

Boreskov Institute of Catalysis, Novosibirsk, Russia  
Institute of Cytology and Genetics, Novosibirsk, Russia  
ITMO University, St. Petersburg, Russia

# ANT 2019

*Sochi, Russia*  
*October 10-13, 2019*

**III International  
School-Conference**

## **Applied Nanotechnology and Nanotoxicology**

# ABSTRACTS



Novosibirsk – 2019



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**ABSTRACTS**

**УДК 544+546+57.04+615**  
**ББК 24.1+24.5+28.4+52**  
**A67**

**A67 Applied Nanotechnology and Nanotoxicology (ANT-2019).** III International School-Conference/ October 10-13, 2019, Sochi, Russia [Electronic resource]: Abstracts/ eds.: Dr. A.A. Vedyagin, Dr. M.S. Mel'gunov- Novosibirsk: BIC, 2019. URL: <http://catalysis.ru/resources/institute/Publishing/Report/2019/Abstracts-ANT-III-2019.pdf>  
ISBN 978-5-906376-26-8 [Регистрация № 0521900424](#)



**В НАДЗАГ.:** Boreskov Institute of Catalysis, Novosibirsk, Russia  
Institute of Cytology and Genetics, Novosibirsk, Russia  
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The main topics are:

1. Nanotechnology
  - Synthesis of novel nanostructured materials
  - Unique physicochemical features of nanostructures
  - Characterization methods for nanoparticles
  - Nanosize effects in catalysis
  - Nanotechnologies for green chemistry and clean energy
2. Nanotoxicology
  - Toxicology of nanoparticles
  - Toxicity of purified and non-purified nanomaterials, oxidative stress and antioxidants
  - Tissue specific response to nanoparticles
  - Recognition and clearance of nanoparticles
  - Individual resistance/susceptibility to nanocontamination
  - Animal models in nanotoxicology
  - Nanomedicine (nanoparticles as carriers of pharmaceuticals; nanoparticle based contrast agents; targeted delivery to pathology center; therapy with catalytically active nanoparticles; nanoparticles in the transmission of external influences)

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**ISBN 978-5-906376-26-8**

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- Boreskov Institute of Catalysis, Novosibirsk, Russia
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# ANT 2019

## PLENARY LECTURES

PL-1 ÷ PL-5



[Content](#)



## Preparation of Metal/Metal Oxide/Carbon Nanoparticles and their Functionalities and Catalytic Applications

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Metal nanoparticles are mainly synthesized by liquid-phase reduction method or chemical vapor deposition method. The synthesis of metal oxides is mostly through sol-gel method following calcination. The third group of nanoparticles, carbon dot, is prepared using various processes like organic matter reduction, hydrothermal synthesis and vapor deposition methods. However, to control the particle size, we need additional scheme such as emulsion synthesis or dendrimer-capsule methods. Moreover, stabilizers like surfactants, polymers and monolayers are added in order to well dispersions of nanoparticles in liquid media.

The main characteristics of metal nanoparticles is the catalytic property, and they are used for various chemical reactions (Ag, Cu etc.), electrochemical reactions (Pt) and antibacterial protection (Ag). Nanoparticles of Au and Ag involve unique plasmonic effect. Many metal oxides are useful for photocatalysis, and semiconductive metal oxide (TiO<sub>2</sub>, ZnO etc.) is valuable for solar cells. Carbon dot is one of allotropes of carbon materials but possesses the unique properties different from other allotropes. One of properties is the quantum dot behaviour similar to metal quantum dots. Both of them behave as fluorescence probes too.

This report will also introduce some cases of catalytic applications by these nanoparticles. Although Pt is the most effective catalyst among metal catalysts and indispensable on hydrogen evolution reaction in hydrogen fuel cells, the issue is its rather expensive cost. Thus, the alternatives of Pt, which should be cheaper materials than Pt, are searched or the deduction of the Pt amount is the trial. Using Pt nanoparticles with size less than 5 nm, we could deduce the valuable amount of Pt to be about 1 wt% [1]. Supercapacitor is the focussed energy storage device complementary to ion battery. Hybrid supercapacitors consisting of electric double layer capacitor and pseudocapacitor elements are effective but the addition of carbon dots further increased capacitance [2]. Similar efficiency of carbon dots occurred even on ZnO-based dye sensitized solar cells [3].

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- [2] B. Devadas, T. Imae, *ACS Sustainable Chem. Eng.* 6 (2018) 127–134.
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## Modification of the Material Properties via Nanotechnology Approach

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In the current research the two aspects in the area of the materials properties optimization will be discussed. *The first one* is connected with the laser oriented deposition technique use in order to improve the transparency, mechanical hardness and wetting angle of the optical systems operated in the UV-VIS-IR spectral ranges. The comparative results will be shown for the LiF, KBr, CaF<sub>2</sub>, Sc, Al, ITO, etc. materials. *The second one* will be connected with the doping process influence on the refractive, photoconductive and surface organic materials features. The comparative results will be shown for the doped polyimides, COANP, NPP, PNP, polyaniline, PVA, etc. materials. Moreover, some additional optical effects can be shown (rotation of the polarization plane of the light, bio-objects orientation, etc., when nano- and bio-sensitization process can be taken into account.

Partially, the observed phenomena have been previously published in the papers [1-3].

### References:

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## Nanoformulations of Pesticides and Safety - Toxicology and Risk Assessment

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Nanoparticles are ultrafine particles with characteristic dimensions from 1 to 100 nm having properties that are not shared by non-nanoscale particles with the same chemical composition. The size, shape, surface-to-volume ratio, crystal phase and chemical composition are key parameters of these materials relevant for their use as pesticides, and also for their potential toxicity (Hayles, 2017). As a clear definition of nanopesticides is still lacking, it is not possible to answer the question on how many nanopesticides are already on the market.

Conventional pesticides have important drawbacks that limit their use, such as the harmful effect on non-target organisms (including humans), environmental persistence and the emergence of resistant target organisms. The use of nanopesticides would make it possible to overcome these drawbacks (Balaure et al., 2017).

Nanoformulations of pesticides (i.e., nanopesticides) have numerous benefits over conventional pesticides. These include improved formulation characteristics, increased solubility of insoluble active substances, stability of the formulation, ease of application, possibility of slow release of the active substances, prevent an early degradation, selection of pest species, greater efficiency of pesticidal activity, lower application rates and greater environmental safety (Hayles, 2017; Iavicoli et al., 2017).

However, the limited scientific knowledge on the biosafety of nanopesticides, their environmental fate, potential bioaccumulation in the environment and food chain, biological reactivity when dispersed in the environment, and the possible risks to human and environment represent a challenge for risk assessment and for risk management. Furthermore, the current paradigm for assessing the risks of conventional pesticides, including the testing and modeling methodologies, cannot be appropriate for nanopesticides (Damalas and Eleftherohotinos, 2011).

In this scenario, it is mandatory to define nanopesticide hazards and levels of exposure for different populations, dose-response relationships and environmental fate. Besides, the physical-chemical characteristics that affect their toxicity, potential interactions of coformulants with the multiple stressors existing in the agrosystems should also be evaluated (Iavicoli et al., 2017). On the other hand, nanomaterials are capable of binding various moieties on the particle surfaces, thus transporting other substances to various organs and tissues where they can exert potential harmful effects.

### PL-3

Short-term toxicity testing of nanomaterials has identified pro-oxidant and pro-inflammatory properties and adverse effects on respiratory, cardiovascular and nervous systems of animals, as well as their potential endocrine disrupting activity (Iavicoli et al., 2013). Nevertheless, there is a need to assess the toxicity of long-term exposure to low-dose of these materials. In this regard, epidemiological studies carried out on workers occupationally exposed to nanopesticides will allow patterns of worker health linked to job activities and practices to be identified (Iavicoli et al., 2017).

The European Food Safety Authority (EFSA) has developed a tiered framework for toxicological testing of nanomaterials using *in vivo* and *in vitro* toxicological studies. The strategy includes a detailed physicochemical characterization and technical parameters of nanopesticides and coformulants, *in vitro* degradation, toxicokinetics (in particular likelihood and extent of the absorption through skin, lung, and gastrointestinal tract), acute toxicity, skin and eye irritation, skin sensitisation, short-term toxicity and genotoxicity. Depending on the results found in the first tier, additional studies may be needed to assess reproductive and developmental toxicity, and if applicable, immunotoxicity, allergenicity, neurotoxicity, carcinogenicity and endocrine activity (EFSA, 2018).

This presentation will make a multidisciplinary approach on the relevant considerations regarding problem formulation of nanopesticide benefits and drawbacks, and will address the major issues for risk assessment in humans and the environment.

**Acknowledgement.** No specific funding was received for this work.

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## Nanoparticles and Brain

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Nano-sized particles are widespread in nature being our invisible companions and often foes. Nanoparticles come in many forms ranging from trivial fine-grained dust, ash and other environmental pollutants to highly sophisticated viruses. Being small and light, nanoparticles are omnipresent in air and are constantly inhaled by humans. What happens next is fascinating story of nanoparticles ride from nose deep into the brain, which will be uncovered in this presentation. Spirited by interdisciplinary approach in our research we dissected nanoparticles' bodily fate at various angles. For example, we will demonstrate the importance of nasal aerodynamics in nanoparticles delivery [1], then we will show how nanoparticles spread within brain, how do they interact with cellular proteins [2] and so on. Finally, we will highlight our advances in use of nanoparticles in diagnostics of neuronal functions along with other their applications as simple, yet potent, pharmaceutical agents.

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research, grant 18-04-00472.

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## Synthesis of Nanostructured Carbon Materials via Metal Dusting of Ni-Based Alloys

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Carbon nanostructured materials (CNM) produced by catalytic chemical vapor deposition (CCVD) of hydrocarbons (including halogenated ones) still are of particular interest due to their unique physicochemical features that makes them irreplaceable material in a wide spectrum of applications. The catalyst of the CNM synthesis can be generated *in situ* in course of metal dusting (carbon erosion) of bulk Ni-based alloys. Carbon erosion leading to emergence of so-called self-organizing catalyst (SOC) has become rather powerful instrument for the purposeful production of CNM. For instance, such method was also proved to be effective for the decomposition of chlorinated hydrocarbons (Cl-HC) and related waste products to obtain the carbon nanofibers (CNF) with a developed specific surface area and unusual structure [1].

In this lecture, an approach to synthesize CNM via controlled carbon erosion of Ni-M alloyed precursors, as well as the possible areas for the application of the obtained CNM will be outlined.

The first series of the microdisperse Ni-M alloys (M = Fe, Cr, Mo, Pd etc.) was synthesized by co-precipitation of the precursor salts. The resulted material was reduced in an H<sub>2</sub> atmosphere at 800°C to obtain the metallic Ni-M phase. Second series of the Ni-M alloys was prepared by means of a single-stage mechanochemical alloying of individual metallic powders in a planetary mill. In both the cases, the formation of corresponding Ni-M alloys (solid solutions with face-centred cubic lattice of Ni) was confirmed by XRD method.

Synthesized Ni-M alloys were studied as precursors for the SOC catalysing the growth of CNM during the H<sub>2</sub>-assisted CCVD of hydrocarbons (C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>-C<sub>4</sub>-mix) and halogenated HC (CF<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, organochlorine wastes) at T = 600°C. The kinetic studies on carbon deposition process were carried out in a gravimetric flow reactor equipped with McBain balances. The synthesis of enlarged batches of CNF materials was performed in a horizontal quartz flow tube heated by Brother XD-1200NT furnace (China). The morphology, structure and textural features of the produced CNM were examined by SEM, TEM, BET, XPS etc.

## PL-5

Interaction of the Ni-M alloy with carbon precursor results in its rapid disintegration driven by metal dusting. The CCVD of  $C_2H_4$  over Ni-Cu alloy is seen to be accompanied by very fast and spontaneous emergence of submicron metallic particles functioning as active centres for further growth of carbon nanofibers (Fig. 1). Only 5-7 min is required for complete wastage of Ni-M alloy playing a role of precursor for *in situ* SOC preparation.

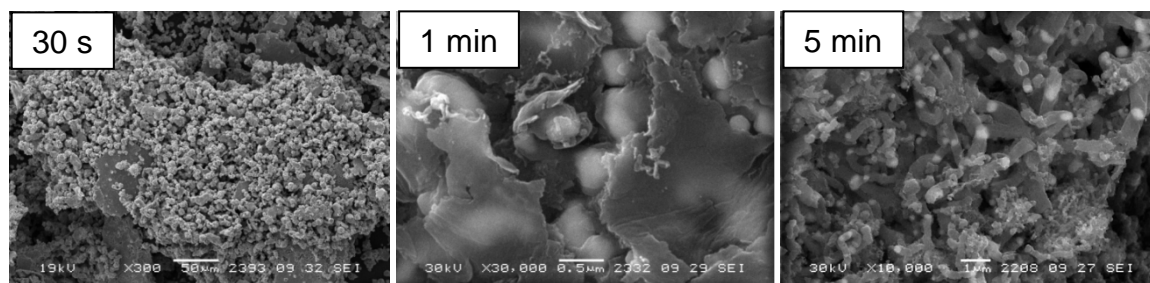


Fig.1. Carbon erosion of Ni-Cu (10%) alloy resulting in emergence of active particles (white contrast spots) catalyzing the growth of CNF. Reaction gas  $C_2H_4/H_2$ , 600°C.

Introduction of M = Pd, Pt, Cr into Ni-alloy was shown to have positive stabilizing effect on catalytic activity and stability of nickel. In its turn, the Mo metal was revealed to have the most significant impact upon catalytic performance of Ni in CCVD of 1,2-dichloroethane (shortened induction period along with doubled yield of carbon product).

The carbon filaments produced by CCVD of halogenated HC over SOC are characterized with apparent segmental structure in which the fragments of densely and loosely packed graphenes are stacked with regular order (Fig.2). The formation mechanism implies the determining role of Cl species interacting with active particles. More features of segmented CNF examined by Raman spectroscopy, BET and XPS will be shown during the presentation.

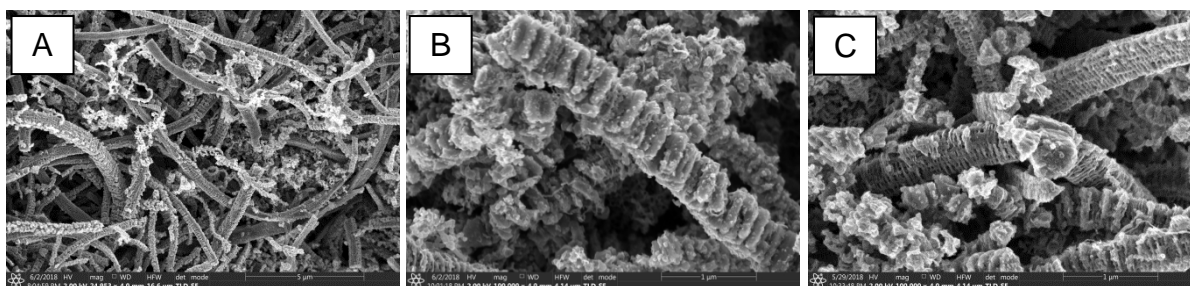


Fig.2. FESEM micrographs of the segmented CNF produced on self-organizing catalysts during  $H_2$ -assisted CCVD of  $C_2H_4Cl_2$  at 600°C: A – Ni-Pd(5%); B – Ni-Mo(8%); C – Ni-Pt(5%).

**Acknowledgement.** This study was supported by RFBR (research project No. 18-29-19053-mk).

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# ANT 2019

## KEYNOTE LECTURES

KL-1 ÷ KL-5



[Content](#)



## High-Electron Density Nanomaterials for Theranostics

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During stages of cancer treatment up to 60 % of patients undergo radiation therapy. However, being widespread, this method has a number of limitations due to the adverse reactions of perifocal (normal) tissues. To increase the efficiency of radiotherapy, radiosensitizers, that enhance the sensitivity of tumor tissues to irradiation, are being developed. As radiosensitizers interact with cancer cells and tumor microenvironment, any changes caused by the radiation therapy can significantly affect the effectiveness of the drug. In addition, detailed pre-clinical trials are necessary to define the optimal dosage regimen of the irradiation and the radiosensitizer. In order to amplify the radiation inside the tumor cells the prototypes of agents (nanoantennas) are developed. The effect is achieved as irradiation of high electron density materials triggers the Auger cascade and formation of free radicals. There are several important things to be mentioned. First of all, synthesis of nanoantennas from bioinert metal oxides is preferable as minimizes effect of the drug in the absence of radiation. Secondly, the small size of the nanoparticles (under 50 nm) functionalized by special surface groups for delivery into tumor cells allows to localize the radiation in the desired area that leads to the decrease of the radiation dosage. Thirdly, doping of the crystal lattice with different elements provides the necessary conditions for the upconversion of the near infrared (NIR) laser and, consequently, allows to diagnose the local distribution of the nanoparticles in tissues. As a main result colloidal injectable fluids based on doped hafnium, tantalum and gadolinium oxides less than 50 nm in size for radiologic theranostics of oncological diseases have been already synthesized by our group.

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research, grant 18-29-11078.

## Nanomaterials - New Challenges

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Recently attention in the scientific world is focused on the study of nanoparticles and the development of nanotechnology, that is, technologies aimed at obtaining substances and materials in the size range up to 100 nanometers in at least one dimension.

The cost of products and goods produced by the nanoindustry exceeds 1 trillion \$.

Now in the field of nanotechnology employs about 2 million people.

World achievements in the field of nanotechnology are used in the production of more than 80 groups of consumer goods over 600 types of raw materials, components and industrial equipment.

Nanomaterials are obtained from a variety of materials ranging from carbon and metals to ceramics, various polymers and gases. Physicochemical properties such as large surface area, mechanical strength, optical activity and chemical reactivity make nanoparticles unique and suitable candidates for a variety of applications ranging from medicine to the nuclear industry. Therefore, the volume of production of nanomaterials is growing every year.

Studies have been conducted on the effects of nanomaterials on various organisms from plants and microorganisms to mammals. It showed that due to physicochemical, mechanical and electronic differences between bulk particles and nanoparticles derived from the same material, Toxicological data for bulk toxins cannot be used to assess the toxicity potential of nanoparticles. One example is metal ions (titanium, silver and gold ions), which are chemically inert and essentially non-toxic. However, the reduction of ionic metals into nanoparticles leads to an exponential increase in their area of specific and surface reactivity; thus, the particles become more toxic.

All these unusual properties of nanomaterials allow us to consider them as new challenges facing humanity.

## KL-3

# Investigation of Advanced Carbon Nanostructures Using Synchrotron Radiation

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By accelerating electrons to near-light speed, radiation sources like synchrotrons generate brilliant beams of light from Terahertz to X-rays, which are used for academic and industry research. Therefore, synchrotron is the power tool for investigation of advanced carbon nanostructures also. Imagine techniques ensure their visualization, X-ray diffraction methods characterize the degree of crystallinity, spectroscopy provides information on the nature of chemical bonding.

Prof. H.W. Kroto (Nobel Prize laureate for the discovery of fullerenes) predicted that “21<sup>st</sup> century will be the carbon age”. This is greatly due to the diverse structural forms and functions of carbons. Controlling the physicochemical properties of carbon materials on the nanometer scale (nanocarbons) will be core technology for obtaining novel nanocarbons with new and extraordinary functions [1]. Nanocarbons include various forms of carbon in the range from carbyne to nanoporous materials. At present, it is accepted that chemical functionalization of carbon nanostructures (CNS) can extend the field of application of these nanosystems in nanoelectronics, green chemistry, clean energy, sensorics, medicine, etc.

In this lecture will be presented results of combined investigations of atomic structure and electronic properties of functionalized carbon nanostructures and their derivatives using synchrotron radiation for different applications, among them, for nanoelectronics [2]; clean energetics [3]; aerospace. Major attention will be paid to discussion of changes appeared in atomic and electronic structure of CNS under functionalization, the nature of chemical bonding between CNS and atoms/molecules or their ensembles during and after functionalization of CNS, new details on mechanism of CNS functionalization, the chemical state of atoms used for functionalization.

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## New and Future Developments in Photocatalytic Water Splitting

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Solar-driven photocatalytic water splitting has been considered as environmentally friendly and economically viable method to capture and store solar energy into clean and renewable hydrogen fuel; the approach conceptually similar to photosynthesis in plants. However, low solar-to-hydrogen efficiency and low hydrogen production rate are the most fundamental barriers that needs to be overcome in order to improve overall water splitting efficiency. Although substantial advances have been made in improving photocatalytic water-splitting process, the design of highly efficient, visible-light responsive photocatalysts with potential to be economically viable is still a major challenge. This work will focus on advances achieved in preparation and application of various photocatalytic systems, including Z-scheme photocatalyst systems and hybrid natural–artificial photosynthesis systems. The work will also introduce strategies for tuning structural and morphological properties for enhancing photocatalytic performance of modified semiconductor photocatalysts. Finally, we will present concluding remarks and future directions of photocatalytic water splitting for solar energy conversion.

**Acknowledgement.** Financial support for this study was granted by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects III 45001).

## Highlights and Perspectives of Nanoparticle Fabrication and Shape Control for Nanotoxicology in the Ural Center for Shared Use “Modern Nanotechnology”

Shur V.Ya., Shishkina E.V., Gunina E.V., Zubarev I.V., Kuznetsov D.K.,  
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The study of nanoparticle toxicity (nanotoxicology) needs production of the stable suspension of high concentration of model pure nanoparticles (NPs) with required composition, sizes and shapes. The laser ablation in water gives the unique ability to produce the stable suspensions of pure noble metals and metal oxides with required parameters. The suspensions of Au, Ag, CuO, NiO, ZnO, Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, PbO, and CdO NPs with narrow size distribution function, concentration up to 0.5 g/l and high enough stability have been produced to study the impact of the nanoparticles on the biological tissues and cells.

The pulsed Yb fiber laser (1064 nm, 100 ns, 21 kHz) has been used for ablation of the pure metal target in deionized water and subsequent fragmentation. The NPs synthesis was performed in several stages: (1) treatment of the target surface by focused laser beam scanning, (2) laser ablation of the target, (3) additional laser fragmentation of the suspension without the target, (4) heating for NPs reshaping by growth and aggregation [1], (5) drying of the suspension to increase the concentration.

The technologies optimized for given material allowed to produce the suspensions of spherical NPs with averaged sizes from 10 to 60 nm with up to month stability (Fig. 1). The size distribution function has been measured by particle size analyzer Zetasizer Nano ZS (Malvern Instruments, UK) and by statistical analysis of the images obtained by scanning electron microscope Auriga CrossBeam (Carl Zeiss, Germany). The NP composition has been determined by confocal Raman microscope Alpha 300 AR (WiTec, Germany). The structure of the individual NPs has been extracted from the electron diffraction patterns obtained by transmission electron microscope JEM-2100 (JEOL, Japan).

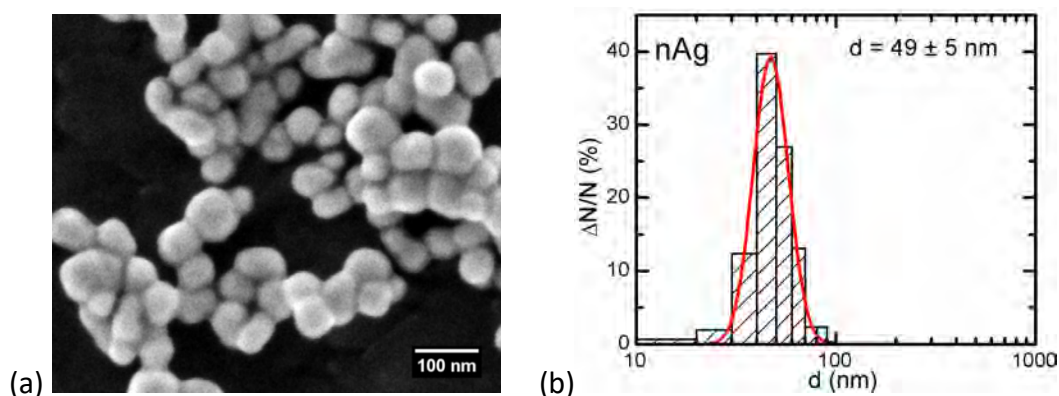


Fig. 1. Ag NPs produced by laser ablation in water: (a) SEM image, (b) size distribution function.

## KL-5

The total content of metals in the tissues of liver, kidneys, spleen, and brain of the rats long-time administered by NPs was obtained using atomic emission spectrometer with inductively coupled plasma iCAP 6500 Duo (Thermo Scientific, USA). The freeze-dried homogenized tissues were subjected to acid ignition with the help of a MARS 5 microwave accelerated reaction system. The content of NPs of paramagnetic metals has been revealed by electron paramagnetic resonance (EPR) method by means of EPR spectrometer EMX Plus (Bruker, Germany).

The impact of NPs on alveolar macrophages has been *in vivo* studied by atomic force microscopy (AFM) by means of probe nanolaboratory NTEGRA-Therma (NT-MDT, Russia). It was found that phagocytosis of NPs leads to nanoscale change of the cells surface morphology. The sizes of surface nano-depth pits revealed by AFM on the cells of rats administered by NPs are close to the NPs sizes. Such pits were absent on the surface of the reference cells. The positions of NPs in the rat tissue and induced destructions have been revealed by scanning transmission electron microscopy (Fig. 2) by means of Merlin (Carl Zeiss, Germany). The NPs neurotoxicity may be associated not only with mechanisms specific for a certain composition. Any inhaled NPs are able, after deposition in nasal cavity, to be transferred along the olfactory nerve fibres, thus bypassing the blood-brain barrier. Therefore, brain neurons may be damaged like any cells due to mechanisms common for all metal NPs (Fig. 2). Neuron's myelin sheath contains magnetite NPs. There are areas of demyelination in axon's sheath, where the electron-dense NPs are detected.

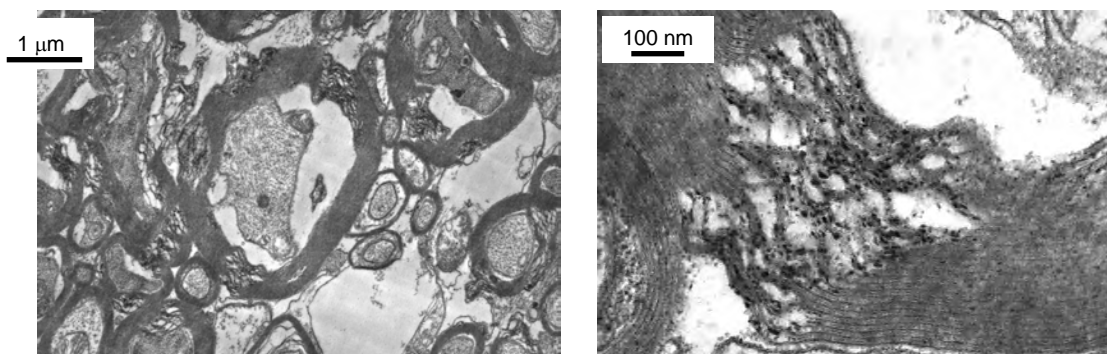


Fig. 2. STEM image of rat brain. A neuron's myelin sheath containing magnetite NPs.

The presented methods have been used for research in collaboration with Ekaterinburg Medical Research Center for Prophylaxis and Health Protection of Industrial Workers [2].

**Acknowledgement.** The equipment of the Ural Center for Shared Use "Modern nanotechnology" School of Natural Science and Mathematics, Ural Federal University was used.

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# ANT 2019

## ORAL PRESENTATIONS

OP-0 ÷ OP-24



[Content](#)



## Balancing between Technological Advantages and Toxicological Jeopardy of the Nanoobjects

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Nowadays, nano-sized objects have penetrated almost all areas of human life. It is hard even to imagine that some of the artificial materials surrounding us were created without a touch of the magic wand called “nanotechnology”. Modern chemical industry is one of the bright examples of application area, where nanotechnologies have significantly changed the basic concepts. Among the variety of nano-sized objects, **nanocatalysts** [1-3], **carbon nanomaterials** [4] and **nanocomposites** [5], and **nanostuctured ceramic materials** [6, 7] should be mentioned especially. On the other hand, the “nanotechnological coin” has reverse side. The advantages of the nanotechnological approaches quite often are balanced by serious disadvantage - unacceptable toxicity of the nanoproducts or manufacturing processes [8].

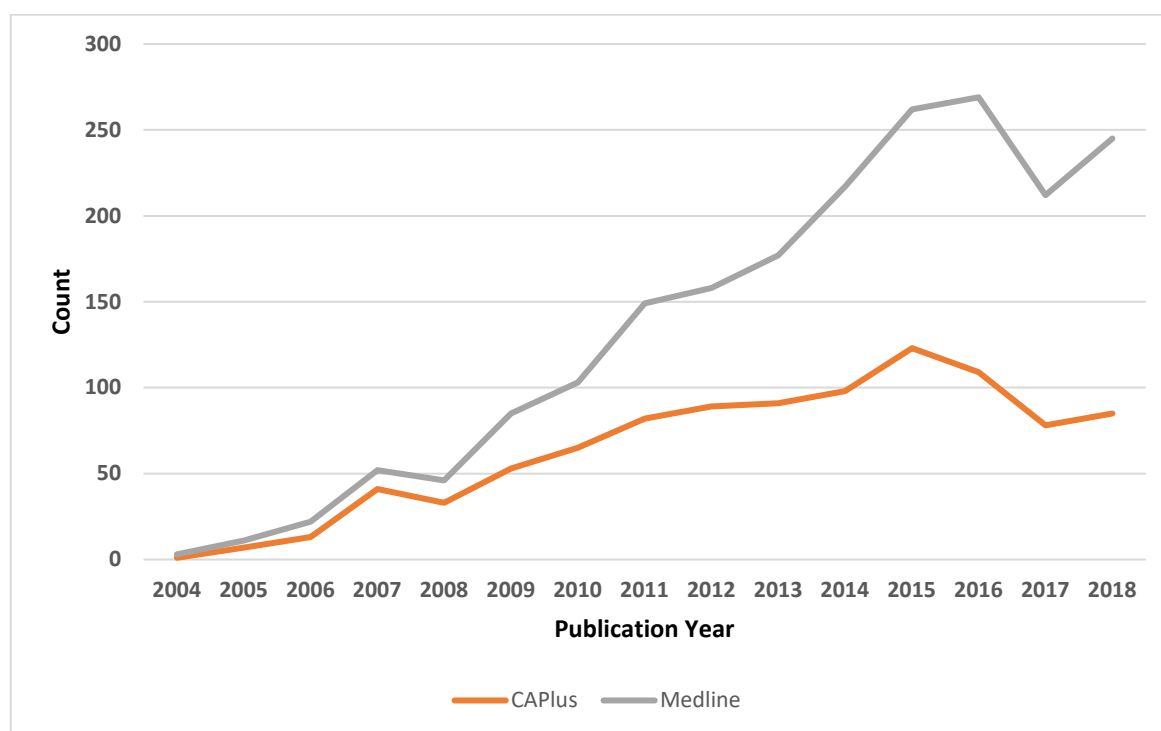


Figure 1. Dynamics of the publications related to the “nanotoxicology” concept based on the CAPlus and Medline databases (SciFinder platform). Data for 2018 are incomplete.

Fig. 1 shows the distribution of the publications indexed with regard to the “nanotoxicology” concept. The search was performed on the basis of CAPlus and Medline databases using SciFinder platform at the end of January, 2019. The total amount of papers is

1.5 thousands, and the earliest is dated by 2004. As seen, a rapid growth of the publication number is observed after 2007-2008. For 2015-2016 it achieves its maximum.

With regard to the found paper, the search on controlled terms of the Medline database gave 8.5 thousand publications, and 97% of them are journal articles including 12% reviews. The most frequent terms are **toxicity** (8450 papers), **drug effects** (6465 papers), **animals** (5101 papers), **chemistry** (4720 papers) and **metabolism** (4880 papers).

The studies in the field of nanotoxicology are performed worldwide, and three of the most active countries are **United States of America** (269 papers), **China** (274 papers) and **India** (127). The main language of the publications is **English**. The papers are published in a wide variety of journal. Thus, the papers presented in three of the most active journals correspond to just 13% of the total amount. These journals are **Nanotoxicology** (546 papers), **International Journal of Nanomedicine** (269 papers) and **Environmental Science and Technology** (227 papers).

As it was already noted, nanotoxicology deals with the toxicity of nanomaterials. In general, nanoparticles can be divided into **combustion-derived nanoparticles** (for instance, diesel soot), **manufactured nanoparticles** (carbon nanomaterials including nanotubes and nanofibers) and **naturally occurring nanoparticles** (for example, from volcanic eruptions). According to the CAS registry numbers, the most frequently reported in the publications on nanotoxicology substances are **silver** (1106 papers), **titanium** (1017 papers) and **titanium oxide TiO<sub>2</sub>** (875 papers). Besides them, typical nanoparticles that have been studied are alumina, zinc oxide, carbon black, carbon nanotubes, and buckyballs.

**Acknowledgement.** This work was supported by the Ministry of Science and High Education of Russian Federation (Project AAAA-A17-117041710086-6).

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## Structure, Texture and Morphology of the Nanoparticles Formed by Relativistic Electron Beam Irradiation of Carbon Black

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Carbon black (CB) is a readily available material. It is characterized as a highly disordered structure on various organization scale levels. This fact suggests the possibility of the occurrence of rapid dynamic structural, morphological and textural transformations in the initial globular particles under the influence of high-energy electron beams and laser irradiation with the formation of other nanosized multi-morphological carbon forms (i.e. onions, nanocages, nanocapsules, rosette particles, nanostacks of graphene sheets), having essentially wider set of new properties [1-5].

This work was aimed at studying the nanostructure, texture and morphology of coarsely and finely dispersed carbon black samples after irradiation with a continuous relativistic electron beam to determine the relationships in their formation using HRTEM, EPR and adsorption methods.

We used of the powders of carbon black. Primary particles in these samples have the shape of globules of different diameters: 100-300 nm (CDCB, T-900 grade) and 10-50 nm (FDCB, P-267E grade) according to technical specifications. Relativistic electron beam irradiation ( $E=2.5$  MeV) of carbon black samples was performed at an ELV-8 accelerator (Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences, Novosibirsk). The nanostructure and morphology of particles of the initial and irradiated CDCB and FDCB samples were studied with a JEM-2100 transmission electron microscope (JEOL) in the high resolution mode (accelerating voltage 200 kV, resolution 0.145 nm). The images obtained were processed with Digital Micrograph program package (Gatan). Additionally, EPR measurements (X-band, 9.74 GHz) were performed on EMXplus spectrometer (Bruker) at 25°C. The textural characteristics of the initial and irradiated CB samples were obtained from analysis of the nitrogen adsorption-desorption isotherms at 77.4 K, taken with an ASAP-2020M volumetric vacuum static analyzer (Micromeritics).

According to the HRTEM data (fig. 1) the initial globules (table 1) indeed transform into nanocapsules of different size with different height of graphene layers (table 2) under continuous beam of 2.5-MeV accelerated electrons irradiation. Structural transformations of the carbon framework significantly affect the texture, decreasing the specific surface area and porosity, but increased the mean nanopore diameter (table 1, 2).

The observed EPR-spectra of the irradiated samples (CDCB, FDCB) were changed significantly after high-energy electron beam irradiation of the initial CB. The intensity and shape of EPR signal from of the formed nanocapsules may be due to the presence of partially



## OP-01

delocalized or localized  $\pi$ -electrons in the new graphene layers of small length, as well as on the edge defects in such layers.

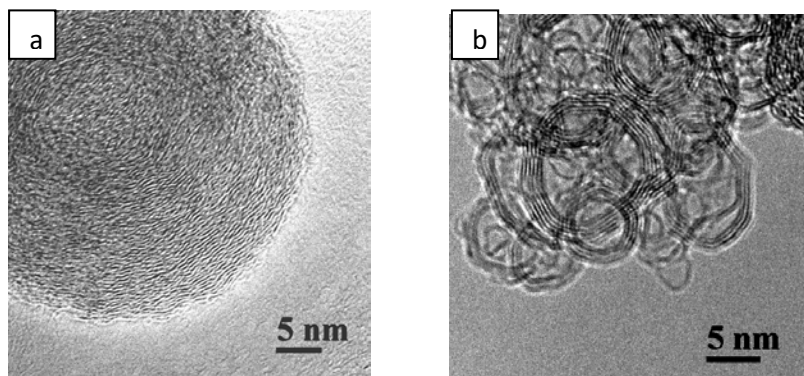


Fig.1. Particle nanostructure and morphology in the (a) initial and (b) irradiated of FDCB.

Table 1. Characteristics of the structure, morphology, texture of initial CDCB and FDCB

Sample	Nanoglobule size (D), nm	Spacing between graphene layers, $d_{002}$ , nm	Length of graphene layers, nm	$S_{BET}$ , $m^2 g^{-1}$	Porosity, $\epsilon$ , %	Mean $D_{pore}$ , nm
CDCB	100-300	0.36-0.40	0.4-3.0	11	6.3	13.5
FDCB	10-30	0.36-0.37	0.4-1.3	250	55.1	10.0

Table 2. Characteristics of the structure, morphology, texture of irradiated CDCB and FDCB

Sample	Nanocapsule size (D), nm	Spacing between graphene layers $d_{002}$ , nm	Number of graphene layers in shell	$S_{BET}$ , $m^2 g^{-1}$	Porosity, $\epsilon$ , %	Mean $D_{pore}$ , nm
CDCB	200-500	0.355	> than 100	3	3.8	26.6
FDCB	5-50	0.365	5-20	59	34.5	18.2

**Acknowledgement.** The study was performed within the framework of the government assignment for the Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences in accordance with the Program of Basic Research of the State Academies of Sciences for the period 2013–2020, direction V. 45, project V.45.2.8. (state registry no. in the Integrated State Information System for Account of Research and Development for Civil Purposes AAAA-A17-117021450093-7).

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## Specific Surface Area of Metal-Organic Frameworks

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Porous metal-organic frameworks (MOFs) are the nanomaterials with ordered structure of mutually arranged inorganic connectors, organic linkers, and the within pores with apertures in the range of 0.5 – 3 nm, usually. Significant part of MOFs have a so-called impermanent porosity, which forms as the response of their structure to the external conditions: depending on the latter the material can be totally nonporous, or microporous. Such transitions can be reversible or irreversible, even under cryogenic conditions typical to, e.g. nitrogen porometry. All this introduces ambiguity in interpretation of porosity studies, and makes the problem of characterization of MOFs' porous structure significant.

In this talk we discuss the possibilities of the BET method for the specific surface area measurement for MOFs. Application of the BET method to microporous materials is traditionally not recommended due to special mechanism of micropore filling different from adsorption on a flat surface. However, starting with 2000-xx the significant advance on testing of MOFs with the BET method coupled with theoretical calculation of the specific surface area accessible for spherical probes of known size have been performed by Dr. Snurr's group [1–3]. As it was shown, both values coincide within 10% or better for the considerable number of structures. That have become possible due to application of the special restriction criteria to the BET method regarding the range of pressures [4,5]. Only a part of MOFs with intermediate pores in a range 2-3 nm fell out from a general trend [3].

According to our knowledge, even if the applied restriction criteria is fulfilled, this is not sufficient for proper application of the BET method. We elaborated the more suitable technique to apply the BET method [6], which returns the falling-out group of MOFs into the range of the 10% deviation between BET results and theoretical calculations. Thus, one can conclude that despite on serious distinctions between the mechanisms of micropore filling and adsorption on a flat surface, the BET method can be applied with a known accuracy as a testing technique for the majority of MOFs.

**Acknowledgement.** This work is supported by Ministry of Science and Higher Education of the Russian Federation (project AAAA-A17-117041710079-8).

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## Synthesis and Catalytic Properties of Nanoalloys of Immiscible Metals

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Bi- and polymetallic nanoparticles (nanoalloys) are attracting increasing interest in solving the fundamental problems of physics and chemistry, taking into account their practical use in modern technologies: catalysis, the creation of magnetic instruments and optical converters, biosensors, medical diagnostics and therapy, etc. Of particular interest are nanoalloy systems formed by thermodynamically immiscible or partially miscible metals. Due to the peculiarities of the nonequilibrium state, such alloys possess a complex of physical, chemical and electronic properties of the surface that are inaccessible in equilibrium bulk alloys, which opens up prospects for the creation of a new class of catalytic materials.

The report highlights a synthetic approach to the preparation of nanoalloys of immiscible metals, based on reduction thermolysis of specially prepared single-source precursors. Three types of precursors were used to prepare nanoalloys: double complex salts, for example,  $[\text{RhEn}_3]_2[\text{Pd}(\text{NO}_2)_4]_3 \cdot n\text{H}_2\text{O}$ ; mutual solid solutions of salts of metals, such as  $(\text{NH}_4)_2[\text{IrCl}_6]_x[\text{PtCl}_6]_{1-x}$ ; microheterogeneous mixtures obtained by rapid precipitation of supersaturated joint solutions of metal salts under non-equilibrium conditions - “[Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>/(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>”.

For each investigated bimetallic system, the targeted synthesis of precursors was carried out on the basis of the analysis of physical and chemical properties of the components of the resulting alloy. The selection of the conditions for the decomposition of precursors, resulting in obtaining the nanoalloys of the desired morphology and structure, was carried out by simultaneous thermal analysis with mass spectrometric recording of the evolved gases (TG–DSC/EGA–MS). In the experiments, the modes of temperature exposure and gas environment varied. The stages of the nanoalloys formation during thermolysis were studied in-situ by X-ray powder diffraction using a synchrotron radiation source. Intermediate and final products of the thermolysis were characterized at room temperature. The information obtained provided the ability to control the properties of synthesized nanoalloys.

Developed reliable methods for nanoalloys producing in the systems: Au-Ir, Au-Rh, Au-Ir-Rh – immiscible in solid state; Au-Pt, Pd-Rh, Ir-Pt, Ir-Pd, Pd-Ru, Ni-Mo – are limited regions of existence of solid solutions. The catalytic activity of prepared nanoalloys was studied in three model processes: the reaction of CO oxidation, in testing the activity and stability of the active component of three-route catalysts for the neutralization of exhaust gases; electrochemical hydrogen oxidation/evolution (HOR/HER) and oxygen evolution/reduction (OER/ORR) reactions; the process of obtaining carbon nanofibers from 1,2-dichloroethane. The thermal

### OP-03

stability of the samples was studied using an in situ prompt thermal aging procedure (PTA) and UV-Vis diffuse reflectance spectroscopy. The result of the research is the development of a convenient and technologically advanced synthetic approach to obtaining a new group of materials, the active base of which are alloys nanoparticles and composite structures of immiscible metals.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 16-13-10192.

## Obtaining Nanostructured Materials Based on Segregating Aluminoborosilicate Systems

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The widespread use of transparent glass-ceramic materials characterized by high dispersion of nanoscale crystals, low light scattering, and high thermal and chemical resistance made it possible to design new generation devices for structural optics and microelectronics. [1]

A special feature of nanostructured materials is the characteristic dependence of functional properties on the geometric dimensions of structural elements. An important aspect of the application of nanotechnology in the synthesis of glass-ceramic materials is the possibility of isolating nanoscale crystals in the directional crystallization of glass. In this case, nanostructured sitalles (glass-ceramics) containing crystals with molecular sizes can be obtained. [2]

The majority of technical sitalles are synthesized on the basis of glasses of aluminosilicate systems into which other components can be introduced to modify the composition and control of phase transformations, to obtain the glass structure with the necessary structure and properties. To obtain a homogeneous crystalline structure of the sital, it is necessary to create in the glass a high concentration by volume of uniformly distributed crystalline nuclei -  $(10^{12}-10^{15}) / \text{cm}^3$ . It is obvious that the precrystallization metastable phase separation of a supercooled melt (glass) with the formation of phase boundaries initiates the formation of nuclei. Metastable glass segregation is a special state of a non-equilibrium system, with separated glassy phases (droplet and matrix), whose compositions are close to crystalline phases or eutectic, in the fields of crystallization of which segregation occurs. The uniform distribution of nuclei, their amount and size in glass depends on the cooling rate of the melt and the rate of diffusion of ions. At low temperatures, high viscosity of the melt and insufficiently intensive movement of ions leads to a decrease in the size of liquation regions and an increase in their amount.

The sequence and nature of the crystallization of the glass system  $(\text{MgO} \cdot \text{Al}_2\text{O}_3) - \text{B}_2\text{O}_3 - \text{SiO}_2$ , whose compositions are in the area of metastable segregation along the  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 - 2(\text{MgO} \cdot \text{Al}_2\text{O}_3) - 5\text{B}_2\text{O}_3$  section and their influence on the properties of synthesized sitalles were investigated.

The study of the microstructure of hardened glass in the areas of metastable segregation of systems and chemical analysis of various sample sites using electron microspectral analysis showed that the drop-shaped phase with droplet sizes of 30-40 nm is equally distributed in the matrix phase of the glass. [3]

## OP-04

It was revealed that the process of crystallization of cordierite glasses containing up to 20% B<sub>2</sub>O<sub>3</sub> passes stepwise, by the formation of stable and metastable phases, differing in different values of temperature coefficient of linear expansion (TCLE). The results of the study make it possible to synthesize sitalles with certain thermal parameters by stopping further crystallization of glass at the stage of formation of a certain amount and the ratio of the necessary crystalline phases. [4]

Particular interesting part is the technology of obtaining nanocomposite materials, in which the nanocrystalline phase is introduced into the matrix using glass-crystalline filler containing up to 60-80-nanoscale crystals. Since the nanoparticles in the glass crystal are screened from the environment by the surface amorphous layer, therefore, the volumetric properties of the material will dominate in the nanoscale structure. Glass-composite dielectric materials with temperature coefficient of linear expansion  $(18-25) \cdot 10^{-7}K^{-1}$  with high heat resistance were obtained.

It is shown that by changing the content of B<sub>2</sub>O<sub>3</sub> in the glass, it is possible to change the optical density, the values of the temperature coefficient of linear expansion and the Hv of the glass-ceramics without changing the composition of the main crystalline phases. It was revealed that transparent sitalles with high technical parameters should be synthesized on the basis of glasses with metastable segregation.

Thus, the obtained nanoconstructed material (transparent sital) has an internal nanostructure in the field of the formation of stable and metastable phases with certain, thermal-physical, mechanical properties [5].

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## Photoluminescence Spectroscopy of Rh<sup>3+</sup> Ions in Estimation of the Thermal Stability of Bimetallic PdRh/La-Al<sub>2</sub>O<sub>3</sub> Model Catalysts

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During the last century, large amounts of carbon monoxide, unburnt hydrocarbons and nitrogen oxides incoming to atmosphere as a part of exhaust gases from automobile engines have faced an important and complicated environmental problem. Starting from this time, so-called three-way catalytic systems became one of the most intensively studied catalysts. Besides the growing interest to non-precious metal oxide catalysts for utilization of the mentioned emissions, systems based on platinum group metals still remains of wide usage showing superior activity. Among them palladium and rhodium attract much attention as active components. Being applied for purification of engine exhaust gases, the three-way catalysts are known to undergo rapid deactivation during the heating to the temperatures of 800 °C and above. The main reasons of the deactivation processes are migration of active components, sintering, and phase transformations of the support.

As it was numerously reported, rhodium is known to behave in unusual manner being heated to high temperatures. It starts to interact intensively with supports (alumina, ceria) and disappears from the surface. Both the strong metal-support interaction and the depletion of Rh surface concentration are responsible for the changes in catalytic activity. Recently we have demonstrated that formed Rh<sup>3+</sup> ions can diffuse into the bulk of alumina, where they initiate local phase transformations of the support with formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at lower temperature than it should happen in accordance with phase diagram [1]. All this leads to an irreversible encapsulation of rhodium inside the nanoparticles of corundum being formed.

An introduction of lanthanum in the form of isolated ions in the bulk of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, first of all, improves the thermal stability of the latter. Secondly, it leads to an appearance of new luminescence sites of Rh<sup>3+</sup> in the bulk of alumina at temperatures near 800 °C. It is important to note that  $\gamma$ -phase only is registered by the X-ray diffraction analysis in this case. According to spectroscopic data, the coordination of Rh<sup>3+</sup> ions near La ions in the case of Rh/(4%La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>) system is close to their coordination in lanthanum hexaaluminate [2]. Thereby, Rh<sup>3+</sup> ions can be applied as a luminescence probe to study their diffusion from the surface of the La-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support into its bulk [3]. In the case of monometallic Rh/La-Al<sub>2</sub>O<sub>3</sub> and bimetallic Pd-Rh/La-Al<sub>2</sub>O<sub>3</sub> catalysts, diffusion of Rh<sup>3+</sup> ions into alumina during high-temperature treatment can be analyzed by luminescence technique within the extended temperature range of 800–1100 °C [4].

## OP-05

The present research was aimed to study the features of formation of La impurity sites in the alumina bulk at different methods of the initial alumina modification. Interaction of these sites with  $\text{Rh}^{3+}$  ions followed by diffusion of the latter into the bulk during calcination the samples under oxidative/reductive conditions was also investigated. The temperature range of 800–1000 °C was studied, since no irreversible encapsulation of  $\text{Rh}^{3+}$  ions inside the corundum phase should take place at such conditions. Three methods of alumina modification by La were examined: bulk, surface and inter-boundary modification. It was found that surface modification does not lead to formation of La sites in the alumina bulk within the studied temperature range and, consequently, no luminescence of  $\text{Rh}^{3+}$  ions was observed.

Preliminary thermal treatment of the modified support also affects the evolution of the luminescence sites. As presented in Fig. 1, the rate of  $\text{Rh}^{3+}$  ions diffusion and their localization in the nearest surrounding of isolated La ions is significantly higher for the initial support (THL) if compare with that calcined at 1000 °C (THL1000).

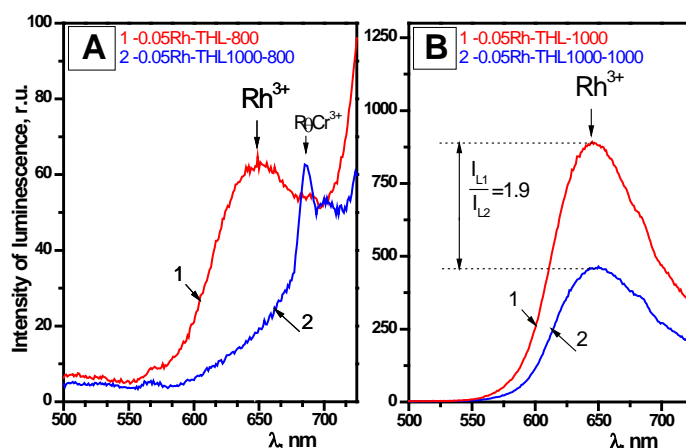


Figure 1. Luminescence spectra  $\text{Rh}^{3+}$  ( $\lambda_{\text{ex}}=415$  nm) for the samples based on initial (THL) and preliminary calcined (THL1000) 4% $\text{La}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  support after aging at 800 (A) and 1000 °C (B).

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research, grant 19-03-00660.

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## Study of Influence of the Composition of Ni(Mg)AlO<sub>x</sub> Catalysts, Prepared by Mechanochemical Route, on their Properties in Aqua-Phase Furfural Hydrogenation

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The possibility of fuel and valuable chemical compounds producing from various types of biomass is currently an important area of research. Furfural is one of the most popular compounds for the further production of various chemical substances. Catalytic hydrogenation of furfural is a complex process, leading to the various types of products in demand in the petrochemical industry. The creation of active catalysts, which allow to purposefully regulate requests for certain products, is a necessary requirement.

The aim of the work was to establish the relationship between the composition of Ni-containing catalysts based on Ni(Mg)Al-LDH, obtained by an environmentally friendly mechanochemical method, and their activity and selectivity in the reaction of aqua-phase hydrogenation of furfural.

The synthesis of Ni(Mg)Al-LDH by the mechanochemical method was performed in two stages. At the first stage, mechanochemical activation of initial mixture (Al(OH)<sub>3</sub>, Ni(Mg)(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>) was carried out in an AGO-2 planetary mill (ZAO NOVITs, Russia). The weight ratio between the steel grinding bodies and the activated mixture was 20 : 1, the time of activation was 30 min, and the centripetal acceleration of the grinding bodies was 1000m s<sup>-2</sup>. At the second stage, the aging of the samples was conducted under vigorous stirring of the mixture of mechanically activated components and distilled water at the weight ratio water : sample=10 : 1 on a magnetic stirrer at 65 °C for 2 h. After this time interval, the sample was washed with distilled water, dried initially in air at room temperature for 12 h and then in a drying oven at 120 °C for 2 h. Structural properties of synthesized samples was investigated by X-ray diffraction (XRD) with using D8 Advance (Bruker) X-ray diffractometer (CuKα radiation, λ=1.5406 Å) by scanning with step of 0.05° and accumulation time of 5 s/step at 2θ diffraction angles between 5 and 80°. Phase composition determination was made with using ICDD PDF-2 database. The concentrations of the metals (Ni, Mg, Al, Fe) in the solid samples after their dissolution were determined by inductively coupled plasma atomic emission spectroscopy (Varian 710-ES device).

Liquid-phase hydrogenation of furfural in the presence of synthesized catalysts was examined using a steel autoclave. Before the reaction, Ni (Mg) Al-LDH samples are pre-oxidized and reduced in a stream of hydrogen (600 °C). Catalyst loading was 500 mg. Catalyst

## OP-06

was pre-reduced in 40 ml of distilled water with hydrogen at temperature of 50 °C and pressure of 0.5MPa for 0.5 h under stirring. After the catalyst pre-reduction, 5.0 mL of furfural and 60 mL of distilled water were loaded into the autoclave. Hydrogenation was performed at a specified temperature and constant hydrogen pressure. The reaction mixture was stirred by a magnetic stirrer at 1400 rpm to prevent external diffusion limitations. The reaction was controlled by measuring the volume of consumed hydrogen with a mass flow meter. The quantitative determination of the reaction products was carried out by GC in a capillary column.

Three series of catalysts with different ratios of  $(\text{Ni} + \text{Mg}) / \text{Al} = 2, 3$  and  $4$  were synthesized by a mechanochemical method. Within each series, the nickel fraction  $\text{Ni}/(\text{Ni} + \text{Mg}) = 0, 0.1, 0.3, 0.5, 0.7$  and  $1$  was varied. It was found that the ratios of metals, calculated on the basis of chemical analysis data, almost completely correspond to theoretical ones. This indicates that complete reaction between the initial components in the process of mechanochemical synthesis occurred. According to XRD data, the diffraction patterns of all samples contain reflexes characteristic of the LDH phase. Moreover, with an increase in the of nickel fraction in the NiMgAl-LDH composition, the peaks become more blurred, which may be due to an increase in the defectiveness of the obtained samples.

The study of catalysts obtained on the basis of Ni-containing LDHs in the reaction of furfural hydrogenation showed that the degree of furfural conversion, as well as the selectivity of the formation of certain products, strongly depends both on the  $(\text{Ni} + \text{Mg})/\text{Al}$  ratio, and the nickel fraction in the samples. With an increase in the ratio of  $(\text{Ni} + \text{Mg})/\text{Al}$  the activity of the catalysts decreases. Moreover, the degree of conversion of raw materials for two-component NiAl-LDH catalysts does not exceed 55%. In this case, the main products of the reaction are furfuryl- and tetrahydrofurfuryl alcohols. When the ratio  $\text{Ni}/(\text{Ni} + \text{Mg}) = 0.3$  and  $0.5$ , the maximum activity of the catalysts in each series is reached. Thus, for catalysts with  $(\text{Ni} + \text{Mg})/\text{Al} = 3$  and  $4$ , the complete conversion of furfural is achieved for samples with  $\text{Ni}/(\text{Ni} + \text{Mg}) = 0.5$  with selective (more than 60%) formation of tetrahydrofurfuryl alcohol.

**Acknowledgement.** The work was financially supported by the Ministry of Science and Higher Education of the Russian Federation in accordance with the Program of fundamental scientific research of the State Academy of Sciences for 2013-2020 in direction V.46, project V.46.2.4. (project registration number AAAAA17-117021450095-1). Synthesis and investigation of structural properties of the NiMgAl-LDH was funded by the Russian Foundation for Basic Research according to the research project No. 18-03-00476 (AAAA- A18-118121190005-7).

## Efficiency Destruction of Ibuprofen onto Magnesium Ferrite Catalyst

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Pharmaceutically active compounds (PhACs) and their metabolites are widespread in waste, ground, surface and even drinking water representing a great threat to human health and the aquatic ecosystem [1]. The risk of contamination with antibiotics, hormonal and nonsteroidal anti-inflammatory drugs due to their high stability, low volatility, accumulative and mutagenic properties. It is important to note, that most drugs are not removed during the purification of waste and drinking water, due to the low efficiency of the treatment plants in the removal of PhACs and their metabolites. This leads to the relevance of the development of new materials and technologies for the treatment of natural and waste waters.

The highest efficiency in solving the above problem is ensured by the use of catalytic methods, first of all *Advanced Oxidation Processes (AOPs)*, in conjunction with effective Fenton-like catalysts [2]. The main advantage of AOPs is the possibility of complete “mineralization” of organic pollutants due to the generation of strong oxidizing agents based on oxygen-containing reactive particles, predominantly hydroxyl radical (OH<sup>•</sup>). One of the promising Fenton-like catalysts are metal ferrites, in particular MgFe<sub>2</sub>O<sub>4</sub>, due to their chemical stability, non-toxicity and high catalytic activity to a wide range of organic pollutants [3].

In the present work catalytic properties of obtained Fenton-like catalysts based on MgFe<sub>2</sub>O<sub>4</sub> nanoparticles during oxidative destruction of non-steroidal anti-inflammatory drug ibuprofen (IBP) was studied. The influence of the conditions of the catalytic process (concentration of the catalyst, concentration of the precursor of OH-radicals (H<sub>2</sub>O<sub>2</sub>) and the pH of the aqueous solution) on the efficiency of IBP decomposition was established.

In accordance with the obtained results (Fig. 1), it was found that the optimal conditions for the complete destruction of IBP within 40 minutes are the following: C(MgFe<sub>2</sub>O<sub>4</sub>) of 0.5 g/L, C(H<sub>2</sub>O<sub>2</sub>) of 20.0 mmol/L and the pH of the aqueous solution of 6.0.

## OP-07

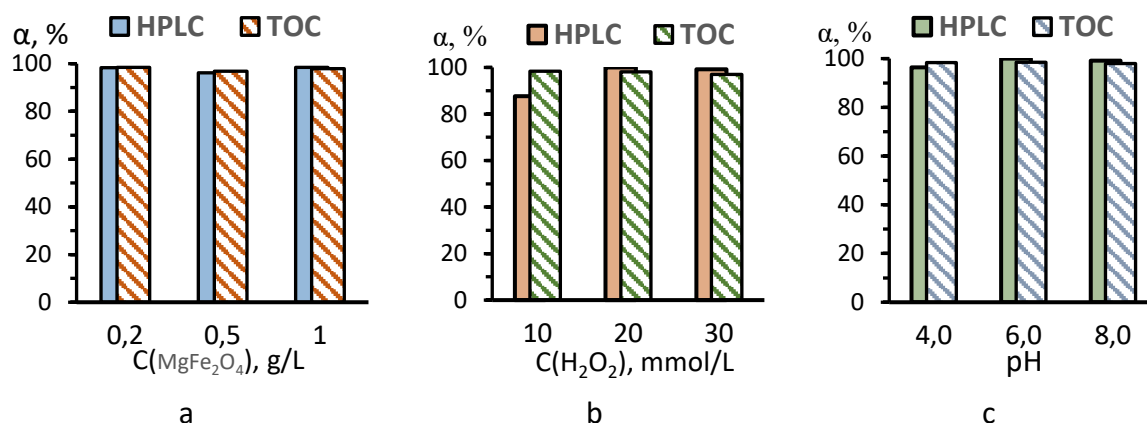


Fig. 1. Effect of catalyst (a) and  $\text{H}_2\text{O}_2$  (b) concentration, solution pH (c) on the degree of IBP catalytic destruction ( $\alpha_{\text{HPLC}}$ , %) and mineralization ( $\alpha_{\text{TOC}}$ , %) after 40 minutes.

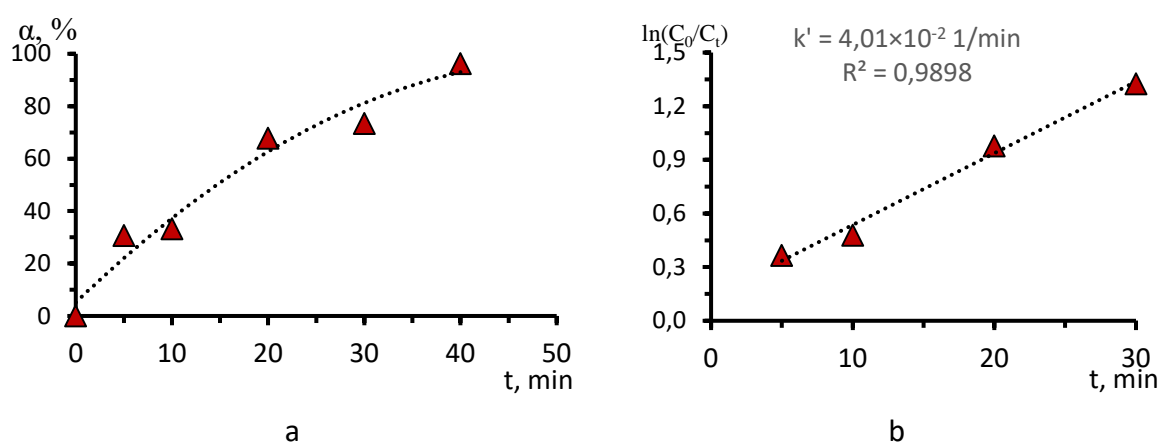


Fig. 2. Dependence of the IBP destruction degree on the contact time (a) and the destruction kinetics in the linear coordinates of the pseudo-first order model (b). Reaction conditions:  $C(\text{MgFe}_2\text{O}_4)$  0.5 g/L,  $C(\text{H}_2\text{O}_2)$  20.0 mmol/L and pH 6.0.

According to Fig. 2a complete mineralization (oxidative degradation) of IBP (100%) is achieved in 40 minutes. The dependence of the destruction degree ( $\alpha$ , %) on time has a monotonic character, and the kinetics of the catalytic process is described by the pseudo-first order model ( $R^2=0.99$ ) (Fig. 2b). The calculated value of the apparent rate constant is  $4.01 \times 10^{-2} \text{ 1/min}$ , which is at the level of similar kinetic characteristics of the most efficient catalysts, described in the literature [4, 5]. Thus, the present study indicates the prospects of using of the obtained catalyst for the purification of aqueous media from PhACs.

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## Methods of Regulating of the Alumina Catalyst Supports Mechanical Strength: an Experiment and a Model Using the Decision Trees and Random Forest

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Alumina is widely used as a support of catalysts for oil refining processes (hydrotreatment, reforming, isomerization, hydrocracking, and others) [1]. General regularities in the formation of the alumina pore structure from reprecipitated hydroxide and its strength characteristics have been revealed [2, 3].

The solid material strength is determined primarily by the strength of its solid particles. The strength of finely dispersed materials with the open porosity is largely determined by the properties of contacts between the corresponding particles, by textural characteristics, and it is laid on the stages of material synthesis. In addition, the mechanical characteristics of the supports and catalysts exhibit a very strong scatter of values, illustrated in box plot (fig. 1a), and the distribution of these values is usually unsymmetrical (fig. 1b).

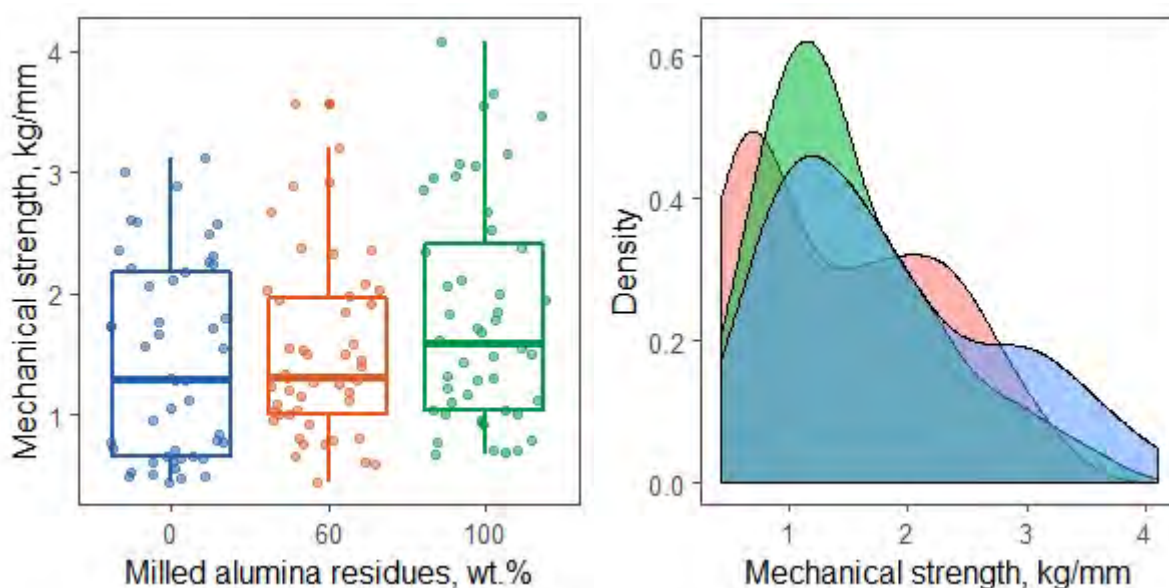


Fig. 1. (a) The strength of alumina supports versus the content of milled residues. (b) The density distribution of the support mechanical strength. Colors are the content of the milled alumina residues in the support: blue – 0 wt.%, red – 60 wt.%, green – 100 wt.%.

This is due to the specifics of the finely dispersed materials: the deviation of the granules from the regular geometric shape, inhomogeneities and defects of the porous structure, and even with the intensity of the extrudate molding. Therefore, when determining the

mechanical properties of carriers and catalysts, it is necessary to take into account their statistical nature.

Decision trees and a random forest are the methods for studying of the statistical relationship between one dependent variable (the mechanical strength in our case) and several independent variables (predictors). Today, these methods are widely used for forecasting and classification problems in marketing, banking, biology, and medicine. Decision trees are effective when the relationships between the predictors and the dependent variable are non-linear, and the variables have asymmetrical distributions. The trees are resistant to emissions and missing values. Based on the foregoing, the decision trees and the random forest are ideal tools for modeling of the support and the catalyst mechanical strength.

This work is aimed to investigate the strength characteristics of composite supports for catalysts based on  $\gamma\text{-Al}_2\text{O}_3$  which were prepared using milled residues of the dried or calcined supports, to study the relationship of these characteristics with the textural parameters of the supports and methods of their preparation, and to build a statistical model of the strength of alumina catalyst supports based on the obtained dependencies.

Measurement of the strength of supports was carried out on a Lintel PK-21 strength meter under static conditions by cross-section method. The number of tests per sample is 48. Statistical processing of the results of strength measurements with the determination of central tendency measures and variability measures, preliminary data preparation, and also predictive modeling using the decision tree and the random forest methods were carried out in the R programming environment.

When constructing a model of the decision tree and the random forest, the average mechanical strength of the supports was considered as a dependent variable and the mass fractions of the dried and calcined support, the textural characteristics of the carriers (specific surface values, true helium density, porosity), as well as synthesis conditions (temperature and calcination rate, amount of acid peptizers) were used as independent variables.

It is shown that the constructed tree and the random forest are in good agreement with the experimental data and accurately predict the value of the independent variable.

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research (Project No. 18-33-00791).

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## Monoterpene Alcohols Amination for Pharmaceutical Applications over Gold Catalysts

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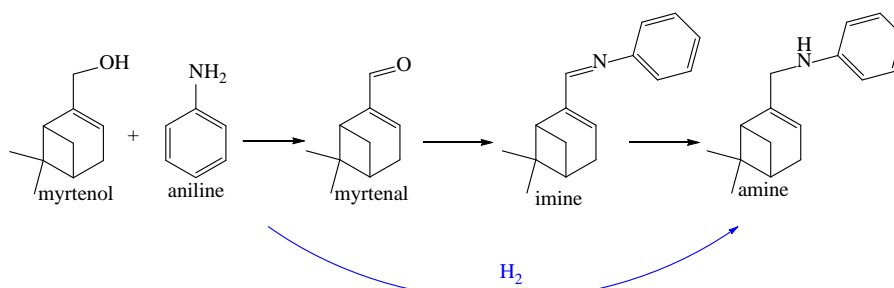
Amines are important chemicals that are widely used as agrochemicals, dyes, polymers and pharmaceuticals. An effective approach towards complex amines is catalytic one-pot alcohol amination proceeding via consecutive dehydrogenation of the alcohol to the carbonyl compound, a further reaction of the latter with an amine followed by C=N bond hydrogenation by hydrogen generated in the first step. Biomass-based alcohols such as terpenoids possess a large potential as a starting material in production of efficacious chemicals needed for human disease prevention and therapy [1]. The process efficiency is preserved only when the impact of side reactions is minimized which is important in the case of highly reactive terpenoids. The main objective of the present work was to study general regularities of catalytic one-pot terpene alcohol amination and develop an approach for direct production of terpene amines.

One-pot terpene alcohols amination was studied in the presence of nanosized gold-containing catalysts supported on different metal oxides (ZrO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>) with equimolar amounts of the substrates in the temperature range of 413-453 K under nitrogen pressure (9 bar). The gold catalysts on metal oxides (ZrO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>) were prepared by DP method, pretreated under oxidizing or reducing atmospheres and characterized by TEM, XPS and TPR/TPO-MS.

The results of our work have shown that gold catalysts are rather active in one-pot amination of a natural terpene alcohol myrtenol leading to preferential hydrogenation of C=N bond in the final step instead of a more reactive C=C group of myrtenol (Fig. 1) [2, 3]. The product distribution and conversion were found to depend strongly on the support nature, catalyst redox activation and the active metal component composition [2, 3]. Among the tested catalysts, Au/ZrO<sub>2</sub> with both acidic and basic surface sites afforded optimum consecutive myrtenol transformations resulting in complete conversion of myrtenol and selectivity to the target amine of ca. 52% [2]. The basic sites on the metal oxides surface were suggested to be required for the initial alcohol activation, while availability of protonic groups was important for the target amine formation.



## OP-09



**Fig. 1.** One-pot myrtenol amination with aniline over Au catalysts [2].

Differences in activity and selectivity for pre-reduced and pre-oxidized catalysts were proposed to be mainly related to a different degree of the support basic properties modification by residual ammonia [3]. The reaction kinetics was modeled based on the mechanistic considerations with the non-catalytic and the catalyst deactivation step introduced into the mechanism [4]. To improve selectivity to the desired product an effect on the reaction of external hydrogen sources, including molecular hydrogen, alcohols, formic acid, was studied [5, 6]. Predominant hydrogenation of either C=N bond or both C=N and C=C bonds in the presence of Au/ZrO<sub>2</sub> catalyst was observed depending on the type of hydrogen source, addition time or reaction temperature. The hydrogen donors introduction was efficient for controlled hydrogenation of the C=N bond [6]. Application of 2-propanol allowed an increase of selectivity to the target amine with the maximum yield of 68% compared to 52% without any additive. The substrates structure was varied to obtain potential biological active compounds. A good correlation was found between the substrate structure and reactivity using the Hammett equation [7]. The biological activity of the selected amines was studied helping to identify a new type of inhibitors of TDP1, an important target for antitumor therapy [8].

**Acknowledgement.** This work was supported by the Ministry of Science and Higher Education of the Russian Federation (project no. AAAA-A17-117041710075-0).

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## Synthesis of Functional Carbon Nanostructures on Self-Organizing Ni-M Catalysts

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Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have a unique set of physico-chemical properties, which makes them popular and, in some cases, indispensable material in a wide range of applications. [1]. One of the most common reasonable methods for producing CNMs on an enlarged scale is the catalytic deposition of carbon from the gas phase. A variety of hydrocarbons are used as a carbon source, including ones containing various heteroatoms. This method has also proved to be effective for the decomposition of chlorinated hydrocarbons (Cl-HC) and related waste products to obtain the CNF with a high specific surface area and unique structure [2].

The Ni-based system is approved to be the most active and stable catalyst for this process due to high resistance of nickel towards chlorination. Earlier we have reported on the efficiency of Ni-based self-organizing catalysts (SOCs) in catalytic chemical vapor deposition (CCVD) of various halogenated hydrocarbons. Synthesis of SOC is based on the phenomenon of metal dusting of bulk Ni-M alloys that serve as precursors of catalyst. Metal dusting (or carbon erosion) caused by decomposition of Cl-HC results in rapid and full disintegration of Ni-M alloys with emergence of disperse metallic particles catalysing further growth of CNFs [3].

The carbon fibers produced on SOC from decomposition of Cl-HC (Fig. 1) were shown to be characterized by unique segmental structure [4].

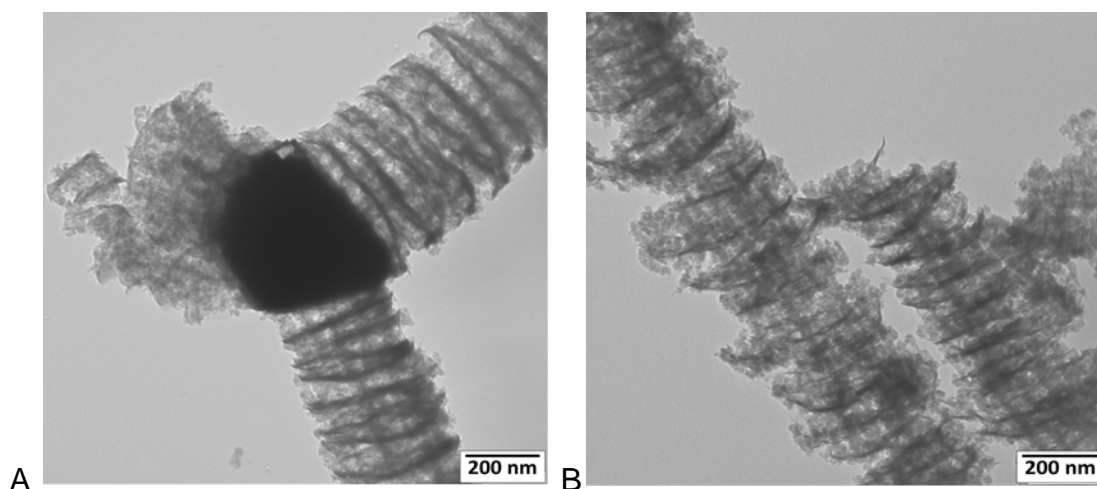


Figure 1. TEM images of carbon material produced by decomposition of DCE over Ni-Fe (A) and Ni-Pd (B) alloys. Reaction mixture: DCE/H<sub>2</sub>/Ar, T = 600°C, reaction time – 2 h.

## OP-10

According to EDX data, the carbon surface may contain up to 0.5 at. % chlorine. It is well known that in many cases the effectiveness of the use of CNT and CNF in various applications is determined by the presence and composition of surface functional groups.

The report will present data on the functionalization of carbon fibers under the conditions of joint and separate decomposition of 1,2-dichloroethane and various oxygen- and nitrogen-containing substrates. It will be shown how the presence of oxygen or nitrogen in the mixture affects the rate of CNM formation during the catalytic decomposition of chlorohydrocarbons, as well as its textural and structural parameters. The possible areas of application for produced functionalized CNF will also be discussed in the presentation.

**Acknowledgement.** The reported study was supported by RFBR (research project No. 18-29-19053-mk).

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## OP-11

### The Study of Cartilage Cells Morphology Grown on the MWCNT Array

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Hybrid technology of bio- and nanoelectronics are actively developing in recent years. Functional carbon based nanomaterials are modern trend in nanoelectronics. Carbon nanotubes are widely used in this area due to their unique mechanical, electrical and optical characteristics. CNTs are well-studied material and their properties can be modified by synthesis and treatment processes. Additionally CNTs have similar dimensions with components of biological cells; their mechanical characteristics are near to protein structures properties.

Multi-walled carbon nanotubes (MWCNT) arrays were produced by catalytic plasma-enhanced chemical vapour deposition (PECVD) synthesis. As the initial substrates, monocrystalline silicon wafers with catalytic pair of Ti (10 nm) and Ni (2 nm) were used. CNT synthesis was performed on plasma chemical deposition unit “PlasmaLab System 100” (“Oxford Instruments”). MWCNT synthesis consists of 3 stages: oxidation of catalytic layer, reducing annealing and grown stage. The grow stage was performed at temperature of 600 °C in acetylene and ammonia flow and plasma power of 20 W RF and 30 W LF during 2 min.

MWCNTs array with the average length of 5 μm was synthesized for this research. CNTs have the outer diameter ~30 nm. The morphology of these nanotubes is shown on Fig. 1.

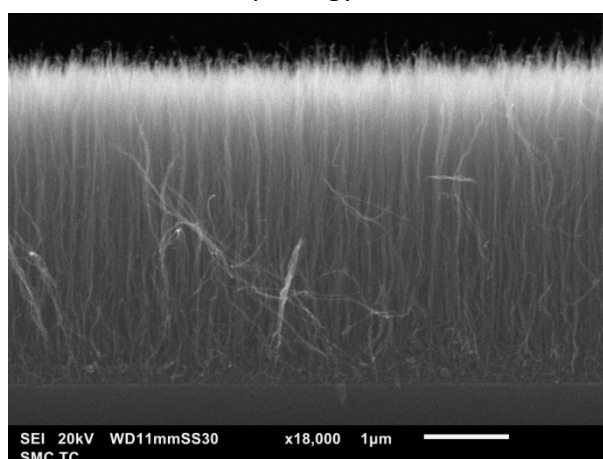


Fig. 1 - SEM image of MWCNT array

In this work cell culture of chondroblasts was extracted from human articular hyaline cartilage. For the formation of suspension with necessary doze, cells were cultivated in

## OP-11

nutrient medium “Sreda 199” (“Biolot Ltd”), with 10% fetal bovine serum addition. 2 ml nutrient medium and 10% fetal bovine serum in doze  $\sim 10^5$  cell/ml, was added in every alveolus and incubated samples by 37 °C for 24 and 72 hrs in thermostat with 5 % CO<sub>2</sub> atmosphere. Nutrient medium was removed after incubation. Cells were fixed for 30 min in 2.5 % glutaraldehyde, washed for 2 min in phosphates buffer for 3 times and dehydrated consistently in 3 ethanol solutions (50, 70, 96 %) for 2 min in every solution.

Experimental and control samples with cells after 24 and 72 hours were fixed by glutaraldehyde and completely dried at room temperature. The study of cells surface structure was performed with SEM (Fig. 2). Clear silicon substrates and silicon substrates with sputtered catalyst for MWCNT synthesis (10 nm Ti and 2 nm Ni) were used as control samples.

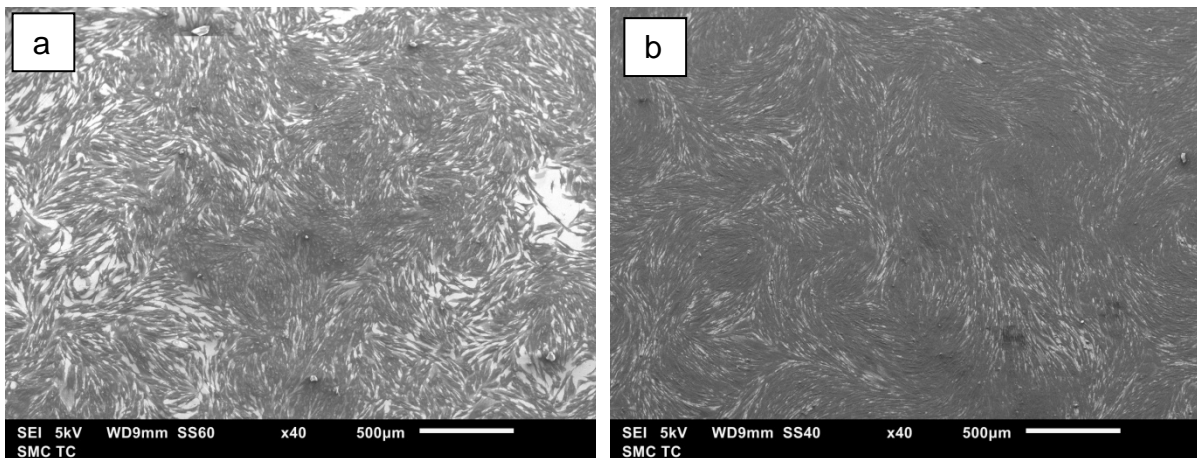


Fig. 2 - SEM of cells proliferating for 24 (a) and 72 hours (b) substrate with MWCNT array

The comparison of cells grown on experimental and control samples demonstrated an absence of the toxic effect on cell viability. No pathological changes in cell morphology were observed. The elongated shape of cells indicated the adhesion of chondroblasts to the surface of substrates and the beginning the active phase of proliferation. The investigation of cell growth over time (24 h and 72 h) showed an increase in cell mass: a dense allocation of cells over the samples was observed after 24 h of incubation, and a homogeneous cell monolayer was formed after 72 h. It was found that the samples stimulated the formation of intercellular interactions and conglomerates and promoted for oriented cell growth. This effect was observed mainly on samples with an array of nanotubes. Cell size was about 50-100  $\mu\text{m}$  which is typical for the studied in the work cell culture. The investigated substrates have high adhesive properties, stimulate the active growth of chondroblasts and can be widely used in the fields of bioelectronics and nanomedicine.

**Acknowledgement.** This work was supported by the project of the Ministry of Science and Higher Education of the Russian Federation (14.578.21.0234 RFMEFI57817X0234). The studies were performed using MIET Core facilities center “MEMS and electronic components”.

## Hafnium Oxide Nanoparticles Modified with Polymer Shell

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Nowadays, there are several approaches in cancer treatment: surgery, chemotherapy, radiotherapy and immunotherapy. However, two of the most common non-invasive approaches (chemo- and radiotherapy) have their own drawbacks, the main one being the death of the healthy tissue as well as of the malignant ones [1,2]. Another issue in cancer treatment is the diagnostics techniques. While computed tomography (CT) provides a high spatial resolution to illustrate the biological structures of the body, a large dose of contrast agent is needed as medications used nowadays have low contrast [3].

Nanoparticles (NPs) of high-Z elements have been recognized as a material that may help to overcome these issues via a specific distribution in cells and the enhancement of radiotherapy through radio sensitization [3]. Sol-gel methods of synthesis provide an easy and effective way to get NPs with controlled composition, size, and morphology. Even greater advances are accomplished if aerogels are obtained as these materials possess high specific surface area and porosity. Nowadays, they are used as catalysts, thermal insulation, particle detectors, supercapacitors and in many other applications [4].

During this work nanoparticles of hafnium oxide with fluorescent mark and polymeric shell were designed. In order to obtain hafnium oxide nanoparticles a controlled hydrolysis of hafnium *n*-butoxide was performed (Figure 1). A simple sol-gel reaction allowed to obtain a stable gel that was further exposed to the supercritical drying in CO<sub>2</sub>. Fluorescent mark was added during sol stage in order to provide visualization of nanoparticles for the biological tests.

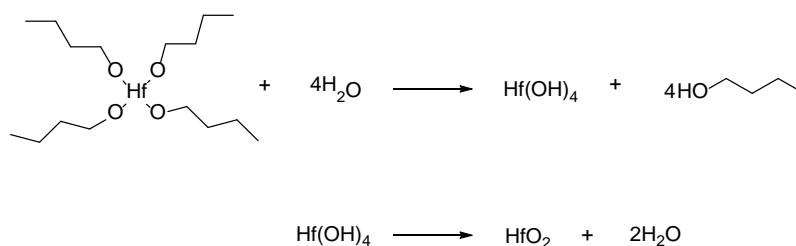


Figure 1. Hydrolysis of Hf *n*-butoxide

Furthermore, in order to improve stability of nanoparticles in water and biological media a polymer layer was introduced. Nowadays, one of the most popular polymers for the surface modification of metal and metal oxide nanoparticles is amphiphilic block co-polymer PEG-PCL. Choice of this polymer was also founded on the FDA approval to use it in the biological systems in order to prevent protein corona formation [5]. Polymers with different ratios of

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hydrophobic/hydrophilic parts were synthesized and tested to find the best composition to provide stable water sols.

The nanoparticles were characterized by TEM, IR-spectroscopy, Nitrogen adsorption, DLS measurements. Polymer was characterized through IR-, NMR-spectroscopy, DSC, GPC. Cell viability tests were conducted to state the biocompatibility of the nanoplatform.

**Acknowledgement.** This work was supported by the Grant of Russian Foundation for Basic Research, grant N 18-29-11078.

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## Yekaterinburg Nanotoxicological Team's Experience in Assessing Experimentally Adverse Health Effects of Metal Oxide Nanoparticles

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Nanoparticles (NPs) of Fe<sub>3</sub>O<sub>4</sub> were produced in a chemical technique and nanoparticles of Ag, Au, CuO, NiO, Mn<sub>3</sub>O<sub>4</sub>, PbO, ZnO, TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> - through laser ablation. In some experiments, we compared particles of a given chemical composition having different diameters, while in others – equidimensional nanoparticles of different metals or metal oxides (Me-NPs). We used two experimental models: a single intra-tracheal instillation of Me-NPs 24 h before the bronchoalveolar lavage procedure (collecting) and the repeated intra-peritoneal injections during 6-7 weeks in non-lethal doses. Besides, we carried out long-term inhalation experiments with NPs of Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and NiO.

We have demonstrated that NPs are much more noxious as compared to their fine micrometric or even submicron counterparts and are usually the more toxic the smaller their dimensions within the nano-scale range. We found also that toxicity of Me-NPs strongly depends on their chemical nature, solubility and mechanisms of action specific for a given metal in any chemical form. Solubilization of Me-NPs in biological milieus plays an important part in their toxicokinetics which can prevail over that of the physiological mechanisms controlling their distribution, retention and elimination. On the other hand, thanks to the high activity of these mechanisms, the organism is not defenseless against the impact of Me-NPs.

The nonspecific responses of the organism to the impact of Me-NP included: changes in the cytological and some biochemical characteristics of the bronchoalveolar lavage fluid caused by the deposition of particles in the lower airways; various manifestations of systemic toxicity, particularly expressed damage to the liver and kidneys; some cytological signs of a likely onset of hyperergic inflammation; moderate neurological disturbances presumably associated with possible penetration of Me-NP into the brain from the blood (in which its concentration rises as a result of proven solubilization of metal oxide nanoparticles in biological media), and with the transport of nanoparticles from the nasal mucous membrane along the olfactory pathway; a paradoxically low manifestation of pulmonary pathology explained by low chronic retention of nanoparticles in the lungs; a genotoxic effect on the organism level even under low chronic exposure for which systemic toxicity is mild enough.

As a protective measure, the toxicity and even genotoxicity of Me-NPs can be significantly attenuated by adequately composed combinations of some bioactive agents in innocuous doses.

## Spider Web as a Natural Nanocomposite Material for Eco-Friendly Applications

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Nature is rich on examples of such organic-inorganic systems, which supply superior toughness and were found in different tissues from abalone shells[1] to human bones[2]. While humanity comes to know more about these natural processing, the importance value of the hierarchical structures becomes obvious for definition how the living world functions. This denotes thrilling prospects based on the concept of converting hierarchically ordered structures properties to novel material functions. This approach opens up opportunities for innovative materials applications in the fields of energy and sustainability, medicine, nanobiomedical technology and many others[3].

Along with its biocompatibility, biodegradability and notable mechanical properties, spider silk may become a suitable candidate for broad eco-friendly applications[4]. One of major challenges of producing spidroin-based materials involves a comprehensive understanding of spider silk proteins and their assembly into fibers. These insights can provide the possibility to develop spider silk-based materials as biocompatible devices and controlled release systems.

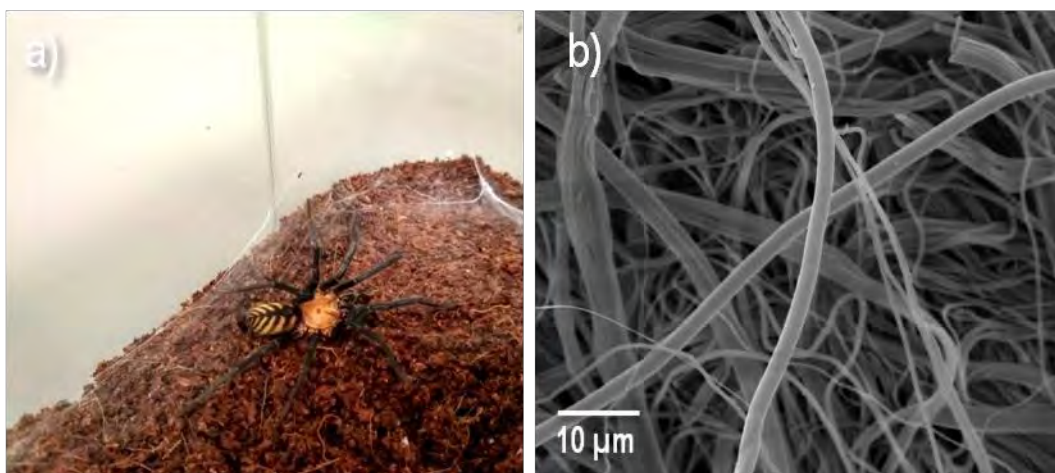


Fig 1. a) *Linothele Fallax*, b) SEM image of native spider silk

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**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 18-79-00269.



## Formation of Phenolic Acid Layer on $\gamma$ -AlOOH Nanoparticles Surface and Their Antioxidant and Membrane-Protective Activity

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In the reported study we prepared gallic and caffeic acid modified  $\gamma$ -AlOOH nanoparticles. We proposed mechanism of phenolic compounds binding on the alumina, suggesting covalent and electrostatic interactions. Most of the properties of alumina NPs are unchanged, but there is partial reduction of surface charge. Prepared samples are colloiddally stable hydrosols.

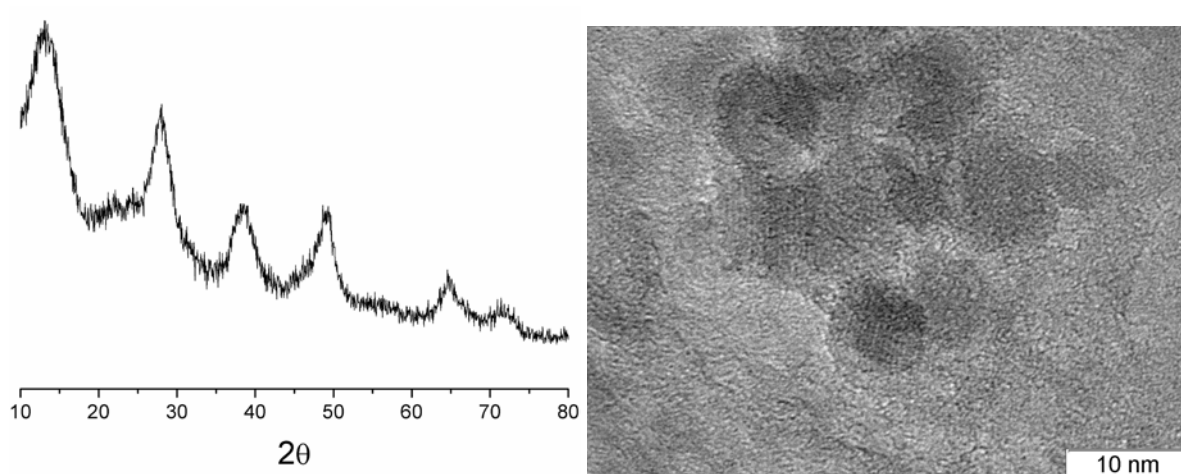


Fig. 1. XRD pattern (left) of and TEM image (right) of the prepared alumina samples.

Using the cellular model system (red blood cells of mammals) and non-cellular medium containing animal lipids, a primary assessment of cytotoxicity (hemolytic activity) and antioxidant activity of aluminum oxyhydroxide-based nanoparticles containing phenolic acids as an active substance was carried out. The highest antioxidant activity was observed for nanoparticles with a high content of phenolic acid. However, due to the ability of aluminum hydroxide to interact electrostatically with the negatively charged surface of the erythrocyte membrane and cause aggregation and sedimentation of erythrocytes as a result of heterocoagulation, a protective effect in the cell model system can be obtained only with the use of this compound in a relatively low concentration.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 18-73-00212.

## Hemolytic Activity of Aluminosilicate Nanoparticles with Different Morphology

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At the moment, there are several promising areas for the use of porous aluminosilicates nanoparticles in medicine at the stages of laboratory research or clinical trials. These areas include the development of drug carriers with a prolonged release, systems for parenteral administration of drugs, targeted delivery, entero- and application sorption.

Development of drug delivery systems of prolonged action, as well as systems for targeted drug delivery is aimed primarily at solving the problems of antitumor therapy. In general, treatment with chemotherapeutic drugs is carried out by the method of intravenous parenteral administration. In this case, there is a direct interaction of both the drugs themselves and the matrices carrying them with the blood plasma. Of great importance in this is the presence of toxicity and hemolytic activity in carriers.

Hemolysis is the process of destruction of red blood cells with the release of hemoglobin into the environment. The widespread use of a number of drugs is limited due to their high hemolytic activity. Red blood cells can be considered as models for studying the interaction of cells with drugs or their carriers, and hemolysis correlates with other cytotoxicity tests.

The study of hemolysis is the simplest and fastest method of studying the effect of materials on biological membranes. In vitro hemolysis studies have shown hemolytic activity in a number of natural silicate minerals - chrysotile sepiolite and palygorskite, kaolinite, montmorillonite and illite.

In the present work, the hemolytic activity of samples of synthetic porous aluminosilicates obtained under hydrothermal conditions was studied for the first time. Samples of layered silicates with the structure of montmorillonite ( $\text{Na}_{2x}(\text{Al}_{2(1-x)}, \text{Mg}_{2x})\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , where  $0 < x < 1$ ), zeolites of various structural types (Beta, Rho, Pau) and aluminosilicates with the halloysite structure ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ). The samples differed in chemical composition (aluminum content), morphology (layers, plates, spheres, nanotubes), in porous-texture and micro-structural characteristics, as well as in particle sizes. The study of the effect of parameters mentioned above on the hemolytic activity was performed.

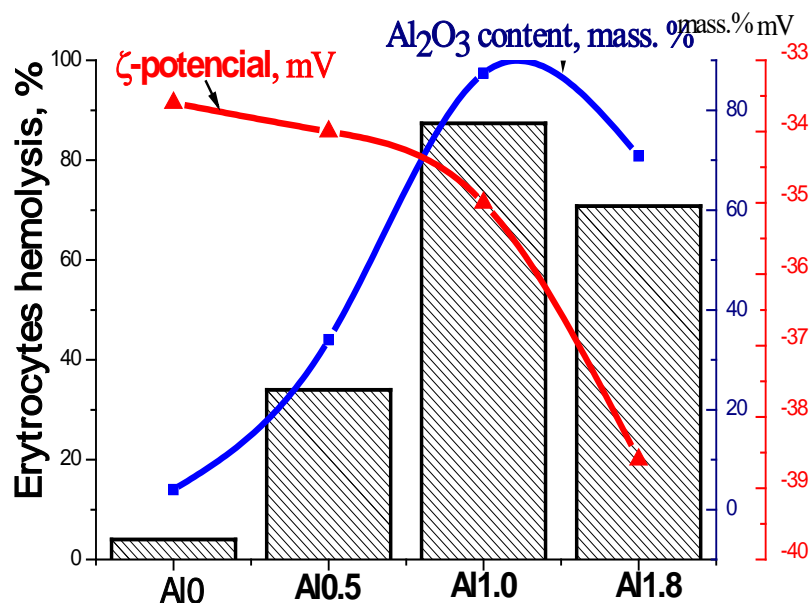


Fig. 1. Correlation of hemolytic activity, surface charge and aluminum content for montmorillonite samples

It was found that all samples of the studied synthetic aluminosilicates have hemolytic activity, which must be taken into account when developing drug delivery systems with intravenous parenteral administration or in contact with blood plasma.

The results of the study show that the surface charges of the particles and their morphology undoubtedly affect the hemolytic activity. The aluminum content of the samples may also have a negative impact on the appearance of toxicity, but the presence of hemolytic activity in samples not containing aluminum most likely indicates the complex effect of several factors on the toxicity of samples.

The degree of carrier toxicity can be significantly reduced by properly selecting their chemical composition, morphology and concentration.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 18-03-00156.

## MOCVD of Pt and Pt<sub>x</sub>Ir<sub>(1-x)</sub> Coatings with High Surface Areas on the Contacts of Electrophysiological Diagnostic Electrodes

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The implantable medical electrodes (endocardial electrodes, electrophysiological diagnostic electrodes, electrodes for neurostimulation, etc.) are widely used to treat and diagnosis of the heart diseases. The above-mentioned electrodes serve as conductors delivering electrical impulses directly to the living tissue, thereby providing their stimulation. The progress in the field of design of medical electrodes based on increasing a surface area of a medical electrode via deposition on its surface biocompatible functional fractal-like coatings. In addition, the modification of electrode surface makes possible to reduce the geometric dimension (diameter / cross-section) of an electrode or its pieces while maintaining electrophysical properties, the quality of biosignal detection and long-term reduction in stimulation thresholds [1].

The platinum and platinum-based coatings combining biocompatibility, corrosion resistance, thermal conductivity and required electrochemical characteristics is one of the most demanded materials for medical electrodes. Being radiopaque material the utilization of Pt-based electrodes [2] facilitated the visualization during diagnostic procedures or operations. The modern trend to complicate the shape and reduce the electrode dimensions includes the challenge to develop highly precise methods to obtain of functional coatings with high surface area and advanced electrochemical characteristics.

The MOCVD seems to be an appropriate method to obtain mono or bimetallic coatings with given component content at low temperature (200–350°C). Taking into account the sensitive of contact material (stainless steel) to oxidation and high temperature, the various strategies to control a surface morphology of Pt-containing coatings have been proposed.

Hence, the features of formation Pt and Pt<sub>x</sub>Ir<sub>(1-x)</sub> coatings on the contacts of EPI electrodes using MOCVD have firstly studied. The Pt-based coatings have been deposited either direct on to the contacts in the hydrogen atmosphere or on to Pd(Ir) interface layers in the oxygen atmosphere. The Pt(acac)<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>Pt(hfac)Py, Ir(cod)(acac), Ir(CO)<sub>2</sub>(hfac) and Pd(hfac)<sub>2</sub> have been used as precursors. The effect of type of precursor and their combination, deposition parameters, gas reagent concentration on composition on the structure and morphology of Pt and Pt<sub>x</sub>Ir<sub>(1-x)</sub> coatings have been studied. The Pt coatings with columnar structure and high ESA have been obtained from Pt(acac)<sub>2</sub> in the oxygen atmosphere in the range of 280–310°C,

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while the using of  $(\text{CH}_3)_3\text{Pt}(\text{hfac})\text{Py}$  leads to formation fractal-like Pt coatings in the hydrogen atmosphere in the range of 200-250°C (Fig.1).

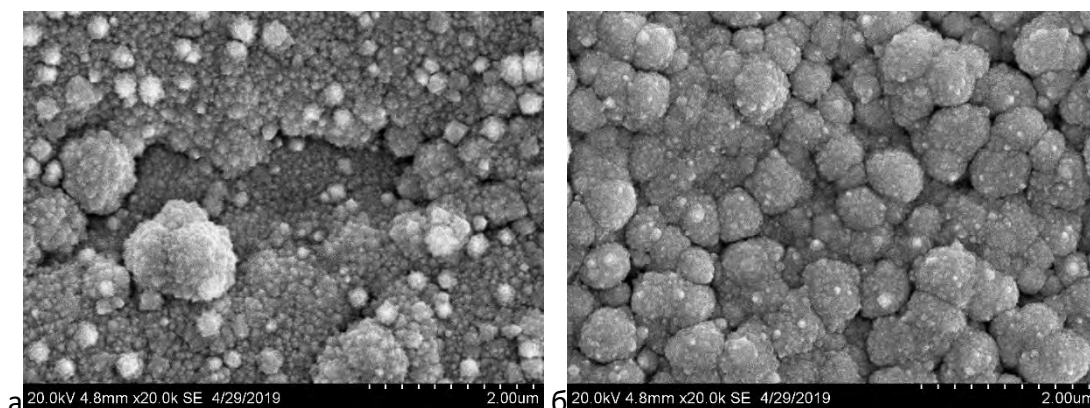


Figure.1. SEM images of Pt coatings with high surface area from a)  $\text{Pt}(\text{acac})_2$  and b)  $(\text{CH}_3)_3\text{Pt}(\text{hfac})\text{Py}$

The novel combinations of Pt and Ir  $\beta$ -diketonate derivatives have been firstly used as precursors to obtain  $\text{Pt}_x\text{Ir}_{(1-x)}$  coatings with  $x > 0.5$ . The effect of deposition parameters and electrochemical activation on the composition and morphology of bimetallic layers has been studied. The charge storage capacity (CSC) values of Pt and  $\text{Pt}_x\text{Ir}_{(1-x)}$  samples evaluated from cyclic voltammetry were in the ranges of 50-400  $\text{mC}\cdot\text{cm}^{-2}$  (PBS solution, 100  $\text{mV/s}$ ).

**Acknowledgements:** The work was supported by the Russian Science Foundation project №. 18-73-00052 "MOCVD of formation of platinum-containing coatings on elements of medical devices"

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## Nanobioarchitectonics: Directed Design of Hybrid Materials

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The production of new scleroprotein based hybrid materials is very promising, since these objects are natural efficient and functional models of durable and lightweight systems that can work in virtually any environment [1]. Spider silk surpasses all the synthetic polymers in mechanical properties, due to its specific hierarchical structure. Nevertheless, there is no complete understanding of the structural organization of spider thread. When introducing metal oxides, nanoparticles (NPs) into the silk structure, conformational rearrangements take place dramatically changing properties of the material. Due to their biocompatibility, these nanocomposites are promising in the field of tissue regeneration, targeted drug delivery, biosensors and bio-imaging [2]. Such innovative composite materials provide analogies to more conventional synthetic polymers, but with enhanced utility due to superior mechanical properties, biodegradability and functionalization.

Spider silk was supplied through an insectarium, in which more than 50 individuals of the funnel-web tarantulas and curtain-web spiders are represented. For instance, silk modified with TiO<sub>2</sub> NPs showing enhanced antibacterial properties was performed for biomedical applications. Then, silk modification with optically active HfO<sub>2</sub> and ZrO<sub>2</sub> NPs was carried out for bio-visualization. The obtained materials were characterized using the complex of physical-chemical methods. The morphology and optical activity of composite materials were analysed (Fig. 1). The development of highly efficient biocompatible agents for complex diagnostics and therapy of diseases is the main scientific challenge the project.

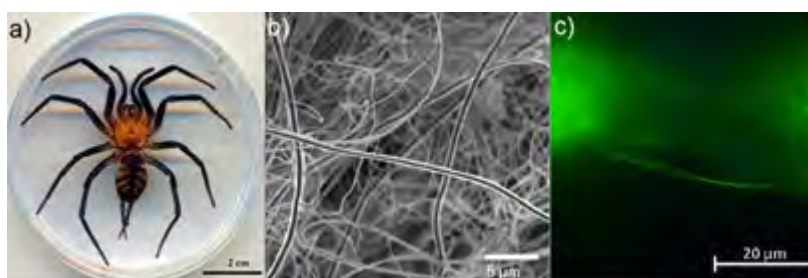


Fig. 1. a) *Linothele Fallax* image; b) SEM image of hybrid material; c) Photoluminescence image of hybrid material

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 18-79-00269.

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## Electrolytes for Lithium Redox Flow Batteries for High Power and High Energy Density Energy Storage

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Instability of oil prices and shortage of natural resources pushes the development of alternative energy sources as well as electric vehicles (EV). To allow this, we need new battery materials which will provide fast and effective energy conversion. According to [1], batteries for EV should have an energy density of 700 Wh/kg by 2030. Metal lithium as anode coupled with organic catholyte has the potential to meet modern requirements. Yet stable towards Li and highly conductive solid electrolyte is needed. On the one hand, Li-based ceramics (such as LATP, LLZO) characterizes by appropriate conductivity ( $\sim 10^{-4}$  S/cm) but degrades in contact with metallic lithium. On the other hand, solid polymer electrolytes (SPE) have the flexibility and good stability to Li but lack conductivity [2]. Our approach combines the advantages of both ceramics and SPE by the fabrication of composite polymeric electrolyte. We have studied separately formation of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  (LATP) ceramics, the polymeric film, and composite Li-conductive membrane. LATP and composite stability and electrochemical performance will be discussed during the talk.

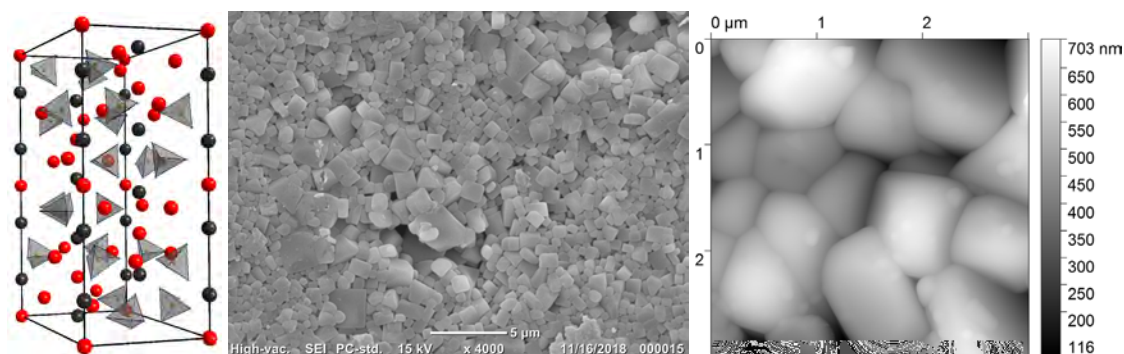


Figure 1. *from left to right* - LATP material crystal structure; SEM and AFM images

**Acknowledgement.** This work was supported by the Skoltech-MIT Next Generation Project “Lithium Redox Flow Batteries for High Power and High Energy Density Energy Storage”.

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## Sol-Gel Synthesis of Tantalum Oxide Nanoparticles for Cancer Theranostics

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An effective approach to cancer treatment is highly significant not only from a scientific but also from a social point of view. According to recent estimates from the World Health Organization, 24.6 million people are living with cancer, and by 2020 it is projected that there will be 16 million new cases of the disease.

In modern clinical practice surgery, chemotherapy and radiotherapy are the most common methods of cancer treatment. Unfortunately, for the most part during the therapy patients face the problem of adverse and toxic side effects in relation to unavailability of an individualized approach to every case of illness. Therefore, the challenge of developing efficiently targeted cancer therapies to encompass personalized medicine is relevance. Theranostics implies simultaneously diagnostic imaging and targeted therapy. Because of the high selectivity of treatment mechanisms, theranostics suggest individualized treatment.

Theranostic nanotechnologies can offer unique characteristics and novel strategies to guide, evaluate, and treat oncological diseases in real time [1]. Nanotechnologies play a vital role in the creation of therapeutic agents formulations, includes the fabrication and utilization of materials at the level of atoms and molecules structures. Unique size-dependent electronic, optical, thermal and mechanical properties of nanomaterials are being exploited today in diverse areas ranging from computer chips to biology and medicine. Also, theranostics is curious about nanoscience in multidisciplinary links chemistry, biology, and physics. Researches on cancer theranostics have been attracting great interest in recent years [2].

Due to physical-chemical properties, high-Z elements are applied in a variety of areas, especially in the theranostics. Tantalum oxide ( $Z_{Ta} = 73$ ) is a strong candidate for this approach, which possesses characteristics of both contrast agent for computed tomography (CT) for bioimaging of tumors and radiosensitizing agent for therapy. The ability of CT to distinguish tissues is based on the fact that different tissues provide distinct degrees of X-ray attenuation, where the attenuation coefficient depends on the atomic number and electron density of the tissues. Recently, tantalum oxide ( $Ta_2O_5$ ) nanoparticles (NPs) have been demonstrated to serve as a CT contrast agent due to its high X-ray attenuation coefficient ( $4.3 \text{ cm}^2/\text{kg}$  at 100 eV) and excellent biocompatibility [3]. Closely monitored doses of ionizing radiation cause damaged to the DNA in cancer cells. Even so, these doses must be accurately delivered to the lump because of its effects both malignant tumor and normal tissues. Radiosensitizers, which increase the sensitivity of unhealthy cells to irradiation, are promising agents that damage tumor tissue by production free radicals (this process is known as radiolysis) [4]. Formation of free radicals is a



result of the emission of secondary radiation by NPs during radio therapy (RT). The interaction of free radicals with DNA and cellular structures induces radical destruction of malignant cells, further apoptosis [5]. During the recent years, tumor-selective radiosensitizers based on noble metal NPs have attracted increasing attention due to their unique physical and chemical properties for usage in RT [6]. Corrosion resistance, low toxicity, and high biocompatibility with body tissues provide nanoparticles of tantalum oxide ( $Ta_2O_5$ ) with a wide range of applications from thin films for a capacitor insulator in random access memory devices to biomedical and clinical applications (implants in orthopedics and dentistry, biosensors, radiographic markers, vascular clips). An additional advantage is a possibility of combining various rare-earth elements in the oxide matrix, that leads to the formation of nanoparticles with adjustable luminescent properties, including up-conversion ones. Upconverting luminescent NPs have a huge potential for biovisualization, because of their high photostability and narrow radiation bands. Moreover, infrared radiation, that is used for the excitation of luminescence, penetrates deeply into the tissue while inducing their minimal autoluminescence.

Recently, tantalum oxide nanoparticles have been manufactured, but the goal is to create the technology of synthesis as efficient as possible. It is known that disperse systems developed for biomedical purposes should have low cytotoxicity, a narrow particle size distribution, and stability both in an aqueous medium and under physiological conditions.

The aim of the present work is to obtain and characterize  $Ta_2O_5$  NPs, to study their properties and cytotoxicity. In this regard, the following objects are the development of a technique of sol-gel synthesis of tantalum oxide NPs; investigation of the physical-chemical characteristics of the produced systems. The production was performed by the sol-gel method. The impact of different process parameters (precursor, a constituent of the dispersion medium, drying process) on the preparation of nanoparticles was investigated in order to reach the optimal conditions of synthesis. The fabricated  $Ta_2O_5$  NPs were characterized by several methods. Particle sizes were measured by the dynamic light scattering (DLS). Surface area, total pore volume, and pore size distribution of the obtained materials were determined by Brunauer-Emmett-Teller (BET) method. X-ray powder diffraction method (XRD) was used to investigate the phase composition of samples. Shape and morphology were investigated by scanning electron microscopy (SEM) and high-resolution transmission microscopy (HR-TEM). Luminescent properties of  $Ta_2O_5$  nanoparticles doped by Eu, Er, Yb under ultraviolet and near-infrared excitation were examined. Cytotoxicity was studied by MTT assay.

**Acknowledgement.** This work was supported by the Grant of Russian Foundation for Basic Research, N 18-29-11078.

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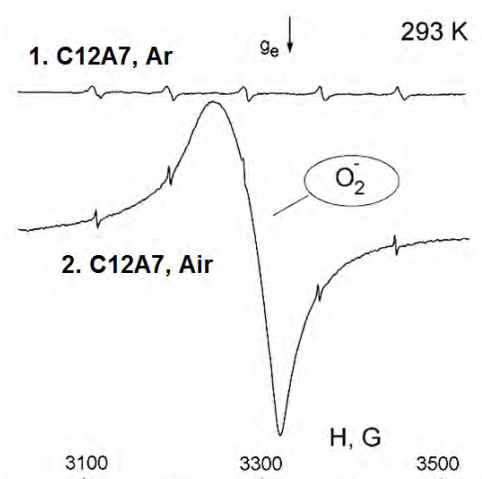
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## Synthesis of Calcium and Strontium Mayenite-Type Aluminates as a Precursor of Oxygen Conductive Ceramics

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Alkaline-earth (AE) aluminate oxide systems with various stoichiometry have a long history of research, due to wide use in various concretes and ceramics. Discovery of the unique chemical and electrophysical  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  (C12A7) properties renewed interest to this materials [1]. These compounds contain a stable cationic framework  $[\text{AE}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}$  (1 unit cell) and sufficiently mobile anion sublattice  $4\text{X}^-$  (AE = Ca, Sr;  $\text{X}^- = \text{H}^-, \text{O}^-, \text{O}_2^-, \text{O}^{2-}, \text{OH}^-, \text{Cl}^-, \text{F}^-, \text{e}^-$ ). The properties of these materials modify in the wide range by simply replacing the  $\text{X}^-$  anions. Materials with  $\text{X}^- = \text{e}^-$  (“electrides”) [2-3] and  $\text{O}_2^-$  are particular interest since they represent as precursors of ceramics with high electron or oxygen-ion conductivity [4].

During this study, various binary hydroxides synthesis were tested (co-precipitation, wet impregnation, Pecchini method etc). It was shown that binary aluminum-AE hydroxide ( $\text{AE}_3\text{Al}_2(\text{OH})_{12}$ ; XRD) can be successfully synthesized using by developed method based on the interaction between thermally activated solid  $\text{Ca}^{2+}$  ( $\text{Sr}^{2+}$ ) and  $\text{Al}^{3+}$  oxides/hydroxides in aqueous solution under mild conditions ( $T < 40^\circ\text{C}$ , ultrasonication treatment). The use of these compounds as precursors allowed us to synthesize dispersed single-phase aluminates AE12A7 at temperatures above  $550^\circ\text{C}$ . Heating of the AE12A7 samples in an oxygen-containing atmosphere ( $>700$ - $1450^\circ\text{C}$ ) resulted in the formation of  $\text{AE}_{12}\text{A}_7:\text{O}_2^-$  material. The presence of  $\text{O}_2^-$  anion radicals was detected by the EPR method (e.g. C12A7; Fig.1 (2)).



**Fig.1.** The EPR spectra of  $\text{C12A7}:\text{O}_2^-$  samples calcined at  $1250^\circ\text{C}$  in Ar (1) or in air flow (2)

## OP-21

In conclusion, simple and efficient method for the synthesis of  $AE_{12}A_7O_{27}$  ( $AE = Ca, Sr$ ) single-phase materials from binary hydroxides was developed. Synthesized materials are considered as precursors of oxygen conductive ceramic due to the high thermal stability.

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research (Project No. 19-03-00834\_A).

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## Nanotechnological Aspects in Design of Oxygen Storage Components

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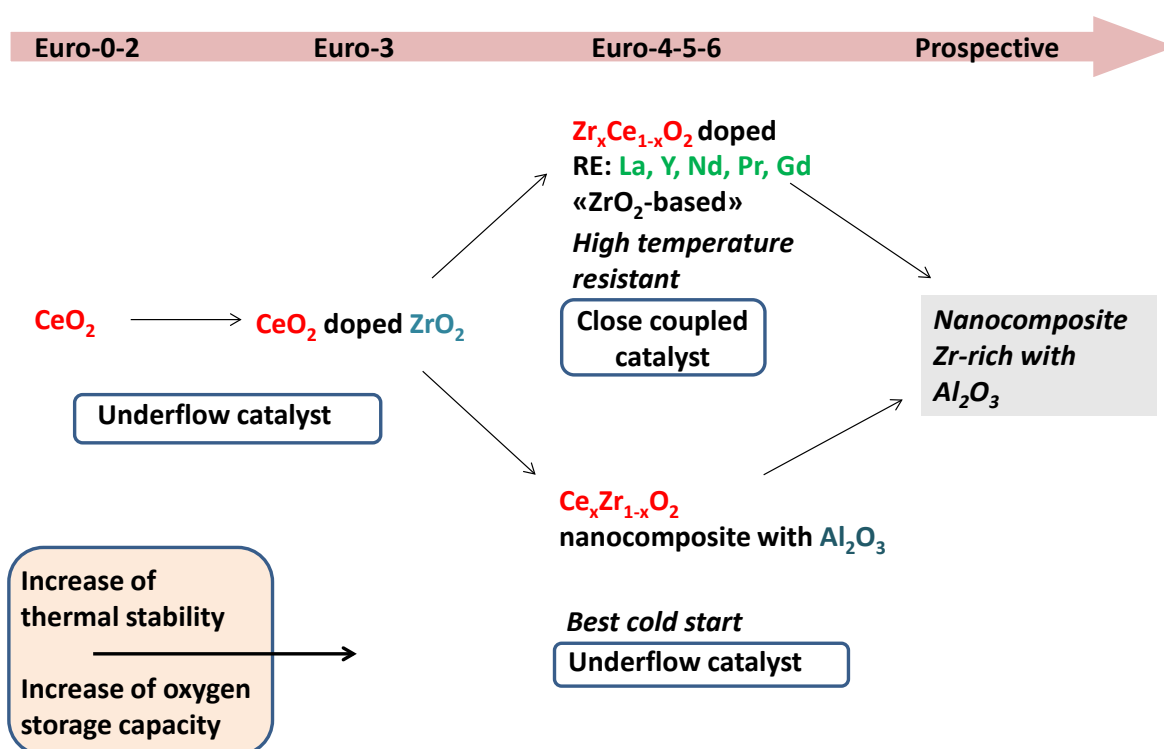
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Widespread application of gasoline vehicles is connected with a global ecological problem due to formation of harmful emissions. Traditionally, this problem is solved by using so-called three-way catalysts (TWC). The main responsibility of TWC is a simultaneous neutralization of CO, unburnt hydrocarbons and nitrogen oxides.



**Figure 1.** Development strategy of CeO<sub>2</sub>-based oxygen storage materials.

On practice, the composition of the reaction gas mixture is being oscillated near the stoichiometric air-to-fuel ratio, thus providing rich or lean reaction conditions. When amount of oxygen in the reaction gas phase is not enough to oxidize all CO and hydrocarbons, participation of lattice oxygen in the oxidation processes is of great importance. The mentioned function can be realized using oxygen storage materials, i.e. materials with enhanced oxygen storage capacity. Among such materials, ceria-based systems are the most commonly used. Additionally, their efficiency can be significantly improved by modification with various promoters. For instance, an introduction of Zr, Y, La, Tb, Gd, Pb and Pr into the ceria lattice results in an appearance of the higher concentration of the defects capable of stabilizing CeO<sub>2</sub> by preventing its sintering. It also increases the thermal stability and efficiency

## OP-22

of the catalyst operation [1]. Therefore, application of the mixed ceria-containing oxides, e.g. CeO<sub>2</sub>-ZrO<sub>2</sub> [2], is promising due to the ability of this system to accumulate oxygen and decrease the deviation of the air-to-fuel ratio from the stoichiometric value, thus significantly increasing the TWC catalytic activity. Schematically, the strategy of ceria-based oxygen storage materials development is shown in Fig. 1.

On the other hand, an interaction of Rh, which is usually added as an active component of TWC, with ceria-based support is known to affect noticeably the efficiency of the oxygen storage function [3, 4], especially after the thermal aging treatment at high temperatures [5]. The present report is aimed to elucidate the possible effects of rhodium and palladium addition into the composition of the oxygen storage materials. Additionally, some results on ceria modification with other additives (e.g., BaO) will be presented. The features of nanocomposite Zr-rich with alumina system will be discussed as well.

**Acknowledgement.** The study was financially supported by the Ministry of Education and Science of the Russian Federation within the framework of subsidizing agreement of October 23, 2017 (No. 14.581.21.0028, unique agreement identifier RFMEFI58117X0028) of the Federal Target Program “Research and development in priority directions of the progress of the scientific and technological complex of Russia for the years 2014–2020.”

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## Nanostructured Metal Oxide Systems Based on MgO for Oxidation and Reduction Processes

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Nanostructured metal oxide materials attract increasing attention due to its various unique properties. Being constituted by nanoparticles, these materials are generally characterized by large values of specific surface area and pore volume. They can be used as effective catalysts, sorbents and antibacterial agents [1].

Sol-gel technology is considered as one of the most attractive ways to synthesize nanostructured metal oxide materials with desired properties and satisfying the requirements of various industrial processes. Sol-gel technique is versatile and convenient route to nanostructured materials due to its fine controllability and inherent simplify.

MgO being prepared by means of sol-gel method is characterized by high textural and structural values. Moreover, it is relatively resistant to sintering at elevated temperatures up to 900 °C. Both these features make the sol-gel prepared magnesium oxide an appropriate support that provides high dispersity and stability of the active component [2].

In the present study, nanostructured  $M_xO_y$ -MgO samples (M = Co, Cu, Fe, Mo, Ni or W) were synthesized by means of a sol-gel approach. Distilled water was replaced by an aqueous solution of inorganic salt precursor at the hydrolysis step. Prepared xerogel and final oxide samples were carefully investigated with a set of physicochemical methods such as low-temperature nitrogen adsorption, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), and diffuse reflectance UV-vis spectroscopy. Differential thermal analysis (DTA) gave some insights into decomposition behaviour of the xerogel systems. XRD analysis has revealed that all the xerogel samples exhibit a turbostratic layered structure due to MgO disordered phase. However, Mg(OH)<sub>2</sub> interlayer distance was found to be significantly increased due to incorporation of the precursor salt anions into the latter. It facilitates the decomposition of Mg(OH)<sub>2</sub> and shifts the corresponding DTA peak towards lower temperature region. Textural and structural properties of the MgO-based oxide systems were found to be strongly dependent on the concentration of transition metal oxide additive. Formation of a joint phase was observed in the case of cobalt oxide only. Additives are believed to be distributed uniformly within the MgO bulk in most the cases. The only exception was WO<sub>3</sub>, which has formed large agglomerates due to low solubility of its precursor [3].

Reductive and oxidative behaviour of the samples was studied by means of temperature-programmed reduction (TPR) and *in situ* XRD methods. The results have revealed that the reducibility of  $M_xO_y$  is affected noticeably by its interactions with MgO matrix. Generally, there

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are two species of transition metal oxide: weakly bonded nanoparticles uniformly distributed within the MgO matrix and strongly bonded  $M_xO_y$  species. The content of each phase determines the redox properties of the  $M_xO_y$ -MgO system. It is important to note that the reduction behaviour of  $M_xO_y$ -MgO during the first and subsequent cycles is different. It can be assigned to the phase transformations taking place at the first cycle. However, starting from the second redox cycle, each system has behaved reproducibly showing the same TPR profile. This feature can be used in a number of applications such as chemical looping processes, dehydrogenation of light hydrocarbons and so on.

**Acknowledgement.** This study was supported by the Ministry of Science and High Education of Russian Federation (project AAAA-A17-117041710086-6).

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## Nanostructured Samples and Nanocomposites Obtained in a Plasma of a Pulse High-Voltage Discharge

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In a plasma of a high-voltage pulsed discharge initiated between electrodes of different composition, samples were obtained containing various nanoscale components. The chemical structure and morphology of the samples was varied by annealing at different temperatures. The composition and structure of the samples were studied by means of XPA, SEM, TEM, IR, Raman, XPS, SQUID.

In the case of copper electrodes, granular samples were obtained. After grinding, the resulting powder contains mainly  $\text{Cu}_2\text{O}$  and up to 6%  $\text{CuO}$  (sample 1). After annealing in air at  $400^\circ\text{C}$ , the composition of the sample changes to  $\text{Cu}_2\text{O}$  (47%) +  $\text{CuO}$  (53%) (sample 2), after annealing at  $900^\circ\text{C}$ , the composition changes to  $\text{CuO}$  (100%) (3). All samples have a nanoscale layered structure. From the analysis of the X-ray line widths of the spectra, it was concluded that in samples (1) and (2)  $\text{CuO}$  is in the  $\text{Cu}_2\text{O}$  matrix as separate nanoscale inclusions. For (1), stepwise changes in the field dependences of the magnetic susceptibility  $M(H)$  (Fig. 1a) are recorded, which are not observed in bulk samples of  $\text{CuO}$  or  $\text{Cu}_2\text{O}$ . Probably, these changes are associated with the rearrangement of the ordering of the magnetic moments of the atoms located in the layer of the interfaces of the  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  phases. Estimated as high photocatalytic activity of samples (1), (2) and (3). Most activity detected for (2).

In the case of the use of electrodes having the composition  $\text{Cu}$  (59%)  $\text{Ni}$  (40%)  $\text{Mn}$  (1%), a sample was obtained consisting of  $\text{Cu}_2\text{O}$  (32%) +  $\text{NiO}$  (68%) (4). After calcining (4) at  $800^\circ\text{C}$ , a sample of  $\text{Cu}_2\text{O}$  (32%) +  $\text{NiO}$  (68%) (5) was obtained, in which a transition from the ferromagnetic to the superparamagnetic phase was detected (Fig. 1b).

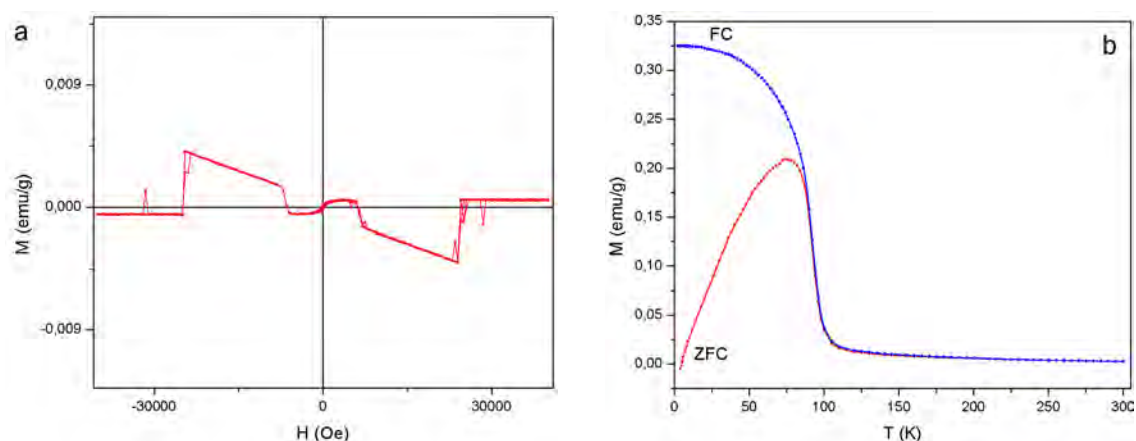


Fig. 1. Dependences  $M(H)$  of sample 1 (a) and  $M(T)$  of sample 5.



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When using W electrodes, a nanocrystalline  $\text{WO}_3$  was obtained; when using Mo electrodes, a powder containing  $\text{MoO}_3$  nano-petals.

In other experiments, polytetrafluoroethylene was additionally placed in the plasma zone. With two different options for the placement of polytetrafluoroethylene in the plasma and using different electrodes, nanocomposites containing the following nano-objects were obtained:

– nanocrystallites with sizes of  $20 \div 200$  nm, composed of  $\text{FeF}_3$ ,  $\text{FeF}_2$  nanocrystals with sizes of  $3 \div 10$  nm and carbon-containing components (Fig.2), after annealing  $\text{FeF}_3$ ,  $\text{FeF}_2$  are transformed into hematite;

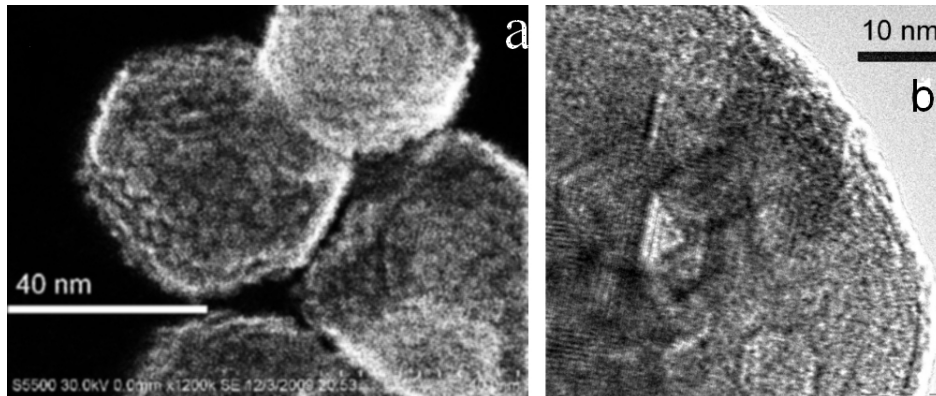


Fig. 2. Nanocrystallites composed of nanocrystals  $\text{FeF}_3$ ,  $\text{FeF}_2$ , recorded at various magnifications, a - ESM, b - TEM data.

– 40–200 nm nanocrystallites composed of  $\text{TiO}_2$  nanocrystals,  $\text{TiOF}_2$  and carbon-containing components, after annealing, the composition of nanocrystallites transformed into anatase;

– Pt nanocrystals, as well as fluorides or metal oxides scattered in a carbon matrix containing a small amount of fluorinated carbon (up to 6%) (Fig. 3). After annealing such samples, powders consisting of platinum nanocrystals, copper oxide nanocrystals, etc., and nano-dispersed PTFE were obtained. After passing an electric current through the samples, carbon nanoforms were obtained in the form of nanoscale ribbons.

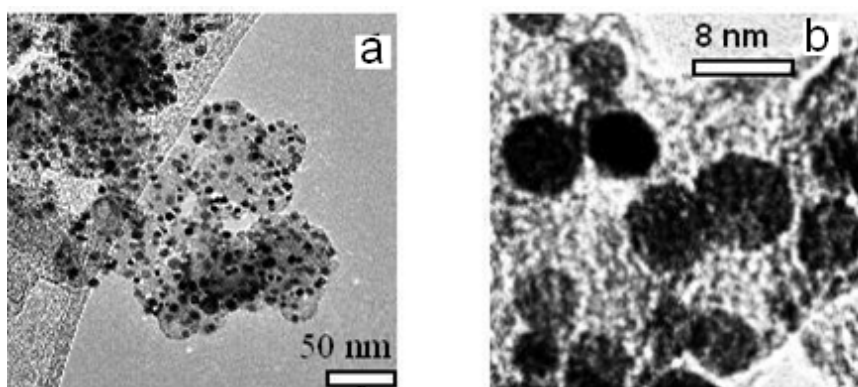


Fig. 3. Platinum nanocrystals in a carbon matrix, TEM data.

Some of the samples are tested for catalytic conversion activity. CO in  $\text{CO}_2$ , as well as tested as anode materials and showed promising results for practical application.

The applied methods for the synthesis of nanomaterials are promising for obtaining a variety of different fluoride, oxide and carbon nanomaterials.

# ANT 2019

## POSTER PRESENTATIONS

PP-1 ÷ PP-18



[Content](#)



## The Enzyme-Like Catalytic Activity of Maltodextrin-Coated Cerium Oxide Nanoparticles

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Cerium oxide (CeO<sub>2</sub>) nanoparticles present a promising object for various applications, including biomedical research [1-3]. The CeO<sub>2</sub> nanoparticles are characterized by a high oxygen nonstoichiometry [2]. The formation of oxygen vacancies leads to the reduction of cerium ions to the Ce<sup>3+</sup> state on the particle surface. Such property correlates with the catalytic activity of cerium oxide nanoparticles and is probably responsible for their biological activity [4].

The efficiency of applying CeO<sub>2</sub> nanoparticles in medicine is directly related to the chemical properties of their surface, which are mostly the result of nanoparticle synthesis techniques. The usage of toxic precursors or stabilizers in the synthesis could significantly limit the scope of biomedical applications of this material. Therefore, the problem of the synthesis of stable and non-toxic CeO<sub>2</sub> nanoparticles is arisen. To date, a large number of methods for the synthesis of CeO<sub>2</sub> nanoparticles have already been proposed [1]. However, the nanoparticles synthesized by the proposed methods do not always satisfy the requirements of biocompatibility. Therefore, in this work we performed the synthesis of non-toxic maltodextrin-coated CeO<sub>2</sub> nanoparticles and the subsequent study of their properties using optical spectroscopy. Synthesis of nanoparticles was performed according to paper [5]. The advantage of this method is the ability to adjust the size of the resulting nanoparticles by varying the concentrations of cerium and maltodextrin compounds, which allows one to change its biological activity.

The optical absorption spectra were recorded with a Helios Alpha spectrophotometer ( $\lambda=190-1000$  nm) equipped with the Vision 32 software. The catalase-like activity of CeO<sub>2</sub> nanoparticles was studied by measuring the optical absorption of the suspensions before and after the addition of hydrogen peroxide. Peroxidase activity of CeO<sub>2</sub> was determined using the TMB reagent (tetramethylbenzidine) by ELISA method.

The cerium oxide was found to demonstrate catalase-mimic activity. This activity appears in the neutral and alkaline media, whereas this behaviour is inhibited in the acidic medium. Maltodextrin-coated CeO<sub>2</sub> nanoparticles also show the peroxidase activity. The activity of cerium oxide increases linearly in the concentration range from 0 to 0.1%.

## PP-1

The research on the possibilities of using this material in biomedical practice requires further studies of its properties, as well as performing an experiment to estimate the cytotoxicity of nanopowder.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 18-79-00188.

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## Catalytic Decomposition of Light Hydrocarbons for Associated Petroleum Gas Utilization

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Associated petroleum gas (APG) is considered a byproduct of oil extraction; in the absence of a possibility of its processing, it is simply flared. In the combustion of APG, tons of pollutants are released into the atmosphere every year to worsen ecological situations in oil-field regions. In this case, significant amounts of valuable chemical raw materials are lost because, unlike natural gas, APG contains ethane, propane, butane, and nonhydrocarbon gases.

In this work, we propose a method for the catalytic decomposition of C<sub>1</sub>–C<sub>4</sub> hydrocarbons with the production of carbon nanomaterials and hydrogen as the main products in order to improve geoecological situations in oil-field regions and to utilize APG. The application of this method makes it possible to obtain a gas mixture with a high hydrogen content and free of carbon oxides; because of this, the separation of hydrogen is facilitated. Previously, we described the use of a Ni–Cu–Fe/Al<sub>2</sub>O<sub>3</sub> catalyst for the decomposition of methane. The study of the properties of this catalyst in the decomposition of other hydrocarbons can extend the range of its application. In this work, we report results of studying the Ni–Cu–Fe/Al<sub>2</sub>O<sub>3</sub> catalyst in the decomposition of a propane–butane mixture over a temperature range of 650–750°C.

The Ni–Cu–Fe/Al<sub>2</sub>O<sub>3</sub> catalyst was obtained by the mechanochemical activation of a mixture of oxides (Fe<sub>2</sub>O<sub>3</sub>, NiO, and CuO) with aluminum hydroxide (hydrargillite) in an AGO-2 centrifugal planetary mill (Novits, Russia; the rotational velocity of drums was 10 s<sup>-1</sup>). Initially, the experiments were performed in a quartz flow reactor with a McBain balance; this made it possible to determine the main rate laws of the formation of carbon deposits on the catalysts. Then, the catalyst was tested in a system with a rotating reactor.

Thus, the above studies demonstrated the effectiveness of the operation of the 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst in the decomposition of a propane–butane mixture in the system with a rotating reactor. At a propane–butane mixture space velocity of 12000 h<sup>-1</sup>, the optimum temperature range was 700–725°C. Under these conditions, the yield of 700–750 L of H<sub>2</sub> per gram of the 70% Ni–10% Cu–10% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst was obtained. The concentration of hydrogen at the reactor outlet was 70–75 mol %. This method of the catalytic decomposition of light hydrocarbons can be used in prospect as a stage in the development of an associated petroleum gas utilization technology in small and distant oil fields.

## Controlled Hydrogenation of Monoterpenoids Oximes and Nitro-Derivatives over Au and Pt Catalysts

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Widespread terpenoids represent the largest group of natural compounds and extensively applied in the food, pharmaceutical and perfumery industry. Terpenoids typically have a complicated structure and often contain several functional groups, which can be hydrogenated. Stereo-, regio- and chemoselective hydrogenation of compounds with multiple unsaturations is commonly considered to be of interest for synthesis of the desired products with a high efficiency. The main goal of this work was to explore competitive hydrogenation of different functional groups aiming at the development of approaches for stereo- and chemoselective hydrogenation of monoterpenoids oximes and nitro-derivatives to valuable compounds.

Liquid-phase hydrogenation of the oximes of monoterpenoids and their nitro-derivatives was carried out in a batch reactor at 373 K under H<sub>2</sub> atmosphere. The reaction mixture was analyzed by GC, GC-MS and NMR. Gold and platinum catalysts comprising Au and Pt on metal oxides, such as TiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, SiO<sub>2</sub>, were prepared by the deposition-precipitation and impregnation methods. The catalysts were characterized by a set of physicochemical methods, including TEM, XPS, XRF, to determine the parameters influencing the catalytic activity.

First, the regularities of carvone hydrogenation were studied in detail. Carvone is one of the most widespread natural monoterpenoids, which is widely used in food and perfumery industry as well as in the synthesis of fine chemicals. Carvone hydrogenation is of great practical interest to obtain a range of valuable products, including dihydrocarvone, which is formed as a mixture of two stereoisomers, has a spearmint-like odor and is used as a flavoring additive in various foods. At the same time carvone is an interesting substrate to explore catalyst activity in stereo- and chemoselective hydrogenation, because it contains an asymmetric center with a specific configuration as well as three types of functional groups, which can be hydrogenated: C=O, conjugated C=C and isolated C=C groups. It was demonstrated for the first time that Au/TiO<sub>2</sub> catalyst promoted stereo- and chemoselective carvone hydrogenation to dihydrocarvone with predominant formation of the *trans*-isomer [1]. This novel approach is of great interest giving a possibility to obtain industrially valuable dihydrocarvone via direct carvone hydrogenation. The highest total selectivity to

### PP-3

dihydrocarvone (62%) was achieved at a nearly complete carvone conversion (90%) after 13 h, with the *trans*-to-*cis*-dihydrocarvone ratio being *ca.* 1.8. As a subsequent step, a one-pot process consisting of sequential transformations of carvone oxime, a key intermediate in carvone synthesis from limonene to dihydrocarvone, was studied. Dihydrocarvone synthesis was shown to occur via carvone formation with subsequent hydrogenation of its conjugated C=C double bond (Fig. 1) [2].

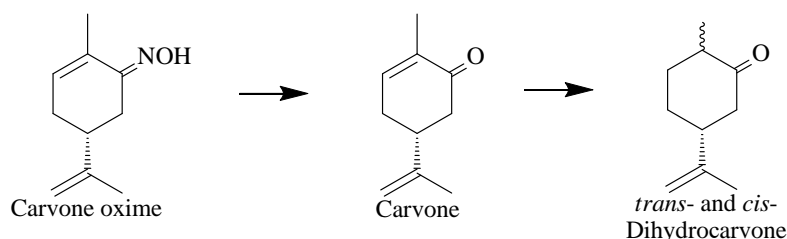


Fig.1. Carvone oxime transformation to *trans*-/*cis*-dihydrocarvone over gold catalysts.

Application of Au/TiO<sub>2</sub> catalyst for both deoxygenation and selective hydrogenation of olefinic C=C functional group is reported for the first time. A combination of these steps provides a possibility to optimize synthesis of dihydrocarvone from carvone oxime. Despite a carvone oxime reaction rate lower than that of carvone, a significant increase in the stereoselectivity towards *trans*-dihydrocarvone was observed when carvone oxime was hydrogenated. The ratio between *trans*- and *cis*- dihydrocarvone was close to 4.0 compared to 1.8 achieved for carvone hydrogenation. Application of the gold catalysts to control selectivity seems to be promising in the particular case of dihydrocarvone synthesis from carvone oxime as well as more general in consecutive chemoselective hydrogenation of different functional groups.

Gold and platinum-containing catalysts were then used for hydrogenation of oxime and nitro-derivatives of menthone, fenchone, camphor. The effect of the catalyst support, active metal and the reaction conditions was studied. Utilization of gold catalyst mainly resulted in deoxygenation of monoterpenoids oximes, while bimetallic AuPt catalyst catalyzed hydrogenation to amines. Higher activity was achieved using titania and alumina supported catalysts. Approaches for direct synthesis of carbonyl compounds and amines with different structures were developed.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 18-33-20175.

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## Nanostructures Formed by Guest Molecules in Disordered Media by Pulsed EPR of Spin Probes

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It is known that some molecules embedded in a biological membrane form nanostructures, such as clusters or aggregates. These structures (protein nanoclusters, lipid rafts, etc.) can participate in different cell processes, for example, in cell recognition and adhesion, signaling, and so on. Despite active research in this field, many features of such structures (mechanism of formation and stability, composition and some functions) remain unclear.

In order to investigate the formation mechanism of such structures in this study, a model nonpolar disordered medium was used to simulate the hydrophobic interior of lipid bilayers. Glassy *ortho*-terphenyl was chosen as such a medium. Two types of stable nitroxide free radicals (spin probes) were used as guest molecules (Fig. 1). The probe concentration was in the range between 0.25 mM and 6 mM. The spatial distribution of guest molecules in a molecular glass was investigated using pulsed EPR. The method applied is based on determining the contribution of electron spin dipolar interaction to the electron spin echo (ESE) decay and allows studying paramagnetic centers with distances between them of the order of several nm.

Two types of spatial distribution were found in these studies. In the case of 1R, the excluded volume around the probe was detected at low radical concentrations (< 2 mM) which is replaced by clustering at larger concentrations. In the case of 2R, the clustering of probes was found for their all concentrations.

It was proposed that these two types of spatial distribution are determined by a relative value of energy of the interaction between host molecules and between the host and guest molecules. To support this suggestion, study of 1R in polar water-glycerol glass was performed, in which host-host interaction is expected to prevail. The obtained results have shown that the probe spatial distribution is indeed random in this case. The proposed two qualitative models are depicted in Figs. 2 and 3.

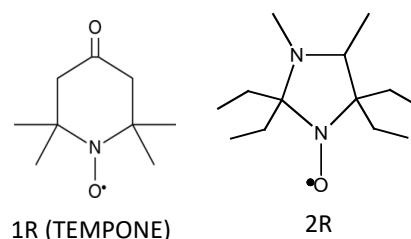


Fig. 1. Chemical structures of nitroxide radicals used as spin probes

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The contribution of the spin dipole interaction to the ESE decay was simulated to obtain the parameters of the radical spatial distribution in *ortho*-terphenyl.

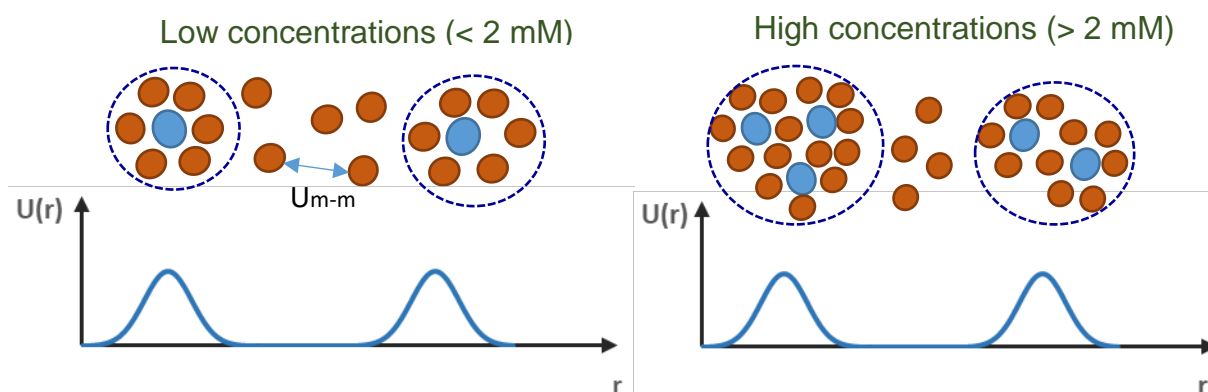


Fig. 2. The model of distribution of 1R in *ortho*-terphenyl

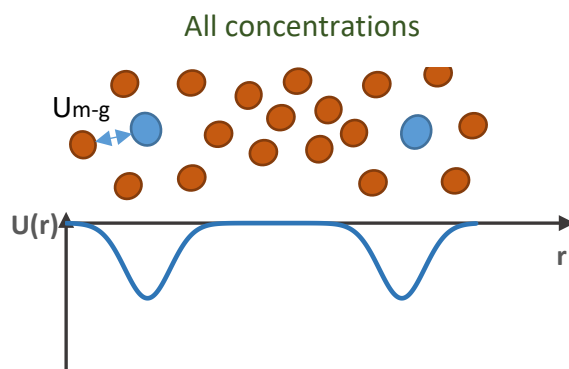


Fig. 3. The model of distribution of 2R in *ortho*-terphenyl

## Synthesis and Properties of Nanocrystalline Calcium Aluminates

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Unique properties of calcium aluminate with  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  stoichiometry (usually labeled as C12A7) were discovered and investigated by H. Hosono et al. [1-3]. These materials possess a stable cation framework  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}$  and changeable anion sublattice  $4\text{X}^-$ . Chemical and electrophysical properties of these materials can be easily varied in a wide range by substitution of  $\text{X}^-$  anions. Particularly interesting are materials with  $\text{X}^- = \text{O}^-$  that supply reactive radical anions in chemical and catalytic oxidation reactions [2] and electriles ( $\text{X}^- = \text{e}^-$ ) that can behave as electron donors in organic reactions or as superbasic supports for heterogeneous catalysts [3].

Ceramic method was usually used for synthesis of C12A7 materials leading to materials with low surface area that are not well suited for catalytic applications. In the current presentation we shall explore the methods of synthesis and properties of nanocrystalline C12A7 materials.

For synthesis of nanocrystalline C12A7 materials in aqueous solution, a mixture of aluminum and calcium hydroxides with required stoichiometry was used as the precursor. The mixture was thoroughly stirred in distilled water for 10 h, filtered and dried at  $110\text{ }^\circ\text{C}$ . Then it was calcined in air at  $600\text{ }^\circ\text{C}$  for 6 h. The obtained sample with mayenite (C12A7) crystallite structure, crystallite size about 15 nm and the surface area about  $80\text{ m}^2/\text{g}$ . In addition calcium aluminates with  $\text{CaO}/\text{Al}_2\text{O}_3$  stoichiometry 1:1 and 3:1 (CA and C3A, respectively) were also synthesized by this method.

Nanocrystalline oxide aerogels are materials with very small particle sizes, high surface areas and pore volumes prepared by sol-gel method usually in an alcohol solution followed by drying in an autoclave under supercritical conditions avoiding collapse of the pore structure. In this study C12A7 aerogels were prepared for the first time starting from a mixture of calcium methoxide prepared by dissolving calcium metal in methanol and aluminum isopropoxide in isopropanol taken in the appropriate ratio.

The surface area of amorphous C12A7 hydroxide obtained after hydrolysis with stoichiometric amount of water, gelation overnight and drying under supercritical conditions was about  $450\text{ m}^2/\text{g}$ . After calcination at  $500\text{ }^\circ\text{C}$  the surface area of C12A7 aerogel was close to  $250\text{ m}^2/\text{g}$  and exceeded that of nanocrystalline C12A7 prepared in aqueous solution by a factor of 3. The surface areas of amorphous CA and C3A aerogels after calcination at  $500\text{ }^\circ\text{C}$  were 330 and  $170\text{ m}^2/\text{g}$ , correspondingly.

One of possible application areas of finely dispersed C12A7 materials is their use in catalytic technologies. Therefore, it was important to study various active sites on their

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surface. After treatment at elevated temperatures in the oxygen-containing atmosphere mayenite samples are known to undergo partial substitution of dielectric oxide or hydroxide anions for  $O^-$  and/or  $O_2^-$  radical anions.

Electron-acceptor and electron-donor sites are very active surface species observed by EPR using the formation of radical cations and radical anions after adsorption of appropriate probe molecules [4]. We observed that sites of both types were present on the surface of C12A7-600 sample. In particular, the concentration of electron-acceptor sites tested using phenothiazine as the probe proved to be as high as on the surface of  $Al_2O_3$  sample with 2.5 times higher surface area.

Remarkable results were obtained after diphenylamine adsorption on C12A7-600. The observed EPR spectrum can be attributed to adsorbed diphenyloxyl nitroxyl radicals. These radicals are formed from diphenylamine in solution in the presence of peroxides due to reaction with hydroxyl radicals. Apparently, the surface of nanocrystalline C12A7 activated in air has a significant concentration of active OH or  $O^-$  radicals. It seems to be a specific feature of this material related to its unique structure that merits further investigation as we did not observe similar signals on any other oxide material. So, C12A7 is likely to have unusual properties in various oxidation catalytic reactions related to the presence of active radicals on its surface.

**Acknowledgement.** This study was supported by the Russian Foundation for Basic Research, grant 19-03-00834.

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## The Correction of *In Vitro* Toxicity of a Silver Nanoparticle Stabilizer in Studies on Endothelial Cells

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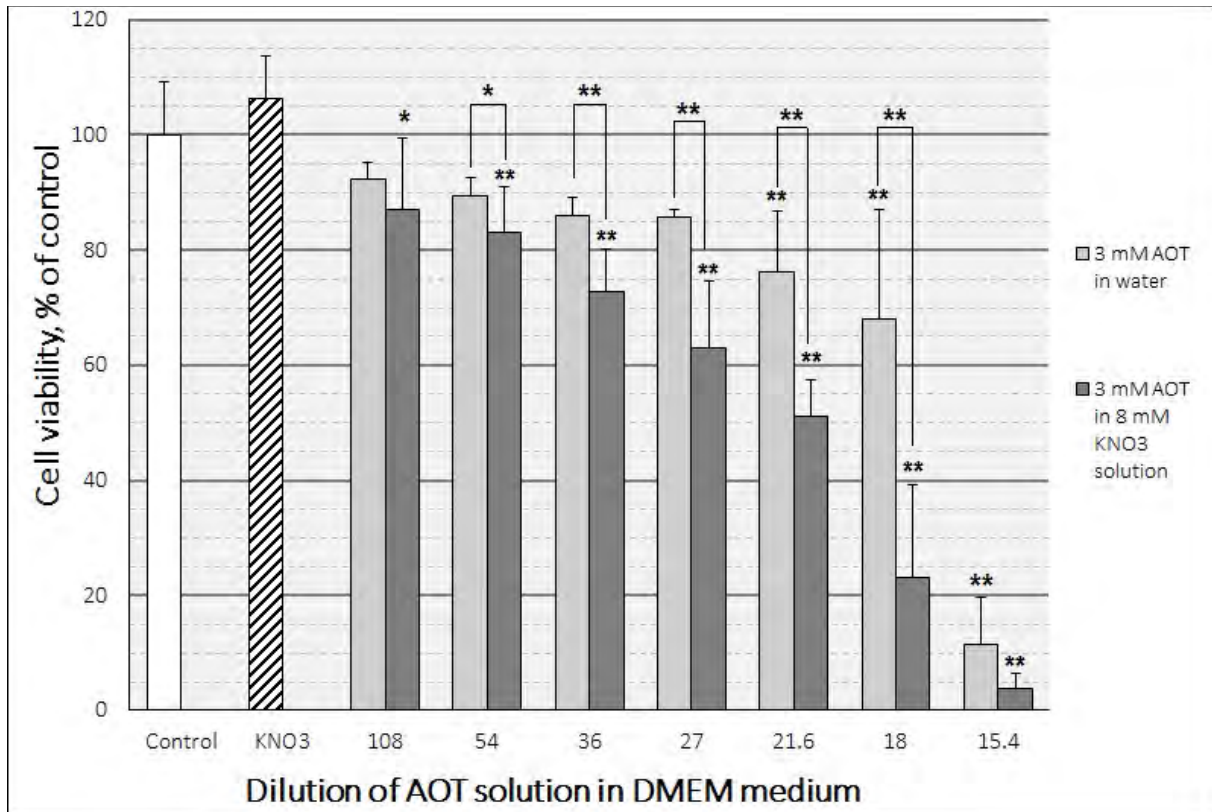
**Background.** Studies on the biological activity of surfactant-stabilized nanoparticles demonstrate an increase in the recent years, the fact which emphasizes the problem of toxicity of such preparations. The presence of surfactant can noticeably increase *in vitro* toxicity of a nanoparticle solution due to the surfactant's effect on a cell culture [1, 2]. To clarify the mechanism of action of anionic surfactant (aerosol-OT, AOT) used as a stabilizer of silver nanoparticles (AgNPs) and to test its toxicity correctly, we used the literary data testifying to the connection between a surfactant toxicity and its critical micelle concentration (CMC) [3]. Also, we took into account that CMC of an ionic surfactant depends on the ionic strength of nanoparticle solution [4]. The increase of AOT toxicity at the ionic strength equal to that in AgNPs solution was previously shown on the Jurkat (human T-lymphoblastic leukemia) cell line [5]. There are reasons to assume that this effect resulted from the decrease of the CMC and the corresponding increase of micelle concentration in AOT solution [6].

**The aim** of the present work was to estimate the influence of ionic strength in the control AOT solution on its toxicity towards the other cell line, namely the endothelium EA.hy926 cells.

**Methods.** Two 3 mM AOT solutions were prepared, one in distilled water, the other in 8 mM potassium nitrate (KNO<sub>3</sub>) solution; here KNO<sub>3</sub> solution simulated the conditions met by AOT when used as an AgNPs stabilizer at the concentration of 3 mM. EA.hy926 cells were incubated for 24 hours with both AOT solutions added at the following dilutions in DMEM medium: 108, 54, 36, 27, 21.6, 18, and 15.4. The cytotoxic effects of the AOT solutions were further evaluated by means of MTT assay. Distilled water and 8 mM KNO<sub>3</sub> solution were used, respectively, as a negative control and a KNO<sub>3</sub> toxicity control.

**Results** showed that AOT in the KNO<sub>3</sub> solution was more cytotoxic than the AOT solution in pure water (Fig. 1). The CMC values obtained for AOT were 2.8 mM in water and 1.7 mM in the KNO<sub>3</sub> solution. Respectively, the concentration of micelles in water,  $3 - 2.8 = 0.2$  (mM) was noticeably lower than in the KNO<sub>3</sub> solution,  $3 - 1.7 = 1.3$  (mM). Hence, the reduction of cell viability after treatment with KNO<sub>3</sub>-containing AOT solution may be explained by the increased contribution of micelles to the cytotoxicity of this surfactant.

**Conclusion.** Basing of the conducted research, it is possible to conclude that cytotoxicity of ionic surfactant solutions is markedly influenced by micelle concentration, determined by the CMC value of the surfactant. The principle presented in this work, for the correction of stabilizer toxicity by control measurements in studies of the biological effects of metal nanoparticles, can be used also in applications of surfactants' solutions for medical purposes.



**Fig. 1.** The viability of EA.hy926 cells after 24 h incubation with different dilutions of AOT preparations (MTT assay). Data are represented as mean  $\pm$  standard deviations from 6 independent measurements. The differences between treated samples and controls were analyzed by one-way ANOVA followed by Dunnett's *post-hoc* test. The differences between types of AOT solutions at the same dilution were analyzed using Student's *t*-test. \* -  $p < 0.05$ ; \*\* -  $p < 0.01$ .

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## A Computational Search for the Novel High-Energy Compounds with HNIW-Like Caged Structure

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HNIW is known as one of the most powerful high-energy density compounds. Its molecules have highly strained carbon-nitrogen cages with six attached nitro groups. Several co-crystals based on HNIW mixed with other molecules were successfully synthesized. However, all of them provide limited energy releasing.

An alternative way to increase the performance of HNIW was proposed. Various HNIW substituted derivatives were considered that contained silicon and fluorine atoms [1]. According to these calculations, some derivatives possess improved characteristics in comparison with the pristine HNIW cage. Such derivatives are regarded as promising high-energy density materials.

Here we present a comprehensive theoretical study of new HNIW derivatives. Their structures and properties are studied with density functional theory approach. Mechanisms of their pyrolysis are revealed via *ab initio* molecular dynamics. Reactions of their decays are additionally explored by the following the intrinsic reaction coordinates; corresponding transition states and activation barriers are defined. Thermodynamic and kinetic stabilities are evaluated in terms of binding energies, Gibbs energies, strain energies, and lifetimes extracted from the Arrhenius law. Indices of chemical reactivity were derived from the frontier electronic orbitals in accordance with the Koopmans' theorem.

It was previously predicted that pristine HNIW molecules could form crystalline chains and networks via methylene molecular bridges [2]. However, it is not known whether HNIW derivatives are able to form similar structures. At the first step in order to answer this question, we consider the dimers of HNIW derivatives. Reactions of dimerization were found to be exothermal. We examine the reactivity and characteristics of earlier predicted HNIW derivatives. Fluorine-contained cages possess low stability due to the thermal-induced migration of fluorine atom to silicon.  $\text{CSi}_5\text{H}_6\text{N}_{12}\text{O}_{12}$  cage is found to be the most attractive molecule for the energy applications.

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research (RFBR), project No. 18-32-20139 mol\_a\_ved.

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## Metallicity of Silicon: *Ab Initio* Study of $sp^3$ -Hybridized Silicon Allotropes

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Polyprismanes or [n,m]prismanes are the nanotubes of a special type constructed from the dehydrogenated molecules of cyclosilanes (silicon rings), where m is the number of vertices of the closed atomic ring and n is the number of layers [1]. Thus, polyprismanes are the special type of single-walled nanotubes with an extremely small cross-section in the form of a regular polygon. In this study using density functional theory we have calculated thermodynamic stability, electronic properties, and chemical reactivity of silicon [n,m]prismanes with m = 5, 6, 7, and 8 containing from two to ten layers by means of calculating frontier molecular orbitals, and some reactivity descriptors. Furthermore, we have performed structural optimization of rather long (“infinite”) polyprismanes taking into account periodic boundary conditions and obtained their band structure, density of electronic states, electronic transmission coefficients, and some mechanical properties to predict their behavior as the part of perspective nanotechnology devices and to illustrate the potential of these systems for the future development of next-gen nanotechnologies.

All DFT calculations for the finite [n,m]prismanes were performed using the TeraChem software, and the calculations under periodic boundary conditions were carried out using the Quantum Espresso package. It is found that the considered polyprismanes become more thermodynamically stable as their effective length increases. The character of the energy spectrum of “infinite” systems, as well as the behavior of transmission function near the Fermi level, illustrate that silicon polyprismanes exhibit non-typical for the  $sp^3$ -silicon systems metallic nature. It can be said that silicon polyprismanes turn out to be metals for all considered diameters, i.e., for the Si<sub>5</sub>-, Si<sub>6</sub>-, Si<sub>7</sub>-, and Si<sub>8</sub>-rings. In such a case, it has been found from the partial density of electronic states calculation that the overlapping of bands near the Fermi level is mainly due to the 3p state of silicon atoms. Unexpected properties endowed by the prismane morphology discover new prospects of application of carbon and silicon nanostructures as the basic elements of future electronics.

**Acknowledgement.** The presented study was performed with the financial support of the Russian Science Foundation, grant no. 18-72-00183.

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## Electrochemical One-Pot Synthesis of Nanodispersed SnO<sub>2</sub>-Based Materials for PEM Fuel Cells Applications

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Tin dioxide is known as a perspective material for support of Pt nanoparticles which are used as catalysts for proton exchange membrane fuel cells (PEMFCs). Many researchers reported about improving the durability as well as the ethanol electrochemical oxidation reaction and the carbon monoxide tolerance of the Pt/metal oxide catalysts including Pt/SnO<sub>2</sub> catalysts [1].

In this work for the preparation of SnO<sub>2</sub> powders and Pt/SnO<sub>2</sub>-C catalysts electrochemical dispersion method was used. Two tin electrodes immersed in the aqueous 2M NaCl solution. The electrodes were connected to ac source operating at 50 Hz, current density 1 A cm<sup>-2</sup>. Bulk tin electrodes were dispersed to nanosized particles. The suspension was filtrated; powder was rinsed with distilled H<sub>2</sub>O and dried at 80 °C to constant mass. The diffractogram of freshly prepared metal oxide powder was indexed to the typical tetragonal structure of SnO<sub>2</sub>.

For the Pt/SnO<sub>2</sub>-C catalysts preparation two platinum electrodes immersed in the suspension of as-prepared SnO<sub>2</sub> powders and amorphous carbon Vulcan XC-72 in aqueous 2M NaOH solution. The electrodes were connected to ac source as it was described in [2] and platinum nanoparticles were deposited on SnO<sub>2</sub>-C support.

The proposed method for synthesis of SnO<sub>2</sub> powders and Pt/SnO<sub>2</sub>-C as a result of electrochemical dispersion of metals is technologically simple and environmentally safe because it does not involve the use of organic solvents and capping agents.

The probable mechanisms of the tin and platinum dispersion under ac and electrocatalytic properties of Pt/SnO<sub>2</sub>-C catalysts will be discussed.

**Acknowledgement.** This work was supported by the Grant of the President of the Russian Federation for state support of young Russian scientists - candidates of science (Grant MK-194.2019.3).

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## Features of Electrophoretic Deposition and Physicochemical Properties of Nanostructured Al-CuO<sub>x</sub> Powder Materials

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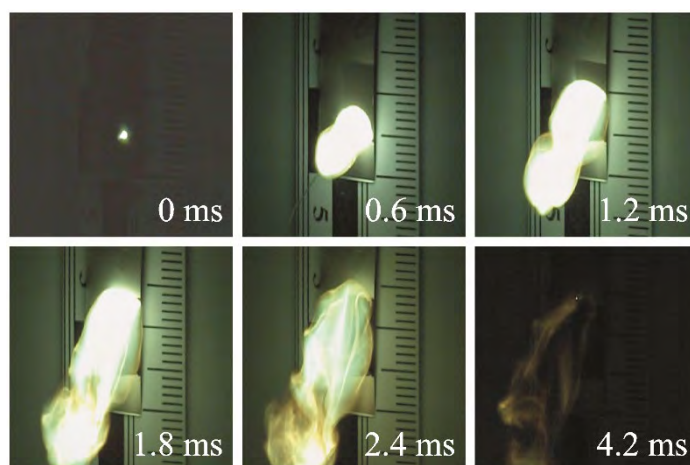
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Development of methods for the formation and study of the energetic materials properties in which fast self-propagating exothermic reactions can take place and which can act as sources of heat is currently an urgent task for a number of applied areas - from microelectronics, self-propagating high-temperature synthesis to alternative energy. Electrophoretic deposition is one of the simplest and cheapest methods for the formation of various composite materials on the surface of electrically conductive materials, including those with complex topological patterns due to the possibility of realizing local deposition.

This paper presents features of electrophoretic deposition process of energetic material based on nano-sized Al and CuO<sub>x</sub> powder materials: the influence of the concentration of the main powder and additional (surface-active materials) components on the stability of the suspension and the deposition rate is established, the dependence of the sediment composition on the ratio of components in the initial suspension is also determined. Formed energy materials were studied using differential scanning calorimetry and thermogravimetric analysis to determine the thermal effects of chemical reactions occurring in them, as well as using high-speed video to determine the velocity of wave combustion.



High-speed video storyboard of the wave combustion process of the Al-CuO<sub>x</sub> energetic material formed by electrophoretic deposition

**Acknowledgement.** This work was supported by grant of the President of Russian Federation (MK-1262.2019.8).

## Theoretical Study of Novel Nitrogen Nanostructures: Structure and Energy Characteristics

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Nitrogen-rich compounds attracted considerable attention for a long time due to their great potential for creating high-energy-density materials (HEDM). Under normal conditions, nitrogen exists as diatomic N<sub>2</sub> molecules with an extremely strong triple covalent bond, making N<sub>2</sub> chemically inert. The energy of the triple bond N≡N is 229 kcal/mol, while the double bond energy N=N is 100 kcal/mol, and the single bond N-N is even weaker, and its energy is only 38.4 kcal/mol [1]. Thus, for nitrogen, the sum of the energies of three single bonds is much less than the energy of the triple bond, which allows one to create the allotropic modifications of nitrogen, consisting of single and double bonds, to store energy that can be used as next-gen fuel elements. Moreover, their subsequent decomposition is environmentally friendly since it leads to the formation of non-toxic N<sub>2</sub>.

Despite the progress achieved in the physics of nitrogen systems, the problem of creating of metastable extended single-bonded allotropic modifications of nitrogen, that can be stable under normal conditions, remains open. In the presented study, we conducted a search for novel nitrogen nanostructures using an evolutionary algorithm USPEX [2-4]. These calculations allowed us to detect a number of unexpected single-bonded nitrogen structures and determine the conditions of their stability. We also found stable nitrogen analogs of traditional well-known carbon nanotubes. For all newly discovered nanostructures, structural, energy, and electronic characteristics were found. Using the VCNEB technique [2-4], the energy barriers for the transition of these crystal structures into the molecular phase, as well as the transition barriers from one crystalline phase to another, were determined. Based on the results obtained, conclusions about the possibility of using such systems as the high-energy-density materials were made.

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research (RFBR), project No. 18-32-20139 mol\_a\_ved.

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**Experimental Data for Characterizing Typology of Metal Oxide Nanoparticles Combined Toxicity and on its Attenuation with Bio-Protectors**

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The broader the use of nanomaterials in various industries, science and medicine, the higher the probability that humans would be exposed to the multi-component impact of respective nanoparticles. Moreover, if one considers not only purposely engineered metal oxide nanoparticles (MeO-NP) but also those generated as by-products in many traditional technologies, such multiple adverse nano-impacts appear to be a general rule. Assessment of cumulative health risks associated with the combined effects of two or more metals and their compounds on the organism has the toxicology of mixtures as its scientific basis although there are some important contradictions between them. It may be explained not only by simplifications characteristic of the widely used methodology of risk assessment but also by extreme complexity of the theory of combined toxicity. This theory is re-considered by authors on the basis of *in vivo* experimental data on binary and some ternary combinations of different MeO-NP (containing oxides of Mn, Ni, Cu, Pb, Zn, Al, Ti, and Si). At the same time, we have shown that the toxicity and even genotoxicity of such combinations could be markedly attenuated by background administration of adequately composed complexes of some bioactive agents in innocuous doses. We believe that, along with decreasing exposures to nanoparticles, enhancing the organism's resistance to their adverse effects with the help of such bio-protectors can be an efficient auxiliary tool of health risk management in related occupations.

## Studying the Possibility of Applying the Ni and Mo Hydrogenating Elements in a Given Ratio to Alumina Prepared by Electro-Chemical Anodizing

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The deposition of transition metal compounds was possible due to the peculiarities of the molecular structure of porous Al<sub>2</sub>O<sub>3</sub>. To obtain nickel oxide nanocatalysts, a matrix of porous alumina with a pore size of about 50 nm and a thickness of 50 μm was used (Fig. 1).

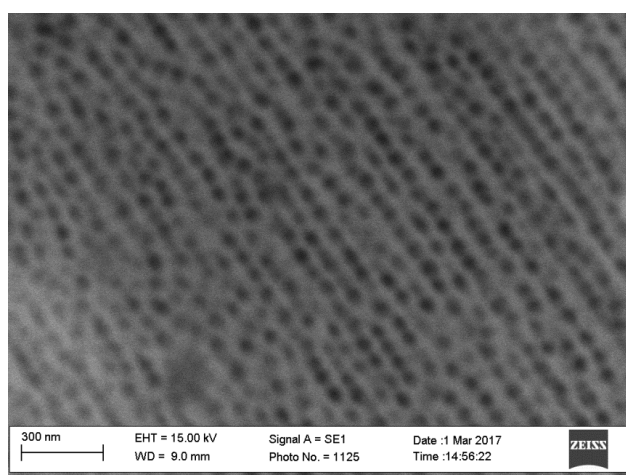


Fig. 1. Image of the plate surface obtained by electrochemical anodizing

The porous alumina plate (Fig. 1) was immersed in an aqueous solution of Ni (NO<sub>3</sub>)<sub>2</sub>, after which the sample was extensively washed with distilled water, dried, and again immersed in the solution. After a certain repetition of this cycle, the plate was annealed in air. Figure 2. shows the image of the surface of the plate obtained using a scanning electron microscope. As can be seen from the figure, on the surface of the plate a mesh structure with filaments ~ 100 nano-

meters was formed. Elemental analysis showed that this structure consists of NiO particles. The presence of nickel oxide was also detected in the pores of the matrix of anodized aluminum. Our studies have shown that, compared with electrochemical deposition, the molecular layering method is the most optimal method for producing nickel oxide-based nanocatalysts.

The introduction of nickel and cobalt nanoparticles into the matrix of aluminum oxide was carried out by the method of periodic dipping of the porous plate in the corresponding solutions with intermediate drying. The porous alumina plate was alternately dipped into aqueous solutions of Ni (NO<sub>3</sub>)<sub>2</sub> and Co (NO<sub>3</sub>)<sub>2</sub>, then washed in water, dried, and again immersed in the solution. After a certain number of cycles, the plate was annealed in air. Figure 2. shows the image of the surface of the plate obtained using a scanning electron microscope with various shooting parameters.

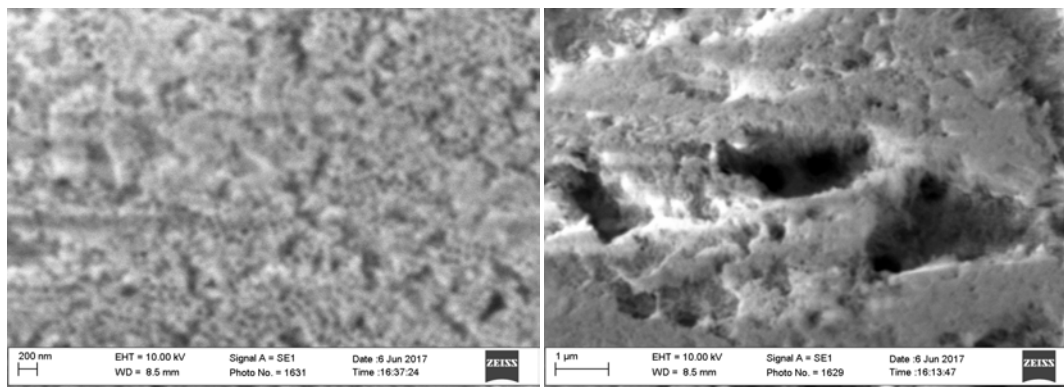


Fig. 2. Image of a plate with deposited cobalt nickel compounds

Elemental analysis data indicate a fairly uniform distribution of nickel and cobalt in the matrix of homogeneous porous alumina. Similar caritin was observed when molybdenum was applied from an aqueous solution of its salt.

1. Using the technology of double anodization, the main parameters of the synthesis were determined and the structure of porous  $\text{Al}_2\text{O}_3$  with a highly ordered arrangement of pores was obtained.

2. Made of oxide structures with different pore diameters of 20 nm, 60 nm and 100 nm, depending on the conditions of anodizing.

3. Nanoscale catalysts based on nickel oxide were obtained using a matrix of porous alumina with a pore size of about 50 nm and a thickness of 50  $\mu\text{m}$ .

4. Methods of scanning microscopy conducted structural studies of porous  $\text{Al}_2\text{O}_3$ , depending on the conditions and at different stages of anodization.

5. The elemental composition in thickness and porosity of the obtained  $\text{Al}_2\text{O}_3$  structures and nickel-based catalysts were studied by scanning microscopy.

6. Nanoscale catalysts based on nickel and cobalt were obtained using a matrix of porous aluminum oxide with a pore size of about 50 nm and a thickness of 50  $\mu\text{m}$ .

7. Elemental analysis showed that a spongy structure was formed on the surface of the matrix of aluminum oxide with filament sizes on the order of several nanometers, and this structure contains nickel and cobalt nanoparticles.

**Acknowledgement.** This work was supported by the Ministry of Innovative Development of the Republic of Uzbekistan under grant number A-12-011.

## New Methods of Synthesis of Bimetallic Coatings for the Catalytic Application in Environmentally Important Redox Reactions

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Bimetallic catalysts promise many advantages when used in environmentally important processes [1]. Methods of “wet” chemistry are widely used for their preparation. However, chemical synthesis is usually a multi-stage process causing significant environmental stress. The development of novel one step ‘green’ synthesis of bimetallic coatings providing composition homogeneity remains an important problem. This work is aimed to apply two original methods: laser electrodispersion (LED) and plasma electrolytic oxidation (PEO) for the direct formation of thin films and coatings based on metallic nanoparticles, alloys or oxides for catalytic applications. The structure of prepared catalysts was studied by TEM, SEM and XPS methods. Their efficiency was compared with known analogues using test redox reactions.

LED [2] produces size-selected nanoparticles as a result of cascade fission of liquid metal drops in the laser torch plasma, in contrast to the laser ablation where particles are formed from metal atoms. Here this method was used for the deposition of bimetallic nanoparticles on the surface of Al<sub>2</sub>O<sub>3</sub> taking the NiPd alloy or mixture of Ni and W or Mo powers as targets. In all cases both components of bimetallic coating were uniformly distributed over the outer alumina surface as metallic and oxide nanoparticles. Even at 0.005 wt.% metal loading the NiPd/Al<sub>2</sub>O<sub>3</sub> catalyst was active and stable in chlorobenzene hydrodechlorination and carbon monoxide oxidation. NiW/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts with the same extremely low metal loading provided effective peroxide oxidation of thiophene.

PEO technique [3] was used for the fabrication of mixed cerium-zirconium-titanium oxides layers on titanium. Catalytic properties of novel “oxide layer/metal” materials were also studied in the peroxide oxidation of sulfur compounds (thiophene, thioanizole and dibenzothiophene) and the desulfurization of diesel fuel. The catalytic activity correlates with the presence of double ZrTiO<sub>4</sub> and Ti<sub>2</sub>ZrO<sub>6</sub> oxides in the coating composition. Another important benefit of the developed systems is the desulfurization of diesel fuel with the unusually high efficiency under mild conditions. The residual amount of sulfur < 10 ppm after treatment meets modern environmental requirements.

**Acknowledgement.** This work was supported by the Program of Development of MSU.

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## The Developing of Compositions and Thermal Conductivity of Zinc Oxide Nanofluids

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Many industrial processes involve heat removal by means of cooling devices. In particular, the problem of the temperature control has become crucial in high heat fluxes applications, such as nuclear fission plants and systems for micro/nano power electronics (MEMS/NEMS). Heat transfer takes place by means of a laminar or turbulent flow of heat carrier flow, usually air, water, mineral oil, ethylene glycol etc. The most important intrinsic limitation consists in the relatively low thermal conductivity of these materials. Water thermal conductivity is the highest among all liquids but is several orders lower than solid materials. Nanofluids represent diluted suspensions of nanoparticles with a diameter of less than 100 nm. Such innovative materials were proposed in 1995 (Choi et al. [1]) to increase thermal conductivity in processes that require highly efficient heat transfer. Within this area, various types of nanoparticles and base fluids have been reported [2]. The present study is devoted to the liquid composition consists of zinc oxide nanoparticles (ZNP) in tetraethylene glycol (PEG200)/kerosene (KO25) base fluid. Zinc oxide nanoparticles were selected due to its well-developed synthesis and existence of the surface modification methodology (e.g., [3]). The composition of the fluid was based on the glycols high thermal conductivity and kerosene low viscosity.

Zinc oxide nanoparticles samples were obtained by sol-gel technique using  $ZnX(II)$  (where  $SO_4^{2-}$ ,  $NO_3^-$ ,  $AcO^-$ ) as precursor, followed by calcination of  $Zn(CO_3)_y(OH)_x$  at 300-400 °C. Preparation methods of 0.5-3 wt.% ZnO/10-40 vol.% PEG200-KO25 nanofluids have been developed using zinc oleate (1-5 wt.%) as a dispersant. Particle size distributions of prepared suspensions were measured by photon correlation spectrometry method. It is shown that nanofluids with a particle size of  $ZnO-Zn(C_{17}H_{33}COO)_2$  lower than 30 nm are stable to sedimentation process. Heat transfer properties of prepared nanofluids were tested by laser flash method (dynamic thermal conductivity; [4]). In addition, the observed thermal conductivity were measured using self-constructed experimental setup. Tested liquids and heating element equipped by thermocouple was introduced into the brass cuvette in thermostating medium (20 °C). An equilibrium temperature ( $T_{eq}$ ) established as a result of heat transfer to a medium and constant heating process. That parameter used to describe observed thermal conductivity. The dynamic thermal conductivity of the optimal ZNP nanofluid (2 wt.% ZnO in 35 vol.% PEG200/KO25) is comparable with that of commercial available liquid MS-20.



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The lower viscosity of the prepared nanofluids leads to a greater observable thermal conductivity at auto-convection mode ( $T_{eq} = 49.7-52.5$  and  $62.1$  °C for MS-20).

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## Shape Control of PbO Nanoparticles Produced by Laser Ablation in Liquid

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The formation of metal oxide nanoparticles (NPs) by laser ablation in water (LAW) and hot water treatment has been studied using Pb as a model metal. The spherical NPs, circular and hexagonal nanosheets, and nanooctahedron shapes have been produced by variation of the ablation parameters and subsequent suspension heating. Various pretreatments of the target surface have been used.

The Yb fiber laser with 1062 nm wavelength and 100 ns pulse duration has been used. The laser beam has been focused on the target surface (fluence 80 J/cm<sup>2</sup>, spot diameter 40 μm). The NPs synthesis was performed in several stages: target surface pretreatment, laser ablation in deionized water, additional fragmentation and heating of the suspension for nanoparticle reshaping and formation of proper shapes [1,2].

The target surface and NPs composition were analyzed by Raman confocal microscope Alpha 300 AR, WiTec. Scanning electron microscope CrossBeam Workstation Auriga, Carl Zeiss, and particle size analyzer Zetasizer Nano ZS, Malvern were used for NPs characterization ( $\zeta$  - potential, sizes and shapes) after each step of the synthesis.

It was found that the laser ablation of the Pb targets aged at ambient conditions, cleaned by LAW and treated by hot water leads to appearance of nonspherical 2D (plates) and 3D NPs (octahedra and rods) in suspension and at the target surface.

The NPs of the classical spherical shape appeared in suspension immediately after LAW (Fig. 1c) and their shape changes rapidly in the heated water. It was found that the octahedra (Fig. 1d) and rods appeared at the target surfaces immersed in the water with temperature about 70°C after several minutes even without laser ablation. Thus, the noticeable role of the hot water treatment during laser ablation in water in formation of the nonspherical micro- and nanoparticles was proved.

The simple model based on growth of seed oxide nanoparticles was applied for explanation of the obtained formation of 3D particles. This process results in growth of PbO spherical nanoparticles and erosion of all Pb surfaces. The PbO NPs played the role of the seeds which phase depends on the target preparation procedure. The 2D particles (plates) appeared by seedless growth (Fig. 1a,b).

The demonstrated influence of the unavoidable hot water treatment should be considered as an additional mechanism for explanation of the results of laser ablation in water especially related to formation of the nonspherical nanoparticles [3].

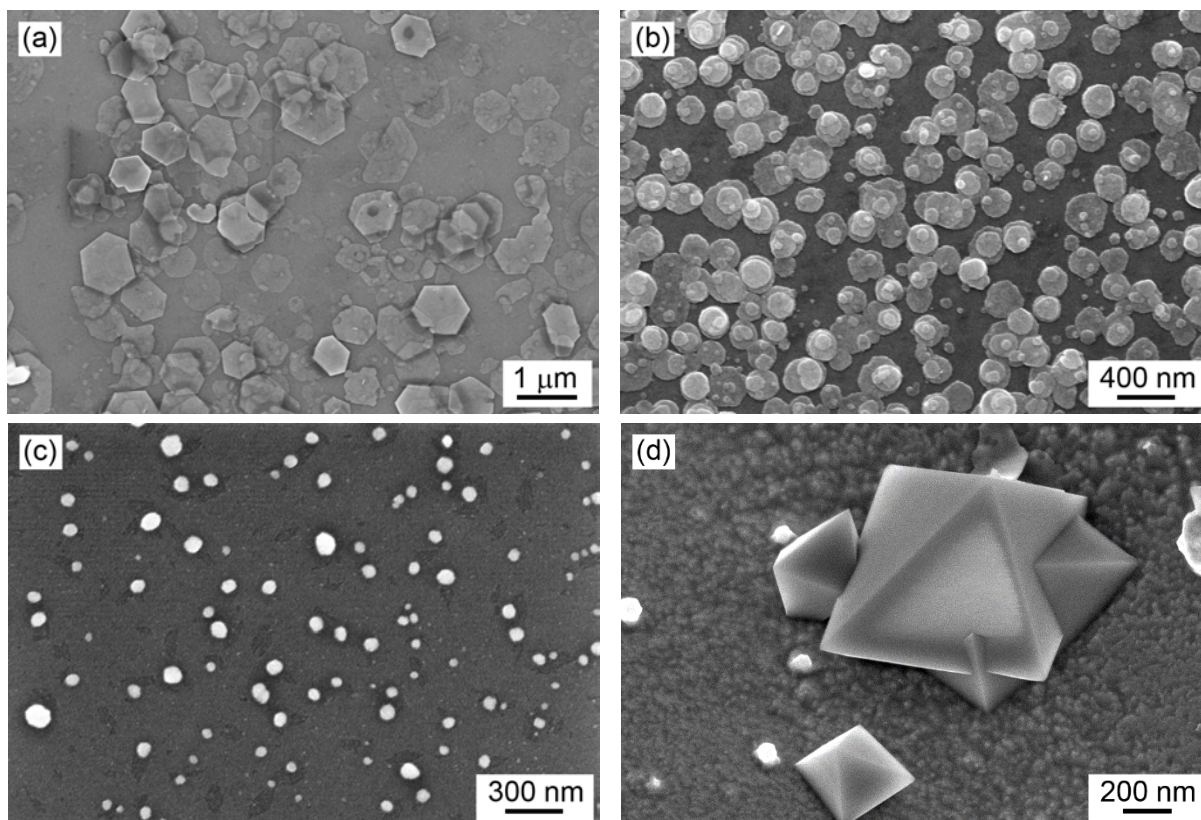


Figure 1. SEM images of PbO micro- and nanoparticles produced by laser ablation in deionized water: (a) hexagonal nanosheets, (b) circular nanosheets, (c) spherical NPs, (d) octahedrons.

The PbO NPs have been used for nanotoxicological research in collaboration with Ekaterinburg Medical Research Center for Prophylaxis and Health Protection of Industrial Workers [4]. The obtained PbO NPs of various controlled shapes can be used for nanotoxicological research and creation of the antibacterial coatings [5].

**Acknowledgement.** The equipment of the Ural Center for Shared Use “Modern nanotechnology” School of Natural Science and Mathematics, Ural Federal University was used. The work was supported by Government of the Russian Federation (Act 211, Agreement 02.A03.21.0006).

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## Creation of Nanoparticles and Surface Nanostructures of Metal Oxides by Hot Water Treatment

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Recently, a simple hot water treatment (HWT) has been used for [1] to creation of metal oxide nanostructures (MONSTRs) on surface of the metals, their compounds, or alloys by a one-step, scalable, low-cost, and eco-friendly process. The HWT involves immersing the metal piece in hot deionized water without any chemical additives. The method was used for durable adhesive bonding [2], for producing superamphiphobic aluminum alloy surface with nanoscale roughness [3] and nanostructure of CuO for optical photoconductive device [4]. Also, HWT can affect synthesis of nanoparticles during laser ablation in liquid [5]. But, to date the MONSTRs formation hasn't been studied systematically. We present the detail study of formation of aluminum oxide nanostructures by HWT at various water temperatures and treatment durations. It was shown that this method can be used for synthesis of water suspension of metal oxide nanoparticles (NPs).

Aluminum compound plate (Al 88.3%, C 6%, O 2.9%) with 0.5 mm thickness was studied. Treatment by hot deionized water has been done at 60 – 100°C during 2 - 30 min with subsequent careful water removing. The plate surface morphology was visualized with nanoscale spatial resolution by scanning electron microscopy (SEM) using CrossBeam Workstation Auriga, Carl Zeiss. To analyze the NPs obtained in water after HWT the suspension drop was dried on the Si/SiO<sub>2</sub> substrate by freeze drier Alpha 2-4 LSC, Martin Christ. The shape and sizes of NPs were revealed by analysis of the SEM images.

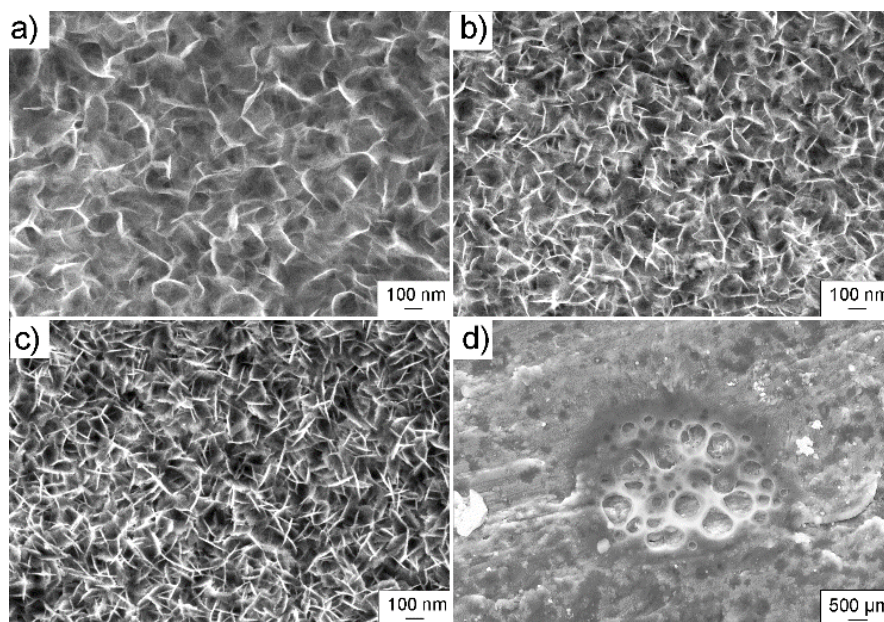


Figure 1. SEM images of aluminum oxide nanostructures on the plate surface after HWT during 30 minutes at different temperatures: a) 70°C, b) 80°C, c) 95°C, d) 100°C.



## PP-17

Moreover, we have investigated the aluminum oxide nanostructures formed after HWT during 30 minutes at different water temperatures. It was shown that below 70°C the nanostructure didn't occur. At higher temperatures the plate surface has been covered by nanostructures with uniform distribution (Figure 1). The nanostructures presented the net of 10-nm-thick nano-sheets mostly oriented perpendicular to the plate surface. It was shown that the density of nano-sheets increased monotonously with water temperature. The plate treatment in boiling water leads to appearance of additional cavitation holes in the plate surface (Figure 1d). The thickness of nanostructured layer varied from 350 to 550 nm. The surface after HWT became super-hydrophilic with stable properties for more than two weeks.

The molecules of aluminum oxide get into the water during HWT. Part of them was re-deposited back to surface, but some part stays in the water [1]. Thus, we have water solution of NPs after HWT. The spherical, dendrite and oblong NPs have been obtained (Figure 2). The mean diameter of spherical Al NPs was about 30 nm for all used water temperatures.

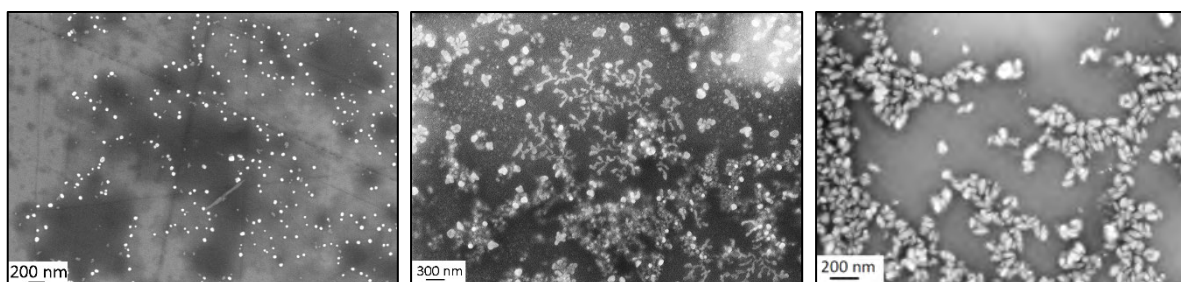


Figure 2. SEM images of Al nanoparticles produced by hot water treatment.

**Acknowledgement.** The equipment of the Ural Center for Shared Use “Modern nanotechnology” School of Natural Science and Mathematics, Ural Federal University was used. The work was supported by Government of the Russian Federation (Act 211, Agreement 02.A03.21.0006).

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## High Kinetic Stability of Silicon Prismanes: Density Functional Theory Study

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Silicon nanoclusters are the subject of intense research, because of their potential use in electronic, optoelectronic, photovoltaic, thermoelectric, and biological applications. In this study using density functional theory, we have analyzed thermodynamic and kinetic stability of elementary silicon prismanes as well as their electronic properties and chemical reactivity indexes. Polyprismanes or [n,m]prismanes are the nanotubes of a special type constructed from silicon rings, where m is the number of vertices of the closed atomic ring and n is the number of layers. Here we considered elementary prismanes with n = 2 and m = 3 – 8. All DFT calculations for the silicon prismanes were performed using the TeraChem software. First of all, we determine their structural characteristics (bond lengths and valence angles) and binding energies. The calculation of vibrational spectra confirmed that these molecular structures correspond to the energy minima. It has been obtained that the most thermodynamically stable of the structures considered is the [2,5]prismane. For every elementary silicon prismane considered, a set of quantum chemical descriptors is defined: HOMO and LUMO energies, ionization potential, electron affinity, chemical potential, electronegativity, chemical hardness and softness, electrophilicity index. We also determine the possible decomposition channels of the elementary silicon prismanes. It was confirmed that the priority decomposition channel for the systems with even m = 4, 6, 8 is the breaking of one of the interplane bonds, whereas for the silaprismanes with odd m = 3, 5, 7 the priority decomposition channel is the breaking of one of the intraplane Si–Si bonds. The minimum energy barrier preventing the decomposition, as a measure of kinetic stability, nonmonotonously depends on m. Using the Arrhenius equation, the estimation of the lifetime of elementary prismanes was made at room temperature (300 K) and at the temperature of 800 K. It was obtained that the elementary silicon prismanes possess high kinetic stability: the estimation of their lifetimes at room temperature gives the macroscopic (“infinite”) values, and their lifetimes at 800 K are greater than microseconds. According to the data obtained, it was concluded that the preferable candidates for the construction of extended systems (nanowires) in the form of silicon polyprismanes for the nanoelectronics applications are the [2,m]prismanes with m = 5 – 7.

**Acknowledgement.** The presented study was performed with the financial support of the Russian Science Foundation, grant no. 18-72-00183.



# ANT 2019

## VIRTUAL PRESENTATIONS

VP-1 ÷ VP-18



[Content](#)





## Bimetallic Catalysts Based on Nanoparticles Pd and Rh in Reactions Involving Hydrogen

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Bimetallic nanoparticles (BM NP) attract the attention of researchers and engineers in connection with their optical catalytic, electrical, magnetic and other properties. A number of properties due to synergies and the mutual ratio of their constituent elements that lead to the emergence of new properties at BNP compared with properties of monometallic woofers, that allows to use them in a variety of applications. BNP properties become dependent not only on the chemical composition and size but also on the morphology of nanoparticles.

Over the past two decades, there has been an increase in the number of studies of nanoparticles based on Pd and Rh. these metals are widely used as catalysts for reactions of C-C- and C-N-binding in many hydrogenation processes in automotive catalysts converters, fuel cells and so on ways to enhance the catalytic activity of these processes lie in a combination of pure metals Pd and Rh, resulting in higher performance, resulting from synergies, as well as a selection of media that plays a significant role in determining the final properties of the catalyst.

This paper presents results of synthesis of bimetallic nanoparticles of transition metal-based Rh and Pd in the solution H<sub>2</sub>O/AOT/isooctane when using flavonoid quercetin (as a reducing agent) and dissolved molecular oxygen whose presence is necessary for the formation of a charge transfer complex [mQr<sup>δ+</sup>...nO<sub>2</sub><sup>δ-</sup>...pMe<sup>n+</sup>] responsible for restoration of metal ions. As a source of salts taken RhCl<sub>3</sub> and PdCl<sub>2</sub>.

Used different methods for the synthesis of NP with type "alloy" Rh-Pd and "core/shell" Pd<sub>core</sub>/Rh<sub>shell</sub> and Rh<sub>core</sub>/Pd<sub>shell</sub> with molar ratio of 1:1 ions. For each type of nanostructures the solution was characterized by coefficients (degree of hydration) - ω=2.0 and ω=5.0. Catalysts obtained by the method of impregnation of granulated media γ-Al<sub>2</sub>O<sub>3</sub> (Redkin catalyst plant) the solution BNP. For comparison, also made from a mixture of catalyst monometallic NP Rh and NP Pd at a ratio of 1:1.

It is shown that in the solution in the presence of ions Rh<sup>3+</sup> and Pd<sup>2+</sup> primarily Palladium ions are restored, and formed NP Pd inhibit recovery ions rhodium. It was as if the joint reconstruction of ions, and advance the restoration of Pd<sup>2+</sup> to nanoparticles with subsequent addition of rhodium salts. Noted enough slow kinetics of formation of NP (~7 days) under these conditions, which is controlled by the dimensions for 52 days. The explanation for this lies in the gradual transformation of the micelles and the redistribution of salts of metals

## VP-1

between them. Optional confirmation of data serve to change the intensity of Raylei scattering, which correlated with the change of optical extinction, under the same conditions. Dimensions of synthesized BNP comprise 1.2-3.1 nm.

Studies of stability of the mixture of the solution NP Rh and Pd have shown that in the solution mix NP blend with an average diameter of  $\sim 2.7$  nm is sustained for at least 25 days. Notes mutual education NP of both mutual residual concentrations of salts of metals, with an appropriate balance of monometallic NP, and decreasing intensity of absorption of electromagnetic radiation in the visible region of the complex quercetin-metal ion.

Received catalytic systems were tested on catalytic activity in the reaction isotopic hydrogen Exchange. This reaction is highly sensitive in regard to the size and structure of the nanoparticles can be used as a reverse control analytical method of their morphology and size. Catalytic studies showed the lack of formation of bimetallic data structures for metals in conditions of the chosen system. For prospective structures of Rh-Pd and Pd/Rh are observed only NP Pd and Rh/Pd structure is revealed the original NP Rh and Pd Clusters (0.7 nm). In the latter case, you change the activation energy of the reaction, but the activity corresponds to the NP Rh of the appropriate size.

For mixtures of NP Rh and Pd of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> identified synergies enhance catalytic activity, which is due to spillover-hydrogen. Hydrogen adsorption on Pd is conducive to its spread over the surface of the media that facilitates the absorption of hydrogen molecules NP Rh or NP Pd yourself easily provide hydrogen depletion, which migrates to the surface in the elemental form.

Declining size NP with increasing  $\omega$  ratio for solutions Rh-Pd and Rh/Pd, as well as when mixing NP Rh with NP Pd relative to original size NP Rh. Catalytic studies confirm this fact - there is complete correlation of the size of the activity.

**Acknowledgement.** This work was supported by the Russian Science Foundation, grant 11-03-90738, [09-08-00758](#).

## VP-2

### Synthesis and Study of the Microstructure of the Components of the Radiopaque Nanocomposite $Fe_3O_4$ -Au-SiO<sub>2</sub>

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Nanocomposites are promising materials in many fields of science and technology. Nanocomposites can be used as contrast agents, agents for targeted delivery of drugs and other substances to cells and organs [1].

The creation of a nanocomposite based on mixed iron oxide, gold, and silicon oxide was proposed in this study. This composite due to the combination of the magnetic properties of  $Fe_3O_4$  and the radiopaque properties of Au is a promising material for computed and magnetic resonance tomography [2, 3].

The microstructure of individual components of the  $Fe_3O_4$ -Au-SiO<sub>2</sub> nanocomposite was studied. The obtained data are presented in Figs 1-3.

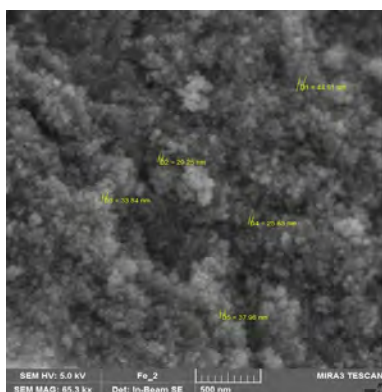


Fig. 1 – SEM-image of mixed iron oxide nanoparticles

It was found that the sample of mixed iron oxide is X-ray amorphous and consists of spherical nanoparticles with a diameter of 30-40 nm.

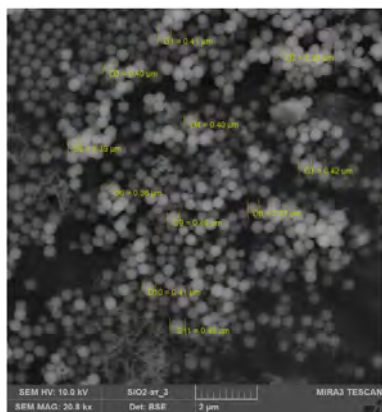


Fig. 2 – SEM-image of SiO<sub>2</sub> nanoparticles

It was established that the particles of silicon oxide have a spherical shape, the particle diameter is about 450 nm.

## VP-2

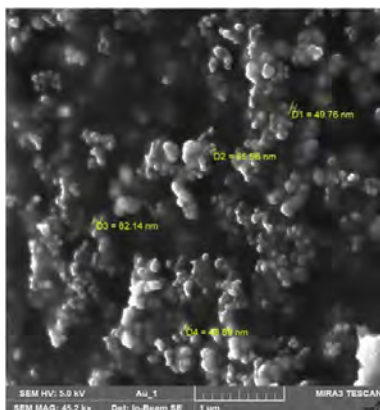


Fig. 3 – SEM-image of gold nanoparticles

The size of gold nanoparticles ranges from 40 nm to 100 nm.

**Acknowledgement.** This work was supported by the Federal state budgetary institution "Fund for assistance to the development of small enterprises in the scientific and technical sphere", contract № 13692GU/2018 since 1st April 2019.

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## Prerequisites for the Use of Nanosilver in Pre-Sowing *Pisum Sativum* Seed Treatment

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Creation and application of nanoparticles are known as one of the most rapidly developing trends in modern nanotechnology. The frequent attempts to apply nanoparticles in agriculture are explained by the number of issues of the conventional seeds treatment methods, e.g. chemical sterilization of seeds.

Conventionally used organic sterilizers have such important disadvantages as high consumption, toxicity, and capability of pathogens to adapt and endure sterilizers. Nanoscale metals show high bactericidal activity, low toxicity and do not accumulate in the human body. Iron, cobalt, copper, manganese and other elements in the nanoscale state can promote growth and development of plants.

Silver nanoparticles are of special interest. While in the nanoscale state, silver shows a drastic increase in catalytic and biological activity. Thus, utilization of nanosilver allows lowering its concentration to several orders, maintaining the level of bactericidal properties.

Two forms of silver nanoparticles were obtained: Ag nanoparticles stabilized with polyvinylpyrrolidone (PVP) and Ag nanoparticles stabilized with quaternary ammonium compound (Didecyldimethylammonium bromide (DDAB)). The synthesis of silver nanoparticles was conducted using the method of chemical reduction.

Optical properties of the synthesized silver nanoparticles were analyzed by spectrophotometry with spectrophotometer SF-56 (OKBLOMO, Saint Petersburg, Russia). The hydrodynamic radius of synthesized silver nanoparticles was measured with photon correlation spectrometer Photocor Complex.

The radiuses of synthesized particles are 50 nm or less, i.e. large fractions are absent. The distribution peaks take place at 50 and 20 nm with the dispersion of 20–100 and 10–40 nm for Ag-PVP and Ag-DDAB, respectively. There is a fraction with radiuses 6–7 nm in both sols. High bactericidal activity is intrinsic for this fraction.

Seeds of pea *Pisum sativum* were treated with different forms of silver. Prior to the mentioned treatment, the seeds underwent no additional processing. Pea seeds treated with solutions of different concentrations (0.05, 0.01, 0.005, 0.001, 0.0005%) were placed in the incubator at a constant temperature of 20 °C without illumination. The key parameters were the average root length and the percentage of germinated seeds.

In case of the treatment with Ag-PVP, Ag-DDAB, DDAB solutions at the concentration of 0.05%, a drastic decrease in the percentage of germinated seeds was observed (down to 30–40%). This indicates a toxic effect of said agents.

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The usage of nanosilver stabilized with PVP demonstrates the best result in terms of root growth as compared with control: average root length is about 40 mm for each concentration used. The treatment of seeds with Ag-DDAB solutions (concentrations of 0.005% and 0.001%) had a positive effect. An average root length was about 42 and 34 mm for said concentrations, respectively, significantly exceeding the length values in control. For Ag-DDAB concentrations higher than 0.001%, a decrease of root length was indicated, showing the inhibiting influence of DDAB. A similar effect was observed when the DDAB solutions were applied: the concentration higher than 0.001% inhibits germination, while lower DDAB concentrations did not demonstrate the level of positive influence intrinsic for Ag-DDAB diluted solutions.

The analysis of the data obtained during the experiment shows that nanosilver treatment agents do not affect the germination of pea seeds adversely at low concentrations. For concentrations higher than 0.005%, a decrease in germination was observed in the case of silver nanoparticles stabilized by DDAB, which is due to the inhibitory action of DDAB.

However, the application of nanosilver may result in a significant positive effect on the length of the root of pea seeds in case of seeds treatment with the agent based on PVP-stabilized nanosilver. Increase in roots length may be reached at low concentrations – only 0.0005%.

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## Catalytically Active Composite Coatings with Self-Organized Porous Alumina Matrix Modified by $\gamma$ -MnO<sub>2</sub> Nanoparticles

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At present, the unfavorable ecological situation is making it necessary to develop new efficient technologies of air decontamination. The problem of reduction of hazardous emissions into the environment can be solved, in particular, through application of catalysts. In many cases, to deposit catalytically active compounds on a metallic substrate, it is necessary to apply a "sublayer" (or a secondary substrate) improving the adhesion to the metallic base and increasing the catalyst specific surface area (SSA). The controlled Al anodization resulting in formation of a thermally and mechanically stable porous oxide layer constitutes a promising method of producing a secondary substrate on Al and its alloys suitable for catalytic processes at temperatures up to 600°C. Such porous oxide coatings with high SSA can be used as matrices for deposition of catalytically active particles, i.e., a basis for creating composite coatings with catalytic properties.

Ultradispersed  $\gamma$ -MnO<sub>2</sub> and  $\beta$ -MnO<sub>2</sub> are active catalysts of oxidation of various volatile organic compounds which is facilitated by their high SSA. In view of the above, application of "ultradispersed  $\gamma$ -MnO<sub>2</sub>/nanostructured Al<sub>2</sub>O<sub>3</sub>/Al" composites appears to be promising in the development of catalytic systems. The aim of the present work is selection of the method of deposition of ultradispersed MnO<sub>2</sub> on the surface of the nanostructured anodic alumina and estimation of the catalytic activity of the produced composites in the reaction of oxidation of CO into CO<sub>2</sub>.

Anodization of Al foil (A99) was carried out in 3% solution of oxalic acid at constant current density  $j_a = 10 \text{ mA/cm}^2$  for  $t = 1 \text{ h}$ . SEM & AFM studies have shown that a "defect porous layer" characterized by the presence of disordered pore openings of a size of 30–50 nm, as well as numerous defects and heterogeneities, were found on the surface of anodic oxide.

MnO<sub>2</sub> has been deposited on the surface of an anodized Al foil using the methods of thermal decomposition of Mn(NO<sub>3</sub>)<sub>2</sub> and K<sub>2</sub>MnO<sub>4</sub>, as well as chemical synthesis, with intermediate drying and subsequent annealing [1]. The application of the technology of thermal decomposition of K<sub>2</sub>MnO<sub>4</sub> at  $T = 220\text{--}230^\circ\text{C}$  enables one to deposit  $\gamma$ -MnO<sub>2</sub> nanoparticles of linear sizes in the range from 20 to 80 nm with predomination of the finer fraction appear in pores and defects of the surface oxide layer. Note that a fine (up to 30 nm) fraction of MnO<sub>2</sub> nanoparticles is present in pores with diameters of up to 80 nm. Thus, one



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can conclude that, under the used experimental conditions, the thermal decomposition of  $K_2MnO_4$  results in formation of  $\gamma$ - $MnO_2$  nanoparticles homogeneously distributed both over the surface and in open pores of anodic oxide film.

It has been shown that the anodized samples modified with  $MnO_2$  nanoparticles catalyze the reaction of oxidation of CO into  $CO_2$  at temperatures above  $180^\circ C$ . So, the produced "ultradispersed  $\gamma$ - $MnO_2$ /nanostructured  $Al_2O_3/Al$ " catalytic systems may prove efficient for the removal of CO and other gases hazardous for human health from the air due to a combination of high specific surface area of the porous oxide matrix and catalytic activity of  $MnO_2$  nanoparticles.

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## Study of Toxicity Heteropolyacids Keggin Type In Vitro and In Vivo

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Polyoxometallates (POM) of Keggin type structure are considered to be a promising and perspective chemical agents characterized by antiviral and antitumor activity. Their production is less expensive than biological preparations and the possibility of varying the structure, chemical composition and properties are very large. However, the high toxicity of POM prevents the creation of drugs based on them. Comparative study of POM of the same structure but different in chemical composition can be useful to determine a basic mechanism of their action. In this work we studied cytotoxic and immunomodulatory effects of heteropolyacids of Keggin type (HPA) in tumor and non-tumor cell cultures. The results were supplemented by the determination of acute toxicity in vivo on albino mice.

Aqueous solutions with  $10^{-2}$  ML<sup>-1</sup> concentration of HPA (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub>, H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub>) manufactured by “Biochem” (France) and their vanadium-substituted analogs (H<sub>4</sub>PMO<sub>11</sub>VO<sub>40</sub>, H<sub>5</sub>PMO<sub>10</sub>V<sub>2</sub>O<sub>40</sub>, H<sub>4</sub>PW<sub>11</sub>VO<sub>40</sub>) synthesized in the Institute of General and Inorganic Chemistry (Academy of Sciences of Belarus) were comparatively assessed. The study of cytotoxic and immunomodulatory effects were carried out in continuous cell lines of human embryo fibroblasts – HEF, canine kidney – MDCK and malignant lung tumor (lung carcinoma) – A-549. Cell lines were cultured in a 5% CO<sub>2</sub> incubator at 37 °C in Minimum Essential Medium Eagle (plus 10% fetal bovine serum) for 24 hours. Then the medium with double HPA dilutions was added to cell lines and they were cultured at 37 °C for 48 hours.

Cytotoxic effects of HPA were determined by standard MTT method. The results of MTT determination of IC<sub>50</sub> (μM/l) after 48 hours cell cultivation with HPA are given in the table.

The study of cytokines was performed by the methods of reverse transcription and polymerase chain reaction (marker J1758, Promega). POM induced expression of cytokine genes in the cells was studied to determine possible mechanism of POM influence on main immunity links. Gene transcription of IL-18, IL-1β, IL-8, TNF-α and gene expression of interferon I, II, III type (IFN- α /β, IFN-γ, IFN-λ) were detected in 24 hours after addition of HPA (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PMO<sub>12</sub>O<sub>40</sub> at dilutions of 1/100-1/500) to HEF cells. They determine the development of T and B cellular and macrophage immunity in macroorganisms that is

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important in anti-infective and anti-tumor processes. Vanadium containing HPA does not change synthesis of mRNA of cytokines in normal HEF cells, however the detected expression of genes IFN-  $\alpha$ , IFN- $\beta$ , IL-18 and IL- 6, is able to activate antiviral immunity.

**Table Cytotoxicity ( IC50) of HPA**

	FHE human embryo fibroblasts	MDCK canine kidney	A-549 malignant lung tumor
<b>H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub></b>	<b>156</b>	<b>125</b>	
<b>H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub></b>	<b>310</b>	<b>125</b>	
<b>H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub></b>	<b>500</b>	<b>250</b>	<b>250</b>
<b>H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub></b>	<b>310</b>	<b>250</b>	<b>156</b>
<b>H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub></b>	<b>310</b>		<b>80</b>
<b>H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub></b>	<b>158</b>		<b>64</b>
<b>H<sub>4</sub>PW<sub>11</sub>VO<sub>40</sub></b>	<b>420</b>		<b>350</b>

HPA acute toxicity (H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub> and H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>) was carried out by injection in doses 3000mg/kg, 2000mg/kg, 1000mg/kg, 500mg/kg, 200mg/kg, 100mg/kg into an empty stomach of albino mice through a metal probe. Clinical signs of poisoning and dead/survived animals were registered within two weeks of observation for DL50 assessment. The obtained results were: DL50 H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub> - 2000mg/kg, DL50 H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> - 1000mg/kg. In our previous researches we found out vanadium-free HPA structures were characterized much lower acute toxicity indexes compared with vanadium containing ones.

Studies of cytotoxicity of POM Keggin type showed vanadium inclusion into molybdenum containing HPA structure increases their cytotoxicity and antitumor activity. These data were supplemented by acute toxicity results in vivo tests.

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research, grant 18-54-00004 Bel\_a and the Belarusian Foundation for Basic Research, contract No. X18P-110.

## Effect of Synthesis Conditions on the Nanostructure of (Ce<sub>1-x</sub>M<sub>x</sub>)<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>y</sub> Catalysts (M = La, Mg)

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Nanostructured composite Ni-containing oxides with the structure of perovskite, fluorite or spinel are promising precursors of Ni reforming catalysts [1]. The phase composition, defectiveness of structure, oxygen mobility and functional properties of these materials depend on their chemical composition and dispersion of oxides, which in turn is determined by the conditions of synthesis [2]. Of particular interest are methods that allow synthesizing composite oxides with a crystallite size of less than 5-10 nm. With such small sizes, so-called size effects begin to appear, leading to changes in the characteristics of the material. Accordingly, in this study (Ce<sub>1-x</sub>M<sub>x</sub>)<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>y</sub> materials (M = La, Mg; x = 0-1; y = 1-1.7) were prepared by polymerizable complex method, and effect of synthesis conditions (calcination and activation temperature, gas medium) on their nanostructure was considered. The samples were characterized by TA, BET, XRD, HRTEM-EDX, HAADF-STEM, SEM, DRS UV-Vis, Raman spectroscopy, and H<sub>2</sub>-TPR. Their catalytic activity was studied in steam/CO<sub>2</sub> reforming of methane (600-800°C, molar ratio CH<sub>4</sub>/CO<sub>2</sub>/H<sub>2</sub>O/He = 1.0/0.81/0.38/2.8).

It was demonstrated that textural, structural, redox and functional properties of (Ce<sub>1-x</sub>M<sub>x</sub>)<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>y</sub> materials were affected by preparation conditions. After calcination in air at 500°C (Ce<sub>1-x</sub>M<sub>x</sub>)<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>y</sub> materials (x ≤ 0.8) contain a CeO<sub>2</sub>-based phase. In addition, for Mg-containing samples, the MgO-NiO solid solution is observed. The growth of molar fraction of M leads to a decrease of the average crystallite size of CeO<sub>2</sub>-based phase and defectiveness of its structure. At an increase of the calcination temperature the partial destruction of CeO<sub>2</sub>-based phase, the formation of Ni-containing phase and an increase of crystallite size were observed. It was shown that after activation of catalysts in hydrogen medium highly dispersed Ni particles were formed. The results of catalytic tests in steam/CO<sub>2</sub> reforming of methane and anti-coking stability of the samples were correlated with the particularity of (Ce<sub>1-x</sub>M<sub>x</sub>)<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>y</sub> nanostructure. The optimal preparation conditions were elucidated.

**Acknowledgement.** This work was supported by Ministry of Science and Higher Education of the Russian Federation (project AAAA-A17-117041710090-3).

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## Biotoxicity of Nanoscale Bimetallic Nanoparticles and (C60)-Fullerene Derivative on *Stylonychia mytilus* and *Staphylococcus aureus*

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Development and wide use of new generation of nanomaterials demands studies of their properties, including influence on live organisms [1]. Therefore, in modern conditions, the development of methodological and theoretical issues in the application of biological test objects (cell cultures, microorganisms, protozoa) in toxicological studies becomes more relevant [2].

The purpose of this work was to evaluate the toxic effect of CuZn bimetallic nanoparticles (NP), differing in the method of preparation, and FeCo, as well as (C60) -fullerene derivative using the single-celled organisms *Stylonychia mytilus* and *Staphylococcus aureus*.

Bimetallic nanoparticles of FeCo and CuZn, differing in the preparation technology (mixture and alloy) with a dimension of about 30 nm and a (C60)-fullerene KV253 derivative representing cationic (C60)-fullerene, bearing four protonated 4-(2-pyridyl) piperazine-1-yl groups were used in the study. Aqueous suspensions of NP (5 mg/ml) were prepared in deionized water. The suspensions of NP were vigorously mixed and sonicated in ultrasonic bath (Sapfir, Russia) at 35 kHz for 30 min. From these solutions 10-fold dilutions were then prepared.

The object of the study was the protozoa *S. mytilus*, cultivated in Lozin-Lozinsky saline solution. As a model bacterial cells we used *S. aureus* 209 P strain, grown for 18 hours in a nutrient medium, normalized by optical density (0.5 units at 450 nm) and washed by centrifugation from nutrient residues at 5000 rpm twice in distilled water. Next, the cells of the protozoa and bacteria were incubated with different concentrations of the NP solutions for 1, 3, 6, and 24 hours in a ratio of 1: 1 by volume with subsequent sowing of *S. aureus* bacteria on nutrient medium in Petri dishes and counting colonies after one day of cultivation at 37°C until visual detection of culture growth or counting the amount of *S. mytilus* after a certain exposure time using a MBS-10 microscope.

The evaluation of the biotest result in the presence of NPs was determined by the cell death reaction after a certain period of time, expressed as a percentage relative to the number of cells before the contact. It was shown that the toxic effect increased with an increasing of contact time and concentration of NPs (Table 1).

In general, CuZn (mixture) NPs had a greater cytotoxicity compared to CuZn (alloy), which indicates their dependence on the production technology, despite the similar chemical composition. The FeCo nanoparticles in the biotest with *S. mytilus* demonstrated lower, and

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with *S. aureus* - higher cytotoxicity in comparison with CuZn NPs. Derivative of (C60)-fullerene provided a greater toxic effect concerning to the protozoa cells comparing to bacterial cells.

Table 1 - Survival of *S. mytilus* / *S. aureus* in contact with nanoparticles

NP	Concentration, mg/ml	Survival,% after n, hours			
		1	3	6	24
Control	0	100 / 99	100 / 74	90 / 66	80 / 65
CuZn (alloy)	0,005	85 / 94	75 / 65	75 / 41	70 / 10
	0,05	75 / 65	75 / 47	70 / 10	60 / 3
	0,5	85 / 30	80 / 25	75 / 6	65 / 3
	5	70 / 11	60 / 6	50 / 3	45 / 1
CuZn (mixture)	0,005	75 / 84	75 / 62	70 / 49	50 / 25
	0,05	60 / 14	60 / 4	25 / 0	10 / 0
	0,5	35 / 5	25 / 3	0 / 0	0 / 0
	5	0 / 2	0 / 2	0 / 1	0 / 0
FeCo	0,005	80 / 46	70 / 35	65 / 18	50 / 16
	0,05	70 / 22	70 / 19	65 / 9	50 / 2
	0,5	70 / 15	60 / 8	55 / 3	40 / 1
	5	65 / 8	60 / 4	50 / 2	40 / 0
(C60)-fullerene KV253 derivative	0,005	75 / 97	75 / 71	70 / 48	55 / 22
	0,05	65 / 87	60 / 46	50 / 25	40 / 13
	0,5	65 / 59	55 / 31	50 / 21	35 / 10
	5	0 / 43	0 / 18	0 / 3	0 / 0

The safety of nanomaterials and nanotechnologies is the most important factor governing their industrial production and implementation. So the experiments show that specific biosensors (*S. mytilus* and *S. aureus*) are very sensitive to the toxic effects of nanoparticles and can play a key role in standardizing the ecotoxicity of nanomaterials, which will provide valuable information in the shortest possible time.

**Acknowledgement.** The authors would like to express appreciation to Dr. Sizova E.A. and Dr. Troshin A.P. for nanomaterials kindly providing.

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## Sorbents for Pharmacology

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*Key words:* carriers, sorbents, modifiers, carbon, porous structure, toxicology

*Motivation and Aim.* Carbon modification of the mineral carrier-aluminum oxide with different porous structure allows to form a hydrophilic-hydrophobic surface compatible with biological tissues and sanitize the body from toxic agents of different nature and size parameters using hemosorption (through blood), enterosorption (per os), application sorption (impact on damaged skin) [1].

*Methods.* Methods for assessing the physicochemical properties of carbon-modified sorbents included x-ray phase analysis, electron microscopy, porous structure studies, and spectrophotometry. Studies on the biological properties and efficacy of carbon-modified sorbents were carried out in animal model experiments using histological, biochemical, immunological and physiological methods in accordance with standard methods

*Results.* Carbon-modified aluminum oxide is a well-loose black crystalline powder with a particle size of 0.1-1 mm, with a predominant pore size of up to 100 nm, at a specific surface area of up to 200m<sup>2</sup>/g, with a hydrophilic-hydrophobic nature of the surface, non-toxic, compatible with biotissues, with sufficient sorption activity on the methylene blue marker up to 30 mg / g, characterized by high antibacterial activity. Biological properties were investigated with enterosorption, hemosorption and application of sorption in model experiments on animals (peritonitis, festering wounds, thermal burns of III degree, acute aseptic inflammation in the uterus, osteomyelitis, model, crush syndrome, poisoning with toxins, etc.). The results confirming high efficiency and necessity of inclusion of the modified sorbent in a complex of preventive and medical measures are received.

*Conclusion.* Technological methods of carbon modification of the surface of aluminum oxide of a certain structure allow to obtain a highly effective safe carbon-mineral sorbent for practical health care.

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## Mouse Core Body Temperature Decrease after Intranasal Injection of Iron Oxide Nanoparticles

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Most studies support the concept that the CNS may be an important target organ for nanoparticle extrapulmonary translocation after respiratory exposure. Certain nanomaterials of organic or inorganic nature, as well as some viruses, were shown to be capable of accumulating in cells of nasal epithelium with consequent translocation into the brain bypassing blood-brain barrier (BBB). For example, nanoparticles (NP), such as carbon, gold, metal (manganese, iron, titanium) oxides, etc., could reach deep brain structures after administration into the nasal cavity where they through oxidative stress can induced neuroinflammation. Earlier it was shown that submicron particles are able to induce local oxidative stress and inflammatory responses in human nasal epithelial cells, thereby leading to nasal inflammatory diseases. Thus, inflammatory response is proposed as the main outcome of contact of mammalian respiratory system with nanomaterials. The present study investigated the size-dependent acute hypothermic response of mouse to intranasal installation of ultrasmall (US) or nano-sized (NS) Fe<sub>3</sub>O<sub>4</sub> particles (8 nm and 30 nm). Using male Balb/c mice we have shown that the application of US- Fe<sub>3</sub>O<sub>4</sub> (5 µl in each nostrils, total dose - 3 mg/kg) into nasal cavity in contrast to NS- Fe<sub>3</sub>O<sub>4</sub> provoked core body temperature decrease ( $\Delta t_{body} = -4.2 \pm 0.8^\circ\text{C}$ ), which starting 5 min after particle exposure and reaching a minimum 30 min later. Nor intravenous neither per oral installation of US- Fe<sub>3</sub>O<sub>4</sub> had any effect on the mouse body temperature. During first 30 min after US- Fe<sub>3</sub>O<sub>4</sub> injection in nasal cavity 3D magnetic resonance imaging reveals significant accumulation of US-Fe<sub>3</sub>O<sub>4</sub> in nasal epithelium, but not in CNS. This indicates the prevalent role of the cells of mouse nasal epithelium in induction of hypothermic response to intranasal installation of US- Fe<sub>3</sub>O<sub>4</sub>. The phenomenon were mediated through the trigeminal innervation of the nasal mucosa since hypothermic effect of US- Fe<sub>3</sub>O<sub>4</sub> could be blocked when the anesthetic procaine was preliminary applied to the nasal cavity. Intranasal injection of mannitol hypertonic solution, known to reduce tissue edema, has also significantly attenuated mouse core body decrease ( $\Delta t_{body} = -1.1 \pm 0.6^\circ\text{C}$ ) compared to vehicle ( $\Delta t_{body} = -4.5 \pm 0.4^\circ\text{C}$ ). This suggests the trigeminal nerve activation upon US- Fe<sub>3</sub>O<sub>4</sub>-induced nasal epithelium cell swelling confirmed using TEM. Water movement into the terminals of trigeminal neurons after US- Fe<sub>3</sub>O<sub>4</sub> exposure was inhibited by DIDS (4,4'-Diisothiocyano-2,2'-stilbenedisulfonic acid), HCO<sub>3</sub><sup>-</sup>/Cl<sup>-</sup> exchanger inhibitor, tetrodotoxin, sodium voltage-dependent channels inhibitor, but not by EDTA, extracellular Ca<sup>2+</sup>-chelator. All the findings suggest size-sensitive manners of nano- and ultrasmall-sized Fe<sub>3</sub>O<sub>4</sub> particles-



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induced trigeminal nerve-dependent hypothermic response. Understanding the ways and mechanisms of such interaction between nanomaterials and organism opens up new approaches to the diagnosis and therapy of neuro-infectious and neurological diseases.

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research, grant 18-04-00472.

## Nanocomposites Based on Sodium Silicates and Boron Cluster Anions [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup>, [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup>, [B<sub>10</sub>Cl<sub>10</sub>]<sup>2-</sup>

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Boron cluster anions [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup>, [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> and [B<sub>10</sub>Cl<sub>10</sub>]<sup>2-</sup> have been used as precursors to form supramolecular structures by the interaction between polyhedral anions and silanol groups of silicates of sodium liquid glass (LG) taken. To modify silicates we used water-soluble triethylammonium salts of boron cluster anions [Et<sub>3</sub>NH]<sub>2</sub>[An] (where An = [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup>, [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> or [B<sub>10</sub>Cl<sub>10</sub>]<sup>2-</sup>), the content of which in the initial compositions with LG was 2–60 wt%. The reaction between (Et<sub>3</sub>NH)<sub>2</sub>[An] and sodium silicates in the presence of NaOH which is contained in LG is accompanied by the replacement of the [Et<sub>3</sub>NH]<sup>+</sup> cations with Na<sup>+</sup> because of the release of triethylamine.

We believe that the [An]<sup>2-</sup> form spatially-branched supramolecular three-dimensional structures due to specific multicenter contacts with silicates (B–H<sup>δ-</sup>...H<sup>δ+</sup>–O–Si, B–Cl<sup>δ-</sup>...H<sup>δ+</sup>–O–Si). The supramolecular structures formed in the silicate matrix in the presence of small additives of boron cluster anions appear to be supramolecular associates, in which boron polyhedral anions function as crosslinking agents for reactive silicates, which are in excess. The strength of intermolecular anion interactions decreases in a number of [B<sub>10</sub>Cl<sub>10</sub>]<sup>2-</sup> > [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> > [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup>. The difference in the number and strength of intermolecular interactions has a direct effect on the formation of supramolecular structures in the silicate matrix, which are distributed in it as associates. We can dimensions of associates formed in the silicate matrix with those of true nanoparticles.

The structuring degree in the LG/[An] system increases with the increasing content of the modifier (Et<sub>3</sub>NH)<sub>2</sub>[An]. Thus, with increasing modifier content of 30% and higher spatially branched network structure can be formed with knots being supramolecular nanostructures built of the boron cluster anions. Such composites have increased deformation resistance, the values of dL/L<sub>0</sub> remain unchanged up to 600°C. Composites of this type are promising for the development of materials with neutron-protective properties.

**Acknowledgement.** This work was supported by the Presidium of the Russian Academy of Sciences through the basic research program no. 35: Scientific Principles of Producing Novel Functional Materials.

## Synthesis of Hydrophobic Materials Based on Oxide Nanostructures

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Superhydrophobic materials are currently of interest for research. Due to their unique properties, they find wide application in different fields of science and technology. These coatings can be applied to any surface, and this is one of the features that made them attractive [1, 2].

Oxide nanoscale materials have great potential because they can be used to obtain an anisotropic rough structure. The roughness of materials is explained by the presence of certain geometry, called «nanoformation», which have a spherical, hexagonal, flake-like, needle shape [3, 4].

The Sol-gel method and electrochemical deposition are promising methods for hydrophobic nanoscale materials producing. This paper presents the results of the synthesis of ZnO, SiO<sub>2</sub> and TiO<sub>2</sub> samples by the sol-gel method.

The composition, size, structure, and properties of the obtained samples were studied by the sessile drop method, dynamic light scattering spectroscopy on the PhotocorComplex setup, X-ray diffraction on the Epyrean 2, scanning electron microscopy (SEM) method on the MIRA-LMH scanning electron microscope with the system of the elemental composition determination AZtecEnergy Standart / X-max 20 (standard) by Tescan.

According to the results of the study by the sessile drop method, it was found that the contact wetting angle of the obtained samples at the interface «liquid» - «solid» was more than 120°. Therefore, this material belongs to the superhydrophobic materials.

At the next stage, the ZnO, SiO<sub>2</sub> and TiO<sub>2</sub> coatings microstructure was studied. Analysis of the images obtained showed that the surface of these samples has a specific roughness due to the particular geometry of the nanostructures.

**Acknowledgement.** This work was supported by the Federal state budgetary institution "Fund for assistance to the development of small enterprises in the scientific and technical sphere", contract 13693GU/2018.

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**Research and Comparative Evaluation of Cell-Phagocytic Activity of the Respiratory Tract in Bronchoalveolar Lavage after Intratracheal Instillation of Nanodispersed Magnesium Oxide**

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Over the past decade, nanomaterials have been actively introduced into various fields of human activity [1]. One of the most widely used nanomaterials is magnesium oxide nanoparticles (MgO). This product of nanoindustry is used in the food industry [2], in medicine, pharmacology, chemical industry, metallurgy and electronics [3]. It is known that MgO nanoparticles are able to generate reactive oxygen species (ROS) [4], to cause lethal changes in cells [5], to accumulate in various organs, leading to pathological changes [6], affect the proteomic and metabolic profiles [7]. They show genotoxicity [5, 6], embryotoxicity [8] and allergenicity [9].

In connection with the widespread occurrence and the available data on the toxicity of MgO nanoparticles, the research aimed at studying the effect of this material on the human body in various routes of intake is becoming more relevant.

The purpose of this work is to study and compare the cellular and phagocytic activity of the respiratory tract in bronchoalveolar lavage after intratracheal instillation of nanodispersed MgO.

Nanodispersed MgO powder of Sigma-Aldrich (USA) production was used for experimental studies. Microdisperse MgO powder was used for comparative analysis. The MgO particle size was estimated using scanning electron microscopy, and the specific surface area of the particles was studied and estimated using the Brunauer, Emmett, and Taylor method. The experiment was performed on the Wistar line white rats weighing 250-300 g. Experimental animals (n = 15) were divided into 3 groups of 5 individuals: the experimental group was exposed to an aqueous suspension of nanodispersed MgO, comparison group - the exposure of an aqueous suspension of microdispersed MgO, the control group was injected with a solvent (distilled water). The concentration of aqueous suspensions of nano- and microdispersed MgO was 0.013 g / cm<sup>3</sup>. Aqueous suspensions were injected in a volume of 0.4 cm<sup>3</sup> per rat; animals in the control group received a solvent in the same volume. 24 hours after instillation, bronchoalveolar lavage was performed. The number of segmented neutrophils (PMNs), monocytes (MO), lymphocytes (LY) and alveolar macrophages (AM) was counted in the selected substrate. Obtained results processing was performed using parametric statistical methods using Student's t-test.

It was established that the MgO study sample contains predominantly nanoparticles with a size of 5–100 nm (71.9% of the total number of particles), which is 50–200 times less than the

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value of a microdisperse analogue (1–5  $\mu\text{m}$ ). The specific surface area of the nanoparticles was  $64.5 \text{ m}^2 / \text{g}$ , which is 9.8 times larger than the value of the microdisperse analogue ( $6.6 \text{ m}^2 / \text{g}$ ).

In the washing waters of the experimental group animals lungs, an increase in the number of PMNs relative to the comparison and control groups was found to be 3.08 times ( $p = 0.0001$ ) and 1.82 times ( $p = 0.002$ ), respectively, and AM relative to the control group, 7.09 times ( $p = 0.0001$ ). In addition, the experimental group animals showed a decrease in MO level relative to the comparison and control groups by 4.50 times ( $p = 0.0001$ ) and 9.33 times ( $p = 0.0001$ ), respectively, LY by 2.91 times ( $p = 0.0001$ ) and 2.83 times ( $p = 0.0001$ ), respectively. The identified changes in the respiratory tract cellular activity are probably due to the inflammatory process caused by the ROS activity induced by MgO nanoparticles [10].

Thus, in terms of the particles size and specific surface area, it has been established that the MgO study sample is a nanomaterial. With water suspension of nanodispersed MgO intratracheal instillation in animals bronchoalveolar washout from the experimental group, the development of a pronounced inflammatory reaction of neutrophilic nature and a sharp decrease in cellular immunity (decrease in lymphocytic monocytic activity), relative to microdispersed MgO was found. The results obtained make it possible to increase the effectiveness of substantiating preventive measures for workers and population, who are exposed to MgO nanoparticles in the production process and products consumption.

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## Surface Nanostructuring of Porous Titanium Sponge Sintered Powders by Means of Anodization

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Currently titanium and its alloys are the most widely used implant materials primarily due to their high biocompatibility, low linear expansion coefficient and absence of toxic effects. Solid titanium implants have been used successfully in orthopedics and traumatology, but unstable anchorage and poor osseointegration compromise their suitability for replacing lost bone tissue. These issues can be circumvented by using implants made of porous Ti, as their structure and physical mechanical properties are similar to those of bone tissue.

Porous powder materials (PPMs) produced from a Ti sponge by applying powder metallurgy methods exhibit a range of unique physical-chemical and biochemical properties, e.g., antibacterial and faster osseointegration. These unique characteristics of compacted titanium sponge arise primarily from the surface structure of powder particles.

A number of studies were dedicated to the formation of bioactive nanotubular oxide coatings on the surface of Ti and porous Ti scaffolds. To the best of our knowledge, there was no reports in the literature concerning the creation of self-organized nanotubular or nanoporous oxide layers on the surface of sintered Ti sponge powder by anodization. Here we prepare and study nanostructured anodic oxide films (AOFs) formed on the surface of sintered titanium sponge powders.

For this study, we used PPM of sponge powder of technical grade Ti with particle sizes in the range of 0.63–1.00 mm. The specific surface area of our specimens was 1350 cm<sup>2</sup>/g. Anodization was performed in an aqueous electrolyte, H<sub>2</sub>SO<sub>4</sub> (10%) and HF (0.15%). Detailed description of the anodization process can be found in [1, 2]. The surface morphology of our specimens was characterized by atomic force microscopy (AFM) and by scanning electron microscopy (SEM). The atomic structure of the specimens was analyzed by X-ray diffraction. Optimal conditions ( $U_a = 15$  V,  $t_a = 60$  min,  $T = 293$  K) for anodization conducive to the formation of a nanostructured oxide layer were established empirically by varying the process parameters and analyzing the recorded data, i.e.,  $j_a(t)$  and  $U_a(t)$  transients.

SEM & AFM imaging of the surface of PPM specimens showed that the constituent microparticles had a developed morphological structure typical of a Ti sponge. After anodizing along with the regions having a regular pattern of pore arrangement, we can see regions consisting of the tubular structure. We establish that anodization of sintered powder of a Ti sponge in an electrolyte H<sub>2</sub>SO<sub>4</sub> (10%) and HF (0.15%) under optimal conditions yields an X-ray amorphous TiO<sub>2</sub> film with a thickness of 250–350 nm and a regular pattern of nanopores and nanotubes with diameters of 30 to 70 nm. Thus, using electrochemical anodization in a

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fluoride-containing water electrolyte enabled us to modify the surface of PPM of a titanium sponge to form a bioactive nanoporous/nanotubular oxide film that ensured hydrophilicity and corrosion resistance of the surface.

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## Priority Directions of Toxicological Research and Hygienic Assessment of Nanomaterials in the Republic of Belarus

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Nanotechnologies are the one of basic directions of the scientific and technical development of the Republic of Belarus. Scientists of the National Academy of Sciences of Belarus have developed «Concept for the development of nanotechnology and nanomaterials». The Republican Association of Nanoindustry is successfully developing, which combines about thirty enterprises.

Nanoparticles and nanomaterials (NP and NM) are actively used in microelectronics, power engineering, construction, chemical and perfume and cosmetics industries, medicine and biology, agriculture, and also some other areas. Such intensive production and widespread use of new in their properties and biological effect nanoparticles and materials requires tackling a number of medical and biological problems. The most important issues are the study of patterns of biological effects manifestations of nanoparticles depending on their chemical nature, shape, size, surface area, charge and other physicochemical features of the structure, as well as dose, route of entry, concentration in target organs and duration of action.

In order to address the issues of hygienic safety, it is necessary to improve existing and develop new methods for studying the toxicity and danger of NPs and NM, taking into account their unique physical and chemical properties and modern international requirements. Research methods should be consistent with the concept of an "integrated research strategy" and be based on *in vivo* and *in vitro* studies. According to this experimental model, the main toxicological studies are carried out on warm-blooded organisms, but in order to limit animal testing, it is constantly necessary to search and implement alternative methods and test systems. The main objective of NM research is to study the systemic toxic effect on the body and specific (selective) effects on individual organs and tissues, as well as long-term effects.

To achieve success in the field of hygienic safety and risk assessment in the production and application of NP (NM) requires focus on solving the following problems:

- development of uniform criteria for the hazard of NP (NM) and methods for their determination/control;
- justification of safe levels of NP (NM) content in the habitat and production facilities;
- classification of NM by hazard classes in accordance with the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) and preparation of NM safety data sheets according to generally accepted rules for chemical products;



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- development and implementation of accurate and informative instruments for determining and controlling NP (NM) in practice;
- assessment of the impact of NP (NM) on the health status of workers and population, identification of risk groups.

Currently, the Republican unitary enterprise "Scientific practical centre of hygiene" is carrying out research on the features of biological action and specific (mutagenicity, carcinogenicity, genotoxicity) toxic effects of nanomaterials based on metals (the research is funded by the state and carried out within the framework of the industry scientific and technical program "Hygienic safety", 2019-2023). It is planned that the results of scientific research will contribute to the solution of the urgent problems of hygienic safety listed in the publication in the production and use of NPs (NM) and will minimize the risk of adverse effects on human health due to the development of nanotechnology.

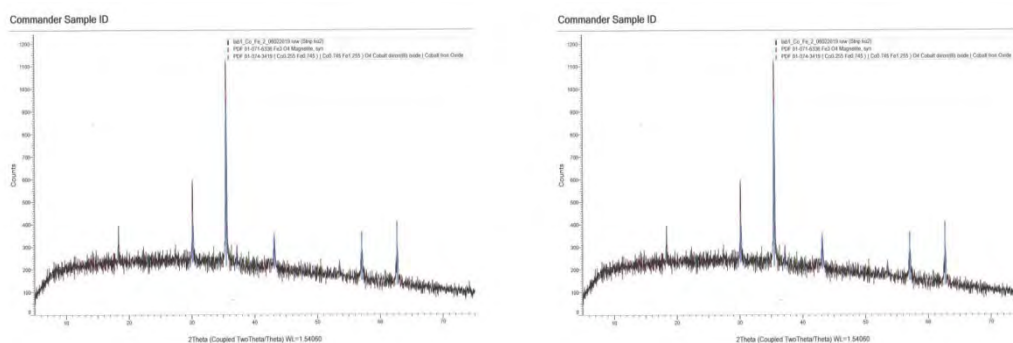
## Synthesis and Study of Cobalt Ferrite in the Reaction of Carbon Monoxide Oxidation

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Manganese, copper-chromium and platinum-containing catalysts are used to oxidize carbon monoxide. In recent years, more and more works on the oxidation of carbon monoxide on ferrite catalysts have appeared in the scientific literature to testify prospects of this trend.

Cobalt ferrite was synthesized by sol-gel technology with combustion. Salts of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and organic reagent were used as precursors. Aqueous solutions of the calculated amounts of salts and organic reagent used as citric acid were stirred on a magnetic stirrer heated for 1 hour. Then they were heated in a drying cabinet, and at a temperature of 130-1500C spontaneous combustion occurred. Further heat treatment of the formed powder was carried out in an EM-G5593V microwave oven (Panasonic) with a resonator volume of 25 l and varying magnetron power 300-800 W with an operating frequency of 2450 MHz. X-ray phase analysis of the products was carried out on automatic diffractometer "D 2Phazer" by Bruker. Note that the size and shapes of the microcrystallites of the synthesized samples were examined on a Hitachi TM3000 scanning electron microscope (Japan).

X-ray phase analysis showed that following the results of the synthesis by the sol-gel method with combustion compound  $(\text{Co}_{0.255} \text{Fe}_{0.745}) (\text{Co}_{0.745} \text{Fe}_{1.255}) \text{O}_4$  is formed (Fig. 1 a). After microwave treatment obtained sample composition does not change, however, the crystallinity increases (Fig. 1b).

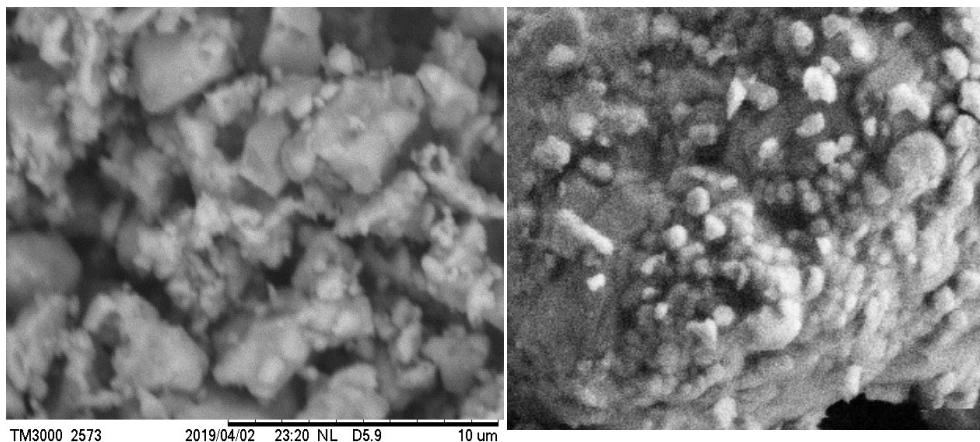


**Fig. 1.** Diffractograms  $(\text{Co}_{0.255} \text{Fe}_{0.745}) (\text{Co}_{0.745} \text{Fe}_{1.255}) \text{O}_4$  obtained by the sol-gel method with combustion (a) and subsequent microwave treatment (b)

Micrographs taken on a scanning electron microscope testify to the phase heterogeneity of the synthesized sample. Sizes of crystallites vary from hundreds of nanometers to tens of

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micrometers although at higher magnification microcrystals of smaller size (within tens of nm) can be observed on the surface of these aggregates (Fig. 2 a, b).



**Fig. 2.** Electron microscopic image of the sample  $(\text{Co}_{0.255} \text{Fe}_{0.745}) (\text{Co}_{0.745} \text{Fe}_{1.255}) \text{O}_4$  after exposure to microwave radiation 800 W., at 10 min. exposure

Experiments in CO oxidation were conducted in a flow apparatus with a fixed bed of catalyst with a ratio of CO: O<sub>2</sub> = 1: (0.4; 0.6; 1: 0.8) in the temperature range 200-250 °C. Chromatographic analysis was performed on CaA zeolite. Samples were pre-mixed with alumina as a binder (active mass was 0.8 grams) dried in air and calcined at 400 °C.

The results of the experiments showed that the conversion of CO to carbon dioxide reaches 35–37% at 200 °C and 80% at 250 °C.

## Perovskites $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$ New Inorganic Antibacterial Materials

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Prevention of infectious diseases through control of pathogenic microorganisms has been a major challenge across the globe. The need for hygienic living conditions prompts new challenges for the development of affordable and efficacious antimicrobial materials that should be environmentally friendly and absolutely non-toxic towards human beings.

Compared to organic hybrid antibacterial materials, fully inorganic antibacterial materials may offer several advantages, such as long-lasting action, stability (chemical, thermal, mechanical), simplified manufacturing and storage characteristics.

The majority of research and interest in the antimicrobial properties of inorganic materials regards their use as antimicrobial coatings of the surfaces of various devices to eliminate survival of microorganisms on surfaces in the environment, community and health care settings that will eventually stop the spread of the diseases.

This is precisely why at the present time searching of the new, stable and effective inorganic antibacterial materials is in progress. Understanding of the key factors influencing on the antiinfective properties and toxicity for humans has fundamental importance for development of effective microbicide.

Whereas full-scale study of complex oxides with perovskite structure was performed in different fields of science, investigation of their antibacterial activity has been started less the 10 years ago. Several publications are available where following perovskites were tested for antibacterial activity:  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  /  $(\text{La}_{0.5}\text{Eu}_{0.5})_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ,  $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ,  $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ,  $\text{LaCo}_x\text{Fe}_{1-x}\text{O}_3$ ,  $\text{CaFe}_x\text{Mn}_{1-x}\text{O}_{3-\delta}$ ,  $\text{BaFe}_x\text{Mn}_{1-x}\text{O}_{3-\delta}$  and  $\text{CaTiO}_3$ . Promising results obtained shows great potential of using oxides with perovskite structure as bactericides for different applications. Minimal inhibition concentration was in the range 3-300  $\mu\text{g}/\text{ml}$ . Investigations were performed both on gram-positive and gram-negative bacteria.

In this paper, we evaluated the antibacterial activity of complex oxides with the perovskite structure  $\text{GdCo}_{1-x}\text{Fe}_x\text{O}_3$  ( $x=0; 0,2, 0,5, 0,8; 1$ ) using gram-positive bacteria as an example - *Escherichia coli* by two methods diffusion method for agar (inhibition zone test) and Shake-Flask method). The minimum inhibitory concentrations (MIC) were determined.

**Acknowledgement.** This work was supported by the Russian Foundation for Basic Research, grant № 18-33-01209.

Scientific researches were performed at the Center for X-ray Diffraction Methods and Nanotechnology, Center for Studies in Surface Science, Center for Thermogravimetric and Calorimetric Research, Resource center Cultivation of microorganisms of Research park of St. Petersburg State University.

## New Approach in Use of Accelerator Mass Spectrometry in Biology

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Accelerator mass spectrometry (AMS) is an extremely sensitive method that can detect the amount of radioactive carbon in biological samples at early clinical or experimental researches. Currently, AMS undergoes rapid development contributing to the emergence of new methods for bioanalytical tracing. The efficiency of AMS is achieved due to the high sensitivity of the instrument, speed of analysis, and versatility of application for the study of various chemical compounds. The development of a new diagnosis method using accelerator mass spectrometry will allow studying virus-cell interactions on the example of pandemic influenza virus A(H1N1)pdm09 with the introduced label of radiocarbon. The technology based on the binding of radiocarbon-labeled substances (carbamide and/or methanol) and carboxyl groups of influenza virus proteins. This process affects only carbon in free carboxylic groups and is not accompanied by a significant change in the structure of the molecule. The reaction takes place in an aqueous medium in the presence of EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) used for binding to a carboxyl group. The reaction conditions prevent the hydrolysis of peptide bonds. This work considers a special case of technology application for obtaining isotopically labeled standards of viral peptides and proteins. Enrichment of the virus-containing liquid with isotope  $^{14}\text{C}$  will allow us to carry out an ultra-precise analysis of the number of penetrated viral particles into the lungs of experimentally infected mammals. The proposed new method of diagnosis of virus-cell interaction is suitable for quantitative and qualitative analysis not only for study viruses, but also for virtually any peptides and proteins containing at least one COOH-group. This method will help to study in-depth the virus-cell interaction and the mechanism of development of high-lethal infection. Due to the fact that the circulation of influenza A(H1N1)pdm09 virus, which caused the pandemic worldwide in 2009, still occurs the study of the mechanisms of pathogenesis of influenza viruses with pandemic potential remains extremely relevant.

**Acknowledgement.** This work was supported by the foundation for Presidium of the SB RAS AAAA-A18-118033090074-0.

## State-of-the-Art in Characterization of Alumina Porous Structure

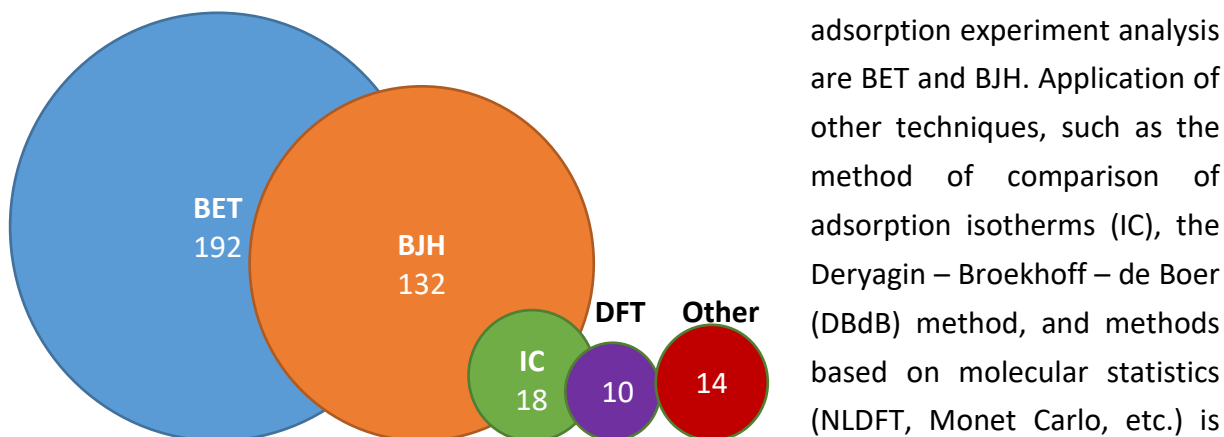
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Traditionally, porous structure of aluminum oxides is characterized by means of nitrogen adsorption at ca. 77.4K. We surfed about 200 publications dating 2018 that are devoted to characterization of alumina, and found (see Figure) that the most widespread methods of

adsorption experiment analysis are BET and BJH. Application of other techniques, such as the method of comparison of adsorption isotherms (IC), the Deryagin – Broekhoff – de Boer (DBdB) method, and methods based on molecular statistics (NLDFT, Monet Carlo, etc.) is less common. Most probably, this is due to usually observed uncertainty of the obtained results. E.g., the values of the specific surface area, which are calculated with all mentioned methods can vary in some cases within 50% error, that is not suitable for proper analysis of other characteristics, such as catalytic activity, porosity evolution during preparation, processing, ageing, deactivation, etc.

Upon our knowledge, the problem can be solved by proper accounting of surface adsorption potential, which in general depends on density of adsorbent, which can vary in the case of alumina from 109 at/nm<sup>3</sup> for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to 118 at/nm<sup>3</sup> corundum. The known variants of BJH, DBdB, and NLDFT-based methods are parameterized with adsorption on amorphous silica surface, which solid density is about 63 at/nm<sup>3</sup>. The second source of deviation is the model of the flat surface. For some materials the surface roughness aspires 50%. In particular cases it can be estimated by means of Connolly algorithms. Both factors yield with a correction coefficient to the reference adsorption values, used in all methods, except BET. Proper accounting of this coefficient reduces the deviations to acceptable 10%. In our presentation we demonstrate this on several particular examples.

**Acknowledgement.** This work is supported by Ministry of Science and Higher Education of the Russian Federation (project AAAA-A17-117041710079-8).



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## Scientific edition

III International School-Conference  
Applied Nanotechnology and Nanotoxicology (ANT-2019)  
October 10-13, 2019 Sochi, Russia

Abstracts Editors:  
Dr. A.A. Vedyagin, Dr. M.S. Mel'gunov

Compiled by: Svetlana Logunova  
Computer processing of text: Yulia Klimova, Aleksey Spiridonov

## Научное издание

III Международная школа-конференция  
«Прикладные нанотехнологии и нанотоксикология» (ANT-2019)  
10-13 октября 2019 года, Сочи, Россия  
Сборник тезисов докладов  
Под общей редакцией: к.х.н. А.А. Ведягина, к.х.н.М.С. Мельгунова

Составители: С.С. Логунова  
Компьютерная обработка: Ю.В. Климова, А.А. Спиридонов

## Издатель:

Федеральное государственное бюджетное учреждение науки  
«Федеральный исследовательский центр «Институт катализа им. Г.К. Борескова  
Сибирского отделения Российской академии наук»  
630090, Новосибирск, пр-т Академика Лаврентьева, 5, ИК СО РАН  
<http://catalysis.ru> E-mail: [bic@catalysis.ru](mailto:bic@catalysis.ru) Тел.: +7 383 330-67-71

## Электронная версия:

Издательский отдел Института катализа СО РАН  
E-mail: [pub@catalysis.ru](mailto:pub@catalysis.ru) Тел.: +7 383 326-97-15

— Объем: 20 МБ. Подписано к размещению: 29.09.2019 —

Адрес размещения:

<http://catalysis.ru/resources/institute/Publishing/Report/2019/Abstracts-ANT-III-2019.pdf>

Системные требования: i486; Adobe® Reader® (чтение формата PDF)

ISBN 978-5-906376-26-8



<http://catalysis.ru/resources/institute/Publishing/Report/2019/Abstracts-ANT-III-2019.pdf>