3rd International School-Conference on Catalysis for Young Scientists

Catalyst Design

ABSTRACTS

Novosibirsk-2009

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Institute of Solid State Chemistry UB RAS, Russia
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3rd International School-Conference on Catalysis for Young Scientists “CATALYST DESIGN”

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ABSTRACTS

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PLENARY LECTURES

PL-1

TEMPLATING MECHANISMS OF CATALYSTS AND ADSORBENTS FORMATION

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There are several mechanisms of adsorbents and catalysts formation among which templating, which plays important role. Templating generally is a process of interaction between structure directing agent (template) and a source of material solid phase. Formation of template/solid phase hydride is usually followed by template removal that results in appearing of pores. Variety of directing agents includes metal cations, surfactants, macromolecules, hard templates. Different templates interact with source via a number forces, including ionic or dispersive interactions, hydrogen-bonding. One also has to distinct soft and hard templating mechanisms. The former involves frustration, when template and source significantly influence one another, the latter is proceeds without tuning of rigid template structure. Depending on template structure the resulting adsorbent or catalyst can have regular or irregular organization of porous space. Structure of resulting material can be ordered on atomic, supramolecular levels, or their combination.

Several examples of templating processes are considered in the lecture. Formation of micrporous zeolites is considered to be guided by small inorganic or organic cations. Several reasons of zeolites crystalline structure formation are formulated, including state of siliceous precursors, role of template, additive cations. Formation of mesoporous silicates and non-silicate materials using ionic or non-ionic surfactants as templates is discussed basing on a frustration principle. Formation of carbons and low-soluble metals or oxides by means of hard-templating mechanism is illustrated with examples of preparation of regular and non-regular materials.

Some examples of application of adsorbents and catalysts prepared via templating mechanisms are discussed. Advantages and disadvantages of templating are summarized.

CATALYSTS DESIGN FOR PRODUCTION OF CARBON NANOTUIBES AND NANOWHISKERS

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Nanowires, nanowhiskers, filaments and nanotubes of different materials are the most important elements of fast developed nanotechnologies. Despite the difference of the structure of these products their formation mechanisms on surface of metal catalysts include some common steps. Thus vapor–liquid–solid (VLS) and the vapor–solid–solid (VSS) mechanisms are widely used to describe the main steps of the 1D nanowire/nanowhisker/nanorod/ nanotube growth. The key feature of VLS growth mechanism is the liquid state of the metal alloy tip during the nanowire growth, which occurs by the formation of a eutectic alloy. Once the alloy tip forms a eutectic, any excess material that is adsorbed from the vapor precipitates out in the form of a nanowire or other 1D material. The VSS mechanism may be realized when the metal alloy tip is supposedly in solid state during the nanowire growth, unlike the VLS mechanism.

In this paper the mechanisms of carbon nanotube and filamentous carbon formation are considered using unified approach based on “metals-carbon” phase diagram analysis and classic nucleation theory. Thus a thermodynamic analysis of the carbon nucleation on the metal surface leads to the master equation for the dependence of critical radius of the carbon nucleus on the reaction parameters, such as the reaction temperature, metal-carbon bond energy, the work of adhesion of the graphite-metal system, the supersaturation degree of catalyst particle by carbon. This equation and the phase diagram approach were used for discussion of scenarios of different carbon deposit formation. Possibilities to increase the yield and selectivity of carbon nanotubes production are discussed in terms of optimization of catalyst composition and optimization of reaction conditions.

It was found that the same approach can be used for the description of the nucleation of BN nanotubes (BNNT) and SiC whiskers. Thus the formation mechanisms of carbon deposits, BNNT and silicon carbide whiskers on metal surface catalysts have some common features. The most important are: (1) the formation of metal particle alloys oversaturated with atoms of forming deposit and (2) the nucleation of corresponding deposits on the metal catalyst surface. The master equations for the dependence of critical radius of BNNT or SiC nucleus on reaction parameters, such as reaction temperature, supersaturation degree of catalyst particles with atoms of deposited compounds, work of adhesion of metal to corresponding atoms (B and N; Si and C), were obtained. These equations combined with the phase diagram approach can be used for the description of different scenarios of BNNT and SiC deposits formation and for the development of the main principles of catalyst and promoters design.

Theoretical results are compared with experimental data.

APPLICATION OF SURFACE SCIENCE METHOD FOR IN SITU STUDING OF HETEROGENEOUS CATALYTIC REACTIONS

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Atomic-level understanding of catalytic processes on surfaces under reaction conditions remains a formidable task for modern surface science. Significant progress in this area was made in the 20th century, when the great number of surface analytical techniques was developed. The first surface science techniques such as LEED, AES, TDS, HREELS, IRAS allowing the investigation of solid surface on the atomic level became commercially available in the early 1970s. The use of these techniques led to an increasing interest to study of well-defined catalyst surfaces, notably a flat surface of single crystals under ultra-high vacuum conditions (UHV). Vast number of works devoted to the study of surface reconstruction, chemisorption, adsorbate-adsorbate interactions, surface diffusion, desorption, and the simplest heterogeneous catalytic reactions appeared over the next three decades. In fact, the results of these UHV/single-crystal studies provided fundamental understanding of the relationships between atomic-level structure and composition of a catalyst surface with its catalytic activity for a number of catalytic systems.

Certainly, the conditions under which most typical surface analytical techniques can be applied are highly idealized. The ultra-high vacuum required for the surface science studies were typically 10 orders of magnitude below than typical pressures used in real technological catalysis. At first, to overcome this pressure gap problem, experimental systems was developed that combined an elevated pressure reactor with an UHV surface analysis chamber. In this case, the catalytic performance of model catalysts can be measured using the elevated pressure reactor, while analysis of the structure and composition of the surface both before and after reaction can be accomplished in the UHV analysis chamber. The main advantage of such experimental systems was that the catalyst can be transferred between the elevated pressure reactor and the UHV analysis chamber rather quickly without intermediate exposure to air or other gases. This approach dominated in the 1990s and designates as ex situ study.

Unfortunately, all catalytic systems are very dynamic and the structure and composition of catalyst surfaces depends very strongly on reaction conditions. For example, the equilibrium with the gas phase at elevated temperatures may lead to surface coverages and adsorbate structures that cannot be observed under typical UHV conditions. High pressures may also produce weakly bonded species, which are absent in UHV. In addition, surface compositions in UHV may differ substantially from the real catalyst conditions and processes that are simply too slow in UHV may become significant at high pressure. It means that the active state of a catalyst exists only during proceeding of the catalytic reactions and can be «killed» by UHV. Correspondingly, the investigation of really «living» catalysts should be performed under working conditions, i.e., while the catalysis takes place. Moreover, it is essentially to combine the spectroscopic characterization of a catalyst surface with simultaneous monitoring of its catalytic performance by on-line mass spectrometry or gas chromatography. Such approach which is developed for the last several years is usually designated as in situ surface science studies [1-4].

Following this tendency, in the 21th century researchers have developed a number of novel surface-sensitive physical methods and have modified existing ones for in situ measurements at elevated pressures. Among them are X-ray photoelectron spectroscopy [1,2,4], near edge X-ray absorption fine structure (NEXAFS) spectroscopy, scanning tunneling microscopy, polarization-modulated infrared reflection absorption spectroscopy and sum frequency generation (SFG) spectroscopy [1,3]. In this contribution we demonstrate novel potentialities of the surface science techniques when they are applied for investigation of the mechanisms of heterogeneous catalytic reactions at elevated pressure in situ, i.e., while the catalysis takes place. The investigations of CO adsorption on Pd, methanol decomposition and oxidation over Pd(111) and Pt(111), methanol oxidation over V_2O_5/TiO_2 oxide catalyst, ethylene epoxidation over Ag as well as propane oxidation over Ni in self-oscillation regime are among the examples of in situ studies.

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PL-4

THE ROLE OF MATHEMATICAL MODELING IN THE DESIGN OF CATALYTIC PROCESSES AND REACTORS

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It is impossible to imaging contemporary science, technology and many other fields of creative activity apart from mathematical modeling [1]. The essence of this methodology is changing of real object by its mathematical "image" and studying of this image with the help of computational methods by computers. The work with not real object, but with its mathematical "image" gives us the possibility to investigate its properties and behavior relatively rapidly and without significant costs, deeply and in details in any real and unreal conditions. The elements of mathematical modeling were used from the very outset of the appearance of exact sciences and it is not accidentally, that the some of computational methods were called in the names of such leading figures of science as Newton and Euler. New birth of mathematical modeling began in the middle of 20 century. It was caused by two reasons: appearance of the first computers and need of creation of nuclear-missile weapons, what could not be realized by traditional methods. Nuclear explosions and missile flights were previously realized using computers with the help of mathematical modeling and only then put into practice. At present none of large – scale technological project is seriously considered without using of mathematical modeling.

As applied to chemical technology M.G. Slinko made an important contribution to development of the methods of mathematical modeling [2]. Industrial catalytic processes are realized in the reactors of different types with fixed bed (adiabatic and tubular), with fluidized bed, with gas-liquid and solid catalyst. Mathematical formulation of chemical and physical processes in such reactors is correspondingly different. The base of the method of mathematical modeling is the idea of multilevel approach to construction of mathematical models of reactors, which includes division of complicated chemical technological process into chemical and physical constituents, separate studying of these processes and synthesis of total mathematical model from the models of individual parts of the process. The first level of the mathematical model of the reactor is the heat- and mass transfer processes in the porous catalyst particles. The kinetic model (dependences of reaction rates from reagent concentrations and temperature) is the component part of this level. The next level of the mathematical model of the reactor is the description of the heat- and mass transfer processes in the catalytic reactor. The apparent reaction rate is the constituent of this level. The apparent reaction rate is either calculated with the use of mathematical model of catalyst particle or experimentally found. Mathematical modeling allows to:

- Study the process with the purpose of prediction of the results of its passing;
- Analyse the stability of the reactor performance;
- In the presence of contingencies on input and output reactor characteristics, optimize the reactor performance and design. The production cost, the quality of products obtained, the aggregate capacity and investments are depending from the reactor performance;
- Reduce the period between laboratory studies and industrial conditions;

The ability to predict the behavior of chemical reactor under the change of the process parameters is the main criterion of mathematical model accuracy.

Several examples of the efficient using of the method of mathematical modeling in the design of catalytic processes and reactors are shown in the lecture.

A theoretical optimization of shaped catalyst dimensions with technologically imposed constraints is presented for operating conditions of a typical methanol reformer. A comprehensive two-dimensional mathematical model of a single reformer tube containing physically sound correlations for heat transfer parameters of holed catalyst particles is used. Three-hole pellet and Raschig rings were used as examples. A general conclusion is made that holed steam reforming catalyst should have maximum catalyst height and minimum diameter determined by requirements of uniform catalyst packing.

A numerical study of the partial oxidation of methane to synthesis gas in a monolith reactor with Pt/Ce-Zr-La catalyst is presented. A dynamic one-dimensional two-phase reactor model of the processes with accounting for both transport limitations in the boundary layer of a fluid near the catalyst surface and detailed molecular unsteady-state kinetic model for surface reactions have been developed and verified with the transient experiments data. The mathematical model was used to explain a transient behavior of the process in the monolith reactor during start-up (ignition). Also studied is the influence on the process dynamics such parameters as linear velocity, equivalent diameter of triangular channel and effective thermal conductivity of the monolith. It was found that higher linear velocity and equivalent channel diameter as well as the worse axial conductivity of solid phase favor decreasing a time delay in syngas production in the Pt/Ce-Zr-La/α-Al_2O_3 honeycomb monolith with a triangular shape channels.

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PL-5

APPLICATION OF FOCUSED ION BEAM TECHNIQUE FOR THE STRUCTURED CATALYSTS INVESTIGATION. CROSS-SECTIONAL STUDY AND SPECIMEN PREPARATION FOR TRANSMISSION ELECTRON MICROSCOPY

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Focused Ion Beam (FIB) technique was originally developed and mostly used in a semiconductor industry. The ability of FIB technique to sputter sample material by precise manner have promoted an application of FIB in the cross-sectional studies of different materials. In case of structured catalysts FIB can be used to reveal several characteristics of catalyst such as internal porous structure and monolith support /catalysts coating properties. In combination with Secondary Ion Mass Spectrometry (SIMS) FIB can provide information about the spatial distribution of the active component inside a granule of catalyst or catalytic coating. Another application of FIB is 3D reconstruction of internal structure by combination of results from the several 2D cross-sections made at equal interval.

FIB system operates in a similar fashion to a Scanning Electron Microscope (SEM). A beam of Ga+ ions is tightly focused and raster over the surface of sample. As a result of ion/material interaction several processes take place. The main process is the sputtering of material under the primary beam. The sputtered material is removed in form of atoms, neutral or charged clusters and ions that can be detected by SIMS to obtain composition information. Another type of particles generated during beam/sample interaction is secondary electrons that are used to obtain images of surface similar to SEM technique. If the special compound gas is delivered to the beam/surface interaction point, beam assisted deposition take place on the surface of the sample. Several material can be deposited for instance Pt, W, SiO_2, C. A spatial resolution of FIB is mainly depend on a beam current and have range from 8 nm to 500 nm.

The Transmission Electron Microscopy (TEM) specimen preparation is the area where FIB is widely used. The main advantage of FIB specimen preparation is that a specimen can be prepared site specific and materials of any hardness can be studied. There are several limitation applied to specimens prepared by FIB technique. The first limitation is the beam damage that in some materials could prevent the atomic resolution TEM measurement. The second limitation is the maximum size of specimen that usually is 10-15 um wide and 5-7 um deep. The beam damage can be reduced by utilizing the low energy ion polishing of specimen after FIB preparation.

PHOTOCATALYSIS: FUNDAMENTALS AND APPLICATIONS

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Photocatalytic oxidation today is considered by many researches as the only universal technique of air and water purification which are contaminated with low concentrations of dangerous organic, inorganic and biological species.

Titanium dioxide is the mostly used photocatalyst which is being investigated last decades. But in spite of this the detailed mechanisms of photocatalytic processes are still unclear although the major factors which influence the TiO_2 photocatalytic activity are well known and will be discussed in the first part of lecture.

Synthesis of highly active photocatalyst is only one of the varieties of problems which should be solved when the photocatalytic reactors are under development. Other problems concern additional filtering stages, light and air (water) flow distributions, pressure drop, selection of materials for catalyst support etc. Modern approach for solving these problems as well as application results in the Russia and worldwide are the subject of second part of the lecture.

Keywords: photocatalytic reactor, air purification, titanium dioxide.

FUNDAMENTAL AND TECHNOLOGICAL ASPECTS OF HETEROGENEOUS SELECTIVE OXIDATION OF C_1-C_4 ORGANIC COMPOUNDS

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Catalytic selective oxidation is the basis for multiple processes for the production of bulk and fine chemicals. At present, more than 60% of the chemicals and intermediates synthesized via catalytic processes are products of oxidation. Understanding of reaction mechanism and the main factors responsible for selectivity is very important for improving of various industrial processes. Basic principles of selective oxidation of C_1-C_4 hydrocarbons, the mechanism of the hydrocarbon activation, surface oxygen species, their role in selective oxidation, and the origins of selectivity in oxidation and ammoxidation reactions will be discussed in the presentation.

Selective oxidation of methane to methanol continues to be an important area of research and holds considerable potential for use of the large reserves of natural gas. The oxidation of methane over molybdenum and vanadium supported catalysts, and over Cu, Fe-containing zeolites will be considered. Further selective oxidation of methanol to formaldehyde, and formaldehyde to formic acid will be also discussed.

C_2 oxidative chemistry will be presented by the reactions of oxidative dehydrogenation of ethane to ethylene, selective oxidation of ethylene and ethanol to acetaldehyde and acetic acid. New ways of the production of valuable C_2 intermediates in comparison with the traditional methods will be discussed.

Acrolein, acrylic acid and acrylonitrile are among the most important bulk chemicals produced at industrial scale. Propene oxidation and ammoxidation over multi-component oxide catalysts are used in the production of these compounds. The composition of the oxide catalysts, the surface intermediate species, source of oxygen inserted into propene, as well as the overall reaction mechanism will be described. New processes based on amm(oxidation) of propane instead of propene will be also considered.

C_4 oxidative chemistry will be presented by the reactions of n-butane to maleic anhydride, n-butene to butandiene, and isobutene convertion to methacrolein and methacrylic acid.

ALUMINA AND MIXED OXIDE CATALYST SUPPORTS FOR SOPHISTICATED CATALYST DESIGN

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Boehmite (Al_2O_3 x H_2O), Bayerite (Al_2O_3 x $3H_2O$) or the corresponding alumina transition phases (gamma-, theta-, delta- and eta-) crystal structures have been used as carrier materials in a broad variety of catalytic processes. Traditionally the access to these industrially available alumina grades for standard catalytic purposes was established by the Bayer process **[1]**. However, today many catalytic applications request alumina carriers with superior purity levels in order to ensure extended catalyst lifetime and improved catalyst performance. Furthermore, modern high selective catalysts technologies demand catalyst with tailored morphology and desired acidity.

Such aluminas and mono/poly-phase mixed (e. g. REE) oxides with higher purity levels and sophisticated surface design can easily be produced by applying the sol-gel manufacturing process **[2]**. This modern process employs refined aluminium-organic precursors in the manufacturing process. Such refined precursors (e.g. $Al(OR)_3$; -OR = isopropylate, butanolate or hexanolate) are hydrolysed under controlled chemical conditions resulting in higher purity alumina. In addition to the improved purity levels the advantage of this sol-gel process compared to the traditional Bayer process is the advanced control of the micro chemical condensation reaction during the hydrolysis step. This control is responsible for the resulting physical properties of the alumina hydrates (e.g. crystal structure and crystallite size) **[3]**.

Furthermore novel types of high purity aluminas become accessible via the sol-gel process, if other elements are added during the synthesis **[4, 5]**. Dependent on the selection of the element added (e.g. Si or Mg) and its concentration levels the physical properties of the resulting high purity compounds are influenced. Of course in the case of Si addition acidic centres and in the case of Mg basic centres on the carrier’s surface are formed **[6, 7]**. The combination of element doping and variation of crystallite size broadens the range of carrier materials with interesting new properties even further. The influence of crystallite size and element oxide content (SiO_2, MgO or REE) on the thermostability of the calcined catalyst carrier was investigated. Surprisingly both crystallite size and element content strongly influence the phase-transition temperature and, consequently, the surface stability at elevated temperatures **[8]**.

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The selection of surface acidic properties is important challenge in catalyst design and construction.

We have succeeded to determine the concentration of Lewis and Brønsted centres on different phases of own support materials (aluminas and silica-aluminas). The extremale dependence of their concentration from Si-content in silica-aluminas indicates qualitative changes in surface chemistry and morphology with Si-content increasing (Fig. 1).

It was also possible to verify morphological characteristic of support materials through 3D-TEM (Fig. 2).

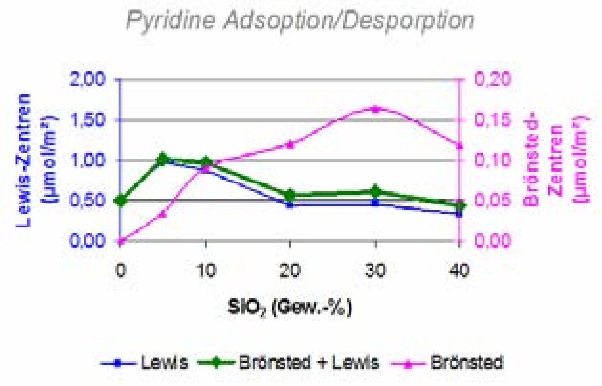

Figure 1. Acidity Measurements on SIRALOX.

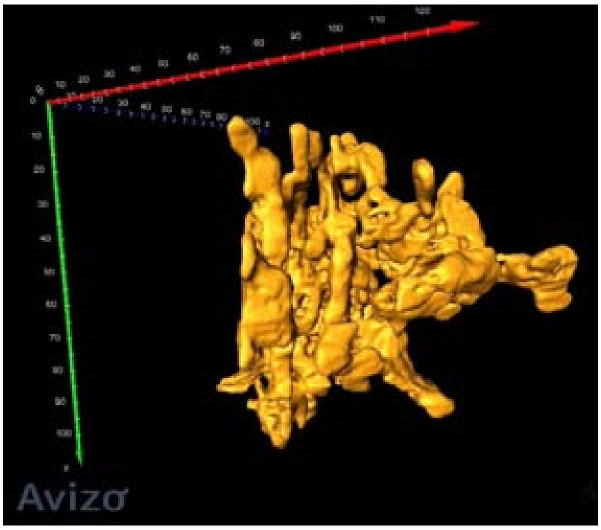

Figure 2. 3D-TEM, gamma-Al_2O_3 (calcined 3h@550°C).

It becomes obvious, that with the industrially available advanced sol-gel process specific requirements of the catalyst carrier can be adjusted.

Keywords: alumina, mixed oxides, tailored acidity

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CATALYSTS AND CATALYTIC LAYERS IN POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

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Fuel cells are electrochemical devices, which convert chemical energy of fuel oxidation reaction into electricity. Some of them can work at room and even subzero temperatures that requires enormously accelerated rate of oxidation reaction.

Efficient approach to the problem involves a combination, called a catalytic layer, of a highly active and stable catalyst with ion and electron conducting media. There are two catalytic layers in the fuel cell. The anode layer is for oxidation and cathode one is for reduction half reactions. The layers are placed between solid electrolyte and corresponding (anode or cathode) current collectors. The anode catalyst transfers the electrons from oxidizes fuel to the current collector and produces protons, which move to the solid electrolyte. The cathode catalyst uses electrons and protons to reduce oxygen to water.

Design of the catalytic layer involves the control of its structure at different spatial scales. At the atomic scale the catalyst surface composition is of primary importance, since it determines exchange current, tolerance to impurities and long-term catalyst stability under over voltage conditions. The next is the level of the catalyst grain, where the type and porosity of the carbon support, size of the catalyst particles, their concentration and distribution over the support affect the performance. The carbon support also serves as an electron conducting medium that transport electrons from fuel to the current collector. At the scale of several tens of nanometers the catalytic layer is a mixture of catalyst grains with ion conducting binder – Nafion. Sometimes hydrophobic binder is also added to the catalytic layer. The size of the Nafion and catalyst agglomerates, amount of the Nafion in the layer and its spatial distribution influence both the proton conductivity and the transport of the reagents to and product from the catalyst.

In the presentation physical chemistry of the processes in the catalytic layers in connection to the performance of the fuel cell are considered along with some modern approaches to the synthesis of catalytic layers.

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ORAL SESSION

I. PREPARATION OF CATALYSTS AND ADSORBENTS

EFFECT OF TiO_2 (ANATASE) MICROSTRUCTURE ON THE THERMAL STABILITY AND CATALYTIC PROPERTIES OF Pt-SUPPORTED TiO_2 CATALYSTS IN CO OXIDATION

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The titanium dioxide of anatase phase is widely used as the support in a number of the important catalysts of environmental protection from nitrogen and carbon oxides. For example platinum supported on the titanium dioxide catalysts are characterized by high activity in CO oxidation. However the anatase phase is metastable and under thermal treatment above 650-700 °C transforms to rutile. Phase transition results in to structural changes and essential decrease in dispersity of titanium dioxide that worsens its properties considerably. In this connection design of new oxide materials with TiO_2 of anatase structure characterized of a high thermal stability is actual.

The goal of this work was to increase the thermal stability of TiO_2 (anatase) by preparation of nanostructured titanium dioxide doped with silica and ceria and its characterization with chemico-physical methods.

The titanium dioxide doped with silica and ceria containing 1-15 wt. % SiO_2 (or CeO_2) has been prepared by impregnation of xerogel TiO_2 with anatase structure by solution of tetraetilortosilan (or solution of ceria nitrate) followed by drying and thermal treatment in the temperature range 300-1100 °C. Supported Pt/TiO_2 and $Pt/Ce\text{-}TiO_2$ catalysts with Pt content of 2 wt. % have been prepared by impregnation of pure TiO_2 and TiO_2 doped with ceria by platinum nitrate solution. The resulting catalysts were dried and calcined in air at 500 °C.

XRD, XPS, transition electron microscopy (TEM) and adsorption methods have been used for the characterization of chemico-physical characteristics of the supports and catalysts under study. Catalytic properties were studied in CO oxidation in a flow reactor. The composition of the reaction mixture was as follows: 0,05 % CO, 5 % H_2O, 6,7 % O_2, nitrogen as balance, GHSV was $1.8 * 10^5$ h^{-1}.

XRD and TEM investigations show that initial titanium dioxide consists of fine crystals of anatase with size about 3-8 nm packed into large aggregates of size 50-100 nm. On the stage of impregnation the solution of modifier introduces into the aggregates of anatase particles being stabilized in there at the subsequent stages of drying and thermal treatment, and prevents coherent sintering of anatase crystals. It results in the significant changes of anatase microstructure after the thermal treatment.

According to XRD and TEM investigations pure TiO_2 calcined at 500 °C represents anatase phase with well ordered crystalline structure (fig.1a).

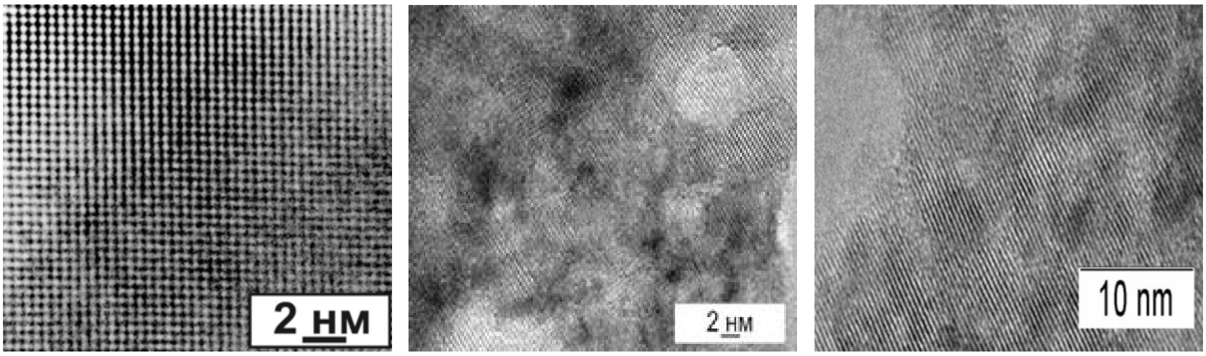

Fig. 1. Microstructure of pure TiO_2 (a) and TiO_2 doped with ceria (b) and silica (c) calcined at 500°C

The titanium dioxide doped with ceria and silica also represents an anatase phase but their crystal structures are distinct from a pure TiO_2 (Fig. 1b, 1c). The crystal structure of titania doped with ceria is nanocrystalline and consists of incoherently intergrown fine anatase crystals with a size of 4-8 nm with formation between them interblock boundaries where Ce^{3+} ions are stabilized.

The microstructure of titanium dioxide doped with silica also consists of highly dispersed particles of anatase stabilized by thin layers of silica. Formation of nanocristaline structure of TiO_2 results in to increase the temperature of anatase to rutile phase transition. For TiO_2 doped with ceria and silica the anatase phase is stable up to 900-1000 °C. The nanostructures formed in the TiO_2 doped with CeO_2 and SiO_2 lead to stabilization of anatase phase, prevent the sintering of anatase particles at high temperatures, and allow modified anatase to retain a larger specific surface area and higher porosity upon heat treatment than pure titanium dioxide does.

Pt/CeO_2-TiO_2 catalyst demonstrates the high thermal stability and high catalytic activity in CO oxidation. Effect of microstructure of Pt/TiO_2 and Pt/CeO_2-TiO_2 catalyst on the activity in CO oxidation has been investigated.

Acknowledgments

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INFLUENCE OF ALUMINA SPECIAL ADSORPTION CENTERS ON PLATINUM PROPERTIES IN Pt/Al_2O_3 CATALYST

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Process of precursor-support interaction (PSI) is basic for creation of supported metallic catalysts. Surface OH-groups of alumina play an important part in H_2PtCl_6 fastening when Pt/Al_2O_3-catalyst is synthesized. They are distinguished in properties [1] and only most basic of OH-groups are capable to the durable coordination binding of $[PtCl_6]^{2-}$ [2]. Thus, a variety of OH-groups composition may change the strength of PSI and so properties of supported platinum will be affected by this interaction.

In this work the surface OH-groups composition is changed by means of impregnation of γ-alumina by organic aluminium salt with the subsequent heat treatment. Aluminium oxalate $Al_2(Ox)_3$ was chosen. Such modification does not change chemical composition of the support. Thermal destruction of $Al_2(Ox)_3$ and phase composition of obtained samples were investigated by differential thermal analysis (DTA) with registration of mass-spectra of gaseous products (STA 449C Jupiter, Netzsch) and by X-ray diffraction (XRD) (DRON-3 apparatus). In accordance with XRD data, heat treatment of aluminium oxalate at 550 °C leads to mixture of γ- and η-Al_2O_3.

The isotherm of aluminium oxalate adsorption on γ-Al_2O_3 at a molar ratio [Ox]/[Al]=1.5, pH = 5 and a temperature of 21±2 °C was obtained. Compositions of impregnating solutions before and after adsorption were determined by liquid-state ^{27}Al NMR (Bruker AC 200 spectrometer). It was established that at given experimental conditions there are predominantly ions $[Al(Ox)_2]^-$ and $[Al(Ox)]^+$ approximately in equal quantities. Content of $[Al(Ox)_2]^-$ anion in solutions may be increased by adding an excess quantity of Ox-ligands. It was shown that about 3 % wt. of alumina may be supported on γ-Al_2O_3 surface by chemical adsorption of $Al_2(Ox)_3$.

The comparison of hydroxyl cover of initial and modified alumina by infrared spectroscopy was realized. Adsorption of platinum (IV) chloride complex was studied for these supports and strength of PSI was investigated by gradient elution [2, 3] and thermal programmed reduction (TPR) (AutoChem-2920, Micromeritics). When H_2PtCl_6 was adsorbed on modified γ-Al_2O_3 (3%Al_2O_3/γ-Al_2O_3) hydrogen consumption at the temperature above

300 °C was grown. This result is explained by increasing part of hard-to-reduction grafted surface platinum species (Fig. 1).

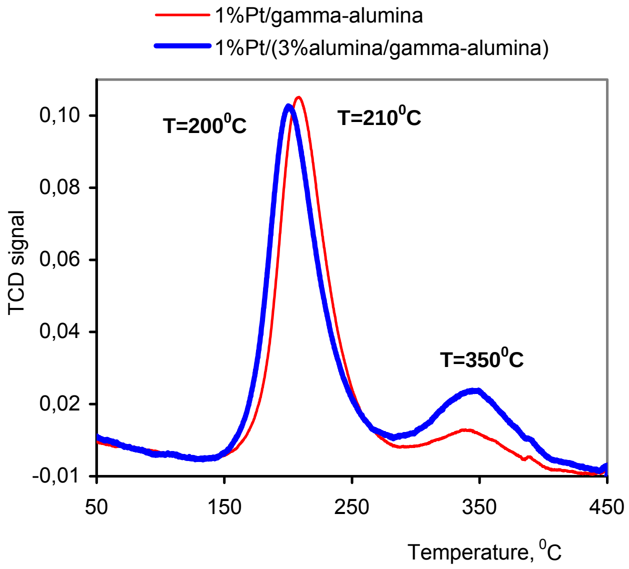

Fig. 1. TPR profiles of 1% Pt/(3%Al_2O_3/γ-Al_2O_3) and 1% Pt/γ-Al_2O_3.

Adsorption properties of supported platinum after catalyst reduction were characterized by CO and H_2 chemisorption. Catalytic properties were studied in model reactions of hydrocarbon transformations.

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DEVELOPMENT OF BIMETALLIC Pt-Sn/TiO$_2$ CATALYSTS FOR SELECTIVE HYDROGENATION OF CITRAL

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Introduction. Hydrogenation of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols is an important reaction in fine chemical and pharmaceutical industries. Higher selectivity to unsaturated alcohols, high conversion and lower polutions can be achieved by application of bimetallic catalysts. The application of an ex situ prepared bimetallic complex as a metals precursor allows a formation of the supported bimetallic nanoparticles of uniform composition and size. The use of the mesoporous oxides synthesized by Evaporation-Induced Self-Assembly (EISA) method with a narrow pore size distribution as support can improve the catalyst performance due to the regular distribution of nanoparticles over the catalyst surface [1,2]. This study is devoted to development of up-to-date bimetallic catalysts on mesoporous titania containing Pt-Sn nanoparticles derived from carbonyl complex for selective hydrogenation of citral.

Experimental. Bulk samples of mesoporous titania were prepared by sol-gel method using Pluronic F127 and Pluronic P123 as a template and titanium tetra-isopropoxide Ti(OiPr)$_4$ as a precursor [2]. Synthesis was carrying at controlled value of a pH in the range of 1.5-1.8 and Pluronic /Ti molar ratio in the range of 0.005-0.008. Aging time was 24 hours. All samples were dried at 100 °C and calcinated at 550 °C for 4 hours.

The Pt-Sn carbonyl complex anion $[Pt_3(CO)_3(SnCl_3)_2(SnCl_2H_2O)]_n^{-2n}$ were prepared and loaded on the mesoporous titania support via either impregnation or adsorption. Several catalyst synthesis parameters have been varied, including the nature of Pt-Sn precursor (carbonyl cluster complex, metal inorganic salts), concentration of Pt-Sn solution (0.5-10 mgPt/ml, 0.3-6 mgSn/ml), solvent used (acetone, ethanol, isopropanol or tetrahydrofuran (THF)). The prepared Pt-Sn/TiO$_2$ catalysts have been characterized by HRTEM-EDX, FTIR and XPS.

Results and discussion. The regulation of specific area, pore volume and concentration of acid sites of bulk mesoporous titania have been achieved by appropriate variation of pH value and surfactant/Ti molar ratio in the initial sol. All samples show similar type-VI adsorption isotherm that reveals mesopores presence. BET surface area and pore volume increase with increasing surfactant/Ti ratio and surfactant molar weight. It was demonstrated that the lower value of pH results in the higher Broensted acid site concentration (BAS) on mesoporous titania and at following impregnation BAS concentration does not affect significantly on the loading of adsorbed Pt-Sn carbonyl complex.

It has been established that narrower size distribution of Pt-Sn particles is achieved by the use of Pt-Sn carbonyl complex instead of metal inorganic salts as a metals precursor. It was also shown that Pt and Sn content in Pt-Sn/TiO_2 catalysts prepared by adsorption of Pt-Sn carbonyl complex depends on solvent nature and increases in a sequence: acetone < ethanol < THF that may be connected with difference of complex solubility in these solvents. The increase of Pt-Sn concentration and ratio of volume of Pt-Sn complex solution to that of TiO_2 lead to increase of Pt and Sn content in Pt-Sn/TiO_2 catalysts from 0.6 to 3 wt. %. The average particle size increases from 1.5 to 3 nm.

The HRTEM-EDX has shown that adsorption of Pt-Sn carbonyl complex (2 mgPt/ml, 1.2 mgSn/ml) from ethanol solution during 24 hrs followed by vacuum activation at 190 °C resulted in formation 1.5 nm particles and narrow distribution of particle size (1-3 nm) in Pt-Sn/TiO_2 catalyst. The chemical states of Pt, Sn, Ti, O, C, Cl elements in catalysts have been determined by XPS. In citral hydrogenation, the bimetallic catalysts showed a TOF of 0.2-3.3 min^{-1} and a high selectivity to unsaturated aldehydes (80-90%) at conversion up to 95%.

Conclusions. The rational preparation procedure of Pt-Sn/TiO_2 catalysts has been developed. The correlation between synthesis conditions vs. physicochemical properties of Pt-Sn catalysts has been established.

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O-I-4

PALLADIUM CATALYST FOR THE SYNTHESIS OF THE 4,10-DIFORMYL-2,6,8,12-TETRAACETYL-2,4,6,8,10,12-HEXAAZAISOWURTZITANE

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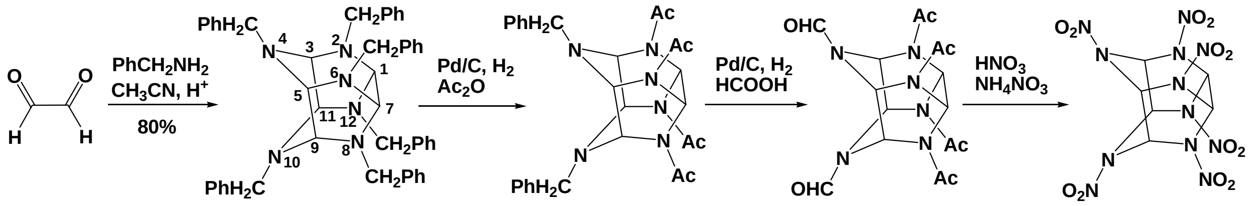
Caged polynitramines are generally known to be high-dense and energy-rich explosives. The caged polynitramine material such as hexanitrohexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.0^{3,11}.0^{5,9}]dodecane, HNIW, CL-20) is prepared via complete removal of all six benzylic groups in hexabenzylhexaazaisowurtzitane (HBIW) during the reductive debenzylation of the latter (see Fig. 1, hydrodebenzylation **1**→**2**→**3**) followed by 2,6,8,12-tetraacetyl-4,10-diformylhexaazaisowurtzitane (TADFIW) nitration. Noble metal catalysts are rapidly deactivating during the latter process [1, 2]. Therefore, careful selection of catalyst and reaction conditions is required.



1, HBIW ***2, TADBIW*** ***3, TADFIW*** ***4, HNIW***

Fig. 1. *Scheme of CL-20 synthesis.*

In preliminary study [2] we studied the porous structure and the morphology of palladium particles for fresh and spent samples of the Pd/C catalyst. The low-temperature (77 K) nitrogen adsorption and the high resolution transmission electronic microscopy (HRTEM) are used. By-products of the hydrodebenzylation process (***1***→***2***) block active palladium particles and decrease the catalytic activity. The agglomeration of palladium particles observed by HRTEM decreases catalytic activity as well.

The overall cost of the CL-20 explosive production is determined by productivity of the HBIW hydrodebenzylation process, so it is essential to improve productivity of the Pd/C catalyst. This task is the main goal of the present study. New types of amorphous noble catalytic systems (Pd-B/C, Pd-B/Al$_2$O$_3$, Pd-B/SiO$_2$) and metal glasses (PdB, PdNiB, NiB) are probed. Pd-B/C samples are found to be more stable in hydrodebenzylation process than all known up-to-date prototypes. Table 1 summarizes results of our findings.

Table 1. HBIW hydrodebenzylation over palladium-based catalyst samples.

№	Catalyst (metal loading, wt.%)	Yield of TADBIW in reaction recycles, %				Summary yield of TADBIW per g of Pd/C catalyst (without regeneration)
		1	2	3	4	
1	Pd/C (10%Pd, Degussa)	80	0	-	-	5.7
2	Pd/C (6%Pd)	82	0	-	-	5.9
3	Pd-B/Al_2O_3 (6%Pd)	0	-	-	-	0
4	Pd-B/C (10%Pd)	86	0	-	-	6.2
5	Pd-B/C (10%Pd)	84	75	75	0	16.8

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BEHAVIOUR OF ZIRCONIUM-NASICON-TYPE PHOSPHATES $Na_3MeZr(PO_4)_3$ WITH Me = Zn, Co, Cu IN THE DECOMPOSITION OF BUTNOL-2

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The plasma chemical technology also offers promise for heterogeneous catalysis as a method for reparing catalysts with unique properties at comparatively low temperatures and under easily controllable conditions. Low-temperature glow-discharge plasmas in various gas media (argon, oxygen, air, and water vapor) could be successfully used for the regeneration and modification of the surface of silica gels, cements, and other sorbents and also iron catalysts of the hydrogenation of CO. During the preparation, modification, and regeneration of catalysts by the method of plasma chemical treatment, surface structures and defects are formed that increase their activity, selectivity, and stability [1-2].

We selected solid electrolytes with framework structures of the Nasicon (Na-superionic conductor) family as objects of study because of their high sodium-ion conductivity, stability toward thermo mechanical actions [3]; the base compound of this family is $NaZr_2(PO_4)_3$ (NZP). Whereas the cationic composition of these electrolytes can vary broadly, they retain the NZP structure with insignificant changes in the unit cell parameters.

The purpose of this work was to determine the influence of thermal and plasma chemical treatments in oxygen on the catalytic activity of complex sodium-zirconium phosphates $Na_3MeZr(PO_4)_3$ with Me=Zn, Co, Cu in reactions of butanol-2.

Catalysts were prepared by the sol-gel method. The catalytic properties of zirconium orthophosphates were studied on a flow unit. The products were analyzed by chromatographing with helium as a carrier gas and a flame ionization detector at 120–360 °C. The acidity of the surface of NZP was determined spectrophotometrically by studying the adsorption of pyridine (Py) from heptane. Plasma chemical treatment was performed in the zone of oxygen glow discharge burning in a vacuum flow alternating current (50 Hz) unit. For this purpose, we used a reactor designed for treating solid samples in a discharge burning zone with simultaneously measuring temperature. The samples were evacuated to a residual pressure of 10^{-4} torr, the discharge current was 200 mA, and the voltage drop between the electrodes was 1.8 kV. Treatment continued for 15 min at 433 K. Violet-pink glow was observed during discharge burning. After treatment, the samples were cooled to room temperature under evacuation. All the samples subjected to plasma chemical treatment had stable activity. Thermal treatment was in the flow of oxygen at 673 K during 40 minutes.

All initial samples catalyzed the dehydration and the dehydrogenation of butanol-2. The least active catalyst (the activity was measured by the yield of products per gram of a catalyst) was sample with Me=Zn, and the most active - the sample with Me=Cu. The yield of ketone depended on the temperature (Tabl 1). After the plasma chemical treatment of NZP, the dehydrogenation reaction only occurred. No butane formation was observed, and the yield of ketone increased on average by a factor of 3 on catalyst with Me=Cu and by a factor of 10 on catalysts with Me=Co, Zn (Table 1). For the temperature region in which the conversion did not exceed 30%, we constructed the Arrhenius dependences ln N–T^{-1}; the activation energies of alcohol dehydrogenation *E*‡ listed in Table 1. We see that the activation energies of dehydrogenation on the initial samples are 1.5–2 times lower than on the sample after the plasma chemical treatment. This can be explained by the strong adsorption of alcohols on the surface center forming during this treatment.

Table 1. Ketone yields (n·10^9 mol\h g), dehydrogenations selectivity (%), activation energies of alcohol dehydrogenation (kJ\mol) for samples $Na_3ZrMe(PO_4)_3$ before and after their treatments.

		Initial			**After thermal treatment in O_2**			**After plasma treatment in O_2**		
Me	**t, °C**	**$n_{МЭК}$**	**S,%**	**E_a, kJ\mol**	**$n_{МЭК}$**	**S,%**	**E_a, kJ\mol**	**$n_{МЭК}$**	**S,%**	**E_a, kJ\mol**
Zn	300	0,7	60	14	1,2	23	21	7	100	46
	350	0,8	28		1,4	17		15	100	
Co	300	3,3	74	17	2,6	84	14	36	100	32
	350	4,2	62		3,2	74		57	100	
Cu	300	5,9	97	44	11,0	92	48	15	100	68
	350	8,2	89		11,3	83		27	100	

This is in agreement with the results from testing the state of the surface of NASICON obtaining by measuring the amount of absorbed pyridine. It was shown that after the plasma chemical treatment the adsorption occurs on centers of two types: with a higher pyridine-adsorbent bond energy and on a centers with a low bond energy. It was shown that on the initial surface the centers with a higher bond energy were absence.

To summarize, we showed that plasma chemical treatment caused deactivation of the centers of dehydration of butanol-2 and increased the yield of ketone by a factor of 3-10. It was shown that changes in catalytic activity correlated with changes in pyridine adsorption after plasma chemical treatment.

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PREPARATION OF NANOSCALE BYNARY OXIDE SYSTEMS VO_x/MgO BY AEROGEL TECHNIQUE

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Nanoscale MgO and MgO-based binary oxide systems are known to be widely used as catalysts and sorbent agents. For example, the aerogel VO_x/MgO system shows the highest catalytic activity and selectivity in oxidative dehydrogenation of propane [1]. Such catalytic behavior could be explained by small crystallite size, high surface area and quite uniform distribution of active sites. From the other hand, nanocrystalline MgO-AP (Aerogel Prepared) was found to be able to react with rather inactive molecule of freon-12 (CF_2Cl_2) [2]. In this case, the doping of MgO-AP with a small amount of VO_x (1-2%) results in significant acceleration of reaction rate causing more profound extent (2 times fold) of MgO transformation into fluoride.

The aerogel method of synthesis of the binary oxide VO_x/MgO system which allows obtaining the nanocrystalline materials within the wide range of V-concentrations has been developed. For the synthesis of aerogel stoichiometric Mg-vanadates the different molar ratios of metals were applied (Mg:V = 3:2 for orthovanadate, and Mg:V = 1:1 for pyrovanadate).

It was established that the surface area of synthesized aerogel hydroxide $VMg(OH)_x$ exceeds 1100 m^2/g and does not practically depend upon conditions of autoclave drying procedure. The process of dehydration of the aerogel hydroxide $VMg(OH)_x$ was investigated by gravimetrical method in order to find the optimal conditions for their transformation into corresponding oxides VO_x/MgO with surface area as high as 450 m^2/g. Surface area of stoichiometric Mg-vanadates turned out to be much lower (especially for Mg-pyrovanadate) than that of doped aerogel oxides VO_x/MgO. Nevertheless, the measured S_{BET} values appeared to overcome considerably the analogues reported elsewhere in literature [3].

The synthesized aerogel oxides VO_x/MgO were studied by a whole spectrum of physicochemical methods. The joint V-Mg phase was not detected even in case of samples containing very high concentration of introduced vanadium. Vanadium atoms are believed to be incorporated inside the lattice of MgO nanocrystals (with average size of 4-5 nm) which results in distortion of initially cubic symmetry (Fm3m) to end up with orthorhombic one (Cmca). This observation was also confirmed by the data of solid state NMR, according to which the part of V atoms in tetrahedral surrounding of oxygen atoms (corresponding to vanadate structure VO_4) grows up with increase of V content in aerogel VO_x/MgO sample. By the EDX analysis data, the developed aerogel method, in contrast to the conventional preparative ways, provides the uniform distribution of vanadium throughout the structure of magnesium oxide.

In general, the developed aerogel technique allowed obtaining the nanoscale binary oxides VO_x/MgO which are characterized with both high surface area and uniformity of V distribution in wide range of vanadium concentrations.

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METHANE STEAM REFORMING ON NICKEL REINFORCED Cr_2O_3-FREE CATALYSTS

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Methane steam reforming (MSR) is one of the most promising methods for synthesis gas production. To carry out the endothermic methane steam reforming reaction (MSR), intensive heat transfer from an outer source to the reaction zone is required. Therefore, the catalyst must have a high thermal conductivity. It is most promising to use catalysts on metallic supports. The peculiarities of the formation of composite reinforced nickel catalysts free of chromium oxide additive, and their catalytic properties in the reaction of MSR were studied in the present work.

To prepare reinforced catalysts, a mixture of components containing 87,5 wt.% Ni, 12,5 wt.% commercial GIAP-3 or NIAP-18 catalyst was mixed with a rubber-based adhesive and applied to reinforcing gauze followed by sintering in a vacuum oven at 760 °C for 2 h.

The prepared catalysts were characterized by XRD, X-ray phase analysis, the nitrogen adsorption at low temperatures, mercury porosimetry and electron microscopy (TEM and SEM). Catalytic activity in the methane steam reforming reaction was determined by the flow-circulating method (750 °C, $H_2O/CH_4=2$, p=1 atm, GHSV 16860 h^{-1}). The samples were reduced at 750 °C in flow of H_2.

According to XRD data, the commercial GIAP-3 catalyst and GIAP-3-based catalytic layer contained the phases of Ni and α-Al_2O_3; catalyst NIAP-18 and NIAP-18-based catalytic layer additionally contained $CaO \cdot 6Al_2O_3$ phase.

Mercury porosimetry studies showed that the catalytic layers had a macroporous structure with the pore volume composed mainly by pores with 15-100 μm radii. According to SEM data, the catalytic layer was a coarse-pored metallic nickel material formed by spherical conglomerates of 2-15 μm in size united at contact sites. Either irregularly shaped individual particles of supported nickel catalyst of size 0.5-3 μm were distributed in the pores

We evaluated the average particle size of supported nickel in the commercial catalysts and catalytic layers using TEM and found out that the nickel particle size increased by a factor of 1.5-2 in the course of preparation.

The conversion of methane on catalytic layers remained stable over the entire period of testing (30 h). Methane conversion on the NIAP-18 – based catalytic layer exceeded this value of the GIAP-3 – based catalytic layer that can be attributed to the interaction of NiO from the metal matrix with dispersed Al_2O_3. NIAP-18 catalyst contained much higher portion of dispersal Al_2O_3 in comparison with GIAP-3. In the course of catalyst preparation at the stage of high-temperature treatment the formation of surface mixed oxides or surface compounds was possible; the reduction of these surface mixed oxides or surface compounds resulted in formation of dispersed nickel crystallites. A comparison of the activity on a unit volume basis showed that the activity of reinforced catalysts was lower than the activity of commercial catalysts by a factor of ~2. It was shown that in contrast to the activity of GIAP-3 – based catalytic layer that one of NIAP-18-based catalytic layer was higher than the activity that corresponded to the commercial catalyst content in the catalytic layer assuming proportional dependence of catalytic layer activity on commercial catalyst content. This can be due to the contribution of a nickel metal matrix to the catalytic activity. In the surface layers of this matrix, dispersed nickel crystallites were formed from a surface mixed oxides consisted of NiO and Al_2O_3.

CALCINATION TEMPERATURE EFFECT ON PROPERTIES OF IRON-CONTAINING SILICA SUPPORTED CATALYSTS IN HYDROGEN SULFIDE OXIDATION REACTION

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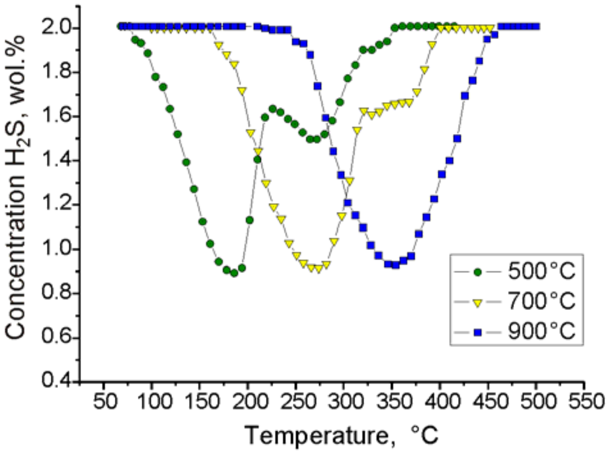
Silica-supported iron-containing catalysts are highly efficient for the environmentally valuable reaction of H_2S oxidation to sulfur, for example, Fe oxide catalyst is used commercially as catalyst for the SUPERCLAUS® process [1]. It is known that the formation of iron disulfide phase due to the interaction with H_2S from the reaction medium is accompanied by an appearance of SO_2 among the reaction products that decreases the selectivity towards sulfur [2, 3]. Thus, the stability of the active phase against sulfidation in the reaction conditions is crucial for the development of the selective catalyst for the oxidation of hydrogen sulfide to sulfur. Although the effect of the preparation condition and the active component precursor on the activity of the supported iron–containing catalysts has been extensively studied, iron(II) sulfate ($FeSO_4 \times 7H_2O$) as precursor of the active component received few attention despite it is needed in properly utilization as the main component of steel-picking chemical waste.

The aim of this topic is to study the effect of the calcination temperature on the catalytic activity of Fe-containing silica-supported catalysts prepared using the iron (II) sulfate precursor. Furthermore, the stability of the prepared catalysts against sulfidation has been compared using the method of temperature-programmed sulfidation (TPS).

The catalysts were prepared by a dry wetness impregnation of SiO_2 with an aqueous solution of iron (II) sulfate. After impregnation the samples were dried at 100 °C and calcined at 400, 500, 600, 700 and 900 °C for 4 hours (denoted as F400, F500 etc.), whereas the iron concentration in the samples of the second series was about 10 wt.% (10FS500 etc.). The nature of the iron-containing species after calcinations was studied by DTG, X-ray powder diffraction, the XPS and Mössbauer spectroscopy. Steady state reaction rate and selectivity of silica-supported catalysts in H_2S oxidation reaction were measured in an external recirculation reactor. Since under the reaction conditions the formation of iron disulfide is slow process, special procedure of the temperature-programmed sulfidation (TPS) was used for the comparison of the catalyst stability against sulfidation.

The comparison of the steady-state reaction rates of the H_2S conversion let us to conclude, that the increase in the calcination temperature led to the rising of the H_2S oxidation rate, which was observed both for 4FS and for 10FS series. The 100% selectivity in the oxidation



of hydrogen sulfide to sulfur was observed for all samples, regardless of the calcination temperature. TPS curves of the 4FS catalysts calcined at 500, 700 and 900 °C are depicted in Figure. A comprehensive analysis of the TPS curves indicates that maximum of the H_2S concentration decrease, that reflects an absorption of H_2S by the catalysts due to transformation of iron oxide to iron disulfide, is shifted to higher temperatures with the increase of the calcinations temperature of the samples. So, we can conclude that the increase in the calcination temperature makes the catalysts more stable against their interaction with hydrogen sulfide.

The results of the X-ray powder diffraction study show that samples calcined at the temperature 400-700 °C do not exhibit any diffraction peaks. The temperature increase up to 900 °C led to the formation of recently observed ε-Fe_2O_3 phase [4], as have been proved by data of Mossbauer's spectroscopy and X-ray powder diffraction. The formation of complex iron (III) compound that contained the hydroxide and sulfate groups as anions is supposed on the basis of chemical analysis, DTG and XPS data in the samples, calcined at intermediate temperature. The identification of the exact structure of these amorphous compounds is rather complicated.

Thus, the increase in the calcination temperature for the supported iron oxide catalysts prepared by impregnation of silica with aqueous solution of iron (II) sulfate improves their activity and stability against sulfidation, probably due to formation of ε-Fe_2O_3 phase.

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O-I-9

DESIGN OF CERMET MONOLITHS FOR HIGH TEMPERATURE CATALYTIC PROCESSES

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High-temperature catalytic processes of hydrocarbons/biofuels combustion and their transformation into syngas by partial oxidation and steam/dry reforming at short contact times are now considered as being attractive for application in the fields of clean energy generation, environment protection, synfuels production etc. The catalysts for these energy-intensive processes should meet a lot of demands such as thermal stability, thermal shock resistance, low pressure drop, efficient heat transfer etc. Monolithic catalysts based upon different substrates such as ceramic (cordierite, γ-Al_2O_3, etc.) or refractory metal foil (Fechraloy etc) honeycombs, metal or ceramic foams were used for these applications. However, there are some problems in using such substrates. Thus, metal foil substrates suffer from oxidation in fuels combustion processes under air excess, whereas ceramic supports possess insufficient thermal shock resistance [1,2]. Besides, refractory metal or ceramic monolithic substrates usually provide only geometric surface area. So, to ensure required catalytic performance, porous layers of active components are supported by washcoating. [3].

This work presents results of design and testing of a new type of monolithic substrates based upon porous $MAlO_y/MAl_x$ cermets produced by hydrothermal oxidation of mechanically alloyed M-Al (M=Cr, Fe) powders. Mechanical alloying is an important synthesis stage to activate the surface of metal particles for oxidation in hydrothermal conditions. Moreover, mechanical treatment favors formation of high-temperature resistant and mechanically strong M-Al alloys. Alloys powder loading into specially designed die fixes the arrangement of large transport pores essential for an easy access of reagents into the monolithic substrate walls. At the hydrothermal treatment stage, aluminum containing in a powdered alloy reacts with water forming a hydroxide. Decomposition of this hydroxide layer by calcinations under air generates mesopores determining the бcermets surface area. At the same time, the volume expansion due to Al oxidation into hydroxide by water provides consolidation of cermet particles into a strong monolithic material. In these materials, metal particles are randomly distributed within the oxide matrix providing good mechanical strength being at least one order of magnitude higher than that for conventional γ-Al_2O_3 support.

Changing the die form allows to obtain a wide range of monolithic support shapes- from simple cylinders and rings to honeycombs and complex integrated structures comprised of cermets with incorporated metal tubes, gauzes etc. Several types of honeycombs were designed and manufactured for different catalytic applications. Thus, for fuels combustion in the catalytic reactor with fluidized bed of inert heat carrier, structured catalysts resistant to abrasion are required [4]. Especially for this reactor, a structured catalyst based on 40 mm diameter cermet monolithic substrate with a big (up to 70%) free volume was synthesized and successfully tested. To produce syngas by the partial oxidation of methane, monolithic catalyst with channels density ~12/cm^2 possessing a high thermal shock resistance was manufactured. For steam reforming of oxygenates (ethanol, acetone), the mini-monolithic catalyst with a high thermal conductivity possessing 20 channels per 20 mm diameter was produced and tested with a good yield of syngas being demonstrated.

Hence, technology of monolithic cermet substrate manufacturing developed in this work and based upon the partial oxidation of powdered metal-aluminum alloys meets requirements for catalysts of energy–intensive processes of a great importance for the hydrogen/clean energy generation and environment protection fields.

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DEVELOPMENT OF SYNTHESIS OF POROUS CARBONACEOUS ADSORBENTS AND CATALYST SUPPORTS FROM HIGH-ASH BIOMASS – RICE HUSK

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The work is devoted to a development of rice husk (RH) conversion process into such porous carbonaceous materials as carbon-silica nanocomposites and carbons possessing predominantly mesoporous or microporous texture. It has become possible because of high content of silica in RH – up to 23 wt % of amorphous silica [1]. The first stage of the RH processing is carbonization in a fluidized catalyst bed (FCB) reactor (contact time of milled RH with the catalyst bed $\tau \sim 1$ s) with obtaining of the carbon-silica nanocomposites. In the dependence on carbonization temperature, the prepared composites possessed specific surface area $A_{BET} = 30 – 250$ m^{2}g^{-1}, total pore volume $V_\Sigma = 0.04 – 0.22$ ml g^{-1} and silica content 33 – 76 wt % with homogenously distributed carbon and silica phases [2]. These composites can find such applications as cheap bifunctional adsorbents and catalyst supports.

As it seemed that silica phase of the nanocomposites might play a role of template in carbon phase, it was decided to try to use the composites as a precursor of carbons with predominantly mesoporous texture. The composites were mixed with powdered equimolar mixture of Na_2CO_3 and K_2CO_3 with the following thermal treatment at 750 – 1000 °C. This approach has allowed to obtain mesoporous carbons with A_{BET} up to 1700 m^{2}g^{-1}, V_Σ up to 1.5 ml g^{-1} and volume mesopore quota more than 80 %. The average pore diameter of the materials was 2–4 nm. TEM images with low and high resolution are presented on **Fig. 1**. The mesoporous carbons are intended to be employed as adsorbents and catalyst supports.

The traditional template synthesis method includes the following steps: synthesis of template mesoporous SiO_2, impregnation of SiO_2 by carbonaceous precursor, carbonization at 500–1000 °C and the last – remove the template SiO_2 by HF or NaOH [3].

The obtaining carbon materials possess texture properties comparable with the properties of carbons from RH. Nevertheless, the traditional way of the materials synthesis is more difficult, expensive and includes the using of a lot of chemicals.

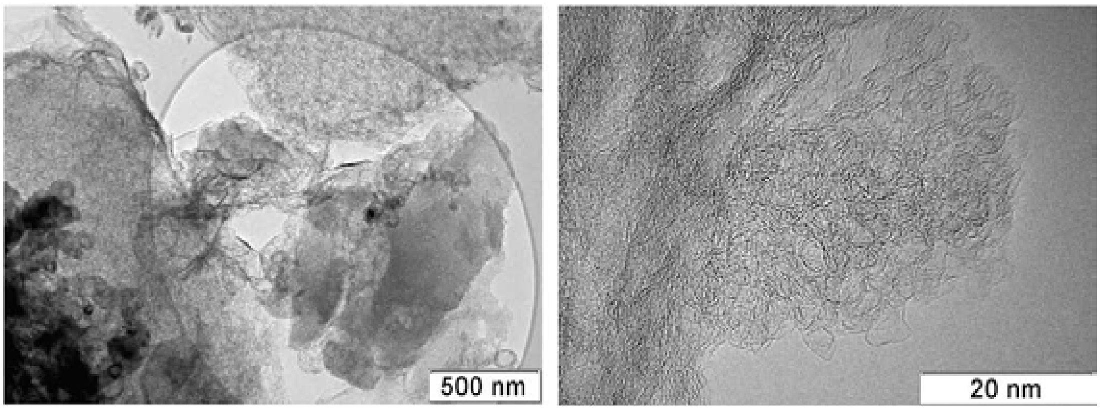

Fig. 1. TEM images of mesoporous carbon sample prepared at 900 °C.

It was also discovered that the carbon-silica composites can be precursors of microporous carbons with high specific surface area – more than 3000 m^2g^{-1} in accordance with BET model. By KOH activation method microporous carbons with A_{BET} up to 3500 m^2g^{-1}, V_Σ up to 3.0 ml g^{-1} and V_μ up to 1.9 ml g^{-1} were obtained at 700–900 °C. Tests of the adsorptive properties of the materials relating to H_2 (at 77 K and 50 bar) and methane (at 273 K and 60 bar) have showed high adsorptive capacities of the materials on these gases. They have adsorbed up to 6.3 wt % of H_2 and 41 wt % of CH_4 [4].

The analogies of the materials – microporous carbons, such as Maxsorb (Kansai Coke and Chemical Co Ltd., Japan) are produced from petroleum coke and pitch also by KOH activation at 700–800 °C but through a preliminary treatment of the precursors by concentrated nitric acid that leads to mordant and toxic wastes. In addition, these materials possess lower texture characteristics (A_{BET} about 2700 m^2g^{-1}, V_μ about 1.2 ml g^{-1}) [5]. A comparison of the technical conditions leads to a resume that the proposing method is cheaper and environmentally more appropriate.

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USP CATALYSTS FOR CNF GROWTH

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Catalytic growth of carbon nanofibers (CNF) results from chemical vapor deposition (CVD) of organic compounds on metal particles of iron subgroup (Fe, Co, Ni) and their alloys with the other metals. Depending on conditions of the experiment it is possible to produce the CNF with different structure. The morphology of CNF can be divided into four types:

- coaxially-cylindrical (nanotube);
- coaxially-conical (fishbone);
- step-like;
- feathery.

Main factors effecting the structure of CNF are: catalyst composition, carbon precursor and temperature of the process. In addition, the size of the active metal particle determines the diameter of growing CNF and can either influence on their structure.

Method of ultrasonic spray pyrolysis (USP) allows one to form catalytic particles with harrow size distribution [1]. The approach is based on the action of ultrasonic processing which makes the precursor solution being sprayed into submicron drops. This spray is to be passed by carrier gas in furnace where its evaporation and formation of catalytic particles occurs. A diameter of formed particles mainly depends on concentrations of precursor solution and frequency of the ultrasound.

We have constructed demo experimental setup for ultrasonic spray pyrolysis and prepared the series of catalysts with composition 78%NiO+12%CuO/MgO using nitrates ($Ni(NO_3)_2*6H_2O$, $Cu(NO_3)_2*3H_2O$, $Mg(NO_3)_2*6H_2O$) as precursors for catalysts. The concentration of salts in precursor solution was varied in the range 0.1-5 mass.%. After passing through furnace the particles were caught by electrostatic filter. Obtained catalysts were tested in reaction of the CNF growth. The products, as well as catalysts, were studied by transmission and scanning electronic microscopy (TEM and SEM).

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SUPER-HIGH SILICA ZEOLITES IN MTH PROCESS

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The current pricing of crude oil has led to increased interest in the use of natural gas or coal as a feedstock for the production of gasoline and petrochemicals. Methanol can be made from such feedstocks via synthesis gas and further converted into gasoline-range hydrocarbons (MTG) or light olefins (MTO) [1]. The conversion of methanol to hydrocarbons is commonly referred to as the MTH reaction.

ZSM-5 zeolite is active catalyst for the decomposition of methanol. The conversion of methanol over ZSM-5 catalysts proceeds via the sequence of steps: methanol → DME → olefins → aromatics and paraffins. The selective production of light alkenes can be attained by selecting optimum reaction conditions or by affecting the catalytic properties of the zeolite. Long lifetime and carburization stability are the significant catalysts requirement. According to mechanism of MTH process, gaseous olefins are primary products, which quickly turn to other hydrocarbons. One of the ways to break secondary transformations of light olefins is the decrease of Lewis acid sites concentration. As the silica modulus increase, the strength of acid sites decreases because of a decrease in the content of Al^{3+} in the zeolite framework. Thus high SiO_2/Al_2O_3 ratios (low concentration of strong acid sites) have resulted in raising light alkenes selectivity.

The main purpose of the work is the producing of effective and stable catalysts for MTH process. Our catalysts are based on zeolites with SiO_2/Al_2O_3 ratios 300-500. The zeolites were synthesized by hydrothermal crystallization with hexamethyleneimine template (175 °C, 30-50 h). The physical-chemical properties of zeolites were characterized by IR-spectrometry and XRD. The concentration of acid centers was studied by the temperature programmed desorption (TPD) of ammonia. The catalysts showed high catalytic activity, the extent of methanol conversion being ~100%. The process was carried out in a flow installation at 390 °C, methanol hourly space velocity of 1 h^{-1} and under atmospheric pressure. Low concentration of acid sites allows the highly selective production of light olefins from methanol. The yield of alkenes C_2-C_4 increases from 25,8 to 29,7% with increasing of SiO_2/Al_2O_3 ratio from 200 to 500. The major products of liquid phase are C_6-C_9 aromatic hydrocarbons (under 84% for the catalyst with SiO_2/Al_2O_3=200) and the yield of aromatics falls with growth of catalyst's silica ratios. Superhigh-silica ZSM-5-type zeolites show prolonged lifetime in MTO process (unto 700 h).

Table. The results of methanol conversion

Distribution of hydrocarbons (wt.%)	M=200	M=300	M=400	M=500
$\sum C_1$-C_4	48,7	37,9	36,9	40,0
alkanes C_1-C_4*	*55,4*	*54,4*	*49,1*	*46,5*
alkenes C_2-C_4	*25,8*	*25,3*	*29,9*	*29,7*
$\sum C_{5+}$	50,9	61,9	62,7	59,8
alkanes C_{5+}**	*1,2*	*1,4*	*1,9*	*1,8*
alkenes C_{5+}	*1,6*	*3,4*	*5,5*	*4,8*
isoaklanes C_{5+}	*9,0*	*17,8*	*22,9*	*21,2*
aromatics	*84,1*	*73,5*	*60,8*	*65,5*
Lifetime, h	430	723	509	100

** – percentage in gaseous faze; ** – percentage in liquid faze.*

Thus one can see that superhigh-silica to aluminum ratios (low concentration of strong acid sites) have resulted in increasing of selectivity toward light alkenes, that is caused by decreasing sharply of the concentration and strength of acid centers as the silica modulus grew. That also result in increasing of coke formation stability and consequently in the catalysts lifetime prolongation.

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O-I-13

MCM-41 TYPE CATALYTIC MATERIALS VIA MICROWAVE SYNTHESIS

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MCM-41 type catalytic materials with their hexagonal arrangement of unidimensional pores and large surface areas (greater than 1000 $m^2 g^{-1}$) fascinate the designers of new selective heterogeneous catalysts in the production of fine chemicals on large scale. Microwave assisted synthesis of mesoporous molecular sieves is a promising method due to several advantages over the conventional hydrothermal method such as homogeneous heating throughout a reaction vessel, more homogeneous nucleation and shorter crystallization times. In this work, incorporation of different metal sources into MCM-41 structure were investigated. Metal solutions were added into the raw materials and then the mixture was treated in the microwave oven using different Si/metal ratios as 25, 50, 75 and 100. The products obtained were characterized by XRD, N_2 physisorption, SEM, EDS and TEM. Metal-MCM-41 type catalytic materials prepared by microwave radiation method having Metal/Si ratio as high as 0.04 were found to preserve the MCM-41 structure having BET surface area values over 1500 m^2/g. The synthesis time of the mesoporous materials was reduced from at least 96 to hours to 30 minutes by microwave-induced heating. The effect of metal amount on the incorporation of metals into MCM-41 structure were compared.

The XRD patterns of the metal-MCM-41 materials synthesized by microwave heating procedure clearly showed the characteristic Bragg peaks of MCM-41 structure corresponding to $d_{(100)}$ and the three reflections. An example of an XRD pattern was given in Figure 1 for Co-MCM-41 synthesized by using cobalt (II) nitrate hexahydrate as cobalt source with a Si/Co mole ratio of 25. Adsorption isotherm of the same sample gave Type IV isotherm which shows mesoporus characteristics.

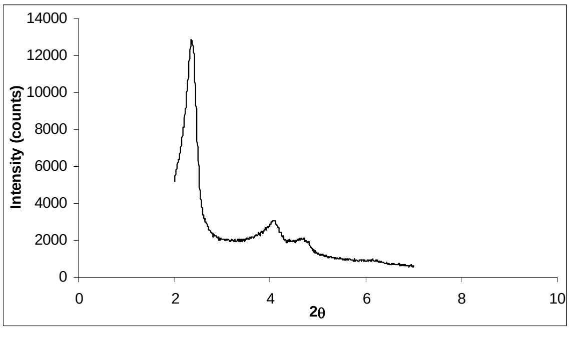

Figure 1. XRD pattern of Co-MCM-41.

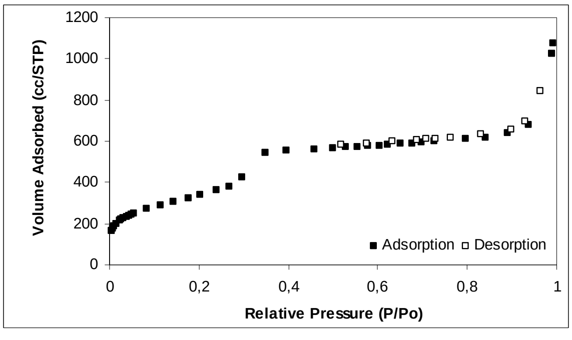

Figure 2. Adsorption isotherm of Co-MCM-41.

The characteristic lattice parameter (the repeating distance “*a*” between the two pore centers) was calculated from the following equation [1]:

$$a = \frac{2}{\sqrt{3}} d_{(100)}$$

A summary of the properties of some samples were given in Table 1.

Table 1. Summary of some Co-MCM-41 materials synthesized from cobalt (II) nitrate hexahydrate

Sample ID	Initial Si/Co mole ratio	Co/Si (mole ratio) in solid EDS	Surface Area (m^2/g) BET	BJH Adsorption Pore Volume (cm^3/g)	BJH Ads. Average Pore Diameter “dp“ (nm)	d_{100} (nm)	Lattice Diameter “a” (nm)	Pore Wall Thickness “δ” (nm)
Co-MCM-41	25	0.045	1305	1.81	2.7	3.7	4.3	0.76
Co-MCM-41	50	0.039	1577	1.62	2.2	4.0	4.6	0.82

Metal-MCM-41 type catalytic materials were successfully synthesized in 30 minutes by using microwave radiation. The MCM-41 structure was not distorted and the BET surface area values over 1500 m^2/g were obtained with metal/Si mole ratios over 0.04.

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ORAL SESSION

II. MECHANISMS OF HETEROGENEOUS CATALYSIS, METHODS OF CATALYST CHARACTERIZATION

ETHANOL DECOMPOSITION ON ALUMINA SUPPORTED NOBLE METAL CATALYSTS

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Recently it has been found that supported noble metal catalysts are active for H_2 production in the ethanol reforming [1]. Comparative studies show that among these samples supported Rh and Pt have one of the best performances especially at the beginning of the reaction [1-3]. Our previous works demonstrated that while the selectivity of H_2 decreased in time, the formation of C_2H_4 increased parallel to it on all alumina supported noble metals [3,4]. The selectivity order of H_2 formation under quasi steady state conditions was Ru>Rh>Ir=Pd>Pt and the selectivity of C_2H_4 formation increased in the opposite way [3].

In the present work we give an account of the catalytic effect of alumina supported Pt and Rh catalysts in the ethanol decomposition. Attention was paid to the surface species produced during the high temperature interaction of ethanol with the catalysts and the changes of the isotope distribution of the products during the decomposition.

The DRIFTS analyses were performed in a diffuse reflectance infrared cell (Spectra Tech), adapted to a BioRad FTS-135 type FT-IR spectrometer. The catalytic experiments were carried out in a fixed bed continuous flow reactor. Ethanol was introduced by bubbling the carrier gas through the ethanol at 298 K and C_2D_5OD was injected into the reacting gas stream. Analysis of the products and reactants was performed with a mass spectrometer (Pfeiffer QMS 200).

The decomposition of ethanol was studied by gradually heating (heating rate 10 K/min) the catalysts in the reacting gas mixture from 370 K. (Fig. 1)

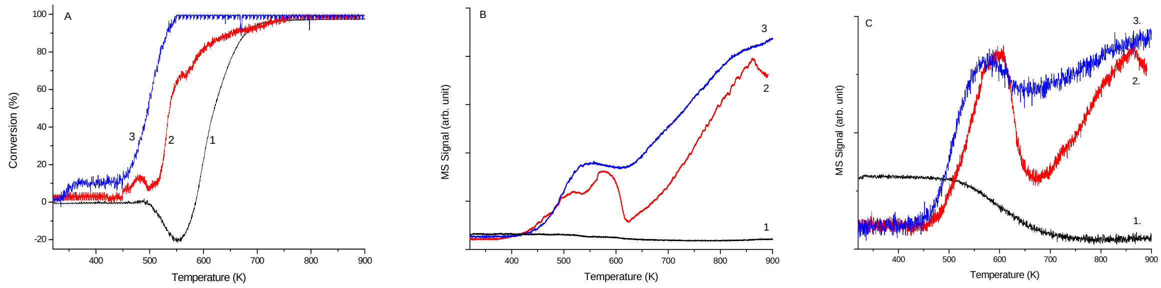

Fig. 1. The conversion (A), the hydrogen (B), and carbon monoxide (C) selectivity in the decomposition of ethanol on Al_2O_3 (1); Pt/Al_2O_3 (2); Rh/Al_2O_3 (3) catalysts.

The decomposition of ethanol was also studied under isothermal conditions at 573 K and 723 K, too. When C_2D_5OD was injected into the reacting gas mixture the H_2 (m/e = 2) formation decreased and the D_2 (m/e = 4) and HD (m/e = 3) evolution increased (Fig. 2) in both cases. From these results we may suppose that H_2 forms in different ways during the reaction.

It was found that not only H_2 but CH_4 and C_2H_4 were also formed with different isotope distributions. On Rh/Al_2O_3 mainly CH_3D and CD_4 were formed in the first 20 minutes and the distribution hardly changed during the reaction. In spite of this on Pt/Al_2O_3 the amount of CD_3H and CD_2H_2 was relatively stable during the reaction and significantly higher than on Rh/Al_2O_3. (not shown)

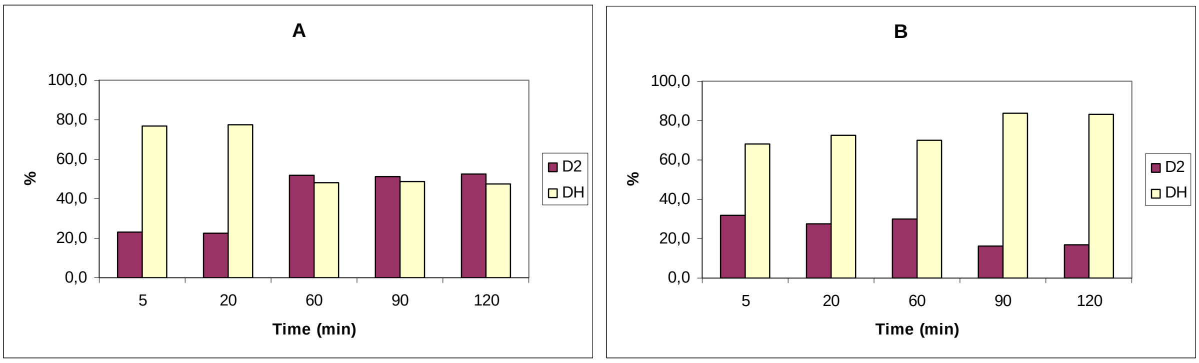

Fig. 2. Hydrogen isotope distribution in the C_2D_5OD pulses, injected different time of the reaction into the reacting stream at 723 K on Rh/Al_2O_3 (A) and on Pt/Al_2O_3 (B) catalysts.

The infrared spectra did not change below 2100 cm^{-1} when C_2D_5OD was added to the ethanol stream. The negative spectral features at about 3713 and 3662 cm^{-1} were more pronounced, and the band intensities at about 3012, 2980 and 2880 cm^{-1} decreased significantly in the first minute. It means that the surface OH and CH_x groups were consumed after C_2D_5OD injection. At the same time new, intensive absorptions were observed at 2700-2900 cm^{-1} attributed to the OD groups on the surface and weak bands were detected between 2300 -2100 cm^{-1} which can assigned to the CD_x species.

The amount of surface carbonaceous deposit was determined by TPO. It was more than 45 times higher on Pt/Al_2O_3 and about 10 times on Rh/Al_2O_3 than the amount of surface metal atoms. On Pt/Al_2O_3 different types of carbon existed on the surface.

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THE XPS STUDY OF OXIDIZED GOLD NANOPARTICLES SPUTTERED IN RF-PLASMA ON TANTALUM FOIL

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The metals of Ib group (copper, silver) are widely used as active components of catalysts in the processes of complete and partial oxidation [1]. Till recently gold was not used since it was believed totally inactive. However in the end of 20-th century it was showed that nanosized gold particles supported on the reducible metal oxides possess high activity in many catalytic reactions [2]. The pathways of oxidation are determined to a great extent by oxygen species, so their nature is a key factor in the understanding of the reaction mechanisms. Unfortunately the coordination and state of oxygen are not established because of certain difficulties in the application of the surface analysis methods (XPS, UPS, AES etc.) in the investigation of oxygen species on the surface of the supported gold catalysts. The most informative investigation of the oxygen species on the gold surface can be performed on the surface of massive samples (foils, single crystals, films). But in case of massive samples investigations the question of “material gap” have no answer. To establish size effect for gold catalysts the generation of gold nanoparticles on model surfaces and its investigation should be performed. For last five years such kind of model systems are studied by some research groups [3,4]. But the most part of produced information is about different ways of gold nanoparticles preparation and its basic properties – particle size and gold oxidation state. The nature of oxygen on gold nanoparticles and the influence of particle size are under studies.

The main goal of the presented work was to study by photoelectron spectroscopy the metallic and oxidized gold nanoparticles obtained by plasma sputtering of the gold in oxygen and/or argon atmosphere. Application of this method gave us opportunity to study the evolution of gold and oxygen states of the oxidized nanoparticles, thermo stability and reaction probability. The comparison with properties of oxidized massive gold surfaces was made.

The experiments were performed using electron spectrometer VG ESCALAB HP equipped with XPS and TPD methods. The polycrystalline tantalum foil (99,99%) was used as a support for gold clusters. Nanoparticles of metallic and oxidized gold were sputtered at room temperature by means of RF-discharge in O_2 and/or Ar atmosphere. No contaminations presence was found during the experiments. The adsorbed on gold nanoparticles oxygen was characterized by means of XPS (Au4f and O1s spectra) and TPD, the reactivity was tested “in situ” using gas flow of CO, by means of dynamic-XPS.

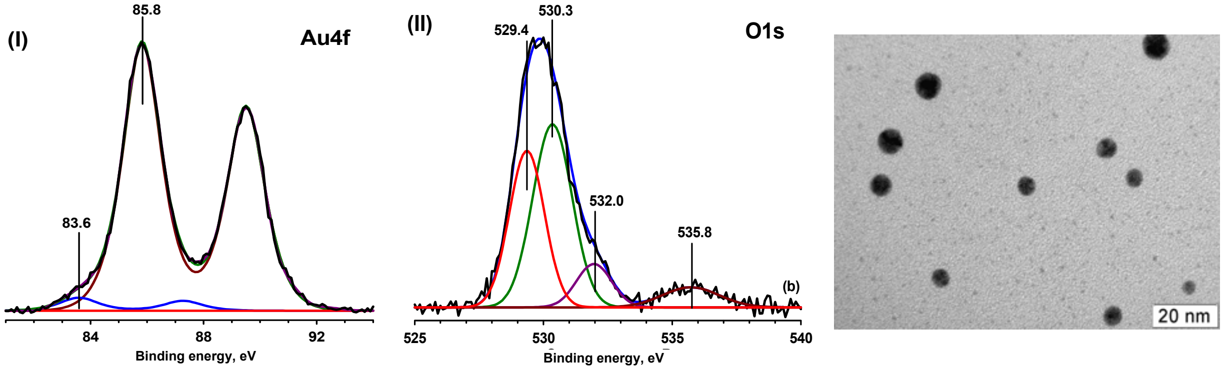

Fig.1. XPS spectra Au4f (I) and O1s (II) of oxidized gold nanoparticles, HR TEM pictures of gold nanoparticles produced using RF-plasma in oxygen atmosphere.

By means of HR TEM the formation in RF-plasma sputtering of gold nanoparticles about 10 nm and less was proved (see fig.1). The XPS data shows the formation of metallic gold nanoparticles in case of RF-plasma in Ar atmosphere and of totally oxidized gold particles in case of RF-plasma in O_2 and O_2+Ar atmospheres. In oxidized gold nanoparticles only one state of gold Au^{3+} and some different states of oxygen were observed. In total the oxygen and gold states observed in XPS spectra of oxidized nanoparticles are similar to their states in nanostructured three-dimensional gold oxide films. Thermo stability of gold oxide nanoparticles was fond to be about 350 K, that is lower than for massive gold oxides. The reaction probability was measured for CO and C_2H_4. Oxidized gold particles were found to be more active in CO oxidation. The highest value of observed reaction probability was $\chi{\sim}10^{-3}$. The form of kinetic curve allows to suppose an autocatalytic mechanism of CO oxidation over gold oxide nanoparticles.

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REDUCTION AND OXIDATION FEATURES PROCESSES XPS INVESTIGATION ON Pd/CeO$_2$ CATALYSTS SURFACE

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Oxidative catalysis is one of the most effective ways decreasing the automotive exhausts toxicity as well as industrial emissions. Therefore, the understanding of processes on the catalyst surface during oxidative catalysis is very important for this further development.

Palladium ceria catalysts are used as sufficiently simple model catalytic systems for fundamental investigation of more complex oxidation processes occurring on the composite multicomponent oxide catalysts surface using for automotive exhaust neutralization.

The aim of this work is the detailed XPS investigation of palladium surface states of 5%Pd/CeO$_2$ catalysts during step-by-step reduction in CO and subsequent step-by-step reoxidation in oxygen.

The catalysts have high low-temperature activity (LTA; $T < 150$ °C), and presence of palladium in two forms: palladium reduced interaction phase (PRIP) (BE(Pd3d$_{5/2}$) = 335.6 – 336.4 eV) and palladium oxidized interaction phase (POIP) (BE(Pd3d$_{5/2}$) = 337.5 – 338.3 eV). Catalysts characterizing by the absence of the above palladium forms are not capable for LTA in CO oxidation reaction. The nature of this palladium forms was investigated in detail in our previous work [1].

It should be noted, that the presence of two phases PRIP – POIP is typical feature for palladium – ceria catalytic systems (fig.1a). However, the mechanism of these phases action occurring on the catalyst surface during interaction of CO + O$_2$ mixes and CO, O$_2$ reagents has not properly studied till now.

The catalyst reduction in CO can be characterized by several steps. The first step is bound with Ox-Red transition Pd^{2+}/Pd^0 at the LTA range (0–150 °C), while cerium oxidation power doesn't change (fig. 1b). During this process palladium ions escape out of CeO$_2$ lattice (POIP) and grow on initial epitaxially fixed PRIP up to large metallic Pd particles. Ox-Red Ce^{4+}/Ce^{3+} transition is observed to occur at more higher temperatures above 120–150 °C (fig. 1c).

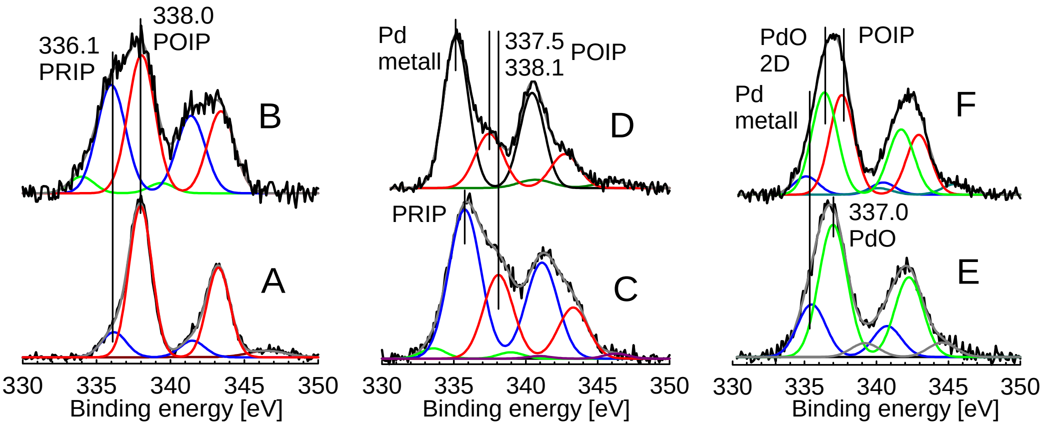

Figure 1. XPS Pd3d spectra of the initial 5%Pd/CeO_2 catalyst (A), the reduced in CO at T = 84 °C (B), 230 °C (C) catalyst, and further reoxidized in O_2 at T = 280 °C (E) и 450 °C (F) catalyst.

OSC of ceria begins to take a part in CO oxidation reaction at temperatures more than 230 °C. Transfer of reduced palladium back in CeO_2 lattice with POIP formation becomes impossible at these temperatures during subsequent reoxidation of catalyst in oxygen. This effect relates with formation of palladium particles size more than critical one. After achievement of this size of palladium particle the epitaxial interface between POIP and PRIP breaks and backward dissolution of palladium in CeO_2 becomes difficult at low temperatures of reoxidation in oxygen (fig.1d). Therefore, reoxidation at T = 280 °C of reduced catalyst leads to the bulk oxidation of part of metallic Pd particles to PdO without POIP formation (fig. 1e).

Heating of the catalyst in oxygen at T = 450 °C leads to disaggregation of PdO particles and following Pd penetration into subsurface lattice layers of CeO_2 with POIP formation as a result of CeO_2 lattice ions mobility. Residual palladium oxide phase can be attributed to 2-dimensional oxide PdO which able to play an intermediate role of transition PdO into POIP intermediate (fig. 1f).

Thus, the presented results allow us to make conclusion that epitaxial interface PRIP – POIP on catalyst surface is necessary for interconvertible transition of palladium in these phases which evaluate the LTA.

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IN SITU XRD INVESTIGATION OF ACTIVATION OF COBALT CATALYST AND MODEL COBALT OXIDE

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The Fisher-Tropsch synthesis is one of the processes producing synthetic liquid fuels and valued chemical compounds from syngas [1]. The supported metallic catalysts are widely used in Fischer-Tropsch synthesis. Cobalt based catalysts are suited to produce high yields of long alkanes. Catalysts are activated by reduction of Co_3O_4 in hydrogen. It is important to understand how the reduction conditions influence the structural parameters of catalyst. It is impossible to study structure parameters and phase composition of catalyst during the activation process in the reactor. When activated process is stopped catalyst reoxidation was observed. In situ X-ray powder diffraction (XRD) was used to characterize phase composition, size and structure of samples. We investigated Co_3O_4 supported on γ-Al_2O_3 and model samples to compare their behavior during reduction process.

Model sample was prepared from cobalt carbonate. Catalyst supported on γ-Al_2O_3 was prepared by the incipient wetness impregnation using a cobalt nitrate aqueous solution.

Results of XRD structural analysis show that in the both samples Co_3O_4 has similar structure namely it contains considerable quantity of vacancies both in tetrahedral and octahedral positions (the occupation of the positions is less than 1). A lack of cations in the samples is observed that means that the condition of a charge neutrality formally is not met. Presumably, compensation of the excess negative charge occurs via partial transition Co^{2+} in Co^{3+} and presence at samples residual carbonate and nitrate groups. The calculated average size of CSD is about 140Å for both samples.

In situ XRD investigations show that reduction process is different for supported and model samples in whole. But there are some features which are the same for both types of the samples. The reduction process for the both types of samples begins at the same temperature (T=180 °C). A series of the experiments for the refinement of Co_3O_4 structure before the reduction beginning has been spent. Structure refinement has shown that in both cases Co_3O_4 is also defective before reduction. The increase in occupation of the octahedral and tetrahedral positions is observed. Also occupation of the additional «non-spinel» positions 16c (0,0,0) is detected. It is possible to guess the structural mechanism of Co_3O_4 reduction: 1) excess oxygen ions leave Co_3O_4 under the influence of hydrogen and temperature, 2) cations fill vacancies and additional «non-spinel» octahedral positions using channels. Presence of cobalt ions in «non-spinel» positions means filling of two adjacent octahedrons jointed by edges, i.e. CoO structure fragments appear in the Co_3O_4 structure both in the model and supported samples. Nevertheless, in model sample appearance of crystal CoO phase is not observed and Co_3O_4 is reduced directly to metallic cobalt (hcp) i.e. model sample is reduced in one step. In contrary supported cobalt oxide is reduced in two steps. Reduction of Co_3O_4 to CoO clearly identified by XRD is the first step. The second step (CoO→Co) begins at 260 °C and it is not fully completed at the temperature 350 °C. At this temperature two phases CoO and Co (fcc) coexist. It seems cobalt ion diffusion into the structure of alumina leads to species that are difficult to reduce. Differentiative solution (DS) experiments confirmed this version. According to DS data there are two cobalt containing phases. One of this phases is determined as Co_3O_4 solutes together with Al ions. It may be combined oxide with Co-Al-O composition. The second phase solutes in the other conditions and is determined as Co_3O_4.

$$Co_3O_4 \xrightarrow{H_2,180^oC} Co(hcp)$$

$$Co_3O_4/\gamma Al_2O_3 \xrightarrow{H_2,180^oC} CoO/\gamma Al_2O_3 \xrightarrow{H_2,260^oC} (Co_{1-x}Al_xO + Co(fcc))/\gamma Al_2O_3$$

Metallic cobalt with hcp and fcc structures is formed as a result of reduction of the model and supported samples correspondingly. Particles of metallic cobalt of hcp and fcc structures have high concentration of stacking faults (SF) i.e. disordering of layer sequence ABABAB… and ABCABC…, respectively. It is observed as the anisotropic peak broadening on the X-ray diffraction patterns. We simulated XRD patterns for metallic cobalt (hcp and fcc) with various concentration of SF. The diffraction pattern simulation showed that Co(hcp) and Co(fcc) structures contained stacking faults with concentration of about 0.2 and 0.1, correspondingly.

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THE COMPARATIVE STUDY OF PHASE COMPOSITION OF Fe-Co CATALYSTS FOR THE MULTIWALLED CARBON NANOTUBES SYNTHESIS

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Carbon nanotubes have aroused the great scientific and commercial interest worldwide due to their unique physical and chemical properties. Composite materials containing carbon nanotubes are perspective objects for developing of the new materials with tailored mechanical, electrical and optical properties. However, the wide practical application of carbon nanotube based materials requires effective catalysts synthesis techniques.

At present catalytic chemical carbon deposition (CVD) method using multicomponent metal catalysts is most suitable among others known methods for low-cost and large-scale synthesis of high-quality nanotube materials. The most important parameter for the production of multicomponent metal catalysts is the homogeneity of the distribution of the components in the catalyst. Thus, the development of adequate approaches of catalysts phase composition control is very important for design of effective catalysts.

In this study we have performed comparative investigation of the phase composition of model FeCo catalysts with different content of active components using X-ray diffraction method (XRD), differential dissolution phase analysis method and transmission electron microscopy (TEM).

FeCo-catalysts supported on Al_2O_3 and MgO were synthesized via polymerized complex route, based on the Pechini-type reaction. For comparison, the samples of individual phases that seemed to be formed during the catalysts synthesis were also investigated. On the basis of elemental composition of catalysts the spinel-like structures formation (with total formula $M(II)_2M(III)O_4$) would be expected as well as formation of solid solutions based on MgO (for FeCo/MgO catalysts).

XRD study demonstrates the presence of spinels with variable composition (in the case of MgO supported catalysts it the presence of highly dispersed MgO was also detected). However, the detailed identification of spinel phases with XRD method is complicated because of similar lattice parameters and high dispersity of active component phases resulting in XRD-lines broadening.

Differential dissolution phase analysis method is based on the gradual solution of the catalyst sample with acid mixtures at increasing temperature with permanent chemical analysis of solutions carried out by means of atomic emission spectroscopy. The constancy of the concentration ratio of different components pointed out the presence of phases with definite composition. The results obtained with this method proved the formation of several phases in each FeCo/Al_2O_3 and FeCo/MgO catalysts. The presence of phases with variable composition was registered for highly dispersed catalysts.

TEM study based on analysis of bright-field and dark-field images, diffraction patterns and EDX spectra of specific catalyst grains (with size 3-10 nm) has also shown the presence of phases with variable composition.

The demonstrated combined approach is used for design of new efficient catalysts for the multiwalled nanotubes synthesis.

EFFECT OF SYNTHESIS CONDITIONS ON PHASE COMPOSITION OF MoVTe(Nb) OXIDE CATALYST FOR OXIDATIVE TRANSFORMATIONS OF PROPANE

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Introduction. MoV oxide catalysts modified by Te and Nb are known to be active in oxidation and ammoxidation of propane to acrylic acid and acrylonitrile, accordingly. High catalytic activity is related to orthorhombic M1 phase of composition $Te_2M_{20}O_{57}$ and selectivity to a pseudo-hexagonal M2 phase of composition $Te_{0.33}MO_{3.33}$ (M = Mo, V, Nb) [1].

In these work we have studied influence of the synthesis conditions on formation of phase composition of $MoV_{0.3}Te_{0.23}(Nb_{0.12})$ oxide catalyst.

Experimental. $MoV_{0.33}Te_{0.23}O_n$ and $MoV_{0.33}Te_{0.23}Nb_{0.12}O_m$ catalysts were prepared by the thermal evaporation of slurry at 80-00 °C or by spray-drying of slurry using a lab spray-dryer (Buchi-290). The ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}*4H_2O$, ammonium metavanadate NH_4VO_3, telluric acid H_6TeO_6 and niobium oxalate were used as reagents. pH of slurry was kept constant (2,9) by the addition of oxalic acid. The resulting solid precursors were calcined in flow He at 550 °C for 2 h.

The catalysts were characterized by BET, XRD, IR and Raman spectroscopy, HRTEM and differential dissolution (DD) methods.

The catalysts were studied in flow-circulation setup at a constant composition of the reaction mixture with a molar ratio $C_3H_8/NH_3/air = 1/1.2/15$ or $C_3H_8/H_2O/air = 1/5/10.7$ at 380-420 °C temperature. Reactants and products were analyzed using online gas chromatography.

Result and discussion. The present study disclosed an essential effect of liquid precursor drying procedure on the phase composition of the final catalyst.

Fig.1 shows the dissolution curves of Mo, V, Te, Nb and the corresponding relationship (V/Mo, Te/Mo and Nb/Mo) as a function of the dissolved amount of the dried samples prepared by spray-drying or by the thermal evaporation. Different drying procedures resulted in different phase composition of four-component sample. The thermal evaporation resulted in formation ternary Anderson-type heteropolyanion $[Mo_1V_{0.28}Te_{0.15}O_m]^{n-}$, Nb remained unbound (Fig1.a). Spray-drying resulted in formation of a four-component Anderson-type $[Mo_1V_{0.28}Te_{0.22}Nb_{0,07}O_m]^{n-}$ heteropolyanion (Fig.1b). In contrast with the four-component sample, drying procedure did not influence on phase composition of ternary sample. Both spray-drying and the thermal evaporation resulted in formation Anderson-type heteropolyanion with a similar composition $[Mo_1V_{0.28}Te_{0.22}O_m]^{n-}$ (Fig.1c).

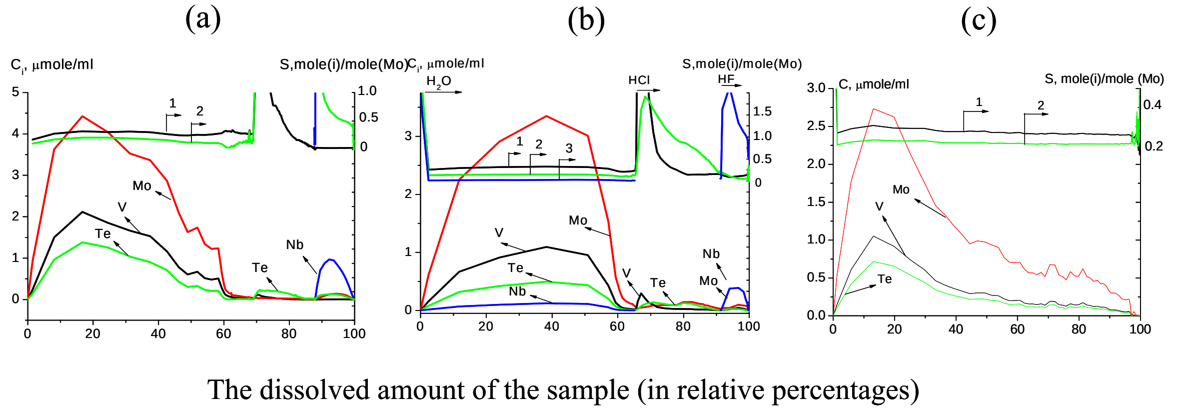

Figure. 1. The concentrations of Mo, V, Te, Nb (C_i, µmole /ml) and the corresponding stoichiograms (S, mole (i)/mole Mo) vs the dissolved amount of the sample (in relative percentages). i – Mo, V, Te, Nb; The stoichiograms: 1 – V/Mo, 2 – Te/Mo, 3 – Nb/Mo;
(a) - MoVTeNb (dry-up); (b) - MoVTeNb (spray-dry); (c) - MoVTe (spray-dry)

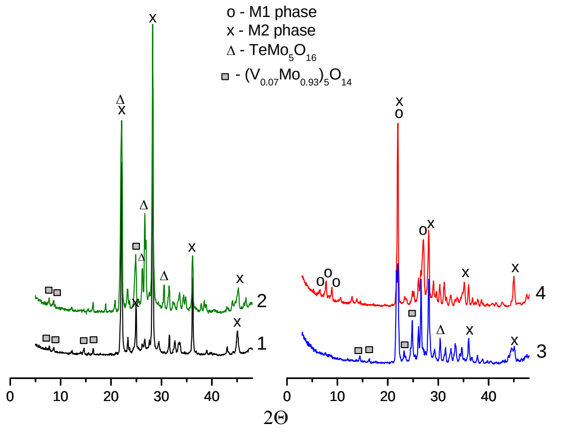

Figure. 2. XRD patterns of samples after heat treatment at 550°C.
1 - MoVTe (spray-dry); 2 - MoVTe (dry up); 3 - MoVTeNb (dry-up);
4 - MoVTeNb (spray-dry)

Fig. 2 demonstrates phase composition of final catalysts calcined at 550 °C in He flow. Heat treatment of ternary precursors resulted in formation of the pseudo – hexagonal M2 phase, independently of drying procedure. Small amounts of $TeMo_5O_{16}$ and $(V_{0.07}Mo_{0.93})_5O_{14}$ phases were also observed (curves 1,2). Similar heat treatment of MoVTeNb precursor prepared by the thermal evaporation resulted in primary formation of hexagonal M2 phase, too (curve 3). Heat treatment of four-component precursors prepared by spray-drying resulted in formation orthorhombic of the M1 phase (curve 4).

Effective catalyst consist of M1 phase and of the M2 phase in ratio 0.9:0.1, in that M1 phase provides the propane activation and M2 phase provides selective transformation of propylene, intermediated in formation acrylic acid and acrylonitrile.

According to data obtained, spray-drying of liquid precursor provides Nb insertion into the heteropolyanion, that is a determinative in formation of catalysts with desired characteristics that are high activity and selectivity.

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EFFECT OF OXYGEN MOBILITY ON CATALYTIC ACTIVITY OF La-Sr-(Mn,Fe)-O MIXED OXIDES IN THE REACTIONS OF METHANE OXIDATION AND NITROUS OXIDE DECOMPOSITION

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Mixed oxides of general formula $LaBO_3$ (B = Mn, Co, Fe, Cu, Cr) constitute a broad class of materials including catalysts for many oxidative processes. Substitutions of foreign M^{2+} (M = Sr, Ca, Ba) cations for La results in either the change of oxidation state of transition metal or the formation of anion defects in the packing of oxygen atoms. Formation of such defect structures influences on oxygen mobility properties, and thus, sometimes directly affects the catalytic properties of mixed oxides [1]. However, the nature of their catalytic activity is still widely debated in the literature. Among the most considerable factors are unusual oxidation states of transition metal, strength of B-O bond and lattice oxygen mobility. In this regard we think that formation of lattice defects by substitution of Sr for La and their effect on oxygen mobility seems to make the most substantial contribution. The main aim of this work was to examine possible relationship between oxygen mobility and catalytic activity in the reactions with participation of oxygen for a series of $La_{1-x}Sr_x(Mn, Fe)O_3$ mixed oxides.

The samples with formal stoichiometry $La_{1-x}Sr_x(Mn, Fe)O_3$ ($x = 0 \div 0.6$) were prepared by both Pechini route and mechanical activation of oxides/salts mixture followed by calcinations in air at 900 °C, characterized by XRD, XPS, differential dissolution phase analysis (DDPA), and tested in methane oxidation in temperature range 600 ÷ 900 °C and in nitrous oxide decomposition at 900 °C. Oxygen mobility was analyzed by steady-state isotope transient kinetic analysis (SSITKA) at 900 °C.

Independently on preparation, unmodified $La(Mn, Fe)O_3$ were single-phase perovskites. For $La_{1-x}Sr_x(Mn, Fe)O_3$ samples, phase composition and degree of Sr insertion in perovskite lattice depends on preparation method, nature of M^{2+} cation precursor and calcination conditions. So, calcination of perovskite prescursors in the reducing conditions (He instead of air) or using of organic ligands (Pechini route) burning out simultaneously with perovskite structure formation lead to the formation of multiphase composites containing layer-structured phase $(La_{1-y}Sr_y)_2(Mn,Fe)O_4$.

For the single-phase systems a specific activity vs x dependence can be explained by formation of oxygen vacancies in perovskite lattice created to compensate the reduced cation charge. Being the possible active sites for competitive N_2O and O_2 adsorption, the vacancies may be responsible for observed inhibiting effect of oxygen on the reaction rate. In case of multi-phase samples formation of layer-structured phase of K_2NiF_4-type in the surface/near subsurface layers of the particles was sufficient to reveal the highest rates of both CH_4 oxidation and N_2O decomposition.

The mechanism of high temperature oxygen transport was elucidated by numerical analysis of isotope responses observed at $^{16}O_2/^{18}O_2$ switches over the samples, considerably differing in phase composition. It was found that introduction of Sr in perovskite lattice gives rise to the appearance of a new fast pathway of oxygen exchange in the bulk of the solid caused by the creation of oxygen vacancies. The highest values of both the content of fast-exchangeable oxygen and the coefficient of oxygen diffusion were found for multiphase samples, containing layer-structured phase $(La_{1-x}Sr_x)_2(Mn, Fe)O_4$. It can be explained, first of all, by the structural features of the layer-structured $(La_{1-x}Sr_x)_2(Mn, Fe)O_4$ phase characterized by reduced oxygen bonding strength, which facilitates the formation of disordered – free channels for oxygen motion in the lattice [2]. Moreover, formation of highly dispersed MnO_x and SrO on the surface can lead to the creation of highly-developed network of micrograin boundaries characterized by enhanced oxygen mobility. Both for manganites and ferrites correlation was observed between oxygen mobility and specific catalytic activity in the reactions of methane combustion and N_2O decomposition.

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NEW APPROACH TO H/D-EXCHANGE USING FOR CHARACTERIZATION OF CATALYST ACIDITY

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The applying of H/D-exchange for characterization of catalyst acidity was proposed some decades ago. In these studies, H/D-exchange technique was used for measuring the acid sites number while the strength of sites was determined by other methods. Though, according to well known reasons, the number and strength of acid sites must be determined by the same method, for example, by widely used low-temperature FTIR spectroscopy of adsorbed CO. However, frequently used techniques turned out to be ineffective for acidity study of catalysts in a new form (like fiberglass materials) that appeared recently in catalysis area [1-3], since their structure is disrupted on a sample pretreatment.

The objective of our work was the development of a special technique that would allow determining both the number and strength of catalyst acid sites at high temperature. For that, we developed a technique similar to Steady-State Isotopic Transient Kinetic Analysis (SSITKA): in a plug-flow reactor under the dynamic adsorption-desorption equilibrium the H_2 flow was replaced stepwise by the D_2 flow with the following mass-spectrometric analysis of changes in labeled atoms concentrations at the reactor outlet. The numerical simulation of H/D-exchange dynamics was carried out in terms of kinetic model. As a result, we revealed that the rates of H/D-exchange depended on samples acidity, estimated the concentration of acid sites as well as the total amount of the exchangeable hydrogen atoms in the catalyst bulk.

For study, we used non-modified leached fiberglass material and that modified by alumina compounds. Besides, the following samples were used as references: 1) zeolite HZSM-5; 2) nanopowder SiO_2 obtained by evaporation in electron beam accelerator; 3) H_3PO_4/SiO_2 obtained by nanopowder SiO_2 impregnation with H_3PO_4.

The concentrations of different OH groups of zeolite obtained by the numerical modeling of the response curves were in a good agreement with the results of acidity measurement by IR spectroscopy of adsorbed CO. The exchange rate of H_3PO_4/SiO_2 sample with weaker acid sites (PA = 1270 kJ/mol) was significantly lower than that of zeolite. As to silica with the weakest BAS (PA = 1390 kJ/mol), the exchange rate was at least by two order of magnitude lower than that for zeolite. Thus, the correlation between the strength of acid site and the rate of H/D-exchange was revealed (Fig. 1).

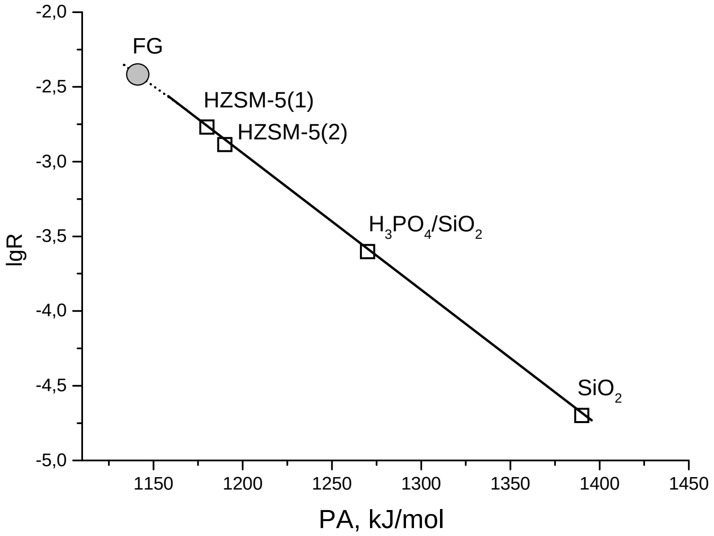

Fig. 1. Correlation between the H/D-exchange rate (calculated per 1 BAS) and *PA*.

By using that correlation curve we estimated the acidity of fiberglass materials in *PA* scale basing on measured rates of H/D-exchange. It amounts to 1130-1140 kJ/mol, i.e. the strength of Brønsted acid sites of fiberglass materials is comparable and even higher than that of zeolite. The lower PA in comparison to HZSM-5 is due to the fact that processes in fiberglass bulk proceed in the same way as if in solution since silica glasses can be referred by physical properties to viscous liquids.

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SYNGAS GENERATION BY PARTIAL OXIDATION OF METHANE: TRANSIENT STUDY

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Catalytic partial oxidation of methane at short contact times is now considered as an attractive technology for the small-scale and distributed production of syngas in the stationary and mobile fuel processing. From a mechanistic point of view, synthesis gas generation may involve either a direct conversion of methane to carbon monoxide and hydrogen or a highly exothermic complete combustion with the available oxygen followed by endothermic secondary steam and dry reforming steps of remaining hydrocarbon. These various routes may depend on the catalyst composition/surface structure (e.g. lattice oxygen mobility/reactivity, state of supported metals such as Pt etc). To discriminate these routes, kinetic methods able to probe the surface reactivity at its nearly constant composition are applied. This study is focused on using the transient (relaxation) experiments to investigate mechanistic features of the partial oxidation of methane (POM) over ceria-zirconia based mixed oxides doped with Pr, Gd or La and promoted with Pt.

Dispersed complex oxides $Me_{0.3}Ce_{0.35}Zr_{0.35}O_x$ (Me=La, Pr, or Gd) were prepared via Pechini route [1,2] and supported on the walls of separate triangular channels of α-Al_2O_3 monolith (wall thickness 0.2 mm, triangle side 2.33 mm, channel length 10 mm) from water suspension ultrasonically dispersed with addition of peptizers and surfactants (loading up to 10 wt.%). Pt (1.4 wt.%) was supported by incipient wetness impregnation with H_2PtC_6 solution. Kinetic transients experiments were carried out using quartz reactors and flow installations equipped with GC and on-line IR absorbance, electrochemical and polarographic gas sensors for different components as described elsewhere [1]. CH_4 concentration in the feed was varied from 7 to 20% with $CH_4 : O_2$ ratio = 2, the temperature range was 650–800 °C and contact times 1-15 ms. Before reaction, samples were pretreated at 700 °C in oxygen stream.

Analysis of experimental data showed that in studied conditions either no delay between responses of CH_4, CO, CO_2 and H_2 (Pr-doped catalyst) or CO_2 appearance after CO and H_2 (Gd-doped catalyst) was observed when switching from He to CH_4+O_2 feed. This demonstrates operation of direct CH_4 pyrolysis-selective oxidation route, which agrees with results of TAP data [3]. Delay of H_2 and CO responses increases with increasing contact time and decreasing CH_4 content. This suggests consumption of primary syngas by reaction with reactive surface oxygen species followed by its generation via secondary reforming reactions on the reduced surface. In this case, the longest delays in CO and H_2 appearance were observed for Gd-doped sample, which can be explained by their generation via formation and decomposition of formate-like species stabilized on this support. For La-doped sample the lowest methane and carbon oxides concentrations as compared to catalysts doped by Gd and Pr were observed during first 5 sec transients. This finding confirms a high adsorption ability of the surface and a high reactivity of oxidized platinum towards CH_4 dissociation. At the same methane conversion, CO_2 concentration is close for Gd- and La-doped samples, but for the latter CO and H_2 concentrations are significantly lower. Last observation shows the carbon imbalance (carbon build-up) and fast oxidation of formed hydrogen, which accelerates with platinum reduction during POM reaction. However, as follows from the analysis of products distribution, the primary process of methane pyrolysis on Pt particles takes place for the La-doped sample as well. Analysis of activity and selectivity of studied catalysts at steady state conditions revealed following row – Pt/PrCeZrO>Pt/GdCeZrO>Pt/LaCeZrO.

Basic approaches to estimation of the constants of key stages of methane transformation into syngas based upon modeling using a system of differential equations with a due regard for the oxygen mobility in complex oxide supports were developed.

This work is carried out in frames of Associated Russian-French laboratory on catalysis.

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NEW METHOD OF STUDY OF HETEROGENEOUS CATALYTIC HYDROGENATION REACTION MECHANISMS BY USING PARAHYDROGEN

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For homogeneous hydrogenations catalyzed by transition metal complexes in solution, the utilization of the nuclear spin isomers of molecular hydrogen has become an established tool for the studies of reaction mechanisms and kinetics. Parahydrogen induced polarization can enhance the NMR signals of reaction intermediates and products by several orders of magnitude and provides the high sensitivity essential for such studies. It has been demonstrated recently [1,2] that PHIP effects can be also observed in hydrogenation reactions catalyzed by metal complexes immobilized on a solid support. At the same time, industrial hydrogenation processes are predominantly heterogeneous and utilize supported metal catalysts. Such catalysts are not expected to produce PHIP effects since the reaction mechanism involved should destroy the original correlation of the two nuclear spins of parahydrogen. In this work, we demonstrate that, contrary to these expectations, supported metal catalysts such as Pt/Al_2O_3 and Pd/Al_2O_3 do exhibit PHIP effects. This fact can be used for the production of spin polarized fluids for MRI applications as well as for developing novel research tools for mechanistic and kinetic studies of heterogeneous hydrogenation processes.

Heterogeneous hydrogenation processes often use highly dispersed supported metals (e.g., Pt/Al_2O_3, Pd/Al_2O_3) as catalysts. Unlike homogeneous hydrogenations which take place on a well-defined single metal center, heterogeneous hydrogenations proceed on a vast surface of a metal cluster. This gives rise to a large number of various interaction possibilities and a variety of relevant and irrelevant species present on the surface during the reaction. As a result, despite a lot of effort devoted to studying the mechanisms of heterogeneous hydrogenation of simple alkenes such as ethylene, the conclusions regarding the reaction mechanism are still controversial. By combining the use of parahydrogen with the heterogeneous hydrogenation processes, it could be possible to develop novel fundamental and practical applications which rely on the substantial amplification of the NMR signals, including the mechanistic studies of heterogeneous hydrogenations and the production of polarized fluids for advanced MRI studies. However, the use of parahydrogen in combination with supported metal catalysts has been postulated to be pointless since the reaction mechanism apparently does not sustain the pairwise addition of hydrogen to a substrate on multiatomic metal crystallites, which is one of the main prerequisites for such applications. The reported results prove that, contrary to the expectations, utilization of parahydrogen in the hydrogenation of propylene catalyzed by highly dispersed supported metal catalysts (Pt/Al_2O_3 and Pd/Al_2O_3) does produce nuclear spin polarization of the reaction product propane, indicating that pairwise addition of hydrogen does take place to a measurable extent.

The pairwise hydrogen addition, while definitely present, is not necessarily the main reaction mechanism. For the catalysts used here, dominating quantities of the product are likely to be formed in the processes which involve random H atoms. For a 100% pairwise addition, the maximum enhancement factor expected under our experimental conditions would be ca. 3470. The one observed experimentally for the Pt(0.6 nm) catalyst was evaluated as ca. 100. Therefore, the contribution of the pairwise addition route can be estimated as ca. 3% if nuclear spin relaxation is neglected [3] However, there are many spin relaxation mechanisms that reduce the observed polarization. For practical applications, hydrogenation of alkynes is of importance, and in particular – the partial hydrogenation of alkynes in the presence of alkenes. For an initial study, we have chosen propyne (methylacetylene). The asymmetric substitution is essential for PHIP observation and also allows us to study stereoselectivity of the hydrogenation reaction

In a more recent study, a microreactor loaded with the catalyst was positioned inside the NMR probe and was imaged while the reaction was in progress [4]. This has made it possible to visualize those regions of the catalyst bed where the hydrogenation reaction was taking place.

This work was supported by the grants from RFBR (08-03-00661, 08-03-00539, 08-03-91102, 07-03-12147), the program of support of leading scientific schools (NSh-3604.2008.3), CRDF (RUC1-2915-NO07), RAS (5.1.1), SB RAS integration grants (67,88).

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ORAL SESSION

III. KINETICS AND MODELING OF CATALYTIC REACTIONS AND REACTORS

O-III-1

KINETICS OF FORMALDEHYDE OXIDATION OVER V/Ti OXIDE CATALYST

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Introduction

V/Ti oxide catalyst is active in formaldehyde oxidation to formic acid [1]. At the present work kinetics of formaldehyde oxidation to formic acid over V/Ti oxide catalyst was investigated.

Experimental

The catalyst of the composition 11% V_2O_5/89% TiO_2 (% mass) was prepared by method described in [1]. The BET specific area of the catalyst was 140 m^2/g. The density of vanadium was 5.2 at/nm^2.

The steady-state activity of the catalyst was tested in a differential reactor in a flow-circulation set-up. The catalyst fraction was 0.25-0.5 mm. The products and CH_2O were analyzed with a gas chromatograph. The kinetic dependence on the conversion of the CH_2O was investigated with the standard reaction mixture: 4% CH_2O, 10% H_2O, the rest was air. The experiment was carried out at 120-140 °C in the 20-85% range of CH_2O conversion. The influence of the CH_2O, O_2 and H_2O was investigated at a constant conversion of the CH_2O.

Results and discussion

In Fig. 1 the selectivities to formic acid (HCOOH) and to carbon oxides (CO, CO_2) are shown as the functions of the formaldehyde (CH_2O) conversion at the temperature range 120–140 °C. The main product of the reaction in the whole investigated range of conversion is HCOOH. Selectivity of its formation is 85-95%. Observed dependences illustrated parallel-consecutive network of products formation. The extrapolation of the HCOOH selectivity to the zero of the CH_2O conversion shows that a parallel share of its formation comprises about 97, 95 and 90% at 120 °C, 130 and 140 °C, correspondingly. CO is obtained by decomposition of formic acid. CO_2 forms during the parallel route. Contribution of the consecutive route increases with the temperature rise.

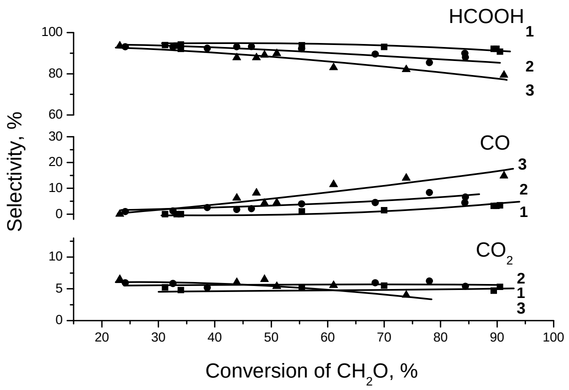

Fig.1. Selectivities to the reaction products as the functions of CH_2O conversion at the temperatures: 1- 120°C; 2 - 130°C; 3 - 140°C

Fig. 2, 3 show a dependence of the accumulation rates of products on the CH_2O (Fig. 2) and oxygen (Fig. 3) concentrations at the CH_2O conversion 60±2% and temperature 120 °C.

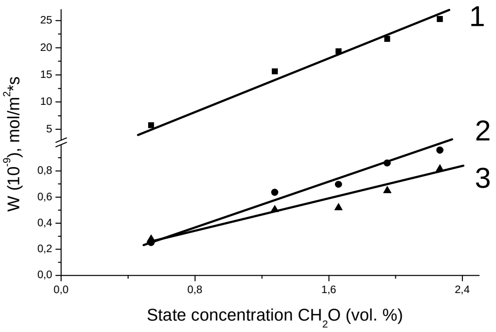

Fig. 2. Rates of accumulation (W) of HCOOH (1), CO (2) and CO_2 (3) as functions of CH_2O concentration. CH_2O conversion is 60%

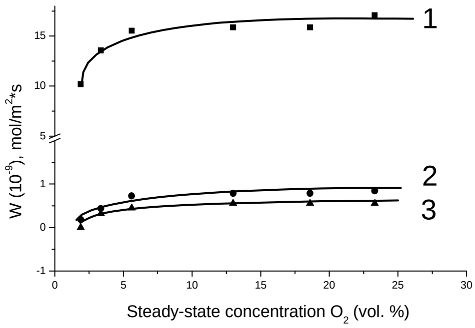

Fig. 3. Rates of accumulation (W) of HCOOH (1), CO (2) and CO_2 (3) as functions of O_2 concentration. CH_2O conversion is 60%

Linear dependence of accumulation rates of formic acid and carbon oxides in the range of entrance concentration CH_2O from 1 to 4% on formaldehyde concentration was obtained. The dependence of reaction product accumulation rate on the oxygen concentration is described by the saturation curves.

Fig. 4, 5 show a dependence of the products accumulation rates at 120 °C (Fig. 4) and selectivities at 120–140 °C (Fig. 5) on the H_2O concentrations at the CH_2O conversion 85±2%. Water accelerates the formation of formic acid and negatively influences on the accumulation rate of CO. Accumulation rate of CO_2 do not depend on the concentration of water. Selectivities change in accordance with products formation rates.

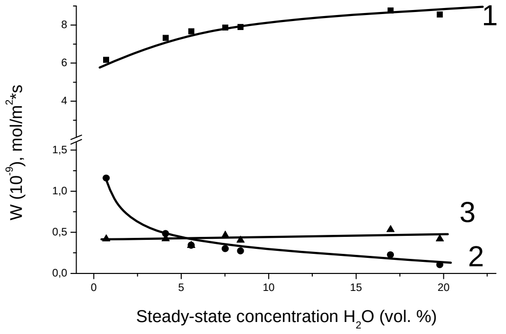

Fig.4. Rates of accumulation (W) of HCOOH (1), CO (2) and CO_2 (3) as the functions of H_2O concentration at 120°C.

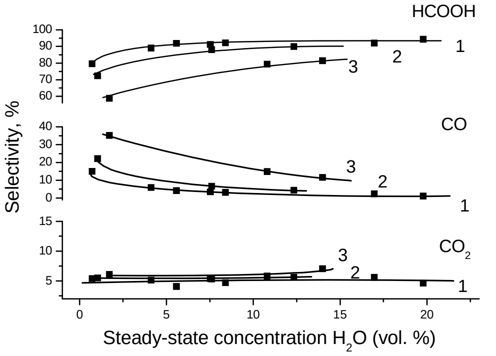

Fig.5. Selectivities to the reaction products as the functions of H_2O concentration at the temperatures: 1- 120°C; 2 - 130°C; 3 - 140°C.

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ALKYLATION REACTOR KINETIC MODELING

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Alkylation of benzene with higher olefines (carbon number from 10 to 14) is one of the last stages in production of linear alkylbenzene sulfonates (LAS), which are used as a base for surfactants production [1, 2]. Presently about 74 % of operating LAS-production plants use traditional HF catalyst [3]. Creation of alkylation reactor kinetic model was the main purpose of this work.

Industrial process kinetic modeling gives the opportunities of important manufacturing characteristics connected with changes in participating substances concentrations direct or indirect prediction. Such characteristics for alkylation process are: desired product and by-product output flows, linear isomers and 2-phenylalkanes percentage in desired product, bromine numbers of products.

Alkylation process technology [1] provides rather wide range of operating conditions, while kinetic modeling allows to determine an optimal unit functioning regime within the range for the specified raw materials composition.

At the same time, industrial process modeling requires solution of problems connected with complex and variable raw materials composition, great number of reactions simultaneous running. Experimental data obtained from operating alkylation unit are limited and carry not only kinetic, but also hydrodynamic, reactor construction information. Separation of purely kinetic information from available data is not possible and, so, reverse kinetic problem solution requires obligatory reactor model formation. Plug-flow reactor model was proposed for hydrodynamic regime description in alkylation reactor, this assumption was confirmed by Péclet number calculation.

Formalized reaction network based on laboratory and thermodynamic analysis data was used while creating of kinetic model:

$$\begin{cases}
C_nH_{2n}\quad (\text{olefine}-1) \xrightleftharpoons[k-1]{k1} C_nH_{2n}\quad (\text{olefine}-2) \\
C_nH_{2n}\quad (\text{olefine}-2) \xrightleftharpoons[k-2]{k2} C_nH_{2n}\quad (\text{olefine}-3,4..) \\
C_nH_{2n}\quad (\text{olefine}-1) \xrightleftharpoons[k-3]{k3} i-C_nH_{2n}\quad (\text{branched olefine}) \\
C_nH_{2n}\quad (\text{olefine-1}) + C_6H_6 \xrightleftharpoons[k-4]{k4} C_6H_5(C_nH_{2n+1})\quad (\text{2-phenylalkane}) \\
C_nH_{2n}\quad (\text{olefine-2}) + C_6H_6 \xrightleftharpoons[k-6]{k6} C_6H_5(C_nH_{2n+1})\quad (\text{2-phenylalkane}) \\
i-C_nH_{2n} + C_6H_6 \xrightleftharpoons[k-5]{k5} i-C_6H_5(C_nH_{2n+1})\quad (\text{branched alkylbenzene}) \\
C_nH_{2n}\ (\text{olefine}-3,4..) + C_6H_6 \xrightleftharpoons[k-7]{k7} C_6H_5(C_nH_{2n+1})\quad (3,4..\text{-phenylalkane}) \\
pseudo-C_6H_5(C_nH_{2n+1}) + pseudo-C_mH_{2m} \xrightleftharpoons[k-8]{k8} \\
\xrightleftharpoons[k-8]{k8} C_6H_4(C_nH_{2n+1})(C_mH_{2m+1})\quad (\text{dialkylbenzene}) \\
C_nH_{2n-2} + C_6H_6 \xrightleftharpoons[k-11]{k11} C_6H_5(C_nH_{2n-1})\quad (\text{unsaturated alkylbenzene}) \\
C_6H_5(C_nH_{2n-1}) + C_6H_6 \xrightleftharpoons[k-12]{k12} C_nH_{2n}(C_6H_5)_2\quad (\text{diphenylalkane}) \\
C_6H_5(C_nH_{2n-1}) + pseudo-C_mH_{2m} \xrightleftharpoons[k-9]{k9} \\
\xrightleftharpoons[k-9]{k9} C_6H_4(C_nH_{2n-1})(C_mH_{2m+1})\quad (\text{unsaturated dialkylbenzene}) \\
pseudo-C_6H_5(C_nH_{2n+1}) + C_mH_{2m-2} \xrightleftharpoons[k-10]{k10} \\
\xrightleftharpoons[k-10]{k10} C_6H_4(C_nH_{2n+1})(C_mH_{2m-1})\quad (\text{unsaturated dialkylbenzene})
\end{cases}$$

where n, m – carbon number of olefine’s molecule, n, m = 10-14.

Elaborated kinetic model was included in alkylation reactor model. Model verification showed good agreement of experimental and calculated values of main process parameters. The model allows to calculate the dynamics of main qualitative and quantative product characteristics under change of raw materials composition or operating conditions, and also to select optimal operating conditions for the specified raw materials composition.

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O-III-3

HIGHER HYDROCARBONS C_9-C_{14} DEHYDROGENATION PROCESS MODELLING ON SURFACE OF PLATINUM ACCELERATORS

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Higher hydrocarbons C_9-C_{14} dehydrogenation process mathematical modelling represents the chain of stages, which involve detailed thermodynamic analysis of processes, mechanism establishment of reactionary mechanism, its formalization, choice of platinum accelerator deactivation pattern, composition of transformation scheme and kinetic model which are based on formalized mechanism of reactions, development of reactor model.

On the base of off-the-shelf conceptions of dehydrogenation mechanism [1] a presumable scheme was composed. Electron molecular structures with use of Gaussian program package bases on quantum-chemical modelling method [2, 3] were calculated and thermochemical characteristics of reactions were evaluated. Thus the results of calculation show that aromatization reaction appears to be the most thermodynamically probable ($\Delta G^0_r \approx -300$ kilojoule/mol). Olefins cyclization, paraffins and olefines isomerization reactions do not run in the present process. Also the reactions of dienes formation with cumulative double bonds are not thermodynamically allowed ($\Delta G^0_r \approx 9$ kilojoule/mol). The presence of isomeric paraffins in product is determined by iso-paraffins dehydrogenation processes which are present in raw materials. All other possible reactions are thermodynamically probable and have approximately the same value of isobaric-isothermal potential ($\Delta G^0_r \approx -50$ kilojoule/mol). In the process the dienes with conjugate and secured double bonds are produced, whereas formation of dienes with cumulative double bonds is not thermodynamically allowed under these conditions.

Transformation scheme, in which carbohydrates were combined into reactionary groups by isobaric-isothermal index ΔG^0_r, was chosen. Kinetic model was based on reduced scheme, which permits to state the value of dehydrogenation transformation rates depending on response time, stuff composition, temperature and pressure in system:

$$\left\{\begin{array}{l}
\dfrac{dC_{\mathrm{C_nH_{2n+2}\,(алкан)}}}{dt} = -k_1 C_{\mathrm{C_nH_{2n+2}\,(алкан)}} - k_3 C_{\mathrm{C_nH_{2n+2}\,(алкан)}} - k_5 C_{\mathrm{C_nH_{2n+2}\,(алкан)}} + k_{-1} C_{\mathrm{C_nH_{2n}\,(алкен)}} C_{\mathrm{H_2}} + k_{-3} C_{\mathrm{C_nH_{2n}\,(циклоалкан)}} C_{\mathrm{H_2}} \\[2ex]
\dfrac{dC_{\mathrm{C_nH_{2n}\,(алкен)}}}{dt} = k_1 C_{\mathrm{C_nH_{2n}\,(алкен)}} - k_2 C_{\mathrm{C_nH_{2n}\,(алкен)}} - k_6 C_{\mathrm{C_nH_{2n}\,(алкен)}} - k_{-1} C_{\mathrm{C_nH_{2n}\,(алкен)}} C_{\mathrm{H_2}} + k_{-2} C_{\mathrm{C_nH_{2n-2}\,(алкадиен)}} C_{\mathrm{H_2}} \\[2ex]
\dfrac{dC_{\mathrm{C_nH_{2n-2}\,(алкадиен)}}}{dt} = k_2 C_{\mathrm{C_nH_{2n}\,(алкен)}} - k_{-2} C_{\mathrm{C_nH_{2n-2}\,(алкадиен)}}
\end{array}\right.$$

$$\left\{\begin{array}{l}
\dfrac{dC_{\mathrm{C_nH_{2n}}\,\text{(циклоалкан)}}}{dt}=k_3C_{\mathrm{C_nH_{2n+2}}\,\text{(алкан)}}-k_4C_{\mathrm{C_nH_{2n}}\,\text{(циклоалкан)}}-k_{-3}C_{\mathrm{C_nH_{2n}}\,\text{(циклоалкан)}}C_{\mathrm{H_2}}\\[2ex]
\dfrac{dC_{\mathrm{C_nH_{2n-6}}\,\text{(арен)}}}{dt}=k_4C_{\mathrm{C_nH_{2n}}\,\text{(циклоалкан)}}+k_5C_{\mathrm{C_nH_{2n+2}}\,\text{(алкан)}}+k_6C_{\mathrm{C_nH_{2n}}\,\text{(алкен)}}\\[2ex]
\dfrac{dC_{\mathrm{C_nH_{2n+2}}\,\text{(изоалкан)}}}{dt}=-k_7C_{\mathrm{C_nH_{2n+2}}\,\text{(изоалкан)}}+k_{-7}C_{\mathrm{C_nH_{2n}}\,\text{(изоалкен)}}C_{\mathrm{H_2}}\\[2ex]
\dfrac{dC_{\mathrm{C_nH_{2n}}\,\text{(изоалкен)}}}{dt}=k_7C_{\mathrm{C_nH_{2n+2}}\,\text{(изоалкан)}}-k_8C_{\mathrm{C_nH_{2n}}\,\text{(изоалкен)}}-k_{-7}C_{\mathrm{C_nH_{2n}}\,\text{(изоалкен)}}C_{\mathrm{H_2}}+k_{-8}C_{\mathrm{C_nH_{2n-2}}\,\text{(изоалкадиен)}}C_{\mathrm{H_2}}\\[2ex]
\dfrac{dC_{\mathrm{C_nH_{2n-2}}\,\text{(изоалкадиен)}}}{dt}=k_8C_{\mathrm{C_nH_{2n}}\,\text{(изоалкен)}}-k_{-8}C_{\mathrm{C_nH_{2n-2}}\,\text{(изоалкадиен)}}C_{\mathrm{H_2}}\\[2ex]
\dfrac{dC_{\mathrm{H_2}}}{dt}=k_1C_{\mathrm{C_nH_{2n+2}}\,\text{(алкан)}}+k_2C_{\mathrm{C_nH_{2n}}\,\text{(алкен)}}+k_3C_{\mathrm{C_nH_{2n+2}}\,\text{(алкан)}}+3\cdot k_4C_{\mathrm{C_nH_{2n}}\,\text{(циклоалкан)}}+4\cdot k_5C_{\mathrm{C_nH_{2n+2}}\,\text{(алкан)}}+3\cdot k_6C_{\mathrm{C_nH_{2n}}\,\text{(алкен)}}\\[1ex]
\qquad +k_7C_{\mathrm{C_nH_{2n+2}}\,\text{(изоалкан)}}+k_8C_{\mathrm{C_nH_{2n}}\,\text{(изоалкен)}}-k_{-1}C_{\mathrm{C_nH_{2n}}\,\text{(алкен)}}C_{\mathrm{H_2}}-k_{-2}C_{\mathrm{C_nH_{2n-2}}\,\text{(алкадиен)}}C_{\mathrm{H_2}}-k_{-3}C_{\mathrm{C_nH_{2n}}\,\text{(циклоалкан)}}C_{\mathrm{H_2}}\\[1ex]
\qquad -k_{-7}C_{\mathrm{C_nH_{2n}}\,\text{(изоалкен)}}C_{\mathrm{H_2}}-k_{-8}C_{\mathrm{C_nH_{2n-2}}\,\text{(изоалкадиен)}}C_{\mathrm{H_2}}
\end{array}\right.$$

Initial conditions $t=0$, $C_i=C_{0i}$, where i- corresponding hydrocarbon (paraffin, olefin and others).

Framed kinetic model will assume as basis of dehydrogenation process mathematical model, which will permit to:

1. Forecast the calculations of process characteristics taking into account specific character of stuff and technological conditions, type of accelerator and analyze the influence of installation behaviour to selectivity process and coke accumulation;

3. Test the platinum accelerators in specific technology conditions and specified hydrocarbon mixture of stuff and determine the optimal technological characteristics of process on working manufacture in real time regime;

5. Calculate the different variants of modernization the working installations with the purpose of promotion the effectiveness of their work.

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O-III-4

KINETIC STUDIES OF THE SELECTIVE CO METHANATION OVER Ni/CeO$_2$ CATALYSTS

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The work is devoted to the studies of nickel-cerium oxide catalysts in the selective CO methanation - a promising method for CO removal from hydrogen-rich gas mixtures obtained by steam reforming/partial oxidation of hydrocarbons or alcohols followed by water-gas shift reaction. As such hydrogen-rich gas mixtures are used for feeding of low-temperature proton-exchange membrane fuel cells, the CO level must be reduced below 10 ppm.

Several catalyst sets have been prepared by different methods. The catalysts prepared by impregnation demonstrated the best performance. After nickel supporting on ceria the catalysts were dried in air and reduced in H_2 flow at 400 °C for 2 h.

The prepared fresh and spent nickel-cerium oxide systems were characterized by means of TPR, TPO, TPD, XRD, XPS and TEM techniques.

The catalyst performance for selective CO methanation in H_2 excess was studied in a flow setup with on-line chromatographic analysis of the reaction products. The dependencies of the catalyst performance on the temperature, inlet composition and feed rate of the gas mixture as well as activation energy and reaction orders have been determined. The experiments were performed at GHSV = 5000 ÷ 80000 h^{-1} and temperature 200 ÷ 400 °C.

It was found that the use of a special procedure for nickel supporting on ceria allowed production of highly active and selective CO methanation catalysts. A series of catalyst samples with various nickel loadings (2-50 wt.%) were prepared. The 10 wt.% Ni/CeO$_2$ catalyst showed the best performance and decreased the CO concentration below 10 ppm in a wide temperature interval with high selectivity. Studies by physicochemical methods (XRD, TEM, XPS) proved small (3-4 nm) nickel particles to be the active component. When exposed to the reaction mixture (reducing atmosphere), these particles reduce to metal nickel; in air (oxidation atmosphere) they re-oxidize to nickel oxide without loss of dispersity. In further experiments the catalyst keeps the activity high.

To analyze the obtained experimental data, a kinetic model has been developed and applied for the process simulation. The model assumes kinetic scheme including the following reactions: CO methanation, CO$_2$ methanation and reverse WGS (feasibility of the latter reaction with this catalyst was confirmed by additional experiments). Figure 1 proves that the model successfully describes the obtained experimental data.

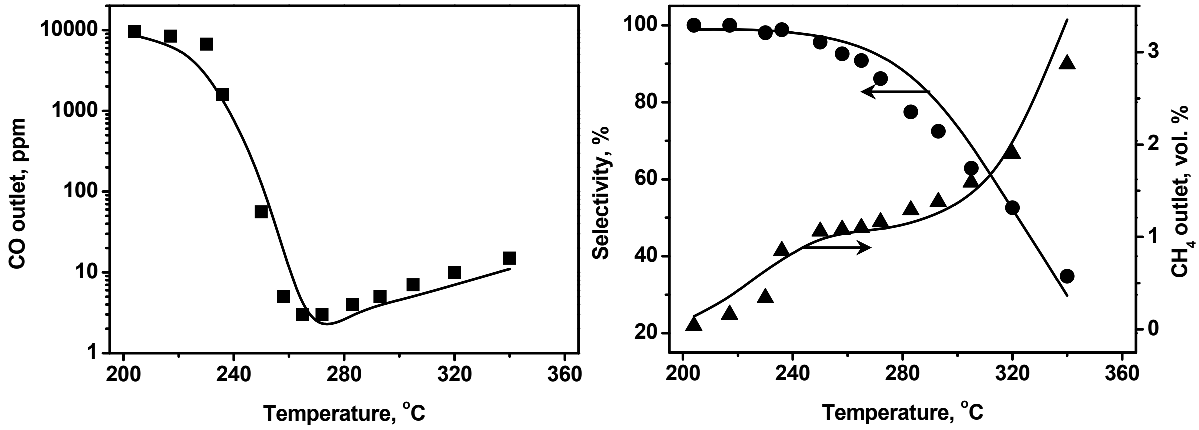

Figure 1: Temperature dependencies of the outlet CO, CH_4 concentration and selectivity for the reaction of selective CO methanation in H_2 excess over catalyst 10 wt.% Ni/CeO_2 (points-experiment, lines – theoretiacal modeling).

The results obtained prove that Ni/CeO_2 is active and selective catalyst for the reaction of CO methanation in hydrogen-rich gas mixtures; it allows reducing CO concentration to <10 ppm within wide temperature interval at selectivity ≥50%.

Acknowledgements

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PREFERENTIAL CO OXIDATION IN HYDROGEN-RICH GAS MIXTURES OVER A Cu/CeO_2 CATALYSTS

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Hydrogen for low-temperature proton-exchanged membrane fuel cell (PEM FC) applications is usually generated by a multistage process including either catalytic partial oxidation, steam or autothermal reforming of hydrocarbons, alcohols or ethers, followed by CO water gas shift reaction. The obtained hydrogen-rich gas mixture contains most often 0.5–2.0 vol.% CO, which poisons the FC anode catalyst and must be removed to a level below 10 ppm. Preferential CO oxidation (PrOx) is one of the promising methods for CO removal from hydrogen-rich gas mixtures. Copper-cerium oxide systems are active and selective catalysts for PrOx [1] and they are chipper than systems based on noble metals.

Several series of the copper-cerium oxide catalysts for preferential CO oxidation were synthesized by various procedures that allowed variation of the textural and morphological characteristics of the samples. The main efforts were focused on finding the optimum catalyst composition and on development of the most feasible preparation procedure. Catalyst screening of prepared samples in PrOx reaction was performed in a fixed-bed U-shape quartz flow reactor (i.d.: 3 mm, catalyst bed length: 30 mm) at atmospheric pressure (Fig. 1). Gas mixture composition was analized by gas chromatograph. It was found that 5 wt% Cu/CeO_2 catalysts prepared by Pechini and impregnation methods showed optimal catalytic characteristics. As CO and H_2 oxidation are very exothermal reactions, it is important for reactor to provide high heat transfer rate. Wall coated microchannel catalytic reactors are favorable candidates for preferential CO oxidation due to high heat and mass transfer rates achieved. The washcoating procedure for the most active copper-ceria catalyst compositions was based on the deposition of water suspension of the catalyst with polyvinyl alcohol as a binder into microchannels of stainless steel platelets. The obtained coatings demonstrated good impact-resistance and were intact after contact with water.

Simple sandwiched (two-plate) and laser-welded microchannel reactors were used for catalyst testing. Catalytic performance of the microchannel reactors were checked using model feeds at WHSV = $50000 – 500000\ cm^3g^{-1}h^{-1}$, $[O_2]_{inlet}/[CO]_{inlet}$ rate = 0.6 – 1.5 and temperature 100 – 300 °C. The results are displayed in Fig. 2.

Using these conditions, operation of 26 paralleled microreactors was tested. To provide process without additional heating of reactors, the heat losses due to contact with ambient air were compensated by the heat release from the oxidation reaction. The experiment proved stable operation of the microreactor assembly under the specified conditions.

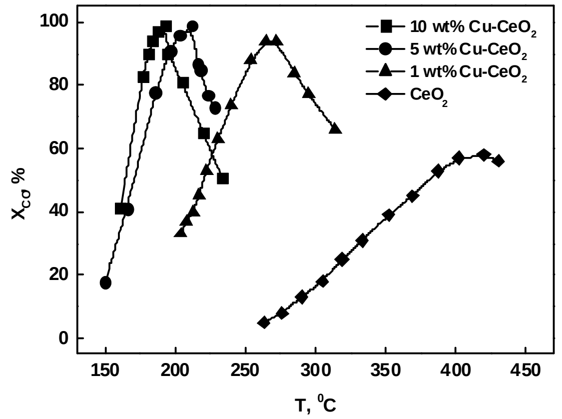

Figure 1. CO conversion as a function of temperature for catalysts with different copper content and for pure CeO_2 synthesized by Pechini method. 1 vol% CO, 1.5 vol% O_2, 10 vol% H_2O, 20 vol% CO_2 and H_2 as a balance. WHSV = 58000 $cm^3g^{-1}h^{-1}$.

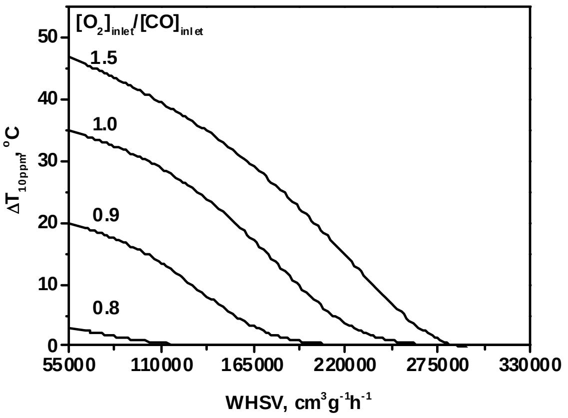

Figure 2. PrOx operational window (ΔT_{10ppm}) as a function of WHSV and $[O_2]_{inlet}/[CO]_{inlet}$. The inlet gas mixture composition is: 1 vol% CO, 0.6–1.5 vol% O_2, 10 vol% H_2O, 20 vol% CO_2 and H_2 as a balance.

Catalytic experiments have been performed that allowed determining the apparent activation energy of the reactions of CO and H_2 oxidation, the reaction orders with respect to O_2 and CO. It was observed [2] that the hydrogen consumption in the absence and in the presence of CO remained the same when the oxygen conversion was incomplete. In other words, the presence of CO does not influence the H_2 oxidation rate in the oxygen excess. It seems reasonable to suggest that the reactions of CO and H_2 oxidation proceed independently using of the same common reagent – O_2. This assumption helps to simplify the mathematical modeling and describe the observed kinetic dependencies by relatively simple equations. Results of numerical modeling of the preferential CO oxidation reaction over Cu/CeO_{2-x} catalysts using estimated kinetic parameters adequately described the observed catalytic dependences and can be used for reactor design.

The work is supported partially by grants BRHE Y4-C-08-12 and MG-2007/04/1 of “Global Energy” Foundation.

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O-III-6

MRI AS A TOOLKIT FOR INVESTIGATION OF AUTOCATALYTIC REACTION FRONTS PROPAGATION

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The classic route of examining only intrinsic kinetics of the reactive process is only meaningful when microscopic inhomogeneities can no longer be detected. Magnetic resonance imaging (MRI) is one of the methods, which gives an approach of opening this black box around the chemical reactor [1]. The work presents an application of MRI for in situ investigation of dynamics of chemical waves propagation in the flowing reactive media. The study is directed to gain information about heat and mass transport as well as main reactants concentration changes during the propagation of chemical reaction fronts in condensed liquid phase. Several autocatalytic non-oscillating chemical systems were examined. For the first time visualization of exothermal chemical reaction wave was performed by means of NMR water chemical shift thermometry [2]. Applied technique allows measuring temperature changes arising in the water medium with accuracy ± 1 °C. Acquired temperature maps allow one to judge about geometries of buoyancy convection flows arising during thermal wave propagation, Figure 1b. Additionally, convective flow was quantified by MRI phase contrast method and antisymmetric convection mode was detected in these experiments, Figure 1a.

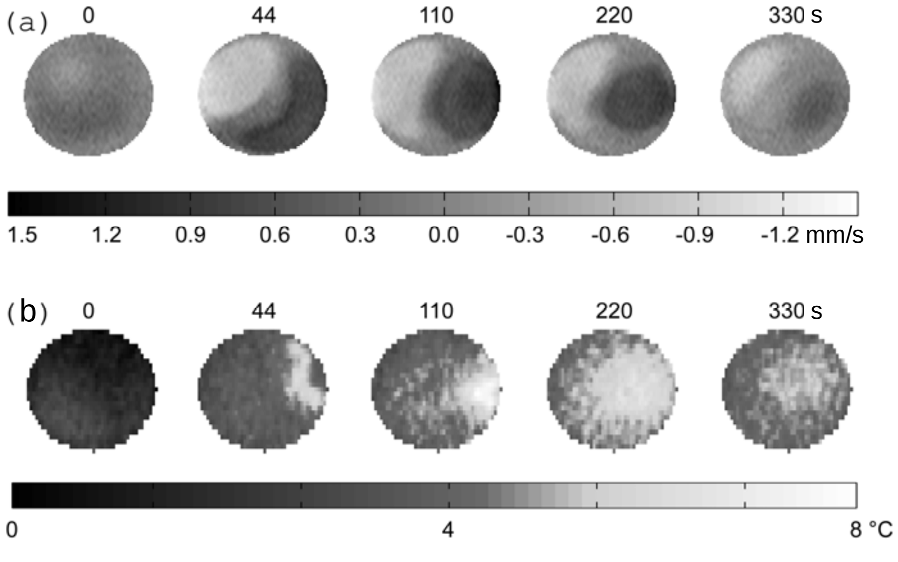

Figure 1. (a) Maps of vertical conponent of convection velocity acquired during the propagation of oxydation front of chlorite-thosulfate reaction in the vertical galass tube of internal diameter 9.1 mm. A horisontal crossections. (b) Temperature maps measured in the same conditons as in (a). A slice thickness is 2 mm in (b) and 1 mm in (a).

Essential part of the work considers the behavior of the reaction fronts in the forced convective flowing media in the packed bed (PB). The conventional optical methods of investigation are unable to provide information about the position of reaction front inside the optically-opaque PB. On the contrary, MRI seems to be a very powerful method of investigation of the processes occurring in the porous media as was shown recently and also in the present work [1,3]. Several effects of the flow dispersion influence on reaction fronts propagation in the PB were found. In particular, for the first time it was shown that stationary (not moving) chemical waves can appear not only in the excitable media flowing in the packed bed, but in bistable systems like chlorite-thiosulfate system as well [3]. Performed model calculations shows that geometry of the forced convective flow in the PB is favorable for acheving limiting bevaviour characterizing by the formation of stationary fronts in the wide range of adverse convective flow velocities [3].

Additionally, the joint action of forced and free convection was considered in the work. By application of MRI for the case of iron-nitric acid system it was found that velocity of the reaction front can spontaneously switch back and forth between constant values of velocities over a certain flow velocity range in the capillary of internal diameter 0.9 mm [1]. Formally two kinds of these periodical switches of the front velocity can be isolated: low- and high-frequency oscillations of front velocity. According to the numerical calculations of the simplified two-dimensional model high-frequency front velocity oscillations can appear due to specific behavior of the free convective flow.

Acknowledgments

Authors are grateful for a support of the present work by grants from the Russian Foundation on Basic Research (08-03-00661, 08-03-00539, 08-03-91102, 07-03-12147), the program of support of leading scientific schools (NSh-3604.2008.3), Civil Research Development Foundation (RUC1-2915-NO07), Russian Academy of Sciences (5.1.1) and Siberian Branch of Russian Academy of Sciences integration grants (67, 88).

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ORAL SESSION

IV. CATALYSIS FOR ENVIRONMENTAL PROTECTION, PHOTOCATALYSIS

SELECTIVE CATALYTIC REDUCTION OF NITRIC OXIDE BY AMMONIA ON Mn(Fe)-SUBSTITUTED Sr(La) ALUMINATES

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INTRODUCTION

Nitrogen oxides are one of the major sources of air pollutant. The selective catalytic reduction (SCR) of NO_x by NH_3 is the most widespread method for utilization of nitrogen oxides containing in automobile exhaust gases [1]. The most active catalyst in this reaction is commercial V_2O_5-WO_3/TiO_2 [2]. The main disadvantage of this catalyst is its instability under conditions of the working automobile engine (600–800 °C). Therefore, the search of active and stable catalysts for this reaction is continued.

Among the various oxide compositions, hexaaluminates are characterized by high-temperature stability and high activity. Their high thermal stability is related to the unique lamellar structure that consists of Al_2O_3-containing spinel block intercalated by mirror planes, in which the largest cations (Ba, Sr, La, etc.) are located. The other feature of hexaaluminates is their ability to form substituted modifications – $LaMnAl_{11}O_{19-\delta}$ [3]. At the same time, Mn-containing compositions, in particular MnO_x/Al_2O_3, show high activity in the SCR, but they also are not very stable [4]. Therefore, it would be expedient to investigate in the SCR Mn(Fe)-substituted hexaaluminates.

The aim of the present work was to synthesize the hexaaluminates $Sr_{1-x}La_xMn_2Al_{10}O_{19-\delta}$ (x = 0; 0.2), $SrFeMnAl_{10}O_{19}$ and to study the influence of the nature of alkaline-earth, rare-earth and transition metals on their structure, texture and catalytic properties in the SCR of NO by NH_3.

EXPERIMENTAL

The hexaaluminates were prepared by co-precipitation of soluble nitrates of ***Al*** and ***M*** (***M*** = Sr, La, Mn, Fe) at pH = 7.5 – 8 and temperature of 70 °C, with NH_4HCO_3 as a precipitating agent [3]. The dried samples were calcined at 700 and 1100 °C.

The chemical contents, structure and texture of the hexaaluminates were investigated by absorption methods, thermal analysis (TG-DTA), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR). The catalytic properties of the samples were studied in SCR of NO by NH_3. The catalyst activity in SCR was tested in accordance with the Light-off test.

RESULTS AND DISCUSSION

The phase composition of the hexaaluminates is determined by nature and contents of components and calcination temperature. According to XRD, the hexaaluminates calcined at 1100 °C indicate that all the samples are multiphase. Except the main phase of the hexaaluminate, the samples contain products of the interaction of Mn, Fe, Al and La oxides.

The hexaaluminates obtained are characterized by high specific surface area, which after calcination at 1100 °C is 20–50 m^2/g.

According to TPR-H_2, the reduction of the samples calcined proceeds in several steps. It can be related to presence of Mn and Fe ions in different states. The amount of H_2 consumed during the reduction of the samples calcined at 700 and 1100 °C increases in the series: $SrMn_2Al_{10}O_{19}$ (1100) < $SrFeMnAl_{10}O_{19}$ (1100) < $SrFeMnAl_{10}O_{19}$ (700) < $SrMn_2Al_{10}O_{19}$ (700) < $Sr_{0.8}La_{0.2}Mn_2Al_{10}O_{19}$ (700).

According to XPS, surface concentrations of elements in the samples $Sr_{0.8}La_{0.2}Mn_2$ $Al_{10}O_{19}$ and $SrFeMnAl_{10}O_{19}$ differ from the volume chemical contents. The main components on the surface are in oxidized state: Al^{3+}, La^{3+} and Fe^{3+}, Mn^{3+} and Mn^{2+}. Amount of Mn^{3+} ions is 65 and 49%, respectively. Sr is predominantly localized on the surface as $SrCO_3$.

The catalytic properties of the hexaalumiantes in the SCR are determined by nature and ratio of their components and calcination temperature. For the samples calcined at 700 and 1100 °C, the NO conversion increases in the series: $SrMn_2Al_{10}O_{19}^{1100}$ (*33%*) ≤ $SrFeMnAl_{10}O_{19}^{1100}$ (*34%*) < $SrFeMnAl_{10}O_{19}^{700}$ (*39%*) < $SrMn_2Al_{10}O_{19}^{700}$ (*50%*) < $Sr_{0.8}La_{0.2}Mn_2Al_{10}O_{19}^{700}$ (*78%*). At the same time the amount of H_2 ($\mu mol/g_{catalyst}$) consumed in the reduction of these samples increases in the same order. Hence, the catalytic activity for the SCR increases with an increase in the amount of accessible oxygen. The study of these hexaaluminates showed that the most selective with respect to N_2 is the $Sr_{0.8}La_{0.2}Mn_2Al_{10}O_{19}$ sample calcined at 700 °C. Mn^{2+} and Mn^{3+} is present on the sample surface, amount of the latter being about 65%.

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PHOTOCATALYTIC WATER SPLITTING OVER Pt/TiO_2 CATALYST WITH Ce^{3+}/Ce^{4+} SHUTTLE REDOX SYSTEM

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Hydrogen as a high-energy fuel has attracted attention all over the world already for several decades. The cleavage of water into H_2 and O_2 by sunlight was shown to be potentially one of the most promising ways for the photochemical conversion and storage of solar energy [1]. For pure hydrogen production it is suggested to use inorganic donors, for example Ce^{3+} ions. Cyclic interfacial electron transfer can be carried out if Ce^{3+} ions are oxidized into Ce^{4+} that are reduced back by applying photocatalytic reduction with simultaneous water oxidation and oxygen evolution.

We used aqueous solution of $Ce_2(SO_4)_3$ for hydrogen, and $Ce(SO_4)_2$ for photocatalytic oxygen production. Oxygen and hydrogen were obtained in different experiments. Water suspension with catalyst and $Ce_2(SO_4)_3$ or $Ce(SO_4)_2$ was placed in a sealed thermostatic oxygen-free reactor and illuminated by a 1000-W high-pressure mercury lamp under continuous stirring. The concentration of H_2 and O_2 was measured by means of a gas chromatograph. The concentrations of Ce^{3+} and Ce^{4+} were determined by a Lambda 35 UV/Vis-spectrometer. Platinized commercial Degussa P25 with 1 % wt. of Pt was used as a photocatalyst.

Oxygen is shown to evolve from the Ce^{4+} solution in the presence of UV-irradiation and semiconductor catalyst; hydrogen is shown to evolve from Ce^{3+} solution under UV-irradiation without any catalyst, but the rate of photocatalytic hydrogen production was higher than the rate of non-catalytic production of hydrogen. Full conversion of $Ce(SO_4)_2$ into $Ce_2(SO_4)_3$ with simultaneous quantitative oxygen evolution was attained (Fig. 1).

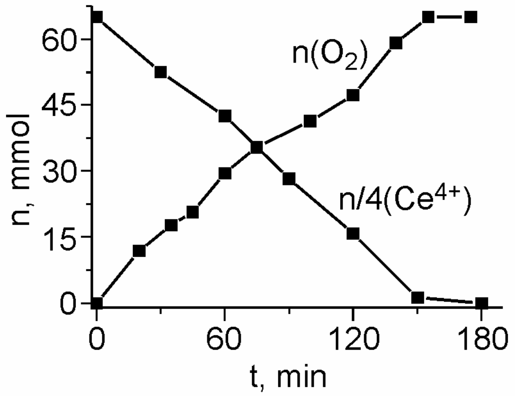

Figure 1: Dependence of the quantity of oxygen evolved on reaction time. Catalyst – 1% Pt/TiO_2 Degussa P25 [2].

The rate of photocatalytic hydrogen production was lower than the rate of photocatalytic oxygen production on the same catalyst. The influence on photocatalytic oxygen and hydrogen production of initial substrate concentration, acidity and catalyst loading was measured. The dependences of both hydrogen and oxygen production on the initial concentration of Ce have a maximum. A kinetic equation for the rate of photocatalytic oxygen production was proposed; constants of this equation were calculated. The mechanism of photocatalytic hydrogen production is more complicated. The optimal catalyst loading for photocatalytic oxygen and hydrogen production is not the same due to the difference in adsorption of Ce^{3+} and Ce^{4+} on the photocatalyst surface. Both hydrogen and oxygen evolve with a high rate in acidic media. Optimal conditions for photocatalytic reactions were found and explained.

Consecutive experiments on photocatalytic water splitting with separate evolution of O_2 and H_2 were conducted. Separate catalysts should be used for hydrogen and oxygen production in the shuttle redox Ce^{3+}/Ce^{4+} system.

We gratefully acknowledge the partial support of NATO grant SfP-981461, ISTC grant 3305, SB RAS integration grants # 36 and 70 as well as SB RAS Presidium grant # 27.56.

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STEAM REFORMING OF ETHANOL OVER $Cu/ZnO/CeO_2$ CATALYSTS

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On-board hydrogen production starting from a suitable liquid source such as ethanol-water mixture which can be easily produced from the biomass, appears to be in the focus of interest in both industrial and fundamental catalysis. It has been found that not only $Cu/ZnO/Al_2O_3$ has high efficiency in the ethanol reforming [1] but CuO/CeO_2 [2] and high surface area CeO_2 [3] are also effective catalysts for this reaction.

In this work ethanol steam reforming was investigated over $Cu/ZnO/CeO_2$. Supports were prepared by coprecititation, and they were impregnated by $Cu(NO_3)_2$ to obtain $Cu/ZnO/CeO_2$ catalysts (Zn/Ce=2:1 and 4:1, the molar ratio of Cu and the support was 1:9).

Catalysts were characterised with BET-surface measurement, XPS, DRIFTS, and TPD. Before measurements the fragments of catalyst pellets were oxidized and reduced.

TPR measurements shows that during the reduction not only the Cu reduces, but the support too. ($Cu/ZnO/CeO_2$ (Zn/Ce=4:1) consumes more H_2, and reduces at lower temperature than the other catalyst. XPS spectra reveal that after reduction Cu(0) and Ce(IV) are present on the surface but Zn almost disappears.

Reaction was carried out in a fixed-bed continuous flow reactor. The analysis of the products was carried out with an Agilent 6890N gas chromatograph. Both catalysts produce H_2, CO_2, acetaldehyde and acetone as main products. In the ethanol reforming a slightly decrease in the conversion (37-40%) was observed at 723 K. At higher temperature, at 923 K a huge decrease occured in the activity of the catalysts. (*Fig. 1*). Over the $Cu/ZnO/CeO_2$ (Zn/Ce=2:1) catalyst we observed higher conversion than over the other sample. The selectivity of the products formation changed only slightly at 723 K, but this value for acetaldehyde increased significantly in time *(Fig. 2)*. The IR spectra registered in the course of the reaction shows that surface acetate species are present on the surface of the catalyst.

Comparing the activity of the samples it was found that the $Cu/ZnO/CeO_2$ (Zn/Ce=2:1) sample shows a better performance than the other catalyst. We may suppose that surface acetate species detected by FTIR measurements can cause deactivation [4].

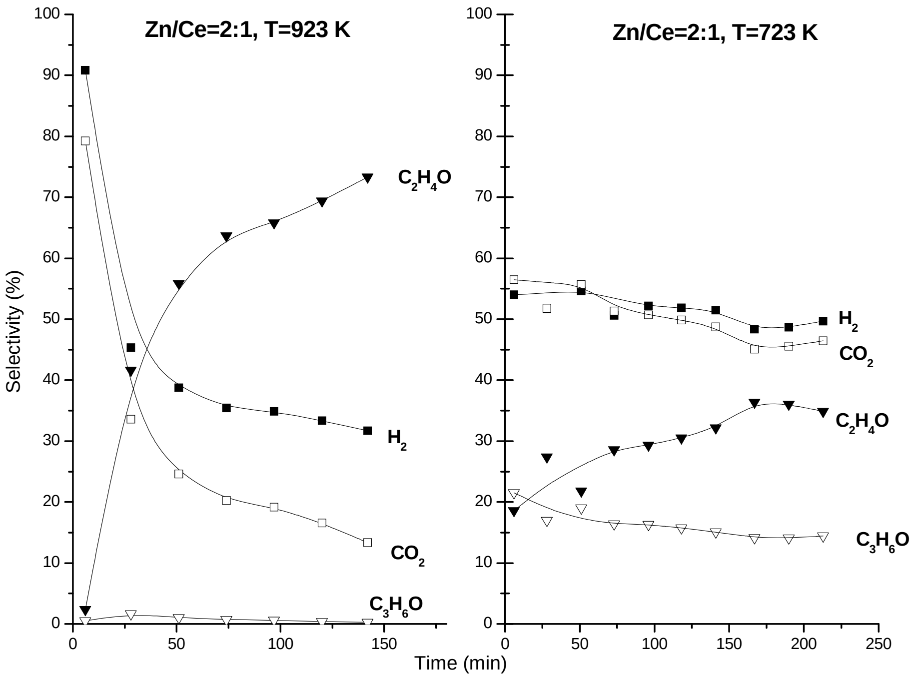

Figure 1.: Selectivities over Cu/Zn/CeO₂ (Zn/Ce=2:1) catalyst under isothermal conditions.

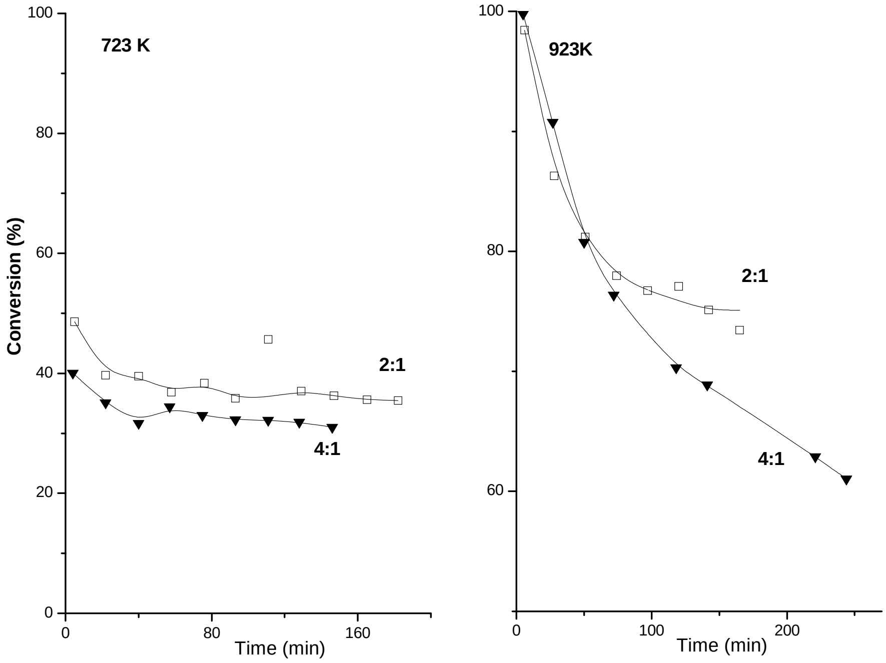

Figure 2.: Ethanol conversion over different Cu/ZnO/CeO₂ catalysts.

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ORAL SESSION

V. CATALYSIS FOR FINE ORGANIC SYNTHESIS, NATURAL GAS AND PETROLEUM CHEMISTRY

COMPARATIVE STUDY OF SELECTIVE GLUCOSE OXIDATION OVER Pt AND Pd CATALYSTS

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Selective oxidation of glucose to gluconic acid is of great interest both from practical and fundamental points of view. Carbon- and alumina-supported Pt, Pd and Pd-Bi catalysts are conventionally used for this process. One of the important technological problems of the oxidation of carbohydrates is over-oxidation and deactivation of the catalysts due to formation of strong M-O bonds on the surface of supported metal particles. Activity of the catalyst and its stability to deactivation depend on the red-ox potential and particle size of the active metal [1].

The aim of this work is a comparative study of the relationship between the oxidation state of the active component of platinum and palladium catalysts and their activity in the reaction of selective oxidation of glucose to gluconic acid. The catalytic performance of Pt- and Pd-based with various dispersity of the noble metal particles was investigated.

The platinum and palladium catalysts supported on mesoporous graphite-like carbon Sibunit were prepared as described earlier [2,3]. All the catalysts were characterized by TEM, low-temperature N_2 adsorption, pulse CO chemisorption and X-ray spectrum fluorescent analysis. The activity of catalysts for the oxidation of glucose dissolved in water was tested in a three-necked glass reactor equipped with a magnetic stirrer (900 rpm) and peristaltic pump for alkali supply (3M NaOH). The experiments were carried out at 60 °C, atmospheric pressure and pH = 8.8-9.2. The initial molar ratio of glucose to noble metal was 750:1. Since the surface of noble metal nanoparticles can be partially oxidized, the activity of both not reduced and preliminary reduced catalysts was tested. For reduction the suspension of the catalyst in water was purged with Ar (30 min), H_2 (60 min) and again with Ar (30 min) at 60 °C. The reaction over reduced catalysts was carried out in the same suspension. The concentrations of glucose and products of the reaction were measured by HPLC analysis using Shimadzu LC-20 Prominence system equipped with a Phenomenex Luna NH_2 column and diode-array detector.

Selectivity and rate of the glucose oxidation over carbon-supported Pd catalysts is reasonably higher than those over Pt-based catalysts. The highest selectivity for Pt/C catalysts does not exceed 30%, while in the presence of Pd/C the selectivity values up to 75% were registered.

We have demonstrated that the Pd/C catalysts exhibit high activity in oxidation of glucose after preliminary reduction only. Non-reduced Pd catalysts show neglible catalytic activity. On the other hand Pt metal particles are much more tolerant to oxidation by air oxygen in comparison with Pd ones. Therefore, the preliminary reduction of Pt catalysts does not result in the increase in their activity in the oxidation of glucose to gluconic acid. Moreover the reduced Pt/C catalysts exhibit lower initial reaction rate in comparison with untreated ones (178 mol $h^{-1}\cdot mol_{Pt}^{-1}$ vs. 119 mol $h^{-1}\cdot mol_{Pt}^{-1}$).

The influence of the mean diameter of the Sibunit-supported platinum metal particles ($<d_{Pt}>$) on their catalytic activity in the glucose oxidation was studied. It turned out that the specific catalytic activity of the Pt/C catalysts normalized to the platinum surface area is independent on the $<d_{Pt}>$ in the range of 1.1-4.5 nm (according to TEM). The platinum surface area was evaluated by pulse CO chemisorption. Thus there is no particle size effect on the catalytic activity of platinum in the glucose oxidation in contrast to the Pd catalysts [1]. Our study of the activity of the 2% Pd/C catalysts showed that the increase in the palladium particle size results in the enhancement of the selectivity of gluconic acid formation. The anomalous influence of the palladium metal dispersion on the selectivity of glucose oxidation was earlier described and related to the deactivation processes (‘oxygen tolerance’ of the catalyst).

In our work we demonstrated that the oxidation state of Pd and Pt influence on their catalytic activity and selectivity of the glucose oxidation. In the case of Pd/C catalysts, an application of preliminary reduced palladium metal particles with low dispersity provides higher yields of the gluconic acid. On the contrary, the utilization of partially oxidized and highly dispersed platinum metal particles is preferential for Pt/C catalysts.

The financial support of RFBR grants 08-03-00823, 08-03-91758 is gratefully acknowledged.

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O-V-2

LIGHT-DRIVEN BIOCATALYTIC REDOX REACTIONS

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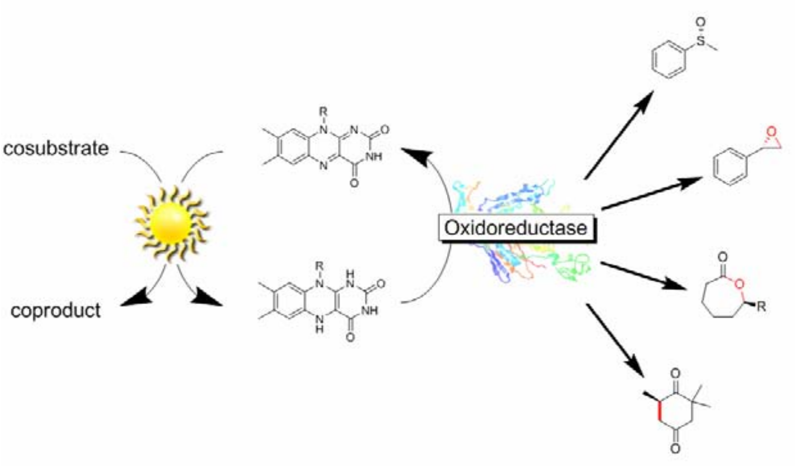
Biocatalysis bears an enormous potential to make industrial production more sustainable. One area that could especially benefit from biocatalysis is organic redox chemistry. So-called oxidoreductases catalyze a wide variety of regio-, chemo-, and enantioselective oxidation, oxyfunctionalization, and reduction reactions. Their major drawback however is their dependence on costly and instable nicotinamide cofactors supplying the enzymes with redox equivalents. [1] Furthermore, these redox equivalents are often delivered to the oxidoreductase via complicated electron transfer chains. As a result, industrial-scale biocatalytic redox reactions, despite their potential, are scarce.

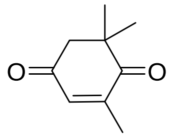
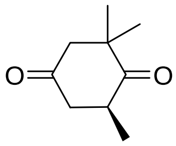
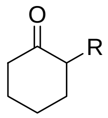
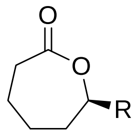
We propose to directly supply oxidoreductases with redox equivalent thereby circumventing the nicotinamide cofactors and electron transfer chains and dramatically simplifying the biocatalytic reaction scheme. To make reducing equivalents available from simple electron donors, we use photocatalysis. Flavins proved to be efficient catalysts [2] to mediate electron transfer from e.g. EDTA directly to the oxidoreductases. Thus, by using visible light (e.g. solar light), enabled us to perform stereospecific oxyfunctionalizations and reductions (Scheme 1).



Scheme 1: Light-driven provision of oxidoreductases with reducing equivalents for enantioselective oxyfunctionalization and reduction reactions.

We report on the setup, characterization, and optimization of this novel reaction setup. The efficiency (in terms of rates and conversion) of enantioselective reduction of conjugated C=C bonds was comparable or superior to the 'traditional' setup (Table 1) while avoiding undesired side-reactions associated with it. Likewise, enantioselective Baeyer-Villiger oxidations were shown to be feasible (Table 1). [3] However, the efficiency fell back significantly behind reported values.

Table 1: Comparison of the efficiency of the traditional reaction schemes with the novel, light-driven system.

Substrate	Product	Conversion [%]		TF [h^{-1}][a]		ee		Ref
		Trad.	hυ	Trad.	hυ	Trad.	hυ	
		86-96 [b]	100	>81[b]	194	37-99[b]	>86	[4,5]
		50	48	394	10	96	97	[3]

[a] calculated for the biocatalyst;

[b] depending on the regeneration system used.

Oxidative uncoupling was identified as major limitation. As a result, reducing equivalents provided by the sacrificial electron donor are wasted to produce hydrogen peroxide and are not delivered to the oxidoreductase. Consequences and potential solutions will be discussed.

Overall, we present a novel and highly simplified reaction scheme to perform biocatalytic redox reactions. The setup is simple, robust, and scalable and will put a basis for future development in the use of enzymes for organic synthesis

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O-V-3

NOVEL CHIRAL NITROGEN CONTAINING LIGANDS FOR CATALYSTS OF ASYMMETRIC REACTIONS

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In recent years homogeneous enantioselective metallocomplex catalysis has achieved impressive results in the field of the synthesis of organic compounds of high optical purity. Asymmetric catalysis is an attractive strategy of the synthesis of optically pure organic compounds and the dominant role in enantioselectivity of catalyst plays the structure of chiral ligand. Thus, design of the ligands of various structural types allows extending the field of application of asymmetric catalysis over the wide range of substrate and reactions. When preparing the ligands most attention was concentrated on the transformations of hydroxy- and amino acids, carbohydrates as well as binaphtyl, biphenyl, ferrocene derivatives. The synthesis of ligands based on steroids and terpenoids received lesser acceptance

Transformations of sesqui- and diterpenes with the purpose of determination of their structure and obtaining of the valuable bioactive compounds have been studied extensively last century. However, these substances have not been considered as convenient starting compounds for the synthesis of chiral elementorganic ligands. Planning the work on the synthesis of chiral elementorganic ligands of novel structural types, we determined the stereospecific transformations of some diterpenes, isolated in sufficient quantities from the phytogenic renewable raw material as the main approach.

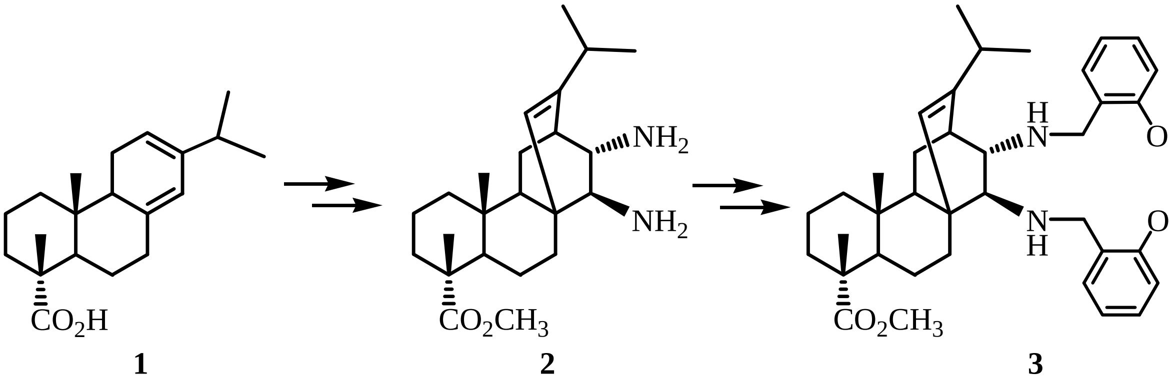
Nitrogen-containing ligands are being used increasingly in asymmetric catalysis. They turn out to be suitable for any type of catalysis and especially for homogeneous catalysis. One of their main advantages over phosphines is their stability to air and moisture. Besides, metal complex catalysts with nitrogen-containing ligands can be based on transition metals less expensive than noble metals.

In our earlier work we developed procedures of synthesis of P-, N-containing ligands starting from levopimaric and dehydroabietic acid, which are part of the composition of the galipot and colophony of the conifers of the Pinus genus [1]. The prepared chiral compounds were used as ligands for catalysts of asymmetric reactions [2]. As a result of our further investigations we developed the new schemas of synthesis of nitrogen-containing ligands on the basis of the transformations of levopimaric acid.

O-V-3

Synthesis of two chiral 1,2-diamines (**2, 3**) was developed on the basis of enantiospecific transformations of adducts of levopimaric acid (**1**) with fumaric acid (scheme 1).

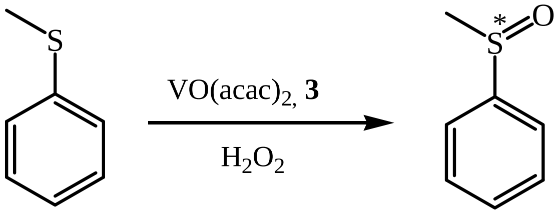
Scheme 1



The prepared new chiral nitrogen-containing compounds are used as ligands of metallocomplex catalysts of asymmetric reduction and oxidation.

In vanadium catalysis hydrogen peroxide could be used as an oxidant. A readily available vanadium complex prepared *in situ* from VO(acac)$_2$ and aminophenol **3** catalyzes the enantioselective oxidation of sulfides with H_2O_2 (scheme 2).

Scheme 2



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O-V-4

SUZUKI REACTION: EXCLUSIVE HOMOGENEOUS OR EXCLUSIVE HETEROGENEOUS CATALYSIS?

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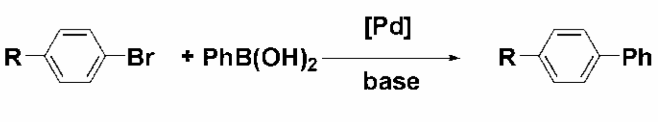
One of the most useful cross-coupling reactions between aryl halides and different reagents (alkenes, alkines, amines, metallorganic compounds) has been the Suzuki–Miyaura reaction that attracts the greatest attention of investigators (Scheme 1). Now it is quite clear that there is no consensus on the catalysis nature of this reaction. Analysis of the literature for only last two years indicates that some researchers advance the hypothesis of catalysis homogeneous mechanism while the others suggest heterogeneous mechanism. It is worth mentioning the most convincing evidence for homogeneous mechanism of the Suzuki reaction. For instance, numerous confirmations of Pd-leaching using wide set of heterogeneous catalyst precursors including Pd nanoparticles were found. Moreover the correlation between activity and amount of Pd dissolved was observed. The relationship between activity and catalyst amount in Suzuki reaction as well as effect of insoluble poison addition and changes in the size of a colloidal nanocatalyst also confirm the homogeneous mechanism.

Scheme 1.



R = H, C(O)H, OMe, COMe, Cl

Unfortunately, the results of the conventional tests on reaction homogeneity-heterogeneity are ambiguous due to the interconversions of different catalyst forms. It can be associated with both varying Pd distribution between different forms during the reaction and the possible compensative effect of the catalytic system which responses (similar to Le Chatelier's principle) to the removal of one of the catalyst forms (for example filtration of solid catalyst or introduction of selective poison for soluble catalytic species) used in the tests. In addition the most complicated case when both homogeneous and heterogeneous catalysis take place simultaneously is impossible to exclude. Note this possibility (especially at high temperature) was distinctly formulated only once in very recently published work [1].

In presented work a new approach to the Suzuki reaction was applied for the first time: studies of the Suzuki reaction selectivity under competitive conditions. The investigation of the selectivity trends allows one to obtain unequivocal answers to important question whether the nature of actual catalyst is unchangeable using different catalyst precursors. Such an approach in particular can be applied to comparative studies of homogeneous and heterogeneous catalyst precursors. In cases when the reaction occurs on the surface of metallic Pd or is subjected to molecular complexes in the solution the equal selectivity of the reaction is highly improbable. The measurement of selectivity under competitive conditions led to results that are irrespective of active catalyst amount. It is also true for the complicated case when not one, but a few of catalytic active species are responsible for activity including homogeneous and heterogeneous catalysts. However in this case the selectivity using different catalysts may change while the fractions of various active species can be depend from catalyst precursor.

The data obtained indicating that selectivity of catalysts formed from different heterogeneous precursors is depending on support nature. The traditional interpretation of such results is the truly heterogeneous catalysis mechanism. However numerous literature data mentioned above suggesting the assumption of the catalytic activity of Pd molecular species formed in the reaction course. In this case the only explanation is the simultaneous reaction proceeding via both homogeneous and heterogeneous pathways. The latter high probably expected in high temperature variant of the Suzuki reaction [1]. The contributions of homogeneous and heterogeneous mechanisms into overall substrate conversion must depend on the catalyst support, since fractions of molecular complexes, “soluble” nanoparticles formed due Pd-leaching from support surface and Pd on support may be distinctly changed depending on catalyst precursor.

So both concepts that are discussed in the literature to be exclusive homogeneous or exclusive heterogeneous catalysis of the Suzuki reaction are not consistent with the data obtained in this work. The relative contribution of heterogeneous catalysis is sufficient to affect the overall selectivity of catalytic system formed during the Suzuki reaction from different catalyst precursors.

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NICKEL CATALYSED HYDRODEFLUORINATION OF PENTAFLUOROACETANILIDE IN IONIC LIQUIDS

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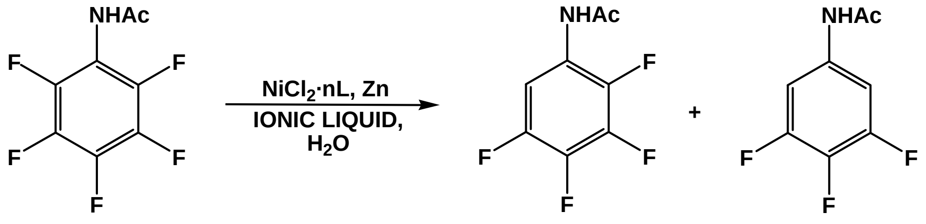
Ionic liquids, being organic salts with low melting points, demonstrate properties applicable for various tasks arising in synthetic chemistry, catalysis, material sciences etc. The inertness of many ionic liquids toward most known salts and transition metal complexes makes them superior to water as solvents for catalysts. The absence of vapour pressures makes ionic liquids attractive as replacements for organic solvents. High thermal stability, broad ranges of temperatures over which they are liquids, and their excellent retention of polar organic substrates allow to use them as convenient media for different synthetic applications. Reusable catalyst – ionic liquid systems make possible facile catalyst-product separation, providing economic incentives for the development of such systems for new processes and as replacements for the existing ones [1-3].

Earlier [4, 5] we observed a highly regioselective activation of aromatic C–F bonds proceeding under the action of zinc in the presence of nickel complexes leading to the formation of 2,3,4,5-tetrafluoroacetanilide (**2**) and 3,4,5-trifluoroacetanilide (**3**). The appropriate solvents for the hydrodefluorination were mixtures of aprotonic dipolar solvents, such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) or N-methylpyrrolidone (NMP), and water, serving as a proton source. Moreover, conversion of **1** and depth of hydrodefluorination depend on the combination of the catalytic nickel complex and solvent [5].

In continuation of our systematic research in this area we investigated the catalytic hydrodefluorination of **1** using ionic liquids as solvents. When the interaction of **1** with zinc in the presence of nickel complexes was performed in ionic liquids instead the aprotic dipolar solvents we observed significant increase of the reaction rate with preservation of the C–F bond activation regioselectivity, leading to formation of ortho-hydrodefluorination products **2** and **3** (Scheme 1).

Scheme 1



1 2 3

L=Bpy, Phen; n=1-3

The performed experiments allowed to establish the dependence of the hydrodefluorination rate on the nature both cation and anion of the ionic liquids. The conversion of **1** as well as the molar ratios of resulting acetanilides **2** and **3** depends on the type and number of ligands in the nickel complexes. The different pathways of hydrodefluorination reaction were observed. Finally the possibility to recovering and recycling of ionic liquids were investigated.

Thus, in the present work we found that ionic liquids can be used as the solvent for the catalytic activation of aromatic C–F bonds by nickel complexes under reductive conditions.

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CATALYTIC OXIDATION OF CYCLOALKENES AND ALCOHOLS IN BIPHASIC SYSTEM

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Catalytic systems based on peroxopolyoxometalates (PPOM) are used actively and successfully in the oxidation reactions of various organic substrates by hydrogen peroxide [1, 2]. Effective homogeneous catalysts composed of $Q_3\{PO_4[WO(O_2)_2]_4\}$ were used in our investigations, where Q^+ – is quaternary ammonium cation (see the Table 1) and anion represents the peroxopolyoxotungstate – tetra(oxodiperoxotungsto)phosphate(3-).

Studies of these catalytic systems were carried out by method of Small-angle X-ray scattering (SAXS) at this point of work. According to preliminary data, investigated samples $[(n\text{-Bu})_4N]_3\{PO_4[WO(O_2)_2]_4\}$ (**I**) and $[Me(n\text{-}C_8H_{17})_3N]_3\{PO_4[WO(O_2)_2]_4\}$ (**II**) dissolved in acetonitrile represent a polydispersed systems. It has been established, that complex (**I**) is similar to monodisperse condition, while (**II**) represents a binary mixture of two fractions. It is most probably, that differences observed are concerned with different nature of Q^+ cation.

Effectiveness of the catalytic systems was tested in organic compounds oxidation reactions by aqueous hydrogen peroxide in diphase systems. As substrates cycloalkenes (cyclohexene, cyclooctene) and alcohols (1-octanol, benzyl alcohol) were used. Carboxylic acids (adipic, suberic, caprylic, benzoic) received, which are included into the list of the basic organic and petrochemical synthesis products, are demanded raw materials for fine organic synthesis. Given acids find a wide application in manufacture of plasticizers, polymers, dyes, cosmetic, biologically active, medical products etc.

As a result of experiments availability of application of catalytic systems based on the tetra(oxodiperoxotungsto)phosphate(3-) in combination with quaternary ammonium cations (Q^+) in reactions of cyclohexene, cyclooctene, octyl and benzyl alcohols oxidation is shown (see the Table 1). Reactions proceed at 93-99% substrate conversions and 60-99 % target product yields from theoretical.

Table 1

Oxidation of the cycloalkenes and alcohols by hydrogen peroxide in the presence of catalytic systems $Q_3\{PO_4[WO(O_2)_2]_4\}$

Substrate (Sub)	**Q^+**	**t, °C**	**[Ox]/[Sub]**	**Yield, %**	**Product**
Cyclohexene	$[CH_3(n\text{-}C_8H_{17})_3N]^+$	90	2	82	Adipic acid
Cyclooctene	$[(n\text{-}C_4H_9)_4N]^+$	85	8	60	Suberic acid
1-octanol	$[CH_3(n\text{-}C_8H_{17})_3N]^+$	90	2	80	Caprylic acid
	$[CH_3(C_7H_{15})_4N]^+$	90	6	75	
Benzyl alcohol	$[CH_3(n\text{-}C_8H_{17})_3N]^+$	83	3	99	Benzoic acid

The presented data is a result of the initial stage of investigations of structure of the peroxopolyoxotungstate catalytic systems, allowing to carry out of effective oxidation of various organic substrates for the purpose of obtainment of mono- and dicarboxylic acids claimed in various industries.

The investigation was carried out at Department of Chemistry and Sciences on New Materials RAS support (project 5.7.3).

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OXIDATIVE PYROLYSIS OF METHANE WITH TREATED Fe/Cr/Al-WIRE

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At present time the information about high-temperature (≥900 °C) catalytic oxidative pyrolysis of methane is practically absent in the literature. The investigations of the oxidative coupling of methane are, basically, fulfilled in particulate bed reactors with heating of a reaction feed. This method has a number of essential deficiencies. The main one is the heating of the quartz reactor and a gas flow up to temperatures ≥ 1000 °C, that initiate gas phase radical processes of oxidation, which can be develop on the walls surface. This circumstance impedes the separation of the catalytic component of oxidative pyrolysis of methane. Besides, the products formed on the catalyst, for example, C_2-hydrocarbons, are less stable at this temperature, than initial methane, and their further transformations into a gas stream can undergo.

The goal of the work was to investigate oxidative pyrolysis of methane in a broad temperature interval (including, and above 1000 °C) with using as the catalyst specially treated Fe-Cr-Al wire [2].

The experimental technique, which allows separate the heterogeneous part of reaction has been developed. In our experiment a cold gas flow contact with heated by electrical current Fe-Cr-Al wire. The part of a gas mixture rush by the catalyst, diluting products of reaction and quickly cooling them to a room temperature (“hardening”).

The support Fe-Cr-Al was previously treated in order to increase its specific surface. This treatment was accompanied by changing of the chemical and phase composition of the surface layer.

The support treatment included operations: degreasing and then heating on air at 1000 °C. New phases: disperse α-alumina and small amounts of hematite form on the Fe-Cr-Al wire surface during heating at temperature 1000 °C on the air [2].

Oxidative pyrolysis of methane on catalyst α-Al_2O_3/FeCrAl is investigated. Values of products selectivities and methane conversion are obtained.

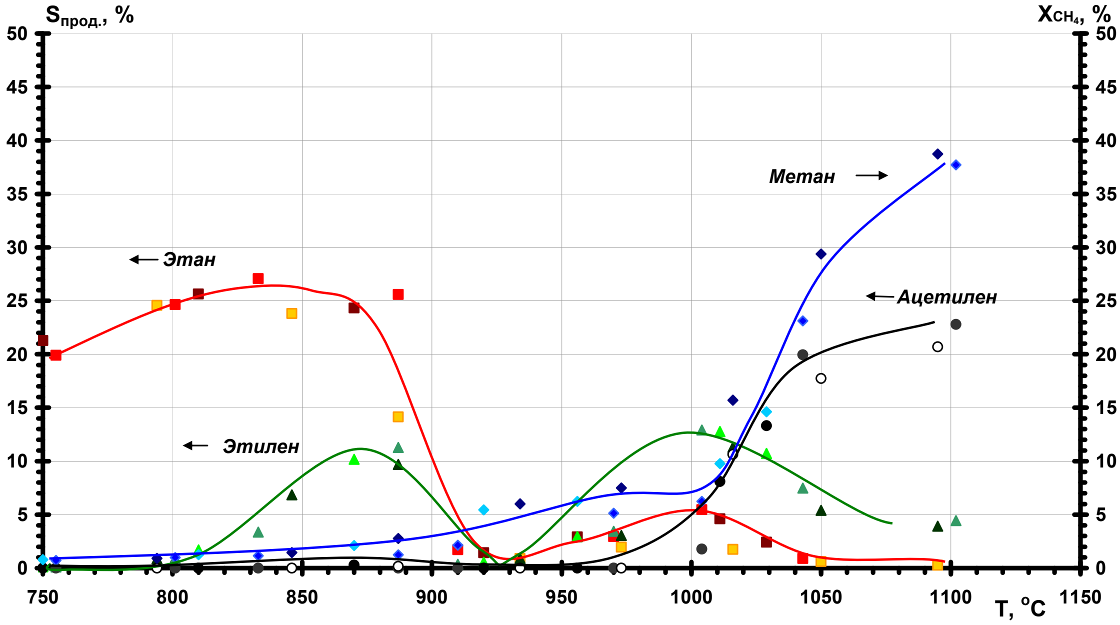

Fig. 1. Methane conversion and products selectivities as a function of the temperature of the oxidative pyrolysis of methane (exhibit data for three reproduced experiments).

It is found that pyrolysis of methane in absence of oxygen proceeds in two temperature regions:

- in interval 600-950 °C with previous formation of ethane and ethylene (values of products selectivity pass through a maximum).
- in region > 950 °C with formation of a little amount of the ethane and ethylene and increasing acetylene selectivity with temperature rising.
- transition zone, which is characterized by close to 0 selectivity of C_2-products and by the maximum formation of carbon and condenced products.

It is shown that the transformation of methane in the presence of oxygen also proceeds in two temperature regions, but these are shifted in the more high temperature interval. For a ratio CH_4/O_2 = 15/1 the first zone is shifted to 1050 °C and for a ratio 9/1 up to 1100 °C. In case of oxidative pyrolysis the transition zone between temperature regions is characterized by the maximum formation of carbon deposits and by the maximum of CO selectivity.

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DESIGN OF MICROSPHERIC Cr_2O_3/Al_2O_3 CATALYST FOR C_3-C_4 ALKANES DEHYDROGENATION

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Olefins and diolefins (propylene, n-butenes, isobutylene, butadiene, isoprene) are sources for producing synthetic rubbers, plastics, motor fuel constituents (MTBE, alkylates) and other important chemicals. The annual bulk volume of olefins, exclusive of propylene, produced by dehydrogenation in Russia is 600-700 thousand tons. In our country two plants use the method of n-butane vacuum dehydrogenation to divinyl (Catadien Process) in the fixed bed of Cr_2O_3/Al_2O_3 catalyst which is supplied by Süd Chemie/ Houdry Division during 30 years. Also about ten plants perform dehydrogenation of isobutane, n-butane and isopentane in the fluidized bed of Cr_2O_3/Al_2O_3 catalyst. The main problem of this technology is low activity and high abradability of Cr_2O_3/Al_2O_3 catalyst IM-2201, which is being used over 30 years. Therefore, the main challenge over many years is developing of new more abredability-resistant, active and selective catalysts for fluidized bed.

In paper [1] was shown that improving of catalytic and strength characteristics of fluidized bed catalyst can be achieved by using of new nanostructured alumina as a carrier, prepared by the centrifugal thermal activation method of gibbsite (CTA product) on the “Ceflar” set-up. Nowadays manufacturing of new catalyst named KDM is developed on experimental-industrial scale in “Altailuminofor” c.c. with the assistance of Institute of Catalysis SB RAS jointly with “AKRP” p.c. In 2007 – 2008 the KDM catalyst successfully passed experimental-industrial tests in “Tobol’sk-Neftekhim” SIBUR Co Ltd.

The aim of this paper is upgrading of KDM catalyst directed at increase of its selectivity, especially in high temperature conditions, decrease of chromium content and determination of optimal thermal activation regime.

There were used CTA products of gibbsite as a carrier during catalyst preparation. Different kinds of gibbsite were provided by several aluminous plants of our country. Catalysts were prepared by impregnation method of CTA products with chrome anhydride solution with promoters [1]. Catalytic characteristics were studied on automatic catalytic set-up in a fluidized bed reactor. State of deposited chromium oxide in obtained patterns was studied using a complex of physicochemical research methods (TPR, chemical analysis, XRD, XPS, DRS).

One ascertain that special structural state of CTA product promote formation of fine-grained nanoscaled particles of active chromium constituent in catalysts [2].

This provides not only higher activity of catalyst, but leads to decrease of chromium content in catalyst in 1.5-2 times in comparison with industrial design. It makes possible to increase selectivity in propane dehydrogenation on catalysts with chromium content 2-4 wet.% lower by the means of nature and content changing of modifying additions (К, Zr, Ce).

Obtained catalysts were studied for thermal stability and coke deactivation resistance. Rise of isobutylene yields, selectivity and coke formation decrease turn out to be observed at calcination temperature higher then in industry (700-750 °C) on about 100-200 °C.

Received results are recommended for preparation of experimental-industrial consignments of KDM catalyst.

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O-V-9

REJUVENATION OF THE NEW-GENERATION CoMo/Al_2O_3 HYDROTREATING CATALYSTS AFTER OXIDIZING REGENERATION

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In present time the industrial hydrotreating catalysts are regenerated by calcination in an oxidizing atmosphere where the carbonaceous (the main cause of the catalysts deactivation) depositions are burn off [1]. Under the high temperatures influence there are a number of undesirable processes occur - sintering of the support accompanied with change of its textural characteristics changing and oxidation of sulfide species with the formation of surface oxygen containing compounds of Co and Mo [2]. These compounds cannot be selectively transformed to the active sites of the hydrotreating reactions such as CoMoS phase type II during the following sulfidation [3]. This results in the catalyst activity decreasing. Recently was found that the treatment of the calcinated catalysts with various agents can increase the activity of the regenerated catalysts. But the reasons of the catalysts activity increase of the and the chemistry of the processes passing on a catalyst surface are not described in the literature.

The aim of this work was to investigate the activation of the calcinated Co-Mo catalysts by treatment with polyglycol aqueous solutions and their mixtures with polybasic carboxylic acids and their characterization with chemicophysical study methods.

The catalytic properties of the samples were investigated after various variants of the regeneration and activation in the hydrotreating of diesel fuel. UV-VIS, XPS, FTIR, Raman and EXAFS have been used for the characterization of chemico-physical characteristics of the catalysts under study.

It was shown that oxidizing regeneration at temperature lower than 550 °C results in the formation of cobalt(II) molybdates and spinel-like cobalt compounds with alumina $CoAl_2O_4$ on a support surface [2]. For the samples sulfided after their calcination, it was shown that:

- XPS spectra analysis reveals the presence both sulfide Co and Mo species and metal compounds of with oxygen environment;
- Raman spectra contains the lines corresponding to oxygen containing species of molybdenum and cobalt which in accordance with a literature data and can be attributed to difficult to sulfide spesies;

- UV-VIS shows a presence in the investigated samples cobalt compounds with an oxygen environment.

Thus low activity of samples after oxidizing regeneration in comparison with the fresh ones could be explained by the presence of difficult to sulfide oxygen containing Co and Mo spesies on the surface.

The treatment of the regenerated catalyst by glycols and polybasic carboxylic acids at elevated temperature before the sulfidation results in the nearly full catalytic activity restoration. For the catalysts treated by chelating agents it was demonstrated that:

- Raman spectra lines corresponding to difficult to sulfide compounds disappeared in after treatment with the complexing agents.
- FTIR and Raman spectroscopy were shown a formation of the cobalt glycol complexes and carboxylic molybdenum complexes in the catalyst pores.
- UV-VIS shows formation of cobalt complexes in a solution in the pores of the catalyst and on its surface.
- According EXAFS data, the structures of Co compounds in the pores solution are identical to that on the catalyst surface, the Mo citrate complexes formation was shown as well.

Thus the treatment of the calcinated catalysts by the solutions of organic chelating agents results in the transformation of the surface molybdates and the cobalt with the support compounds into the carboxylic complexes. These complexes are the best precursors of active sites, are selectively transform to the active sites of the hydrotreating reactions during the sulfiding process.

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CATALYTIC PROPERTIES OF NANOPERIODICAL V-Ti- SILICATE SYSTEMS IN PROCESSES OF PROPANE DEHYDROGENATION

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Rates of consumption of the propylene used for reception of polypropylene, polyurethane foam and a lot of other valuable chemical products increasing all over the world, advance increase in volumes of its manufacture. Therefore improvement existing and development of new ways dehydrogeation of propane in propylene - an actual problem chemical industry [1]. For increase in an yield of propylene in endothermic reversible reaction ($C_3H_8 \leftrightarrow C_3H_6 + H_2$, $\Delta H = 124{,}3$ kJ/mol), which proceeds in processes of propane dehydrogeation (DH) on Cr-or Pt-containing supported oxide systems, it is offered to move the equilibrium of reaction by removal of allocated hydrogen from a reactionary zone, by its burning on special catalysts or to carry out oxidizing dehydrogeation of propane (ODH) at presence of oxygen at the reactionary mixture on catalysts capable to dehydrogenate of propane without essential formation carbon oxides, that doing total process exothermic essentially ($C_3H_8 + 0{,}5\ O_2 \rightarrow C_3H_6 + H_2O$, $\Delta H = -117{,}5$ kJ/mol) and energetically favourable consequently. In processes DH, at 600 °C propylene is obtained with selectivity above 95 % and 35 %-th yield [2] which can be raised by additional circulation of a reactionary mixture; however, that leads to coking of catalysts and necessity of their frequent regeneration. Catalysts for process ODH (basically the supported oxide-vanadic systems) cannot while to compete on a received yield to catalysts DH and are in a stage of development [2].

In this work as catalysts DH and ODH of propane are investigated on the micro-, meso- and bi-porous V-Ti-silicate systems received by directed hydrothermal syntesis with organic templates on the basis of industrially producible pyrogenic amorphous superfine titanaerosile (TAS), identified by methods X-ray diffraction analysis, DTG, FTIR-and DR-UF-spectroscopy and adsorption of nitrogen. Acidity of systems is estimated by method TPD of ammonia and indicators Gammeta. Reaction of propane dehydrogeation was leaded in a flowing tubular quartz reactor at gradual rise in temperature from 250 up to 675 °C on a working mix with concentration 7 vol.% C_3H_8 in rare gas, in case of DH, and containing 3,5 vol.% O_2 in addition at ODH. Products of reaction is analyzed by method gas-solid chromatographies.

It has been established, that both at presence and at absence of oxygen at a reactionary mix amorphous TAS catalyse process of propane dehydrogeation with forming propylene at temperatures considerably below the beginning gas-phase chain reactions thermal destruction of propane. Thus the greatest selectivity shows TAS-1,4 with a specific surface 170 m^2/g in which the titan contains only in the form of isomorphic replacement of ions of silicon by it in matrix SiO_2 and does not form separate phases TiO_2 which presence promotes deep oxidation of propylene up to CO_x during ODH. The last as it has been shown by method TPD of ammonia, can be connected by that the acid centers concerning phase TiO_2 on surface TAS are energetically close to strong acid oxygen inclusived centers of tetrahedrally coordinated the titan, causing activation of propene with formation propylic radicals. Supported catalysts V_2O_5/TAS-1,4 at 600-625 °C gave the maximal yield of propylene more than 50 mol. %. at ODH. At that during the increase in temperature of reactionV_2O_5 was redused, that as it has been certain on adsorption of propylene, is favored its reversible chemisorption and, hence, to increase of an yield. Presence of the titan in structure of the supports promoted to superfine distribution of an active phase and that in O_2- inclusived mixes change of condition V_2O_5 occured no more than up to V_2O_4. In a mix without oxygen, during DH the yield of propylene in 50 % was reached at 650 °C with selectivity above 95 %.

In synthesized out of TAS-1,4 micro-, meso- and bi-porous titanosilicate systems the surface developed up to sizes of the order 1000 m^2/g, thus the isomorphic maintenance of the titan in structure walls times was kept. Own activity of such systems, in comparison with initial TAS, raised also, the yield of propylene received on bi-porous the sample reached sizes, commensurable with the best data resulted in the literature for catalysts ODH of propane. Drawing of an active phase vanadium oxide caused crystallization surfaces of mesoporous the support, diminution of its size and gradual destruction of structure which stability was then is reached by introduction of additives aluminium oxide during synthesis. At ODH of propane such porous samples have shown the maximal yield little bit greater of 50 %, and during DH the yield of propylene above 70 mol. % could be received. In work prospective heterogeneous -homogeneous mechanisms of these processes are discussed.

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O-V-11

SULFATED ALUMINA AND ZIRCONIA IN ISOBUTANE/BUTENE ALKYLATION AND N-ALKANE ISOMERIZATION: CATALYSIS, ACIDITY, ACTIVE SULFATE SPECIES

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Sulfated zirconia (SZ) catalysts attract wide interest because of their high activities in alkane transformations (such as isobutane/butene alkylation and n-alkane isomerization) at relatively mild temperatures. The high activities of these catalysts in such reactions were attributed to superacidic properties of SZ at first. At this moment the superacidity of SZ was subjected to the criticism. At the same time, it was observed no correlation between Broensted sites concentration and isomerization activity [1]. In this connection, one electron oxidation of the alkane by sulfate groups instead acidic activation was proposed. Active sulfate species were attributed with pyrosulfate-type surface species. Such species show a characteristic IR band at 1390-1410 cm^{-1} [2].

The present study aimed to compare acidic and catalytic properties as well as surface sulfate species of SZ (the most active catalyst among sulfated oxides) with those of sulfated alumina SA (less active catalyst in isomerization). Catalytic properties of sulfated catalysts were tested in two reactions: isobutane/butene alkylation (test for acidity) and n-pentane isomerization (test for active surface sulfate species). Activities of SA and SZ in alkylation were similar, except the initial activity when self-alkylation on SZ was observed. At the same time, these sulfated oxides demonstrated a huge difference between isomerization activities (Table 1).

Acidity of SA and SZ was measured by TPD of ammonia and IR of adsorbed pyridine and CO. According to IR spectra of adsorbed pyridine, both sulfated oxides had similar concentrations of Broensted as well as Lewis acid sites. However, the Lewis sites concentration of SZ determined by IR of adsorbed CO substantially exceeded that of SA. Besides the acidity measurement, IR spectroscopy was used to get information about the surface sulfate species of sulfated catalysts. The IR band at 1390-1410 cm^{-1} was observed in spectra of both catalysts. Although its intensity was similar for both samples, its maximum was slightly shifted to a lower frequency for SA (Fig. 1).

Table 1. Catalytic properties of SA and SZ in isobutane/butene alkylalation and n-pentane isomerization.

Sample	SA		SZ	
T (°C)	220		150	
n-C_5 pulse (mmol)	1.7		17	
n-C_5 conversion (wt%)	23.8		97.6	
$m_{C4=}$ (g/g_{cat})	0.5	1.3	0.6	1.3
$C_{4=}$ conversion (wt. %)	99.9	95.9	99.8	97.9
Alkylate yield (wt. %)	190	177	278	207
C_5-C_7 selectivity (wt.%)	34	23	89	39
C_8 selectivity (wt.%)	50	59	9	43

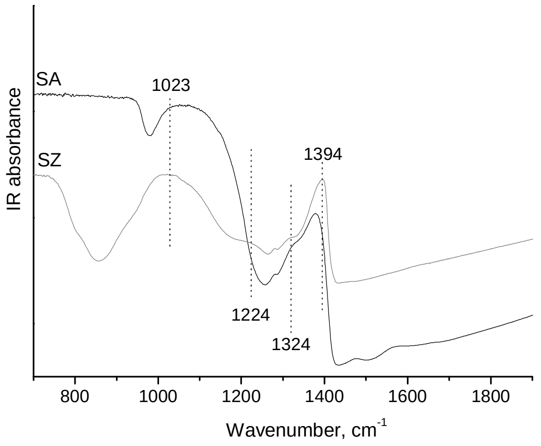

Figure 1. IR spectra of self-supported wafer of SA and SZ.

In summary, both sulfated oxides had similar Broensted acidity that was well-correlated with similar alkylation activities. Although the IR spectra of SA and SZ in the SO stretching frequency region were slightly different; isomerization activities of these samples differed drastically. Most part of studies devoted to the influence of active sulfate species on isomerization activity of sulfated oxides does not consider the role of oxide matrix. It is possible that structure of sites activating alkane on SA differs from that for SZ and other sulfated transition metal oxides, ions of which can participate in one electron oxidation according to the ref [3].

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O-V-12

TOWARDS A BETTER UNDERSTANDING OF THE PROCESSES IMPLYING DURING THE GENERATION OF THE ACTIVE PHASE OF THE CoMo HYDROTREATING CATALYSTS PREPARED USING CHELATING AGENTS

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Molybdenum sulfide promoted by Ni or Co are wildly used for ultra clean fuel production. Recent studies have shown that remarkable improvements of the catalysts activity can be achieved using chelating agents (EDTA, NTA, citric acid etc.) [1]. These compounds allow to arrange Co(Ni) and Mo in the close proximity in the surface species of the catalyst oxide precursor and thus to promote the formation of the active sulfide CoMoS phase of the hydrotreating catalysts [2]. The most studies emphasize the importance of the stages of the solution preparation and the carrier impregnation for the preparation of the catalysts with the use of chelating agents, while the catalysts activation (drying and sulfidation stages) gets poor attention.

The present talk focuses on the activation aspects of the hydrotreating catalyst prepared using chelating agents. The results of extensive characterization study of the oxide surface species formed after the drying step and the sulfide compounds formed after the sulfidation are presented. A special emphasis is put to the influence of oxide precursor drying temperature on the sulfidation behavior and the influence of the activation procedure on the catalysts performance.

An alumina supported CoMo catalyst was prepared by the impregnation of the carrier with a solution contained citrate complex $Co_2[Mo_4O_{11}(C_6H_5O_7)_2]$. To study the drying temperature influence on the sulfidation behavior and catalytic activity the catalyst was air dried at different temperatures (110, 220, 300 and 400 °C). Sulfidation was performed with straight run gas oil (SRGO) spiked with dimethyldisulfide (DMDS) in two consecutive steps: low temperature (230 °C) and high temperature (340 °C). At each step, the gases revealed and the liquids samples were analyzed using gas chromatography (GC) with thermal conductivity detector and GC with Atomic-emission detector respectively. The oxide precursors and sulfide catalyst were studied using XAS, XPS, FTIR, Raman spectroscopy, transmission electron microscopy and element analysis. The catalysts were tested in hydrodesulfurization of SRGO at 3,5 MPa and 340 °C.

Catalyst characterization results coupled with an on-line analysis of the products formed by the DMDS decomposition during the sulfidation of the samples allow to reveal the mechanism of DMDS transformation as well as and the peculiarities of the sulfidation process for the catalysts dried at different temperatures. It was shown that the mechanism of DMDS transformation is similar for all catalysts. But the beginning of the sulfidation strongly depends on the drying condition: the less the drying temperature the later starts the DMDS conversion and oxide precursor sulfidation. In accordance with characterization data the structure of citrate bimetallic complex is not changed at 110 °C, at 220 °C the citrate ligand $(C_6H_5O_7)^{2-}$ undergoes the transformation to itaconic ligand $(C_5H_4O_4)^{2-}$, but Co and Mo are still included into chelating cycle and the coordination of Co towards Mo is not altered. So, during the sulfidation of the catalysts dried at $T \leq 220$ °C the organic ligands are preventing the oxide precursor from the reaction with sulfiding agent. The complexes decomposition occurs during the low temperature activation stage (230 °C) in the presence of sulfidation agents, as a consequence the increasing of the duration of low temperature sulfidation stage is required, but it provides more preferable condition for the active CoMoS phase formation. Under more severe drying condition ($T > 220$ °C) the non-selective decomposition of the organic ligands happens and the formation of the new surface compounds such as surface polymolybdates, the products of Mo and Co interaction with alumina and the various cobalt molybdates occurs. These compounds more easily interact with DMDS but could not be selectively converted to the active centers of HDS catalysts. Thus, the hydrodesulfurization activities of the catalysts are substantially differ and have the best values for catalysts dried at 110 and 220 °C.

The obtained results allow us to conclude that to activate correctly the catalysts prepared using bimetallic complexes with chelating agent it is essential: (1) to save the specific coordination of Co towards Mo occurring in the primary bimetallic complexes during the drying step, it is realized for the catalysts dried at low temperatures, than chelating cycles included Co and Mo are saved; (2) to provide mild condition for the oxide precursor transfer into active sulfide phase, using the prolonged low temperature sulfidation stage and avoiding rapid temperature increasing.

The proposed approach allows to prepare the most active catalyst for clean fuels production.

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ORAL SESSION

VI. CATALYSIS IN ENERGY PRODUCTION, ELECTROCATALYSIS

STEAM REFORMING OF ETHANOL TO HYDROGEN-RICH GAS OVER BIMETALLIC Rh-Co/ZrO_2 CATALYSTS

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In recent years, considerable attention is focused on the development of power generating systems on the base of fuel cells. Since hydrogen-rich gas is the main type of fuel for these power devices, its production from various feedstocks has become an urgent task. Bioethanol, being a renewable resource, is an attractive feedstock for hydrogen-rich gas production.

Analysis of literature showed that among the studied Pd, Pt, Rh, Cu, Co and Ni-containing catalysts, the Co- and Rh-based systems were the most active for ethanol steam reforming. However, the Rh-based catalysts are expensive, whereas the Co-based ones fall behind them by activity, show low coke resistance and rapidly lose activity.

The present work is aimed at the development and systematic studies of supported bimetallic Rh-Co/ZrO_2 catalysts for the reaction of ethanol steam reforming to hydrogen-rich gas. The catalysts were prepared from various precursors by impregnation method. Supported bimetallic catalysts were synthesized by thermal decomposition on the support surface of double complex compound salts (DCCS) comprised of complex anions and cations containing different metals (Rh or Co) as the central atoms. Stoichiometry of the double complex salt strongly determinates the composition of the formed bimetallic phase.

It was shown that ethanol conversion over Rh-Co/ZrO_2 steam reforming catalysts attained 100% at temperatures above 400 °C. All the catalysts provided the maximum outlet H_2 concentration (~50 vol.%) at 650 °C. As an example, Fig. 1 presents the temperature dependences of the outlet product concentrations for the 1wt.%Rh-0.6wt.%Co/ZrO_2 catalyst prepared by DCCS decomposition on the surface of ZrO_2.

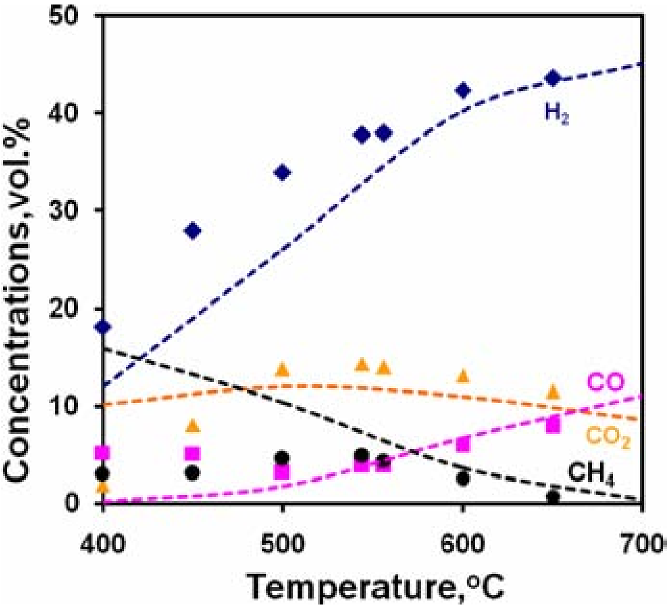

Fig. 1. The temperature dependencies of the outlet product concentrations for the 1wt.%Rh-0.6wt.%Co/ZrO_2 catalyst. The inlet composition: 20 vol.% ethanol, 60 vol.% H_2O, 20 vol.% N_2. GHSV = 10000 h^{-1}.
Points – experiment, dotted lines – calculation of thermodynamic equilibrium values.

The catalysts were characterized by physicochemical methods (XRD, HR TEM, EDX, AES, XRFA). Studies proved formation of Rh–Co solid solution particles over zirconia surface. The nature of the active centers of the Rh-Co/ZrO_2 catalysts is discussed.

Acknowledgements

The work is supported by Integration Project of SB RAS № 112 «Phisico-chemical and catalytic behavior of nano-structural poly-metallic systems, produced by using of double complex compound salts and their thermolysis products as precursors».

SYNGAS PRODUCTION BY AUTOTHERMAL/STEAM REFORMING OF NATURAL GAS AND BIOFUELS OVER MONOLITHIC CATALYSTS

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Transformation of fuels (fossil fuel, biofuels) into syngas or hydrogen is one of the most important tasks of catalysis in the energy-related fields. Catalysts comprised of precious metals and/or Ni supported on complex oxides with a high lattice oxygen mobility are known to be very efficient and stable to coking in autothermal/steam reforming of a variety of fuels including oxygenates [1]. Monolithic substrates with a good thermal conductivity are promising for providing an efficient heat transfer within the reactor to prevent emergence of hot spots/cool zones deteriorating performance [2]. This work presents results of research aimed at design of such catalysts and characterization of their performance parameters at the pilot-scale level.

Several types of heat-conducting substrates including compressed Ni-Al foam, fechraloy foil or gauze protected by corundum layer (either segregated by controlled oxidation or supported via blast dusting) and Cr-Al-O microchannel cermets were used. Stacked flat and corrugated bands of foil were winded into the Arkhimed spiral forming triangular channels. After spark-welding of tungsten rods as electrical current inlets, such a monolithic substrate was used for evaporation of liquid fuels sprayed via a nozzle. Monolithic substrates of planar or cylindrical shapes were washcoated with a slurry of $Ln_x(Ce_{0.5}Zr_{0.5})_{1-x}O_{2-y}$ mixed oxides (Ln = La, Pr, or Sm, x = 0÷0.3) prepared via Pechini route with addition of peptizers and surfactants (loading up to 10÷20 wt.%). Precious metals (up to 1 wt.% of Pt, Pd, Ru), and/or Ni (up to 10 wt. %) with respect to Ln-Ce-Zr-O were supported by incipient wetness impregnation.

Monolithic catalysts were tested in a pilot tubular stainless steel reactor equipped with the electric current heated fuel/water evaporation unit and heating coils to change the catalyst temperature in the reactions of autothermal (ATR)/steam (SR) reforming of natural gas, acetone, ethanol, anisol and sunflower oil. The molar ratios of H_2O/C and O_2/C in the feeds were varied in the range of 1÷7 and 0÷0.5, respectively; the gas flow rate was up to 2 m^3/h

(contact times 5-70 ms) and temperature measured at the end of monolith was changed from 500 to 900 °C.

For all types of studied fuels, stable autothermal performance with the maximum temperature at foil monolith up to 1000 °C was maintained with the inlet feed temperature as low as 200 °C. In these conditions, the oxygen slip was not observed at all contact times. The maximum syngas yield was up to 45% with H_2/CO ratio increasing from ~ 0.8 to 1 with increasing water content up to 10%. In products, along with CO_2 (in the range of 4-6%) some amount of CH_4 (1-2%) and olefins (up to 1%) were observed. This demonstrates occurrence of cracking reactions as well.

For longer contact times, and especially for feeds with too high oxygen content, ignition of fuels at the thermal shield was observed followed by the excessive carbon deposition at walls in the inlet part of the reactor.

In the reactions of oxygenates SR the highest yield of syngas (up to 80% of H_2 + CO content in the converted feed) was achieved for systems with Pr-La-Ce-Zr-O complex oxide promoted by Ni and Pt, only CH_4 being observed as by-product.

At a proper optimization of contact times and feed composition, no coking was observed for hours-long pilot tests even for sunflower oil as a fuel. No carbon build-up was observed for the monolithic evaporator as well. Addition of stack of gauzes or thin–foil monolith after thick-foil monolith allowed improving syngas yield and removing residual olefins from products. No spallation or cracking of the active components supported on metallic substrates was revealed.

Pilot-scale tests of structured catalysts on heat-conducting metal/cermet substrates with supported doped ceria-zirconia complex oxides promoted by precious metals and/or Ni in the reactor equipped with an original evaporator/mixer of water and liquid biofuels revealed their high and stable performance. This provides new possibilities for transformation of a variety of fossil fuels and biofuels into syngas for the fuel cell application.

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DEVELOPMENT OF CATALYST FOR SELECTIVE CO_2 HYROGENATION TO CO

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Biomass-derived fuels and other chemicals are considered as a basic element for sustainable development in the modern world. In recent years, production of biodiesel – one of the main biofuel types - has been growing exponentially in many countries. Biodiesel is produced from vegetable oils and fats by catalytic reaction with an alcohol, typically methanol, which yields glycerine as a by-product. As every ton biodiesel roughly consumes 100 kg methanol and produces the same amount of crude glycerine, the world's methanol demand increases while on the other hand the glycerine market becomes glutted. An interesting option addressing the surplus of glycerine and the request for methanol is to produce methanol from the crude glycerine by the biodiesel producer itself: they will then be less dependent on the methanol spot price, there is a (partial) security of supply of methanol, and their own by-product is used as a green, sustainable feed product.

Process of crude glycerine reforming to produce methanol for re-use in biodiesel plants may consists of three catalytic stages: reforming of glycerine in supercritical water, reverse water gas shift reaction and methanol synthesis. The present work addresses the development of a catalyst for selective CO_2 hydrogenation to CO (reverse water-gas shift, RWGS) towards the optimum gas composition for methanol synthesis (i.e., with the highest possible CO and a low CO_2 content).

Based on scientific literature data [1-3] and available sources on commercial WGS catalysts, we prepared a series of about 20 RGWS catalysts, tested them for catalytic performance and selected the most active ones presented below.

The Cu-Fe/$CeZrO_2$, Fe/$CeZrO_2$, $CeZrO_2$, ZnO/Al_2O_3, Mn/$CeZrO_2$ catalysts were synthesized by coprecipitation of copper, cerium, iron, zinc, zirconium, manganese and aluminum salts taken at the given rations by 5% solution of K_2CO_3. The resulting precipitates were filtered, washed with distilled water, dried in air at 100 °C for 12 h and calcined at 700 °C for 3 h.

The Cu/$CeZrO_2$, Pt/$CeZrO_2$ catalysts were synthesized by incipient impregnation of $CeZrO_2$ (prepared by coprecepitation of cerium and zirconium salts) by copper or platinum salt water solution. Samples were dried at 100 °C for 12 h and calcined at 700 °C for 3 hours.

O-VI-3

Catalysts were evaluated in a fixed bed flow reactor with gas analysis on line. Reaction conditions: $CO/CO_2/H_2/H_2O$ =5/30/60/5, GHSV=10000 h^{-1}, pressure 1 atm., temperature 300-700 °C. Prior to reaction, the catalysts were reduced at 300 °C in reaction mixture for 1 h. The fresh and spent catalysts were characterized by means of TPR, TPO, TPD, XRD, XPS and TEM techniques.

Thermodynamic calculations showed that pressure increase results in preferable methane formation. Therefore, special efforts were made to develop a catalyst highly active for RWGS reaction and inactive for the reaction of CO and CO_2 methanation.

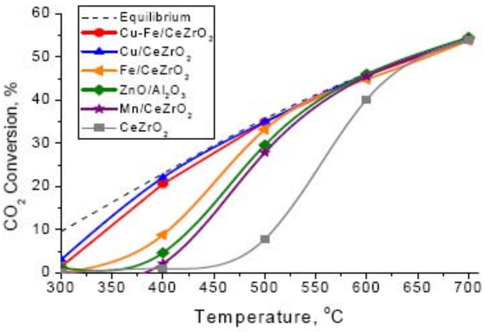

Fig. 1. The temperature dependence of CO_2 conversion.

Fig. 1 presents the results of catalytic performance studies. Cu- and Cu-Fe-based catalysts showed the best RWGS activity. Equilibrium CO_2 conversion on Cu-Fe/$CeZrO_2$ and Cu/Ce-ZrO_2 was achieved at 400 °C. Fe/$CeZrO_2$, Mn/$CeZrO_2$, ZnO/Al_2O_3 showed a lower activity. Pt/$CeZrO_2$ catalyst had activity in the methanation reaction.

In the long-term experiments, Cu/$CeZrO_2$ rapidly deactivated, whereas Cu-Fe/$CeZrO_2$ demonstrated stably and high activity, which remained unchanged even after sample exposure to the air at an ambient conditions. Moreover, neither methane, nor other hydrocarbons were detected among the products of the reaction on the Cu-Fe/$CeZrO_2$ catalyst.

The studies by XRD and HR TEM methods revealed that during pretreatment in the reaction mixture, the catalyst undergoes a structural change that leads to the formation of iron carbides Fe_3C and Fe_5C_2 which may be considered as a part of the active component composition.

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STUDY OF HZSM-5 ZEOLITE MEMBRANE FOR METHANOL DEHYDRATION TO DIMETHYL ETHER

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Abstract: HZSM-5 zeolite membrane catalyst for the synthesis of dimethyl ether (DME) from methanol was prepared by the secondary growth method on the monolithic cordierite surface. This catalyst was characterized by BET, XRD and SEM techniques. It was found that the zeolite membrane covered on the surface of cordierite was dense and uniform. It has a higher methanol dehydration activity and stability for the preparation of DME. Particularly, this catalyst can effectively solve the difficulties of forming of the zeolite, and reduce the cost of the production of DME.

Keywords: zeolite membrane; methanol dehydration; DME.

1. Introduction

DME is a low-emission and environmental friendly energy source, it has shown promise in replacing for diesel fuel [1].But the high cost of DME has seriously restricted its popularized and applied. Catalyst is the key to obtain the high yield and cost-effective DME. Early test results indicate that a high conversion and selectivity for DME can be obtained with pellet HZSM-5 at 200 °C. However, the expensive price, the difficulties in forming and deactivation owing to coke deposition in reaction limited this catalyst amplification. The object of this study is to develop a catalyst which has a high yield of DME and easy scale-up.

2. Experimental

HZSM-5 zeolite membrane catalyst for methanol dehydration to DME was prepared. The detail procedure involves treating the cordierite support [2]; attaching a aluminum layer on the surface of the monolithic cordierite substrate [3]; and synthesizing the zeolite membrane [4]. Beside the variation in the initial seeding solution and the synthesizing solution, the methodology of synthesize HZSM-5 membrane on the cordierite surface was similar to that presented by Aisheng Huang [4]. HZSM-5 zeolite seeds used for preparing colloidal suspensions, and the molar ratio of solution for synthesizing HZSM-5 zeolite membrane was Al_2O_3:38SiO_2:8Na_2O:3000H_2O:17TPABr. The HZSM-5 zeolite membrane catalyst was sealed into a stainless steel reactor. Methanol was used as feed for methanol dehydration to DME. The products were analyzed by using an on-line gas chromatograph with two thermal conductivity detectors (TCD).

3. Results and discussion

XRD patterns shows the high purity HZSM-5 zeolite layer formed on the cordierite surface, and the SEM images show the membrane is dense and uniform (fig. 1). The conversion of methanol can reach 95%; the selectivity of DME is nearly 100% at 200 °C; and the good result last a week, all these are impossible with pellet catalyst.

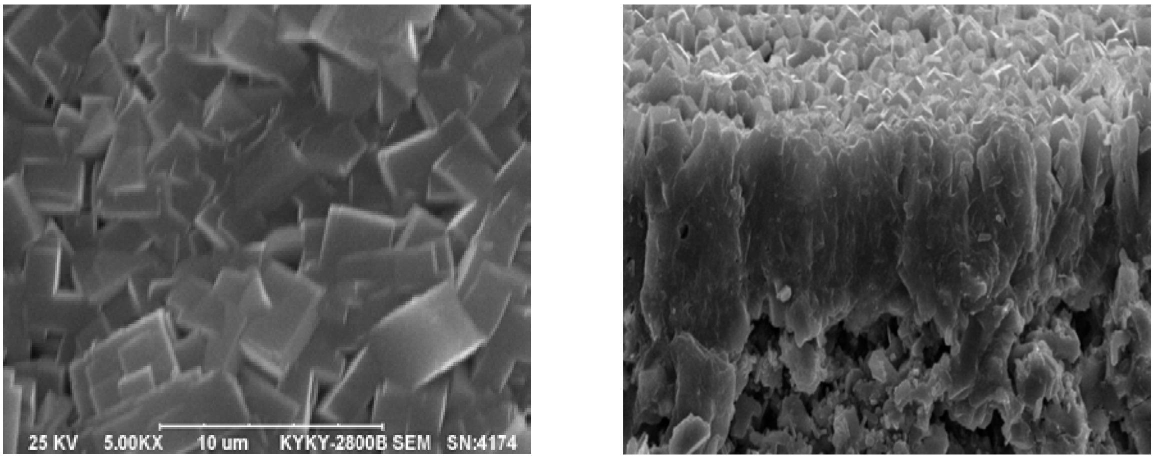

Fig. 1. Micrograph of HZSM-5 zeolite membrane.

4. Conclusions

Secondary growth method is an effective and easy method for synthesis of high quality HZSM-5 zeolite membrane. The activity and stability with membrane are higher than pellet catalyst. As the membrane loading for the monolith is 10.4%, it greatly reduces the amount of ZSM-5 catalyst, which induces the low cost of DME. This finding is of some importance as many new zeolite-catalyzed processes are being commercialized.

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CATALYTIC HYDRODEOXYGENATOIN OF PLANT FATTY ACIDS DERIVATIVES

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Due to the significant increase of the petroleum cost it becomes more perspective to produce engine fuels from the renewable sources.

Widespread biofuels is biodiesel that is usually produced by of transesterification of vegetable oils with methanol. The biodiesel is a mixture of methyl esters of fatty acids (FAMEs).

In spite of a number of its ecological advantages, biodiesel cannot be used in diesel engines without modernization of the engine. The main problems are high viscosity of the biodiesel, its ability to dimerization, low stability and high corrosion activity. The main reason for the quite low operating characteristics of biodiesel is high oxygen content due to the presence of ester groups (11-12 % wet.) in its components. Therefore the FAMEs can be used as a fuel for diesel engines only in a mixture with the hydrocarbon fuels.

Thus the main aim of the present work is a research and development of biodiesel hydrodeoxygenation process in order to obtain high-cetane hydrocarbons – "green diesel".

It should be noted that in contrast to the oil refining it is desirable to use non-sulfided catalysts in this process because of the low sulfur content in the biodiesel. Therefore the development of the new catalysts for biodiesel hydrodeoxygenation (HDO) is also the important aim of the present work.

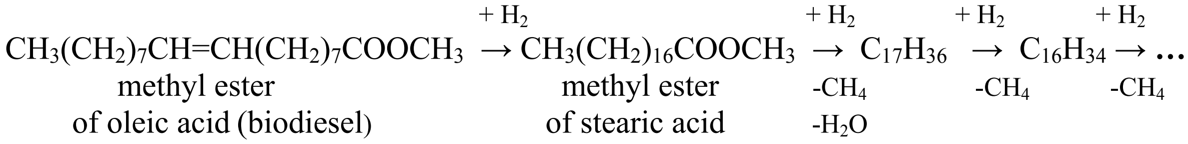
The reaction was carried out with the model compound (decanoic acid ethyl ester and oleic acid methyl ester) and also with the commercial biodiesel produced from the colza oil.

On the first step a lot of hydrotreatment catalysts were tested in biodiesel HDO at the constant conditions. The results of biodiesel hydrodeoxygenation showed that the most active catalysts are Rh/CeO_2-ZrO_2 and Ni-Cu/CeO_2-ZrO_2. It is possible that these catalysts are bifunctional: Rh and Ni-Cu phases activate hydrogen and CeO_2-ZrO_2 support activates oxy-organics.

The biodiesel methanization at the hydrodeoxygenation process is the feature of the nickel-based catalysts. Introduction of copper into the nickel catalysts increases the temperature of the methanization process start from 300-320 °C to 390-410 °C.

O-VI-5

The main products obtained at the 270-400 °C and 0,5-1,5 MPa of H_2 were linear hydrocarbons C_{14}-C_{17} which are formed according to the following reaction scheme:



$$\underset{\substack{\text{methyl ester}\\ \text{of oleic acid (biodiesel)}}}{CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3} \xrightarrow{+\,H_2} \underset{\substack{\text{methyl ester}\\ \text{of stearic acid}}}{CH_3(CH_2)_{16}COOCH_3} \xrightarrow[\substack{-CH_4\\ -H_2O}]{+\,H_2} C_{17}H_{36} \xrightarrow[-CH_4]{+\,H_2} C_{16}H_{34} \xrightarrow[-CH_4]{+\,H_2} \ldots$$

The variation of the process conditions and nature of the catalyst modifier enabled to produce different hydrocarbon products. The obtained experimental data on the examined catalysts stability and selectivity makes it possible to make the conclusions about a possibility of the given process industrial realization.

POSTER SESSION

P-I-1

MECHANOCHEMICAL CATALYST USE FOR GENERATION ACTIVE COMPONENT PRECURSOR OF BULK CATALYST HYDROPROCESSING

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The modern level of methods and technologies of catalysts preparation has an integral feature of active use nonconventional sources of power influence (ultrasound, mechanochemical activation, microwave radiation) which can provide, both the achievement of essentially new level solid substance reactivity end economy or ecological compatibility of manufacture. In particular, nowadays a mechanochemical activation (MA) technique is a basis for creation nonwaste technology catalysts. Thus on a lot of examples it is shown, that received as a result of the MA catalytic systems differ higher activity and selectivity than «wetchemical» analogues [1].

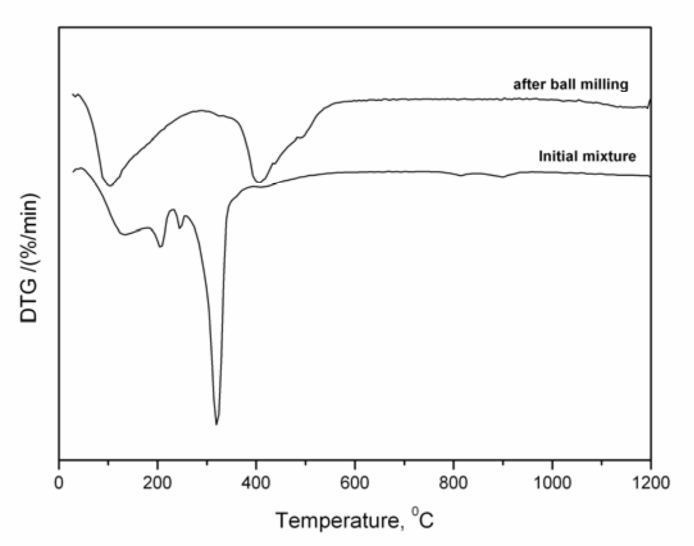
Recently it is offered to carry out mechnochemical activation with use [2] high reactivity compound, in particular compound with which participation reactions with evolution of water proceed. It gives an essential specificity of mechnochemical activation as water promote better interaction between reagents. Besides, hardness of such compound is three-four times less, than waterless ones. It allows to reduce the mechanical loading level and to go for soft condition activation with promotion the efficiency of synthesis at the same time. This type of reactions is called the «soft mechnochemical synthesis».

The aim of the present work were studying the process of interaction Ni and Mo-compoundes and the analysis of the formed products as prospective precursors of active component for bulk catalysts in hydrogenation slurry processes.

It was carried out the MA of the individual compounds : nickel hydroxycarbonate and ammonium heptamolybdate and mixes of these ones in different proportions with regard to metal. The MA were spent in the planet-ball-mill AGO-2C with acceleration factor equal to 30 g. Steel balls of diameter 8 mm were used. The ball-to-powder ratio was about 1:70. The sample were subjected mechanochemical activation in air during 15 minute.

The samples characterized by means of thermal analysis (TG–DTG–DTA), X-ray powder diffraction (XRD). The laser diffraction method were used for particle size analyses.

The received results show that there is a reduction of particle size of nickel hydroxycarbonate from 33 microns down to 2.6 microns in all investigated range with increase in time ball milling, i.e. in this case the mode of crushing is realized. The minimal size of ammonium heptamolybdate particles observed during 5 minutes is 1.7 microns. The further increase in ball milling time leads to agglomeration of particle size up to 4.1 microns. In this case it is possible to speak about realization of the mode of plastic current.



The figure illustrates the DTG curves of the initial mixture before and after the 15 minutes MA treatment. The DTG curve of initial mixture has several peaks, their maxima located at 100-350 °C. These peaks are characteristic for initial nickel hydroxycarbonate and ammonium heptamolybdate. After mechanical treatment the DTG curve represents two peaks, the first one can be connected with the evaluation of adsorbed water (100-120 °C), the second one account for formation of $NiMoO_4$ (390-550 °C). It is proved by XRD data. It's well known [3] that $NiMoO_4$ is the best prospective precursors of active component for Ni-Mo catalysts. It illustrates perceptivity of use mechanochemical activation during preparation of bulk catalysts of hydroprocessing.

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P-II-2

QUANTUM-CHEMICAL STUDIES OF ADSORBED H, O, O_2, OH AND H_2O ON Pt(111) BY DFT

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It is known that the hydrogen oxidation by platinum metals is one of the classical model reaction of heterogeneous catalysis. The reaction is described by Langmuir-Hinshelwood step-to-step mechanism, including dissociative hydrogen and oxygen adsorption with the formation of intermediate species – adsorbed OH-groups. Using the techniques of density functional theory (DFT) the equilibrium states and stretching vibrations of H_{ads}, O_{ads} atoms and OH_{ads}, H_2O_{ads} molecules, adsorbed on the Pt(111) surfaces, have been calculated depending on the surrounding of the metal atoms.

The adsorption of atoms and molecules at coverage of 0.25 ML has been studied by DFT within the local density approximation (LDA). The simulations were conducted using ESPRESSO-3.1 program. We have employed a three layer slab for simulation of Pt(111) surface.

Adsorbed H, O atoms and OH, H_2O molecules can occupy the following states: two threefold hollow sites (fcc and hcp), twofold bridge site and on-top, using only adsorbed species per unit cell (Fig.1). Computed frequency of symmetrical valence vibrations of H_{ads} and O_{ads} atoms occurring perpendicular to the surface heavily depends on the number of metal atoms coordinating with the adsorbed atom. Vibration frequency dramatically increases with decreasing of number of bonds in adsorption center.

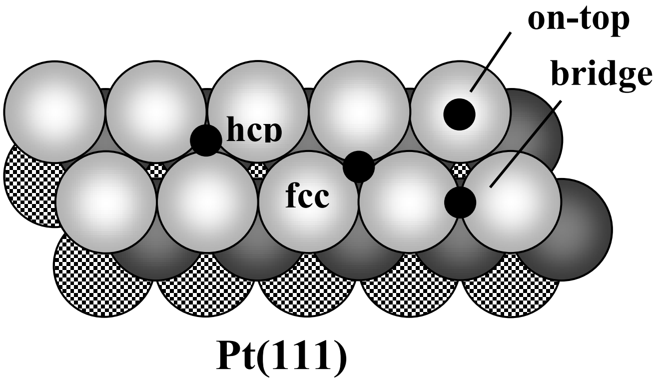

Fig. 1. Schematic top view of the Pt(111) surface: adsorption sites of H, O atoms and OH, H_2O molecules.

Table 1. DFT results for binding energies (E_b), equilibrium heights (r_0) above the surface, bond length (d_0), vibration frequencies (ν = stretch) of adsorbed H, O atoms and OH, H_2O molecules for following adsorption sites on Pt(111) at θ = 0.25 ML.

	Site	E_b, kcal/mol	r_0, Å	d_0, Å	ν, cm^{-1}
H	fcc	-86.6	0.97	-	1218
	hcp	-86.6	0.97	-	1212
O	fcc	-137.6	1.23	-	499
OH	bridge	-75.3	1.71	0.97	427
H_2O	on-top	-14.85	2.26	0.97	265
O_2	bridge	-52.2	1.85	1.35	420

It is demonstrated that the threefold hollow sites (fcc and hcp) for adsorption of H and O atoms are preferred compared to weakly bond energy sites (on-top or bridge). Calculations at 0.25 ML coverage show that OH and O_2 on the bridge sites are more stable than that on the hollow sites or on-top. The appearance of OH-hydroxyl groups during the initial 1st step of H_{ads} + O_{ads} reaction is accompanied by transition of oxygen atom from the hollow site (Pt_3-O_{ads}) into bridge site Pt_2-$(OH)_{ads}$. Water formation in the 2nd step of $OH_{ads} + H_{ads} \rightarrow H_2O_{ads}$ reaction is characterized by the subsequent transition of oxygen atom from the bridge site (Pt_2-$(OH)_{ads}$) into on-top site (Pt_1-$(OH_2)_{ads}$) that is accompanied by cleaning of the centres, active in H_2 and O_2 dissociation (Fig. 2.).

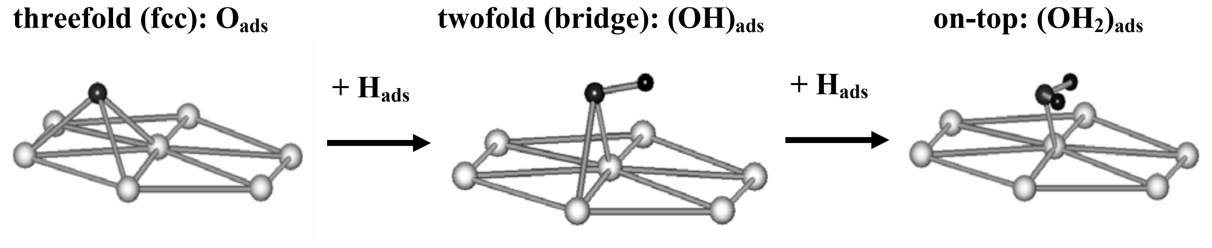

Fig. 2. Transition state geometry for H_2O formation from adsorbed O and H atoms on Pt(111).

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XPS AND UPS INVESTIGATION OF OXYGEN INTERACTION WITH SILVER NANOPARTICLES

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Silver nanoparticles are widely used in catalysis, medicine, optics. The reason why properties of silver nanoparticles differ so drastically from bulk metal is still ambiguous. This problem is particularly important for heterogeneous catalysis. Unique oxidative properties of silver are bound with oxygen species stabilized on metallic and oxidized silver nanoparticles. Therefore, study of silver nanoparticles and their interaction with oxygen or reaction mixture is of considerable fundamental and practical interest.

The objective of the presented work was to study the state of oxygen on the silver particles depending on their size by photoelectron spectroscopy. The experiments were carried out using an electron spectrometer VG ESCALAB HP by VG Scientific (Great Britain). Silver nanoparticles were deposited on the gold support by the convection sputtering in helium or oxygen atmosphere. The TEM method was used to control the particle size.

Comparison of the Ag3d core level and the valence band spectra of silver nanoparticles with the same data obtained for the bulk silver film allowed establishing the peculiarities of electronic structure of nanoparticles. The experimental data give evidence that electronic structure determines the different type of oxygen interaction with silver nanoparticles or Ag bulk.

The oxygen exposure at room temperature results in the formation of the carbonates species on both small and large particles, as can be concluded from O1s and C1s spectra (see fig. 1 and fig. 2, correspondingly). These species seem to be due to the high adsorption ability of background gases (CO, CO_2). When the thick silver film was heated, the carbonates decomposed and the layer of oxide-like silver structure was formed (fig. 1(I)). On the other hand, we could not detect such oxide-like structures after heating of the carbonates layer adsorbed on the silver nanoparticles (fig. 1(II)). One can see the increase of the intensity of spectral features in O1s spectra that are typical for molecular oxygen species.

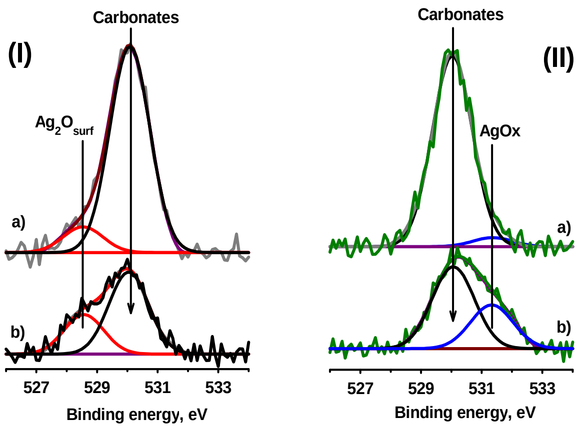

Fig. 1. The O1s spectra of thick Ag film (I) and silver nanoparticles (II) after (a) 10^4 Pa O_2 at RT; (b) heating at 350K.

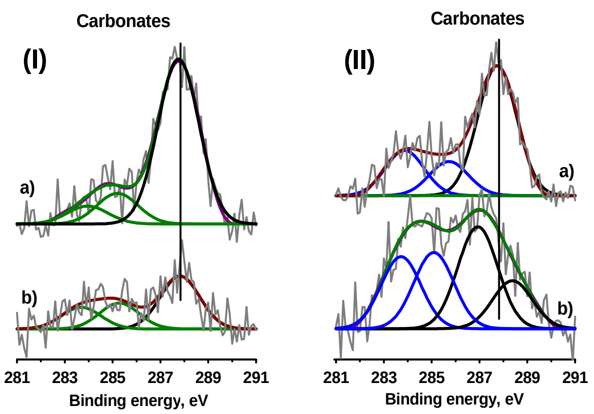

Fig. 2. The C1s spectra of thick Ag film (I) and silver nanoparticles (II) after (a) 10^4 Pa O_2 at RT; (b) heating at 350K.

The C1s spectra (see fig.2) reveal the different mechanism of the decomposition of carbonate species. The heating of carbonate structures on the silver film leads to decrease of the C1s peak intensity. So, the decomposition occurs with the formation of carbon dioxide and atomic oxygen that is in agreement with literature data [1]. For silver nanoparticles, the increase of the temperature results in the increasing of the C1s peak area. One can see the accumulation of the elementary carbon and other carbonaceous species on the surface of silver nanoparticles.

The convectional sputtering of oxidized silver cluster directly in oxygen atmosphere allows avoiding the formation of the carbonate species. Only oxygen species with the binding energy $E_b(O1s)$ >530 eV are formed on the small silver nanoparticles less then 5 nm. Such value of BE is typical for molecular oxygen species. The UPS spectra also show the existence of O-O bonds in these compounds. The increase of the particles size leads to stabilization of atomic oxygen species. The peculiarity of small silver particles seems to be due to existence of great amount of structural defects.

Thus, this investigation showed the substantial changes in the nature of oxygen states on the silver depending on the particles size. The different mechanisms of the interaction of silver nanoparticles and thin film with oxygen and carbon monoxide can be of great importance for oxidation reactions on silver.

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P-II-4

THE CATALYTIC ACTIVITY OF $CoMo/Al_2O_3$ AND $NiMo/Al_2O_3$ CATALYSTS IN THE HYDRODESULFURIZATION OF THE SUBSTITUTED DIBENZOTHIOPHENES

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The main problem arising during the ultra low sulfur diesel production is the removing of refractory S-containing molecules: alkyl substituted dibenzothiophenes (DBT). They can react via direct desulfurization (DDS) leading to the formation of biphenyls or trough hydrogenation (HYD) followed by desulfurization giving first tetrahydro- and hexahydrodibenzothiophenes, which are further desulfurized to cyclohexylbenzenes and bicyclohexyls, correspondingly. To get information about the reaction pathway in the presence of different catalysts and to elucidate the influence of the N-containing molecules and aromatics the model mixtures prepared using different solvents are commonly applied [1-3].

The aim of the present work is to study the influence of the solvent composition on the activity of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts in the hydrodesulfurization (HDS) of the DBT, 4-MDBT and 4, 6-DMDBT. To provide this study the hexadecane, mixture of o-xylol with hexadecane and desulfurized gas oil (DSGO) were used as the solvents. The effect of hydrogen pressure on the activity of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ in the HDS of the alkyldibenzothiophenes has been also investigated.

The catalysts were prepared by impregnation of alumina with a solution containing bimetallic CoMo or NiMo complexes with carboxylic chelating agent and subsequent air drying at temperature 110 °C. The oxide precursors for the sulfidation of the catalysts were heated in flowing H_2S/H_2 gas mixture (10 % vol. H_2S in hydrogen) from room temperature to 400 °C (4 °C/min) and held at 400 °C for 2 h. Reactions were carried out in the batch reactor at 340 °C, the hydrogen pressure was 3.5 or 5.5 MPa. The content of DBT, 4-MDBT and 4,6-DMDBT in model mixture were 500, 250 and 80 ppm respectively. The specific sulfur compounds in the samples were analyzed by gas chromatograph Agilent 6890N, equipped with a capillary column HP-1MS (60.0 m × 250 μm × 1.00 μm) and an atomic emission detector JAS. HDS kinetic constants were calculated assuming pseudo-first order kinetics referred to DBT's concentration.

It was shown, that the reactivity of alkyldibenzothiophenes decreases in the following order: ДБТ > 4-МДБТ > 4, 6-ДМДБТ, irrespective of the solvent nature. It was stated, that the both catalysts provide a lower activity, when the mixture of o-xylol with hexadecane or DSGO was used as the solvent instead of hexadecane. The activity decrease can be explained by the inhibiting effect of aromatic and polyaromatic compounds on the HDS activity. Thus, the DSGO contains 21,7% mono-, 1,89% di- and 0,81% polyaromatics, respectively. $NiMo/Al_2O_3$ catalyst revealed higher activity when the hexadecane was used as the solvent, while the activity of $CoMo/Al_2O_3$ catalysts was higher in the case of DSGO. Therefore we concluded that $NiMo/Al_2O_3$ catalyst is subjected to the greater inhibition by aromatics than $CoMo/Al_2O_3$.

Hydrogen pressure effect on the HDS activity of alkyldibenzothiophenes was investigated using the mixture of DBT, 4-MDBT, 4,6-DMDBT in the desulfurized gas oil. The hydrogen pressure increase from 3,5 to 5,5 MPa led to rising of the activity of both catalyst. It was found, that DBT and 4-MDBT conversion rates were increased in two times, while in the conversion rate of the 4,6-DMDBT run up to three times. The greater increase of the conversion rate of 4,6-DMDBT in comparison with DBT at higher pressure can be explained by preferable transformation sterically hindered S-containing molecules like 4,6-DMDBT via hydrogenation (HYD) route.

Thus, the results obtained make it clear that the solvent used affects strongly the activity of the catalysts in the HDS of the DBT's. Moreover the inhibition effect is more pronounced for the sterically hindered compounds transformed via the hydrogenation (HYD) route. This aspect should be taken into account when the activity of the different catalysts are compared using the model mixtures.

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P-II-5

NEW CATALYSTS FOR REMOVING THE BENZENE IN CYCLOHEXANE FOR OBTAINING ENVIRONMENTAL FUELS

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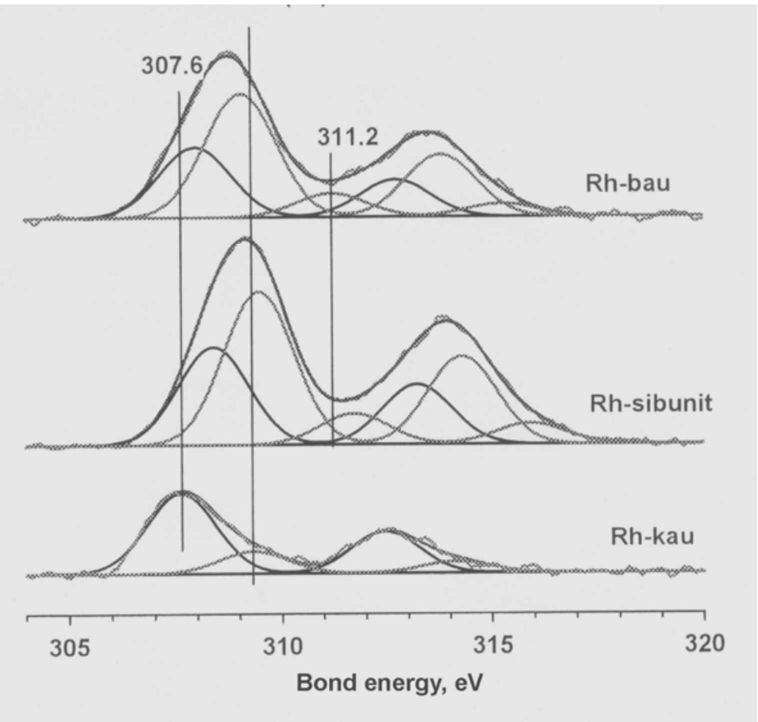
Presence of benzene in fuel leads to formation of strong cancerogen benzoperene at non-complete burn of fuel. According to Euro-4 standard the content of benzene in fuel cannot be more than 1%, whereas according CIS standard the norm is 5%. In Kazakhstan, like in other CIS countries, there is no control for content benzene in fuel. Now the European Union has prepared a new standard, which borders the benzene content in fuel down to 0.1%. The new standard implementation is delaying because of absence the technologies allowing benzene remove.

The highly efficient method of benzene remove in fuels its transformation into environmentally safe cyclohexane. This process needs the new selective catalysts of hydrogenation of the low concentrations of benzene.

We have developed the new Rhodium catalysts laid on different layers. We have used tri-chloral salt of the Rhodium laid on coals and tradition layers. As the layers there have been used the sibunit, birchen activated coal (BAC) and pit activated coal (PAC). Concentration of rhodium varied in limits of 1-3%. The most active catalyst was Rhodium-BAC, providing the reaction velocity two times higher than on other layers.

Benzene’s hydrogenation has been carried at hydrogen pressure of 40 bars and room temperature. The concentration of benzene in a system was 2-3%. Water, alcohol and hydrocarbons have been used as solvents. The highest velocity has been recorded in water, then in alcohol following by hydrocarbons. The medium’s polarity stimulates different forms of rhodium and other components of the system. After the hydrogenation there is no benzene in system, which means 100% conversation.

According to x-ray PES the Rhodium on the coals has different forms from charged to metallic. Sibunit surface has mainly charged ions while BAC has mainly metal atoms. The bond’s energy of Rh^{3+} charged forms is 311,2 eV, while metal rhodium is 307 eV. Basing on this we can suppose that hydrogenation requires Rh^{o} - Rh^{+3} forms.



The ready-to-use catalyst has been modified by Molybdenum salts. This allowed to do selective hydrogenation of benzene on PAC in presence of other aromatic compounds such us toluene, xylene and cumene. The difference of benzene hydrogenation and toluene and cumene hydrogenation was significative while xylene hydrogenation was not detected.

Catalyst modifying by Molybdenum salts increases the benzene’s hydrogenation selectivity in presence of other aromatic compounds.

P-II-6

KINETICS OF H_2, CO AND CH_4 OXIDATION AND SURFACE LAYER PROPERTIES OF HETEROGENEOUS CATALYSTS

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Heterogeneous catalytic systems prepared by H_2-reduction of $Pt(Pd)/M_2O_5$ oxides (M = V, Nb, Ta) were tested in oxidation of small molecules: H_2, CO and CH_4. The catalysts were characterized by XRD, XPS, EM, FTIR, TPD-MS methods sensitive to the surface structure of the catalyst and adsorbates. According to XRD, XPS and EM data, one can concluded that oxygen nonstoichiometry, partial amorphization of the near surface-layer and red-ox M^{4+}/M^{5+} couples facilitate the small molecules oxidation over these catalysts. Activity testing and kinetic studies on mechanisms of these reactions were performed in gradientless reactor. Kinetics of H_2+O_2 reaction over whole catalysts studied obeys satisfactorily Eley-Riedel mechanism: reaction occurs by the interaction of gas-phase H_2 with adsorbed oxygen described. The kinetic regularities of CO oxidation over $Pt(Pd)/V_2O_{5-x}$ are unusual as compared with over metal-oxide systems. In the region of low catalyst activity (CO conversion <20%), the reaction was found to be zero-th in CO and first-order in oxygen. In the high-activity region (CO conversion >95%), the reaction order was first with respect to CO and zero-th with respect to oxygen. Hysteresis phenomena were observed for the $r - c(O_2)$ and $r - c(CO)$ dependences at certain temperatures. The mechanism combining the heterogeneous and heterogeneous-homogeneous mechanisms was proposed; the possible active phase act in the reaction was suggested combining spectroscopic and kinetic data. The reaction of CH_4 oxidation to CO_2 was found to be zeroth in oxygen and first-order in CH_4 concentrations. Different surface structures were found by XPS and EM, the better conversion was achieved when MO_x ($4 < x \leq 5$) non-stoichiometric oxides have been predominant in the layer. The active sites and intermediates formed upon H_2, CO and CH_4 adsorption were determined from XPS, FTIR and TPD-MS data.

THE REASON OF DEACTIVATION OF MODEL PALLADIUM CATALYST IN THE PROPYLENE OXIDATION

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The mechanism of the palladium deactivation in the reaction between C_3H_6 and O_2 on Pd(110) and Pd(551) single-crystals was studied by *in situ* XPS and mass-spectrometry in the mbar pressure range. The activity in total propylene oxidation ($2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O$) during a heating sharply increases at 285, 230 and 210 °C, for oxygen/propylene ratio 1:1, 10:1, 100:1 correspondingly, whereas a quick decrease in the activity was observed at 150 °C during the subsequent cooling ramp.

The activity hysteresis is closely coupled with a hysteresis in the carbon and oxygen content on the surface and in the near-surface region, which was observed by XPS and MS combined study. The state with lower activity corresponds to a PdC_x phase. This phase forms over the Pd surface due to carbon deposition and following partial carbon dissolution in the palladium bulk, leading to immediate catalyst deactivation at low temperature even in an oxygen excess. During heating (210-285 °C), the carbon clean-off reaction by oxygen proceeds and the highest catalytic activity is observed. In cooling from higher temperature regime, the concurrent formation of the surface palladium oxide takes place, which prevents the carbon deposition even at 150 °C. Moreover, it was found that increasing of the oxygen/propylene ratio decreases the propylene conversion. This phenomenon is explained by the inhibiting effect of oxygen adsorption and formation of the surface oxide, which blocks the surface.

Thus, we conclude, that the presence of oxide- and carbon-free metal surface, where propylene and oxygen can adsorb and dissociate, is necessary for high catalytic activity.

Acknowledgements: The study was partly supported by the RFBR grants № 08-03-00454 and № 08-03-00825.

P-II-8

ISOTOPIC EXCHANGE OF O_2 IN THE PRESENCE OF O^- RADICALS ON THE Fe-CONTAINING ZSM-5 ZEOLITES

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Oxygen anion radicals O^- play an important role in various physico-chemical processes, including those taking place on solid surfaces, where their behavior is especially difficult to follow [1, 2]. In this connection, of particular interest are Fe-containing zeolites FeZSM-5. A unique feature of the zeolites is that they allow generating O^- radicals in the concentration which by 2-3 orders of magnitude exceeds that for oxide systems. This is provided by the so-called α-sites, which are special complexes of bivalent iron stabilized in the micropore space of the zeolite matrix [3]. Strong stabilization of the bivalent state prevents the oxidation of α-sites by dioxygen, but they are readily oxidized at 470-520 K by molecules of nitrous oxide leading to the stoichiometric deposition of O^- radicals called the alpha-oxygen for this system, O_α:

$$(Fe^{2+})_\alpha + N_2O \rightarrow (Fe^{3+}\text{–}O^-)_\alpha + N_2$$

This work presents detailed study on the behavior of O^- radicals adsorbed on FeZSM-5 surface in the reaction of O_2 isotopic exchange carried out in a wide range of temperatures (198-513 K). High concentration of O^- in this unique system made it possible to identify two exchange mechanisms, R_0 and R_1, operating in the presence of O_α [4]. The R_1 mechanism (E = 3.5 kcal/mol) dominates in the high-temperature region (323-513K) and can be represented by the follow equation:

$$^{18}O_2 + {}^{16}O_\alpha^- \leftrightarrow [O_3^-]_\alpha \leftrightarrow {}^{18}O^{16}O + {}^{18}O_\alpha^-$$

This mechanism is convincingly supported by several arguments: the first reaction order with respect to O_2; the linear dependence of reaction rate on O_α concentration; the ESR observation of O_3^- species (in other systems); and, according to the isotopic exchange theory, by a twofold excess of the rate of homoexchange over the rate of heteroexchange.

The R_0 exchange (E = 0.2 kcal/mol) is a new reaction pathway that appears at cryogenic temperatures and leads to isotope redistribution only between O_2 molecules, not affecting the isotopic composition of O_α. This exchange mechanism is not quite clear. The necessity of O_α presence without its direct involvement in the exchange process seems to be quite surprising. The reaction may proceed via a hypothetical complex $[O_5^-]_\alpha$, which allows cleavage and redistribution of chemical bonds between two O_2 molecules adsorbed on the α-oxygen. The cleavage and redistribution of so strong bonds at cryogenic temperatures with nearly zero activation energy are an intriguing phenomenon worthy of further study.

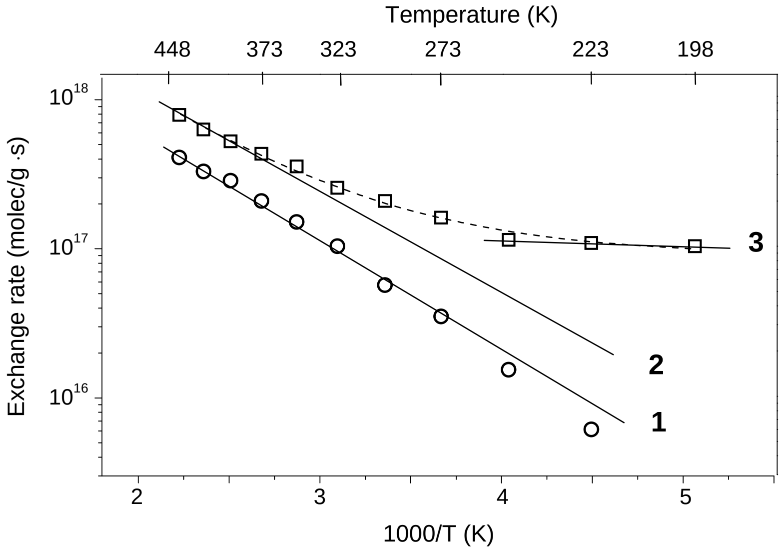

Fig. 1. Arrhenius plot of O_2 isotopic exchange (0.1 Torr, $1.5\cdot10^{19}$ O_α/g):

1) R_1 heteroexchange (E = 3.5 ± 0.5 kcal/mol)

2) R_1 homoexchange (E = 3.5 ± 0.5 kcal/mol)

3) R_0 homoexchange (E = 0.2 ± 0.1 kcal/mol)

Dotted line is a calculated additive rate of homoexchange.

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P-II-9

CATALYTIC OZONATION OF OXALIC ACID WITH COOPER CATALYST

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Catalytic ozonation is one of more effective methods of water treatment. This technique uses oxidation of water pollutants by ozone in presence of catalysts, e.g. different metals, metal oxides. There are many researches of such processes were carried out some last decades. But mechanism of catalytic ozonation is not clear yet. Some authors point out that the mechanism depends on type of using catalyst. That's why it is very important to investigate the process way for every type of catalyst.

This work deals with a new type of catalysts – cooper with cooper oxides on its surface. Catalytic activity of this material in oxalic acid decomposition process was studied and mechanism was proposed. Such indirect methods, as UV-Vis Spectroscopy, FTIR-ATR Spectroscopy, XRD, SEM were used.

As it shown in Table 1, the presence of this catalyst in a system increases oxalic acid decomposition from 7 to 84 %.

Table 1. Oxalic acid decomposition depending on kind of treatment (initial content of oxalic acid – $1*10^{-3}$ M).

Kind of treatment	O_2 without catalyst	O_2 with catalyst	O_3 without catalyst	O_3 with catalyst
Oxalic acid decomposition, %	3	3	7	84

Kinetic diagram of oxalic acid decomposition in catalytic ozonation process was obtained.

It's supposed that the mechanism of oxalic acid decomposition in this case has an oxidation-reduction nature. Oxalic acid decomposition in the presence of cooper catalyst concerns with its oxidation by cooper oxides, which formed on catalyst surface under ozone action.

THE KINETICS STUDY OF LOW-TEMPERATURE 1,2-DICHLOROETHANE CONVERSION ON CATALYSTS SURFACE BY IN SITU FTIR SPECTROSCOPY

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Vinyl chloride is one of the most large-scale products of the industrial chemistry. Vinyl chloride produces via pyrolysis of 1,2-dichloroethane at 480-520 °C [1]. Nowadays, the production of vinyl chloride demands the decision of two problems, namely, the decreasing of harmful exhaust for existing industrial process and the creation of catalytic production of vinyl chloride from 1,2-dichloroethane. Both these problems are related to necessity of study of chemical reactions occurring on a catalysts surface during 1,2-dihlorethane dehydrochlorination. First papers in this area were published in the middle of 90th. It was shown that on oxides surface formation of acetaldehyde took place [2, 3]. Also, two-point mechanism of dehydrochlorination was proposed [4]. Dependence of 1,2-dichloroethane conversion on catalysts acidity was studied on series of binary silicate catalysts [5]. It was found that reaction rate increased with Lewis sites strength.

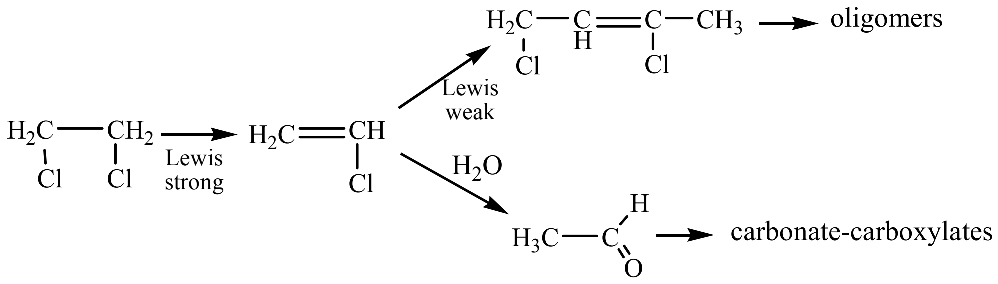
The objective of this work is studying the kinetics of 1,2-dichloroethane dehydrochlorination on well characterized acid catalysts by means of in situ FTIR spectroscopy. As the catalyst H-ZSM-5 zeolite with strong Broensted acid sites was chosen. Alumina and silica alumina catalysts being the most active in this reaction were studied too. Both these catalysts have strong Lewis sites, while strong basic sites exist only on alumina surface.

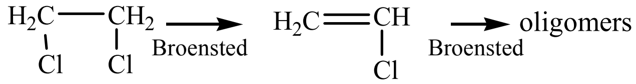
Adsorption 1,2-dichloroethane on H-ZSM-5 zeolite, γ-Al_2O_3 and silica alumina catalyst (15% Al_2O_3, 85% SiO_2) was studied in the temperature range of 25-400 °C. 1,2-dichloroethane conversion started on zeolite at 200 °C whereas on silica alumina catalyst, and alumina already at 100 °C. The complexes of 1,2-dichloroethane and reaction products (vinyl chloride and 1,3-dihlorbutene-2) with the Broensted and Lewis sites were found to form.

It was shown that the formation of H-bond between 1,2-dichloroethane and acidic OH groups of H-ZSM-5 preceded to dehydrochlorination process at 200 °C. The formation of these complexes was proved by band shift from 3602 cm^{-1} (attributed to acid OH groups in channels) to 3350 cm^{-1}. Vinyl chloride converted into oligomers directly at adsorption. Besides, it was shown that vinyl chloride interacted with AlOH groups or water converting into acetaldehyde. Water appeared via interaction of AlOH with HCl. On alumina surface, vinyl chloride converted into 1,3-dihlorbutene-2 and acetaldehyde. The formation of

1,3-dihlorbutene-2 occurred with participation of weak Lewis acid sites. Both vinyl chloride and 1,3-dihlorbutene-2 converted into oligomers on weak Lewis acid sites that resulted in catalyst deactivation. Side reaction of acetaldehyde formation occurred with participation of AlOH groups, similar to zeolite. Unlike to alumina, 1,3-dihlorbutene-2 was not formed on silica alumina catalyst at 100 °C, and oligomers were formed only at 200 °C.

The rate constants of 1,2-dichloroethane dehydrochlorination were calculated for initial period of kinetic curves and after 30 minutes of reaction. The rate constants on alumina and silica alumina catalyst are equal, but on silica alumina catalyst basic sites are absent. It can be concluded that the basic sites do not play any appreciable role in 1,2-dichloroethane dehydrochlorination on this catalysts. The scheme describing main roots of 1,2-dichloroethane conversion was proposed.





Performed study show that the catalyst acceptable for practical purposes should possess only the strong Lewis acid sites, with absence of Broensted, weak Lewis acid and basic sites on catalyst surface.

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STUDYING AND OPTIMIZATION OF MEMBRANE-ELECTRODE ASSEMBLIES (MEA) FOR DIRECT METHANOL FUEL CELL (DMFC)

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There are several significant problems that decrease the efficiency of direct methanol fuel cells (DMFC). These are the low activity of PtRu catalyst in the methanol oxidation reaction, poor stability of electrode layers and methanol crossover through the membrane. The fist one results in the increase of the precious metals (Pt and Ru) load causing the higher prices of DMFC. Low stability reduces dramatically the life span of DMFC. Moreover, methanol crossover significantly lowers the efficiency and performance of DMFC due to the fall of the voltage. The power density and stability of DMFC is directly related to the properties of the MEA, which is the crucial part of DMFC.

In the present work in order to increase the efficiency of DMFC the optimizations of both the MEA properties and proton conducting membranes were performed. Three methods of MEA preparation were studied: (i) deposition of catalytic electrode layer onto the carbon paper surface (CCS); (ii) coating both sides of the membrane with the catalyst material (CCM); and (iii) transferring by hot pressing of both the anode and cathode catalytic layers from polytetrafluoroethylene films onto the surface of membrane ("decal" method). The as-prepared MEAs were studied in DMFC. Moreover, effects of the content of binding material (Nafion) in the electrode layer, type of the catalyst (PtRu black or PtRu/C) (Johnson Matthey Company) and methanol concentration on the polarization characteristics of MEAs in DMFC were also investigated. Structures of MEAs were studied by transmission and scanning electron microscopy. The maximal power density (19 mW/cm^2) was achieved for MEA prepared by CCM method (Fig. 1), this value being close to that reported in literature [1]. On the contrary, the MEA prepared by "decal" method, showed the best stability.

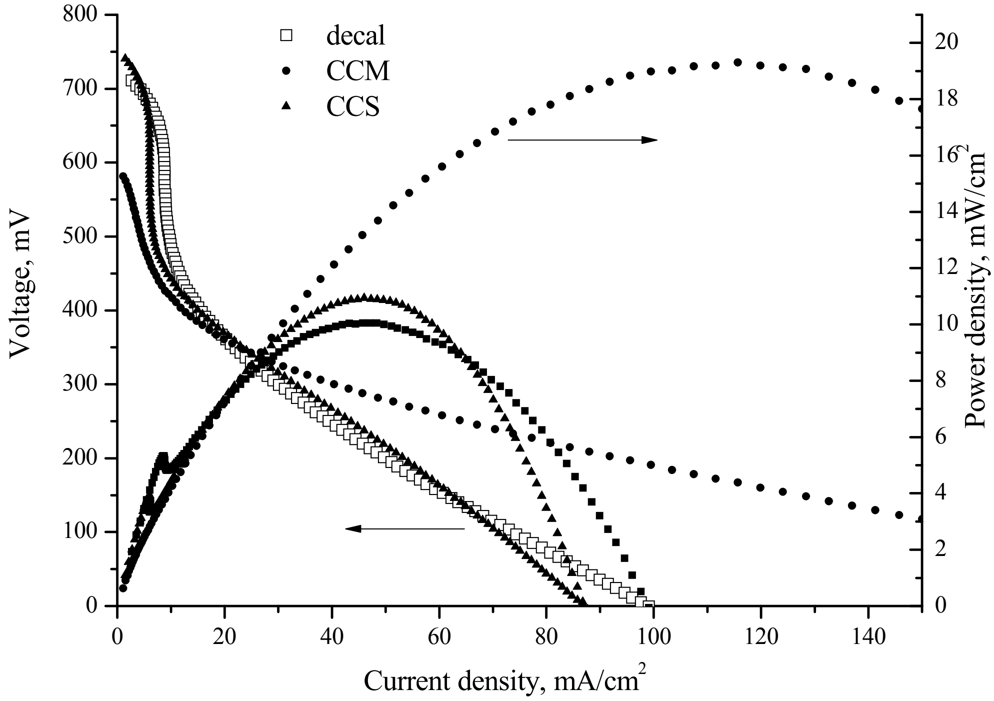

Fig. 1. Effect of the preparation methods of MEAs on their performance in DMFC. Experimental conditions were as follows: ambient temperature, air, methanol 2 M, anode – PtRu black 5 mg/cm^2, cathode Pt black 3 mg/cm^2.

In order to study the effect of methanol crossover, a series of commercial proton conducting hydrocarbon membranes supported by FUMATECH (polysulfone, poly(ether ether ketone), poly(phtalazinon ether ketone)) with low methanol permeability and high selectivity (3-6 relative to that of Nafion) were also studied in DMFC. The polarization curves of MEAs prepared using hydrocarbon as well as nafion membranes were tested and compared under wide range of methanol concentrations.

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PILOT TESTS OF FIBER-GLASS CATALYSTS FOR FLUE GAS CONDITIONING OF COAL-FIRED POWER PLANTS

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One of the most urgent ecological problems in coal electric-power industry is purification of flue gases of power plants from a dust of coal ash. Almost a half of Russian power plants are equipped with electrostatic precipitators (ESPs) for control of particulate matter emissions from. The technology of ESPs modernization known as conditioning – injection of small quantities of SO_3 and its subsequent adsorption on a particles surface – allows to effectively increase of ash electrical conduction. One of the optimal methods of SO_3 introduction to ESPs is controlled catalytic oxidation of sulfur dioxide: $2SO_2 + O_2 = 2SO_3$ (1). It allows to achieve necessary concentrations of sulfur trioxide in flue gases for decrease of flying ash resistivity with simultaneous minimization of SO_3 overshoot.

Prospective catalysts for this technology are catalysts on the basis of fiber-glass supports with platinum and vanadium as active components. Earlier made experiments on laboratory reactor have shown that platinum-containing catalyst on the support modified with zirconium dioxide with low content of platinum mainly in the ionic form possess the best activity in reaction (1) together with good stability [1]. Research of a mixture of conventional granular vanadium catalyst IC-1-6 and the platinum fiber-glass catalyst has confirmed that the given combination provides high activity both at high and low temperatures [2].

For obtaining the direct experimental data not requiring the further scale up, the pilot reactor providing a performance level of SO_3 similar to real process of flue gases conditioning was created at the Biysk Oleum plant. The pilot tests were performed with the composite catalytic cartridges with three-layer catalytic system (platinum fiber-glass fabric – vanadium granules IC-1-6 – platinum fiber-glass fabric), fixed on the metal basis in the form of a mesh belt and rolled into a spiral (Fig. 1).

The following parameters were traced during pilot experiments: gas temperatures at the catalyst bed inlet, middle and outlet; gas flow rate; pressure drop of the catalyst bed; SO_2 concentrations at the entry and exit of the reactor.

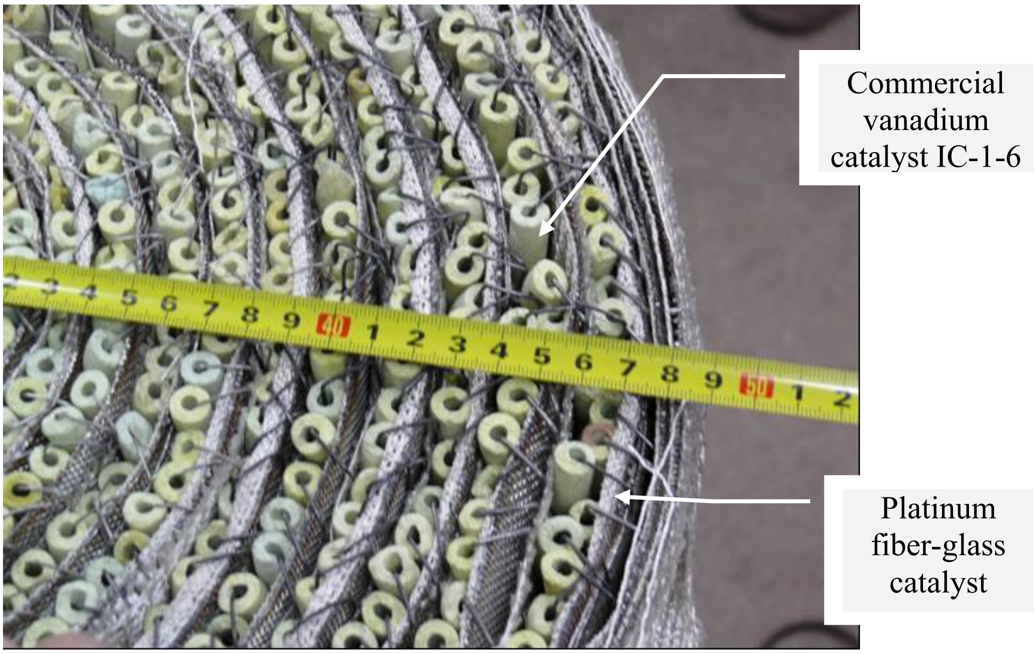

Fig. 1. Structure of the composite catalytic cartridge.

At first the temperature of the composite catalytic cartridge "ignition" has been defined (380-385 °C). It has appeared essentially below of the corresponding temperature for conventional vanadium catalysts (about 410-420 °C for the most of known commercial types) that is rather important advantage of new catalytic system. Then, having stabilized temperature of gas entering into the reactor and varying its flow capacity in a range from 50 m^3/hour to 120 m^3/hour, the optimum gas flow capacity (100 m^3/hour) corresponding to the maximum SO_3 productivity has been defined. After that in the set conditions resource tests of the composite catalytic cartridges for the purpose of studying of their possible deactivation in the conditions of long operation have been started.

The research was performed under the financial support from U.S. Environmental Protection Agency via the International Scientific-Technological Center (ISTC grant #3662).

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INFLUENCE OF THE NATURE OF METAL/METAL OXIDE MODIFIER ON CATALYTIC PROPERTIES OF $Mt/MtO_x/B_2O_3$-Al_2O_3 IN HYDROCONVERSION OF VEGETABLE OIL

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Hydrocarbon diesel fuels produced from vegetable oils do not yield to the best samples of oil origin fuels in combustion value and low-temperature properties, and they greatly surpass them in cetane characteristics and environmental safety at the expense of practically full absence of sulfur compounds and aromatic components. Thus, known today variants of processing of vegetable oils into hydrocarbon diesel fuels as a rule combine hydrodeoxygenation and isomerization reactions which can be carried out on one or two catalysts. Undoubtedly, one-stage processing of vegetable oils is more preferable from the point of technology view as it allows to reduce capital and operating costs. At that for carrying out the process by one stage an appropriate catalyst which optimized functions of hydrogenation (metal site) and isomerization (acid site) is necessary. As stated above such approach exactly was realized in catalytic systems based on Pt, Pd or Ni supported on solid-acid matrices – alumina, alumosilicates, zeolites and others.

In the framework of this paper for development of catalyst of one-stage vegetable oils processing into hydrocarbon diesel fuels it is first suggested to examine bifunctional catalytic compositions based on Pt-, Pd-, Ni-, Co, Mo, W-containing systems with B_2O_3-Al_2O_3 (BA) as a solid-acid support. Catalytic experiments were carried out in a fixed bed flow reactor in H_2 atmosphere at 400 °C, under 4.0 MPa total pressure and WHSV = 5 h^{-1}. Sunflower oil was used in experiments.

It is shown, that on all catalysts, including support BA, decomposition of vegetable oil proceeds with yield of liquid products about 70-85 wt% (see Table). Depending on the nature of catalyst gaseous products of hydroconversion may contain CO, CO_2, C_1-C_4, including light alkenes, and liquid products may contain H_2O, fatty acids, hydrocarbons (alkanes, alkenes, cycloalkanes, arenes).

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Table. Yields of products of sunflower oil hydroconversion on different catalysts, wt%.

Products	Catalyst composition (wt% Mt/MtO$_x$)						
	1Pt	1Pd	15MoO$_3$	15WO$_3$	15NiO	15CoO	BA
Total gas including:	12.57	8.82	9.98	11.52	22.66	10.87	7.28
CO	5.47	3.08	5.67	5.01	0.18	0.52	1.48
CO$_2$	2.52	2.35	2.02	3.62	0.80	1.26	4.04
CH$_4$	0.96	0.19	0.07	0.11	13.50	4.77	0.07
C$_2$-C$_4$	3.62	3.21	2.22	2.77	8.18	4.33	1.69
Total liquid including:	75.90	80.44	80.63	82.15	70.83	80.76	84.89
organic	75.44	80.44	80.46	81.97	65.46	76.00	84.80
water	0.45	0.00	0.17	0.18	5.37	4.76	0.09
Unbalance, not less	11.53	10.74	9.39	6.33	6.51	8.37	7.83

Hydrocracking of triglycerides, containing in vegetable oil, and deoxygenation reactions most efficiently proceed on Pt- and Ni-containing catalysts. At the same time nickel-containing sample (15 wt% NiO) is characterized by presence of alkenes in liquid products of hydrocracking, and it means that hydrogenation activity of the catalyst is depressed. In gaseous products, which are formed on this catalyst, considerable amount of methane is found. In this case, methane is a product of reaction between H_2 and CO, which is formed by means of decarboxylation. For both catalysts in liquid hydrocarbon products presence of heavy cycloalkanes and arenes, and also alkanes with number of carbon atoms in molecule up to 35, which are products of side reactions of cyclization, aromatization and condensation, is found. To diminish these reaction pathways it is necessary to reduce process temperature to 300-350 °C. Analysis of liquid products by sim. dist. confirmed significant amounts of heavy hydrocarbons. Thus, established level of jet and diesel fuel (boiling temperature up to 350 °C) in liquid products of vegetable oil hydroconversion does not exceed 63 wt%. Content of gasoline fraction is about 5-7 wt%.

OPTIMIZATION OF METAL-ACID PROPERTIES OF HYDROISOMERIZATION CATALYST BASED ON SULFATED ZIRCONIA-ALUMINA

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Present-day requirements to gasoline claim significant restrictions of aromatics content, especially benzene. One of the ways to diminish benzene level in gasoline retaining its high octane number is to transform benzene to methylcyclopentane (MCP) by hydroisomerization. To provide these reactions both metal and acid sites are required. Traditional skeletal isomerization catalyst Pt/SO_4^{2-}-ZrO_2 (Pt/SZ) does not suit in this case because of high acidity and depressed hydrogenation activity. Side reactions such as alkanes cracking and naphthenes ring opening readily take place on strong acidic sites. Hydrogenation activity is not enough to eliminate benzene totally. In this work we study effect of alumina on metal-acid properties of Pt/SZ and compare activity and selectivity of sulfated zirconia-alumina catalysts in benzene and heptane hydroisomerization.

Catalysts were prepared by mixing sulfated hydrous zirconia and pseudoboehmite with following calcination and Pt incorporation (Pt content is 0.3 wt%). It is shown by IR-spectroscopy with pyridine and CO as probe molecules (Table) that the number of Bronsted acid sites and strong and medium Lewis acid sites decreases as alumina is incorporated into the catalyst. It is explained by dilution effect. Such modification of acidity strongly influence on catalytic activity in n-heptane hydroisomerization. The temperature at which 50% conversion is achieved rises from 120 to 267 °C as alumina content in Pt/SZ grows to 67.5 wt%. Maximal selectivity of iso-C_7 formation corresponds to Pt/SZA-67.5 and at 50% conversion its value reaches 94.2%.

As shown by H_2 chemisorption Al_2O_3 modifies hydrogenation properties of Pt/SZ. Pt chemisorption capacity, expressed in H/Pt ratio increases with alumina content growth (Table). It is provided by increase of amount of Pt, which is located on Al_2O_3 and does not affected by sulfate-ion.

Table. Hydrogen chemisorption capacity and distribution of acid sites for studied samples

Sample	Al_2O_3 content, wt%	100×(H/Pt)	Bronsted acidity, µmole/g	Lewis acidity, µmole/g		
				weak	medium	strong
Pt/SZ	0.0	0	32	530	90	3.5
Pt/SZA-18.8	18.8	0				
Pt/SZA-47.8	47.8	0				
Pt/SZA-67.5	67.5	44	9	250	60	2.0
Pt/Al_2O_3	99.7	85	0	350	29	3.5

Hydroisomerization of n-heptane-benzene mixture was studied at 1.5 MPa and 300 °C. Incorporation of alumina into Pt/SZ leads to increase of benzene conversion from 68 to 96-99%. At the same time optimized acidity of Pt/SZA-67.5 sample diminishes alkanes cracking and naphthenes ring opening reactions and provides selectivities to isoheptanes and cycloalkanes 93 and 96% respectively. Thus, for benzene-heptane hydroisomerization catalyst with 67.5 wt% Al_2O_3 content has optimal relation between acid and metal functions. It provides maximal yields of C_{5+} hydrocarbons (100 wt%), iso-C_7 (21 wt%) and cycloalkanes (52 wt%).

Hydroisomerization of industrial benzene-containing fraction confirmed high efficiency of catalyst with optimized metal-acid properties.

HYDROISOMERIZATION OF n-HEXANE ON Pt- AND Pd-CATALYSTS, SUPPORTED ON Zr-PILLARED MONTMOROLLONITE

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Pillared clays compose one of the most widely stuted family among the new groups of microporous materials which have shown catalytic aptitude in acid mediated reactions like isomerization [1]. We have shown that Pd or Pt on aluminium-pillared-acid-activated-sodium montmorillonite catalyst is two to three times active than the zeolitcontaning catalysts [2].

In this study, we investigated with the Zr-pillared-acid-activated-sodium montmorillonite (ZrCaHMM) supported Pd and Pt (0,35 wt.%) as catalysts in the hydroisomerization of n-hexane.

The starting clay mineral is an Tagan bentonite (Kazakhstan). Natural CaMM activated by sulfuric acid and then was pillared by $ZrOCl_2$ with different concentration: 2,5; 5,0 and 7,5 mmol/g clay. Pt and Pd were supported by impregnation method. The n-hexane hydroisomerization reaction was carried out in a tubular quartz reactor under atmospheric pressure using n-hexane as reactant in the reaction temperature range 250-400 °C. Space velocities of n-hexane submission was 1,74 $hour^{-1}$, molar ratio of H_2: n-C_6H_{14} = 3:5. The products were analyzed by gas chromotographically.

By X-ray diffraction (XRD) analysis it was shoun that the basal spacing d (001) of montmorillonite sample (CaMM) after activation by sulfuric acid increases from 13,5 to 14,2 Å. When the clay is pillared with Zr polyhydroxycations the basal spacing increases to about 15,5 Å that testifies about expansion of clay layers. The specific surface area (BET) of Zr-pillared samples was 184,0-249,9 m^2/g.

The total acidity of the solids calcined at 500 °C was evaluated by temperature programmed desorption (TPD) of NH_3 adsorbed at 110 °C. TPD-curves of ZrCaHMM and Pt-, Pd/ZrCaHMM-catalysts are characterized by three maximums of NH_3 desorption. Introduction of Zr in acid activated Ca-montmorillonite sample increases considerably the total amount of desorbed NH_3 and maximums of NH_3 desorbtion shifted in more hightemperature area. The catalysts resulting from the impregnation of Pt and Pd on the Zr-pillared acid activated MM inducted higher acidity.The catalytic properties of Pt- and Pd/ZrCaHMM-catalysts in hydroisomerization of n-hexane are presented in table.

For all the catalysts when increasing the reaction temperature from 250 to 400 °C the total conversion increases. The catalytic performance of the Zr-pillared CaH-montmorillonite supported Pt is superior to the Pd/ZrCaHMM-catalysts as shown in table. With Pt- and Pd/ZrCaHMM catalysts isomerization reactions are the major processes in all temperature ranges and the isomer selectivity remains constant and very high between 97,4 and 100%. Products of the hydrocracking reaction appears when the reaction temperature was 350-400 °C for Pt and 400 °C for Pd-catalysts. The conversion of n-hexane to isomers on Pd- and Pt/ZrCaHMM-catalysts is correlated with the amount of middle acid centers.

Table. Hydroisomerization of n-hexane on Pt- and Pd/ZrCaHMM-catalysts

Content Zr, mmol/g. clay	T, °C	α,%	S_{C4+}	Yields, wt.%					
				ΣC_1-C_4	i-BUT	2,2DMB	2-MPEN	3-MPEN	Σiso C_7-C_8
For Pt-	250	1,1	100	-	-	0,11	0,28	0,57	-
catalysts	350	19,1	100	-	-	5,21	2,07	11,6	-
2,5	400	48,3	97,9	0,96	4,97	3,31	24,1	14,9	-
	250	3,9	100	-	-	-	2,08	1,85	-
5,0	350	24,3	99,5	0,12	0,74	0,96	14,1	7,65	-
	400	43,0	97,4	1,8	3,95	2,57	21,9	12,2	-
7,5	250	12,9	100	-	-	-	8,17	4,75	-
	350	26,9	96,6	0,56	0,39	1,22	15,5	8,08	-
	400	48,3	97,7	0,89	3,29	3,18	24,4	13,9	-
For Pd-	250	-	-	-	-	-	-	-	-
catalysts	350	6,6	100	-	0,2	0,1	3,5	1,5	1,3
2,5	400	19,2	98,1	0,4	1,5	0,7	10,4	4,9	1,3
	250	-	-	-	-	-	-	-	-
5,0	350	5,8	100	-	0,1	0,1	2,9	1,4	1,3
	400	14,8	97,8	0,4	0.8	0,6	7,8	3,8	1,4
7,5	250	5,8	100	-	-	-	3,1	2,6	-
	350	18,0	99,9	-	0,4	3,5	8,2	4,7	1,2
	400	31,7	97,5	1,1	1,5	1,4	17,5	8,9	1,1

This work reports the preparation of Zr-pillared acid activated montmorillonites with stable microporous structure and different acidities. The Pt/ZrCaHMM-catalysts showed a high activity and isomer selectivity in the hydroconversion of n-hexane and suppressed the hydrocreacking reaction. The study showed that it was possible to prepare from Tagan montmorillonite new materials with characteristics that make them suitable for catalytic applications.

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CATALYTIC OXIDATION OF NATURAL PRODUCTS WITH HYDROGEN PEROXIDE

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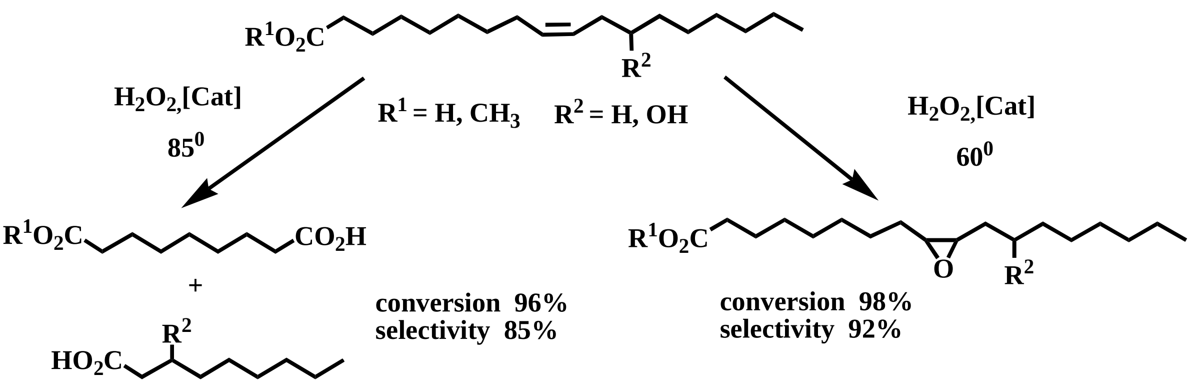
Possibilities of the utilization of products of wood-chemical industry in the producing of valuable chemicals by now have been far from being exhausted. Promising method for functionalization of labile natural compounds is oxidation with hydrogen peroxide in the presence of bifunctional catalytic systems possessing the properties of metal complex and phase-transfer catalysts. These catalysts allow producing important chemicals of practical value including epoxy compounds, mono- and dicarboxylic acids by means of oxidation of various organic substrates in mild conditions with good yields [1].

Investigations of oxidation of different types of unsaturated natural products have been carried out. Various factors having the influence on the yields of products in the reactions of the oxidation with 30% hydrogen peroxide aqueous solution in the presence of the system based on the tetrakis(oxodiperoxotungsto)phosphate(3-) in combination with quaternary ammonium cations have been studied [2].

As a result the efficient methods of oxidative functionalization of fatty acids obtained from nonedible natural raw material have been developed. Oleic and ricinoleic acids were used for epoxide and mono- and dicarbonic acids synthesis with yields up to 90%. The most active catalytic system for the unsaturated fatty acids oxidation is tetra(diperoxotungsto)phosphate methyltrioctylammonium.



Scheme 1. Oxidation of fatty acids.

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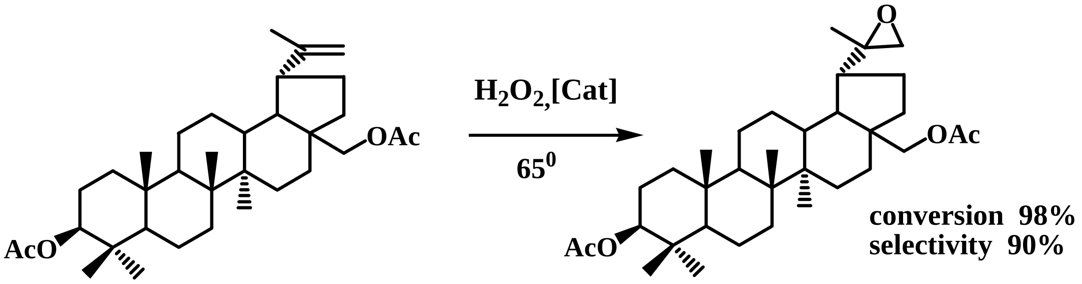
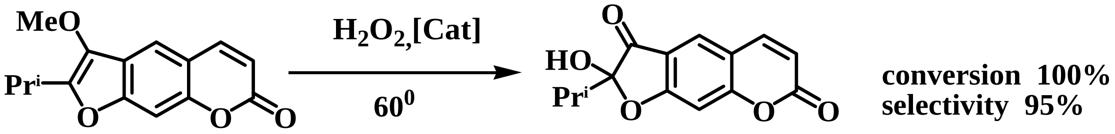
The above mentioned catalytic systems were applied to the mild-conditions oxifunctionalization of natural products with complex structure. Efficient synthesis of derivatives of these substances can be used in preparation of new biologically active compounds.

Betulin is a triterpene isolated from birch bark. It possesses a wide spectrum of valuable biological activities and is regarded as a precursor for synthesis of antivirus and anticancer pharmaceuticals. Tetra(diperoxotungsto)phosphate methyltrioctylammonium was found to be the most active catalyst in the oxidation of betulin and its derivatives. The highest selectivity of the reaction of betulin diacetate oxidation was achieved at 60 °C in 4 h.



Scheme 2. Oxidation of betulin.

Peucedanine is a plant coumarin having a useful biological activity either. Oxidation of peucedanin with 30 % solution of hydrogen peroxide proceeds with 100% conversion in 1 h yielding 2-hydroxyoreoselon.



Scheme 3. Oxidation of peucedanin.

Thus the efficient methods of selective catalytic oxifunctionalization of various available natural products have been developed. The oxidation reactions proceed in mild conditions with the use of environmentally friendly oxidant.

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ISOMERIZATION OF N-HEXANE AND STRAIGHT-RUN GASOLINE OIL FRACTION OVER HIGH-MODULAR ZEOLITE

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Currently, the content of aromatic hydrocarbons in motor fuels is strictly regulated. In high-octane gasoline production, the yield of iso-hydrocarbons with high octane numbers exhibiting better ecological indicators in comparison with arenes tends to increase. The use of high silica pentasyl type zeolites (HSZ) with high silica modulus is a possible way to increase the yield of iso-alkanes by straight-run gasoline upgrading.

The purpose of the work was to study the parameters of isomerization of n-hexane and straight-run gasoline oil fraction over a zeolite with the silica modulus 100 and to choose the optimum temperature range of the process.

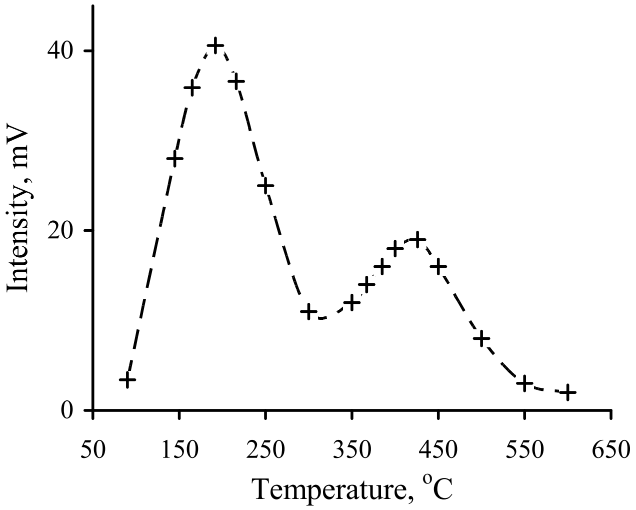

Figure. The thermodesorption spectrum of zeolite catalyst.

One of the most important characteristics of zeolite catalysts is their acidity that could be determined from the adsorption of probing molecules possessing basic properties. Figure shows the thermodesorption spectrum of HSZ, obtained using the method for thermoprogrammed desorption of ammonia.

The spectrum possesses 2 types of acidic sites: low-temperature acidic sites with the maximum temperature 190 °C and concentration 440.6 μmol/g and high-temperature acidic sites (405 °C and 270.1 μmol/g, respectively). The catalytic activity of HSZ is generally controlled by the high-temperature acidic sites represented by OH-groups, which are associated with the aluminium atoms of the zeolite crystal lattice.

In order to choose the optimal process parameters, the isomerization was carried out as a model reaction of n-hexane conversion, since the straight-run gasoline oil fraction is a complex multicomponent system.

The feedstock used was a straight-run gasoline (overpoint 180 °C) of the following composition (wt. %): arenes – 16.7, isoalkanes – 47.5, cycloalkanes – 14.8, and n-alkanes – 18.9; the octane number was 66 points. The conversion was carried out in a flow installation at a reaction temperature of 300-420 °C, a volumetric flow rate of 2 h^{-1} and atmospheric pressure. The reaction products were analyzed by gas chromatography using the chromatographic data. The results of feedstock processing over the investigated sample are given in Table.

Table. Influence of the process temperature on the composition of the products of raw hydrocarbon conversion.

Hydrocarbon raw materials/Raw hydrocarbons	Yield of products, wt. %	Process temperature, °C			
		300	340	380	420
n-hexane	isoalkanes C_{5+}	15,6	28,8	26,8	23,5
	arenes	6,0	23,5	46,6	57,3
	n-hexane conversion, %	42,6	73,9	86,4	93,3
Straight-run gasoline	isoalkanes C_{5+}	37,1	34,2	34,0	32,4
	arenes	37,4	40,3	46,7	47,4
	octane number	89	90	91	92

In the course of n-hexane processing over a high-modular zeolite catalyst, the conversion increases with the temperature, and at 420 °C nearly all initial n-hexane is completely converted (93.3%). The reaction products are mainly presented by all isomers, with iso-decanes prevailing, whose yield exceeds 15 % wt. at the temperature 380-420 °C. The maximum isomerization activity of zeolite is observed at the temperature 340 °C, and a further increase in temperature gives rise to increase in the yield of arenes in reaction products.

Unlike the catalysts manufactured via aromatization of n-hexane, the gasolines produced by conversion of the straight-run gasoline fraction contain a fairly large quantity of both iso-alkanes and arenes. This is likely to be due to the interaction of the feedstock components. The catalyst exhibits a stable activity in the entire temperature range under study, which allows high-performance gasoline to be produced.

OLIGOMERIZATION OF OLEFINS ON SUPERACID CATALYSTS

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Oligomerization of gaseous olefins is a process widely used in industry for a preparation of different useful products and for a “liquification” of gaseous fractions for fuel production [1]. Isooctane is one of the most important and ecologically friendly components of fuels. Isobutene can be effectively dimerized into an isooctenes mixture under the action of different solid superacids - sulfated metal oxides [2, 3].

This work is dedicated to olefins, mainly isobutene oligomerization on novel superacidic catalyst – sulfated tin oxide (table 1).

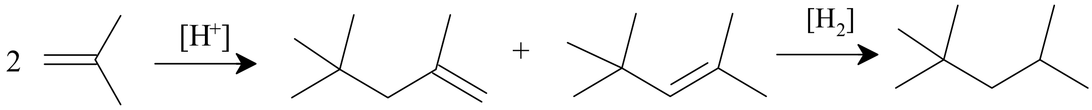

Table 1.

№	Catalyst	Temperature, °C	Yield, %		
			C_8	C_{12}	C_{16}
1	5% $NiSO_4/SnO_2$	18	7	87	6
2	H_2SO_4/SnO_2	18	2	68	30
3	H_2SO_4/SnO_2	120	48	48	4
4	5% $NiSO_4/SnO_2$	150	54	44	2
5	H_2SO_4/SnO_2	150	54	43	3
6	H_2SO_4/SnO_2	180	73	27	0

It is clearly seen from the table above that the temperature increase from 18 to 180 °C seriously increases the isooctenes content and decreases the content of C_{12} and C_{16} olefins. The comparison of 4 and 5 entries reveals that the presence of Ni^{2+} ion does not effect the process.

The dimerization of hexene-1 is also effectively catalyzed by sulfated tin oxide at 60 °C (table 2).

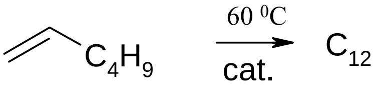

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Table 2.

№	Catalyst	Yield C_{12}, %
1	$6N\ H_2SO_4/SnO_2$	87
2	5% $NiSO_4/Al_2O_3$	92
3	10% $Fe_2(SO_4)_3/Al_2O_3$	65
4	SnO_2	0

It is seen from Table 2 Ni^{2+}ion also does not effect the dimerization process.

Even a hardly polimerizable olefin – cyclohexene - is converted into a C_{12} dimer (table 3).

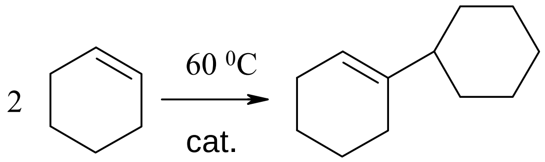

Table 3.

№	Catalyst	Yield C_{12}, %
1	$0.3\ M\ H_2SO_4/SnO_2$	43
2	5% $NiSO_4/SnO_2$	12
3	5% $NiSO_4/Al_2O_3$	15
4	10% $Fe_2(SO_4)_3/Al_2O_3$	26

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RESIN ACIDS IN THE SYNTHESIS OF NEW CHIRAL CATALYSTS FOR ASYMMETRIC REDUCTION PROCESSES

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Asymmetric reduction of prochiral ketones is an attractive method for the synthesis of building blocks for processes of fine organic synthesis. Meanwhile asymmetric catalysis is an efficient way for performing the reduction, while only catalytic amount of chiral inductor is required for conducting this process. The structure of chiral ligand plays the dominant role in the enantioselectivity of catalysts. Thus, design of the ligands of various structural types allows extending the field of application of asymmetric catalysis over the wide range of substrates and reactions. The disadvantage of the catalysts which are usually being used is their high cost caused by the multistage synthesis of chiral ligands or the need for optical resolution. It is considered to be reasonable to utilize the large-tonnage by-products of arboreal plant processing such as galipot and colophony which contain resin acids in optical pure form. Thus the present research is aimed at developing of the methods of chiral ligands synthesis starting from the available natural raw material containing resin acids.

Phytogenic diterpenes have been under intensive investigation for many years. Owing to their availability and unique structures, these compounds have been widely used as starting materials for the production of highly effective drugs and chiral reagents. Procedures of synthesis of P-, N-containing ligands starting from tricyclic diterpenes were described in literature. The prepared chiral diphosphines, diphosphinites, amines, azomethines and ureas were used as ligands for catalysts of asymmetric reactions [1].

As a result of our further investigations we developed the new schemas of the synthesis of nitrogen containing ligands on the basis of the transformations of resin acids. Synthesis of chiral ureas and thioureas was developed starting from the adduct of abietic acid which is formed while heating galipot with fumaric acid. Chiral nitrogen-containing ligands were synthesized and used for preparation of chiral Ru and Rh complexes.

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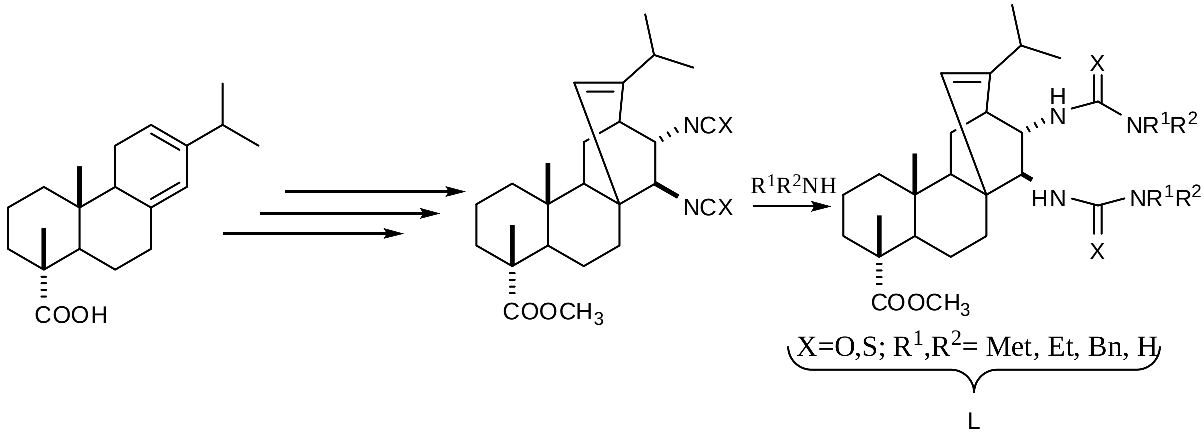
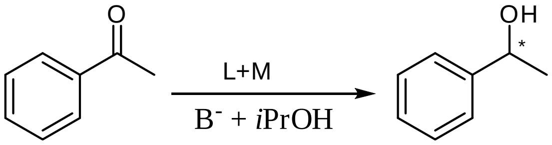


Testing of the catalytic activity and stereo selectivity of synthesized complexes was carried out in the reaction of acetophenone hydride transfer reduction. The conversion of acetophenone catalyzed by urea and thiourea complexes with Rh(I) and Ru(II) was carried out in boiling isopropanol at a ratio of [Ligand]/[Metal-complex]=3, 2 or 1.5. The complexes were prepared *in situ* directly before the reduction. Potassium hydroxide or sodium isopropilate were used as bases.



M=$[Rh(COD)Cl]_{2,}$ $[Ru(COD)Cl]_2$

For all the examined catalytic systems no signs of the formation of phenylethanol were registered at temperatures below 65°. Depending on conditions of the reduction the mixtures enriched by (+)–(R)- or (+)–(S)– phenylethanol were obtained.

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THE MODIFICATION OF RHODIUM CATALYSTS BY TIN AT DEHYDROGENATION OF LIGHT ALKENES' MIXTURE IN ALKALI MEDIUM

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The passing oil gas is not the only source of energy, but it can be effectively used as source of such valuable products like light unsaturated compounds – ethylene, propylene, butylene and isobutylene, which are the base of a huge number of oil products and are the base of polymers industry. While ethylene and propylene are much in demand in the world market, the initial compounds ethane and propane in passing oil gas are burned in torches at the oil fields. By the experts assessment the burn of 1 million m^3 of passing oil gas of Tengiz oilfield gives less than 20,000$, while dehydrogenation of 200 tons of containing ethane with further polyethylene and polysterol synthesis would raise the figure to 110,000$. Thus, the oil chemistry at its maximum developing increases country's GDP. It must be also underlined the negative environmental impact of passing gas burn.

The process of dehydrogenation of light alkenes is carried out by two methods: either in oxidizing or in alkali medium. The bimetal promoted catalysts on the base of platinum group metals are the most perspective. It has been identified that the modifying additives improve laid active metal catalytic properties. It is also favourable as in that case dehydrogenation is carried out in alkali medium, which is better than oxidizing one, where educed hydrogen is losing by converting into water. It can be mentioned that dehydrogenation is usually made for individual light alkenes, while the possibility of dehydrogenation of their mixtures is still unsolved.

In this message there have been reported the results of development of dehydrogenation catalyst in alkali environment, which gives olefins and hydrogen from alkenes. Moreover, the process had been carried out in unbalance conditions, which considerably accelerate and extend process. Earlier we mentioned that Rhodium catalyst in unbalanced conditions shows high activity in dehydrogenation of light alkenes' mixture. The promotion of catalyst has been made by tin.

The dehydrogenation of light alkenes' mixture was carried out in flowing mode with constant control of contact gas composition. The process was conducted in following modes: a) in absence of hydrogen; b) in presence of hydrogen; c) in presence of water's vapour; d) in presence of both hydrogen and water's vapour. At first two cases the process goes in balance conditions. Inserting water's vapour in systems leads to unbalance conditions by combining homogeneously adsorbed dissipative structures.

The results of this work show that the modification of base Rh/Kl (natural klinoptilolit) catalyst by tin and potassium compounds leads to increasing of its catalytic activity at the dehydrogenation of light alkenes and to rising of its selection on propylene. The maximum output of olefins is achieved in system Rh/SnO/K_2O/HKl / water's vapor, and the yield was 30-32%, which is much higher than on Rh/SnO/HKl or on base Rh/NKl.

The catalyst contains the active metal and the natural zeolits which are responsible for catalysis of redox reactions reaction with strong and multiple acid centers. The power and quantity of active centres on Rh/SnO/K_2O/HKl have been determined by method of ammonium' termoprogramed desorption (TPD). The quantity of middle powerful centers on Rh/SnO/K_2O/HKl is falling 3-4 times comparing with Rh/HKl, and concentration of powerful centers almost fall twice, whereas at these conditions the quantity of fable centers on Rh/SnO/K_2O/HKl is increasing.

Thus the modification of catalyst by tin leads to remarkable fall of the power and the quantity of active centres. It's evidently that the quantity of active centres is decreasing because of acting of covered metal, where the restoration process takes place. This process is getting intensive when it's carried out at unbalance conditions. Finally it was found that selection of dehydrogenation is increasing as tin's content increases as well, at this time selection of possible cracking and isomerision process are declining.

DEVELOPMENT OF A NOVEL RU-BASED ELECROCATALYST FOR PEMFC

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World energy consumption has increased almost in 15 times during the last decade. Mineral fuel usage as a primary energy sources has led to that for 50 years emissions of carbonic gas in an atmosphere have increased in 4.5 times. Besides mineral sources are limited. Hence, one of the primary goals of modern power is to find the ways of overcoming of environmental problems arose.

Taking into account the modern economy inquiries, the most significant is **a** creation of stationary and reserve installations for manufacture of the electric power and heat on the basis of fuel elements (FE), and also power plants on the basis of FE for vehicles and portable electronic devices. Though FE various designs already for a long time are used in practice, new types of FE development (cheaper, using new kinds of fuel, more power-intensive, tiny temperatures working in a wide range, including and negative) is an important problem. Now a low-temperature fuel cell polymer electrolyte membrane (PEMFC), intended for transport, stationary or portable application, uses exclusively platinum catalyst. It creates significant difficulties of their expanded application, that is caused by increase in market cost of platinum. The cardinal decision of this problem is a refusal of platinum use and its replacement with the electro catalysts on the basis of ruthenium, which costs essentially below cost of platinum. Thus, however, specific activity and stability to degradation should concede a little to systems on the basis of platinum.

The present paper presents a study of the RuM/C and RuMSe/C (M – Co, Ni, Fe, V) electrocatalysts based on physical–chemical characterization through scanning electron microscopy (SEM) and electrochemical kinetics towards the oxygen reduction reaction (ORR) in acid media by rotating disk electrode (RDE).

Electrocatalysts were synthesized by using $RuCl_3{\cdot}H_2O$ and salts: $CoSO_4{\cdot}7H_2O$, $FeSO_4{\cdot}7H_2O$, $NiSO_4{\cdot}7H_2O$, $VOSO_4{\cdot}2H_2O$, $CoSeO_4{\cdot}6H_2O$ и $NiSeO_4{\cdot}4H_2O$ as precursors. Carbon black (Vulcan XC-72) was added in a proportion to achieve 20 and 30 wt.% (metal-basis) loading. The systems were refluxed under argon at 600 °C for 1 h and then under hydrogen at 350 °C for 1 h.

Results indicate an electrocatalyst with chemical composition of RuCoSe/C (2:1:1), 20 wt.%. The electrochemical kinetics study (RDE) resulted in an electrocatalyst with high activity towards the ORR, preferentially proceeding via 4e$^-$ charge transfer pathway towards water formation (i.e., $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) at 60 °C (fig. 1).

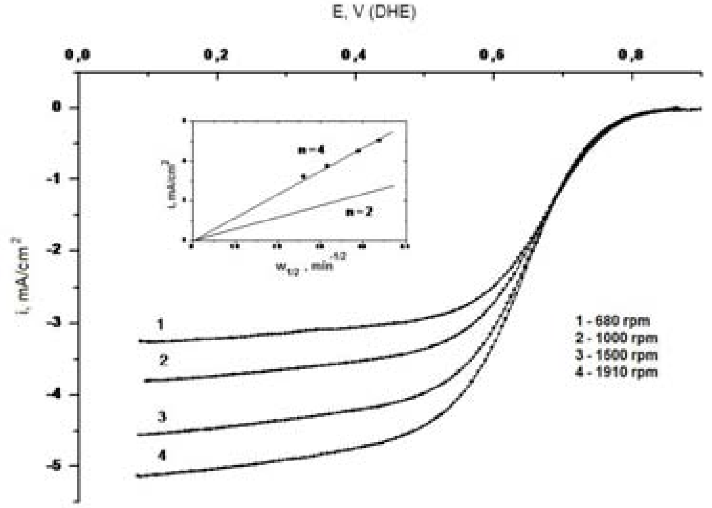

Fig. 1. ORR curves for the 20 wt.% RuCoSe/C (2:1:1) in 60 °C O_2-saturated 0.5M H_2SO_4. Rotation rate = 680-1910 rpm and scan rate = 5mVs^{-1}.

SEM images showed 3–6 nm nanoparticles (fig. 2).

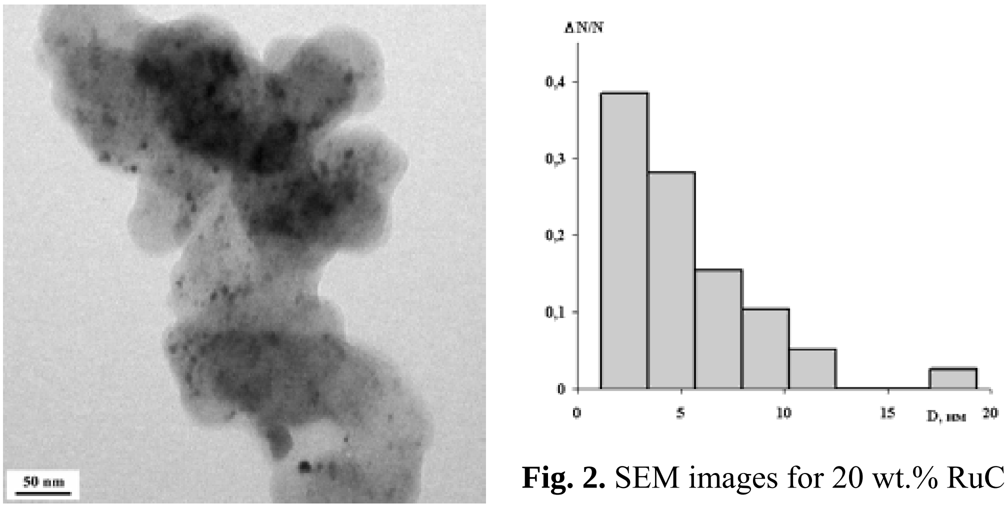

Fig. 2. SEM images for 20 wt.% RuCoSe/C (2:1:1).

Comparison of systems developed with reference literature data [1-2] showed electrocatalyst synthesized had higher activity in ORR. Nevertheless catalysts obtained yield to monoplatinum catalyst therefore we propose to research into their optimization.

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DESIGN OF ASSYMMETRIC MULTILAYER MEMBRANES FOR SYNTHESIS GAS PRODUCTION

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Mixed ionic-electronic conducting (MIEC) oxide composites comprised of electronic conductors and ionic conductors are the most promising membrane materials due to combination of mechanical and chemical stability with a high oxygen permeability provided by interfaces as paths for fast oxygen diffusion [1]. Dense MIEC ceramic membranes have a great potential for catalytic high-temperature processes including methane reforming into syngas. However, for thick membranes, the bulk diffusion limits the oxygen permeability. For thin membranes, kinetics of the surface processes on both membranes sides becomes the rate-limiting. In this case, supporting a porous oxide layer with a high rate of O_2 activation on a dense non-porous MIEC layer membrane or using a microporous MIEC substrate is known to increase the oxygen flux. However, the fabrication of such membranes is still a challenge because of difficulty in obtaining porous supports with desirable properties in terms of pore size, gas permeability, thermal/mechanical stability and compatibility with MIEC materials by thermal expansion coefficients (TEC). One of the promising solution is to use a robust macroporous substrate on which MIEC nanocomposite layers with graded porosity and chemical composition would be consecutively deposited.

The aim of this work is elaboration of synthesis procedures of MIEC nanocomposites comprised of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC) and $La_{0.8}Sr_{0.2}Fe_{1-x}Ni_xO_{3-\delta}$ (x=0.1-0.4) ($LSFN_x$) perovskites, investigation of their structure and transport properties and design of multilayer membranes based on such nanocomposites supported on the macroporous metallic plates made from Ni-Al alloy compressed foam of a high thermal and mechanical stability due to segregated corundum surface layer.

Experimental. Starting $LSFN_x$ and GDC were prepared by modified Pechini route. Nanocomposites were synthesized via ultrasonic dispersion of starting powders in the solvent with addition of surfactants followed by drying and calcination at 700-1370 °C. Structural and transport properties of the samples were studied by XRD, TEM, EXAFS, H_2 and CH_4 TPR, O_2 TPD, oxygen isotope exchange, thermogravimetric measurements of oxygen chemical diffusion, impedance spectrometry.

The fabrication of a supported multilayer membrane was performed in the following steps. First, to fill cells of a Ni-Al foam plate and smooth out its surface geometry, several layers of a coarse-dispersion composite $LSFN_{0.4}$+GDC. Further, for filling macropores between particles of a coarse-dispersion composite and formation of mesoporous layer, several layers of high-dispersion composite were supported. The gas-tight layer was fabricated by coating GDC slurry on the support with composite layers. To attain sintering at 1200 °C, such additives as Cu, Ag and Bi nitrates and $MnFe_2O_4$ (MF) were used.

Results and discussion. The nanocomposite surface/lattice oxygen mobility and reactivity estimated by different methods depend on $LSFN_x$ composition and increase with sintering temperature exceeding significantly the level found for separate $LSFN_x$ and GDC. Such non-additive increase of the oxygen mobility in nanocomposites could be caused by an efficient conjugation of ionic and electronic fluxes at the interfaces of nanocomposite components.

To obtain a high-quality multilayer membrane, the supporting procedures of porous MIEC composite layers and gast-tight GDC layers were elaborated and optimized. For this purpose, the dispersion and sintering temperature of MIEC composite, the nature of solvent and surfactant, the solid phase content and surfactant concentration were varied.

The composite $LSFN_{0.4}$+GDC paste and slurry containing isopropanol as a solvent and polyvinyl butyral as a surfactant showed the best result for fabrication of macro- and mesopores layers. The shrinkage of porous composite layers is minor when composite powders presintered at 1100-1200 °C were used. Furthermore, a higher (up to 1100 °C) sintering temperature of supported porous composite layer prevents cracking of dense GDC+MF layers. To facilitate sintering of GDC layers, the addition of copper and MF was the most effective. As a result of this optimization research, a good quality of gas-tight GDC+MF layers was ensured.

Testing of membrane reformer prototype was carried out in the temperature range of 800-950 °C. Due to specific features of GDC+MF composite possessing a high oxygen permeability and phase stability only in reducing conditions, it was possible to estimate the oxygen permeation flux jO_2 only under operation conditions of methane autothermal reforming. In studied range of parameters, jO_2 was varied in the range of 5-10 cm^3 O_2/cm^2min. Methane conversion was varied within 50-90 90%, and hydrogen and CO selectivities were in the range of 70-90%, all parameters increasing with the temperature and steam/C ratio in the feed.

This work is supported by Project 57 of RAS Presidium Program No.27 and ISTC 3234 Project.

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Firm DONAU LAB AG, Switzerland, and branches of firm in all East-European countries more than 37 years represents the equipment of manufacturing of the leading West-European producers, such as Metrohm (automatic IC, autotitrators, VA, pH-meters, the equipment for process-lab), Buchi Flawil (the express-extractors, NIR analyzers, melting point analyzers, spray-drying, rotational evaporators), Buchi Uster (reactors from small lab till pilot), Applikon (solutions for the industry based on process electrochemical analyses, IC, process VA). Tens companies-manufacturers of our program are applying the newest technologies, long-term experience in manufacture and high culture in methodical maintenance. They cooperate with DONAU firm for many years on the basis of agreements on representation of their production in the countries of the Donau regions, Russia and CIS.

Branches of group DONAU LAB AG have the presence in 18-th the countries of the East Europe. In the majority of these countries we are engaged sales at the state and regional levels and we have the offices consisting of highly skilled experts.

We aspire to improve a network of the companies and offices as much as possible full to correspond to requirements of our Clients. So, in 2008 it was accepted and the decision to increase presence of the company in territory of Russia by opening of additional offices in the cities of St.-Petersburg, Nizhni Novgorod, Novosibirsk is realized. In plans of the company to represent the interests and in Uralsk region.

The equipment which we represent in the market is used in various branches for the decision of a plenty of problems, such as petrochemistry, chemistry, high technology, the general chemistry, synthetic materials. One of priority directions of activity is the science.

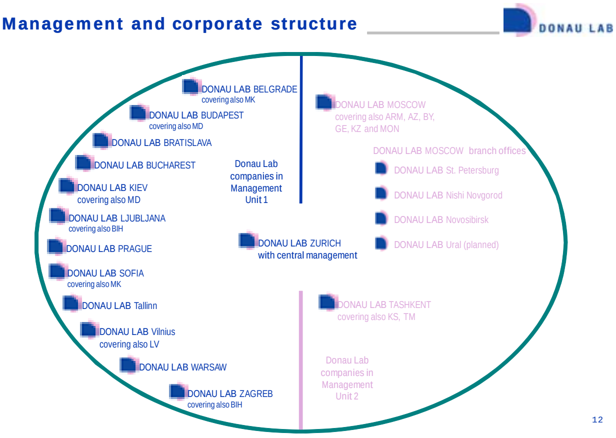
Our clients are leading scientifically research institutes and the industrial enterprises having the laboratories, among them:

- Lomonosov Moscow State University;
- D. Mendeleev University of Chemical Technology of Russia;
- Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences;
- Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences;
- Novosibirsk state university;
- Tomsk state university;
- Sibur-Tomskneftekhim (NIOST);
- Scientific research institute of polymers;
- Niznekamskneftekhim and others.

If it is necessary for you to solve essential problems in laboratory or technological process our experts and experts of the companies-manufacturers will help to find the decision, choice the equipment, offer the methods of solutions of your problems based on world experience of applications. Our experts will make start-up of the equipment, provide the training of your personnel, and offer the warranty and post warrantee service.

Our company and partners – manufacturers of the equipment on a regular basis develop the models and methods, which response of market need. As a vivid example dryer Nano Spray Dryer B-90 and the device for definition of melting point Melting Point M-865 of Swiss firm BUCHI were presented on the international exhibition ACHEMA-2009.

Donau Lab Moscow will be glad to cooperate with you at regional and federal levels.



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CONTENT

3rd International School-Conference on Catalysis for Young Scientists “CATALYST DESIGN”

Abstracts Editors: Evgeny V. Starokon

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