Krasnoyarsk, Russia
golubkov.va@icct.krasn.ru

Gorkusha Aleksandr
Boreskov Institute of Catalysis
Novosibirsk, Russia
deepforesttt922@gmail.com

Guda Alexander
Southern Federal University
Rostov-on-Don, Russia
guda@sfedu.ru

Ignatova Nina
Siberian Federal University
Krasnoyarsk, Russia
nyignatova@sfu-kras.ru

Immen Aleksandra
Boreskov Institute of Catalysis
Novosibirsk, Russia
immen@catalysis.ru

Ionin Vladislav
Institute of Chemistry
and Chemical Technology of SB RAS
Krasnoyarsk, Russia
ionin.va@icct.krasn.ru

Isaev Denis
Institute of Solid State Chemistry
and Mechanochemistry SB RAS Novosibirsk,
Russia
isaev@solid.nsc.ru

Ivkina Daria
State Research Center of Virology
and Biotechnology VECTOR, Rospotrebnadzor
Novosibirsk, Russia
ivkina_di@vector.nsc.ru

Kaichev Vasily
Boreskov Institute of Catalysis
Novosibirsk, Russia
vvk@catalysis.ru

Kakuliia Iylia
Voronezh State University
Voronezh, Russia
kakuliia@phys.vsu.ru

Kalinin Ivan
Lomonosov Moscow State University
Moscow, Russia
rus.ivan4@gmail.com

Kalinina Polina
Novosibirsk State University
Novosibirsk, Russia
P.kalinina@g.nsu.ru

Kapishnikov Aleksandr
Boreskov Institute of Catalysis
Novosibirsk, Russia
avl97@mail.ru

Kardash Tatyana
Boreskov Institute of Catalysis
Novosibirsk, Russia
kardash@catalysis.ru

Kazakova Eva
Boreskov Institute of Catalysis
Novosibirsk, Russia
eva@catalysis.ru

Khainovskiy Mark
Novosibirsk State University
Novosibirsk, Russia
interstellar.ocean@gmail.com

Khametova Elina
Udmurt State University
Izhevsk, Russia
elinaphanilevna851@gmail.com

Kharchenko Nadezhda
Novosibirsk State University
Novosibirsk, Russia
nadya-kharchenko@mail.ru

Khramov Evgeny
National Research Center «Kurchatov
Institute» Moscow, Russia
Khramov_EV@nrcki.ru

Khrapova Ekaterina
Ioffe Institute
Saint Petersburg, Russia
arganella@yandex.ru

Khusnutdinoff Ramil
Kazan Federal University
Kazan, Russia
khrm@mail.ru

List of Participants

Kiruanov Aleksei
Novosibirsk State Technical University Novosibirsk, Russia
leha.kiryanov.00@mail.ru

Kiskinova Maya
Elettra Synchrotron
Trieste, Italy
maya.kiskinova@elettra.eu

Konovalova Viktoriia
Budker Institute of Nuclear Physics of SB RAS
Novosibirsk, Russia
v.konovalova@g.nsu.ru

Kolybalov Dmitry
Novosibirsk State University
Novosibirsk, Russia
d.kolybalov@g.nsu.ru

Kondranova Anastasia
Nikolaev Institute
of Inorganic Chemistry SB RAS
Novosibirsk, Russia
a.kondranova@gmail.com

Konovalova Anna
Synchrotron Radiation Facility SKIF
Novosibirsk, Russia
eliminator400@yandex.ru

Konovalova Valeria
Boreskov Institute of Catalysis
Novosibirsk, Russia
lekorux@gmail.com

Konovalova Viktoriia
Budker Institute of Nuclear Physics
of SB RAS
Novosibirsk, Russia
v.konovalova@g.nsu.ru

Korlyukov Aleksandr
A.N. Nesmeyanov Institute
of Organoelement Compounds RAS
Moscow, Russia
akorlyukov@gmail.com

Kotsun Alena
Nikolaev Institute
of Inorganic Chemistry SB RAS
Novosibirsk, Russia
kotsun15@gmail.com

Krasnov Pavel
International Research Center
of Spectroscopy and Quantum Chemistry,
Siberian Federal University
Krasnoyarsk, Russia
kpo1980@gmail.com

Kriventsov Vladimir
Boreskov Institute of Catalysis
Novosibirsk, Russia
kriven@mail.ru

Krivonogov Artem
Boreskov Institute of Catalysis
Novosibirsk, Russia
akriv@catalysis.ru

Krot Anna
Lomonosov Moscow State University Moscow, Russia
Anna.d.krot@gmail.com

Kudiiarov Viktor
Tomsk Polytechnic University
Tomsk, Russia
kudiyarov@tpu.ru

Kuznetsov Sergey
Prokhorov General Physics Institute
of the RAS
Moscow, Russia
kouznetzovsv@gmail.com

Larichev Yurii
Boreskov Institute of Catalysis
Novosibirsk, Russia
ylarichev@gmail.com

Lavrukhina Svetlana
Nikolaev Institute
of Inorganic Chemistry SB RAS
Novosibirsk, Russia
x-rayspectroscopy@mail.ru

Lazarenko George
Tomsk State University
Tomsk, Russia
laz@phys.tsu.ru

Lazarenko Vladimir
National Research Center «Kurchatov Institute» Moscow, Russia
vladimir.a.lazarenko@gmail.com

List of Participants

Letyagin Gleb
Institute "International Tomografic Center"
of SB RAS
Novosibirsk, Russia
gl@tomo.nsc.ru

Levichev Evgeniy
Budker Institute
of Nuclear Physics of SB RAS
Novosibirsk, Russia
skif@srf-skif.ru; E.B.Levichev@inp.nsk.su

Lobanova Evgeniya
ITMO University
Saint Petersburg, Russia
elobanova@itmo.ru

Logunova Svetlana
Boreskov Institute of Catalysis
Novosibirsk, Russia
logunova@catalysis.ru

Lomakin Makariy
Ioffe Institute
Saint Petersburg, Russia
lomakinmakariy@gmail.com

Losev Evgeniy
Boreskov Institute of Catalysis
Novosibirsk, Russia
losev.88@mail.ru

Malygina Aleksandra
SRF SKIF Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
a.b.malygina@srf-skif.ru

Mamedova Malahat
Institute of Petrochemical Processes
named after Academician Yusif
Mammadaliyev Baku, Azerbaijan
memmedova-melahet@mail.ru

Marchuk Alexander
Boreskov Institute of Catalysis
Novosibirsk, Russia
alexander.s.marchuk@gmail.com

Martyanov Oleg
Boreskov Institute of Catalysis
Novosibirsk, Russia
oleg@catalysis.ru

Marukhin Artem
Immanuel Kant Baltic Federal University
Kaliningrad, Russia
Marukhin.artem.o@gmail.com

Matveenko Ekaterina
University of Tyumen
Tyumen, Russia
matveenko-katya@mail.ru

Merentsov Alexander
M.N. Mikheev Institute of Metal Physics UB RAS
Ekaterinburg, Russia
Alexander.Merentsov@urfu.ru

Mikhailov Yakov
University of Tyumen
Tyumen, Russia
y.a.mikhajlov@utmn.ru

Mikhnenko Maxim
Boreskov Institute of Catalysis
Novosibirsk, Russia
m.mikhnenko@catalysis.ru

Mineev Alexey
Novosibirsk State University
Novosibirsk
mineev.a.m@yandex.ru

Minin Maksim
IMC Group
Moscow, Russia
minin@imc-systems.ru

Mishanin Igor
N.D. Zelinsky Institute
of Organic Chemistry RAS
Moscow, Russia
arnochem2@yandex.ru

Mishchenko Denis
SRF SKIF Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
q14999@yandex.ru

Mordkovich Vladimir
Technological Institute
for Superhard and Novel Carbon Materials
Moscow, Russia
mordkovich@tisnum.ru

List of Participants

Moskalenko Ivan
ITMO University
Saint Petersburg, Russia
i.v.m.rostov.yar@gmail.com

Murzina Anastasia
Novosibirsk State University
Novosibirsk, Russia
a.murzina@g.nsu.ru

Naranov Evgeny
A.V. Topchiev Institute
of Petrochemical Synthesis RAS
Moscow, Russia
naranov@petrol.chem.msu.ru

Naumkin Viktor
Kutateladze Institute
of Thermophysics of SB RAS
Novosibirsk, Russia
vsnaumkin@itp.nsc.ru

Nazarov Artem
Lobachevsky State University
of Nizhny Novgorod
Nizhniy Novgorod, Russia
nazarov.artem6230@gmail.com

Nikitenko Denis
L.M. Litvinenko Institute
of Physical Organic and Coal Chemistry
Donetsk
nykytenko.dv@gmail.com

Nishchakova Alina
Nikolaev Institute
of Inorganic Chemistry SB RAS
Novosibirsk, Russia
nishchakova@niic.nsc.ru

Pakharukova Vera
Boreskov Institute of Catalysis
Novosibirsk, Russia
verapakh@catalysis.ru

Panafidin Maxim
SRF SKIF Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
mpanafidin@catalysis.ru

Pankin Ilia
The Smart Materials Research Institute
at the Southern Federal University
Rostov-on-Don, Russia
ipankin92@gmail.com

Parmon Valentin
Siberian Branch
of the Russian Academy of Sciences
Novosibirsk, Russia
secretary@sbras.nsc.ru; parmon@catalysis.ru

Pastukhova Zhanna
MIREA - Russian Technological University
Moscow, Russia
pastuhova@mirea.ru

Platunov Mikhail
SRF SKIF Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
m.s.platunov@srf-skif.ru

Pnevskaya Anna
The Smart Materials Research Institute
at the Southern Federal University
Rostov-on-Don, Russia
annpnevskaya@yandex.ru

Poliakova Tatiana
Lomonosov Moscow State University
Moscow, Russia
poliakova.radiochem@mail.ru

Polyakova Kristina
University of Tyumen
Tyumen, Russia
polyakova.k.s.99@gmail.com

Polyutov Sergey
Siberian Federal University
Krasnoyarsk, Russia
polyutov@mail.ru

Ponosova Ekaterina
Southern Federal University
Rostov-on-Don, Russia
ponosova02@bk.ru

List of Participants

Popova Anna
Institute of Coal and Coal Chemistry of SB RAS
Kemerovo, Russia
h991@ya.ru

Protsenko Bogdan
The Smart Materials Research Institute
at the Southern Federal University
Rostov-on-Don, Russia
bprocenko@sfedu.ru

Pryanichnikov Stepan
Institute of Metallurgy UrD RAS
Ekaterinburg, Russia
stepian@yandex.ru

Rajput Priyadarshani
Southern Federal University
Rostov-on-Don, Russia
priyadarshanirajput22@gmail.com

Rashchenko Sergei
V.S. Sobolev Institute of Geology and
Mineralogy SB RAS
Novosibirsk, Russia
rashchenko@igm.nsc.ru

Rubanik Darya
Southern Federal University
Rostov-on-Don, Russia
missdare.dr@gmail.com

Samsonenko Arkady
Institute "International Tomografic Center"
of SB RAS
Novosibirsk, Russia
a.samsonenko@g.nsu.ru

Saraev Andrey
Boreskov Institute of Catalysis
Novosibirsk, Russia
asaraev@catalysis.ru

Savvinykh Maria
Synchrotron Radiation Facility SKIF
Novosibirsk, Russia
m.a.savvinykh@srf-skif.ru

Semenov Valentin
St. Petersburg State University
Saint-Petersburg, Russia
val_sem@mail.ru

Semushkina Galina
Nikolaev Institute
of Inorganic Chemistry SB RAS
Novosibirsk, Russia
spectroscopy@mail.ru

Shabanova Marina
Boreskov Institute of Catalysis
Novosibirsk, Russia
sbvmari@catalysis.ru

Shaforostov Aleksandr
IMC Group
Moscow, Russia
shaforostov@imc-systems.ru

Sharaya Svetlana
Boreskov Institute of Catalysis
Novosibirsk, Russia
s.sharaya@g.nsu.ru

Shefer Kristina
Novosibirsk State University
Novosibirsk, Russia
shefer@catalysis.ru

Shibaeva Valeria
G.A. Krestov Institute of Solution Chemistry
RAS Ivanovo, Russia
leric2009@yandex.ru

Shmakov Alexander
SRF SKIF Boreskov Institute of Catalysis SB RAS
Novosibirsk, Russia
shurka@catalysis.ru

Skorynina Alina
Southern Federal University
Rostov-on-Don, Russia
alinaskorynina@gmail.com

Smetanina Ksenia
Lobachevsky State University
of Nizhny Novgorod
Nizhniy Novgorod, Russia
smetanina-ksenia@mail.ru

Smirnova Anastasiia
Lomonosov Moscow State University Moscow,
Russia
smirnova.anastasia2304@gmail.com

List of Participants

Smirnova Kristina
Novosibirsk State University
Novosibirsk, Russia
k.smirnova1@g.nsu.ru

Snegireva Anna
State Research Center of Virology and Biotechnology VECTOR, Rospotrebnadzor
Novosibirsk, Russia
kozlovskaya_aa@vector.nsc.ru

Sonina Alina
N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of SB RAS Novosibirsk, Russia
belalina04@gmail.com

Sterkhov Evgenii
Institute of Metallurgy UrD RAS
Ekaterinburg, Russia
altximik@mail.ru

Sukhanov Andrei
Federal Scientific Research Centre «Crystallography and Photonics» RAS
Moscow, Russia
sukhanov.ae15@physics.msu.ru

Sukharina Galina
Southern Federal University
Rostov-on-Don, Russia
gbsukharina@sfedu.ru

Sulgin Aleksandr
State Research Center of Virology and Biotechnology VECTOR, Rospotrebnadzor
Novosibirsk, Russia
sulgin_aa@vector.nsc.ru

Suturin Sergey
Ioffe Institute
Saint Petersburg, Russia
suturin@mail.ioffe.ru

Suvorova Marina
Boreskov Institute of Catalysis
Novosibirsk, Russia
ms-suvorova@yandex.ru

Sychev Valentin
Institute of Chemistry and Chemical Technology of SB RAS
Krasnoyarsk, Russia
sychev.vv@icct.krasn.ru

Timralieva Alexandra
ITMO University
Saint-Petersburg, Russia
timralieva@itmo.ru

Tishin Anton
State Research Center of Virology and Biotechnology VECTOR, Rospotrebnadzor
Novosibirsk, Russia
tishin_ae@vector.nsc.ru

Titova Sofia
Voronezh State University
Voronezh, Russia
titova@phys.vsu.ru

Titova Svetlana
Institute of Metallurgy UrD RAS
Ekaterinburg, Russia
sgtitova@mail.ru

Trotsky Yuriy
Institute of Chemistry and Chemical Technology of SB RAS
Krasnoyarsk, Russia
qishankruy@gmail.com

Trushnikov Andrey
Ural Federal University
Ekaterinburg, Russia
andrean200023@mail.ru

Tsybulya Sergey
Boreskov Institute of Catalysis
Novosibirsk, Russia
tsybulya@catalysis.ru

Tumanov Ivan
Boreskov Institute of Catalysis
Novosibirsk, Russia
tumanov@g.nsu.ru

Turishchev Sergei
Voronezh State University
Voronezh, Russia
tsu@phys.vsu.ru

Usoltsev Oleg
Southern Federal University
Rostov-on-Don, Russia
oleg-usol@yandex.ru

List of Participants

Vakhrushev Sergey
Ioffe Institute
Saint Petersburg, Russia
s.vakhrushev@mail.ioffe.ru

Valeev Rishat
Udmurt Federal Research Center of UB RAS
Izhevsk, Russia
rishatvaleev@udman.ru; rishatvaleev@mail.ru

Verbitskaya Polina
Novosibirsk State University
Novosibirsk, Russia
p.verbitskaya@g.nsu.ru

Vinokurov Zakhar
Boreskov Institute of Catalysis
Novosibirsk, Russia
vinzux@mail.ru

Vitoshkin Igor
Khristianovich Institute of Theoretical
and Applied Mechanics of SB RAS Novosibirsk,
Russia
ghatu0oosj37@mail.ru

Vorfolomeeva Anna
Nikolaev Institute
of Inorganic Chemistry SB RAS
Novosibirsk, Russia
vorfolomeeva@niic.nsc.ru

Yazovskikh Ksenia
Physical-Technical Institute
Udmurt Federal Research Center UB RAS
Izhevsk, Russia
k.yazovskikh@bk.ru

Zakharov Boris
Boreskov Institute of Catalysis
Novosibirsk, Russia
b.zakharov@yahoo.com

Zakharov Nikita
Institute of Coal and Coal Chemistry of SB RAS
Kemerovo, Russia
2metil4@gmail.com

Zavorin Alexey
Boreskov Institute of Catalysis
Novosibirsk, Russia
zavorin_alexey@mail.ru

Zharkov Dmitry
Institute of Chemical Biology
and Fundamental Medicine
Novosibirsk, Russia
dzharkov@niboch.nsc.ru

Zharnikov Michael
University of Heidelberg
Heidelberg, Germany
Michael.Zharnikov@pci.uni-heidelberg.de

Zimonina Anastasiia
State Research Center of Virology and
Biotechnology VECTOR, Rospotrebnadzor
Novosibirsk, Russia
ana.zimonina@mail.ru

Zolotarev Mikhail
Synchrotron Radiation Facility SKIF
Novosibirsk, Russia
m.k.zolotarev@srf-skif.ru

Zubavichus Yan
SRF SKIF Boreskov Institute of Catalysis SB
RAS Novosibirsk, Russia
yzubav@gmail.com

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Сибирского отделения Российской академии наук»
630090, Новосибирск, пр-т Академика Лаврентьева, 5, ИК СО РАН
http://catalysis.ru
E-mail: bic@catalysis.ru Тел.: +7 383 330 67 71

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E-mail: pub@catalysis.ru Тел.: +7 383 326 97 15

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