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"CATALYST DESIGN: from Molecular to Industrial Level"

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ABSTRACTS

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The proceedings include the abstracts of plenary lectures, oral and poster presentations of the following areas:
- **Preparation of catalysts and adsorbents**
- **Mechanisms of heterogeneous catalysis, methods of catalyst characterization**
- **Kinetics and modeling of catalytic reactions and reactors**
- **Catalysis for environmental protection, photocatalysis**
- **Catalysis for fine organic synthesis, natural gas and petroleum chemistry**
- **Catalysis in energy production, electrocatalysis**

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PLENARY LECTURES

PL-1

BIOLOGICALLY INSPIRED CATALYSTS for SELECTIVE C-H and C=C OXIDATION REACTIONS

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The selective functionalization of C-H and C=C bonds remains a formidable unsolved problem, owing to their inert nature. Novel alkane and alkene oxidation reactions exhibiting good and/or unprecedented selectivities can have a big impact on bulk and fine chemistry by opening novel synthetic methodologies. These goals are targeted in our research efforts via design of iron and manganese catalysts inspired by structural elements of the active site of non-heme iron and manganese enzymes. Designed catalysts are environmentally benign because they use catalytic amounts of non toxic Mn and Fe metal ions, H_2O_2 as oxidant, and operate under mild experimental conditions (pressure and temperature). The fundamental mechanistic aspects of the catalytic reactions, and the species implicated in C-H and C=C oxidation events is also studied with the aim of building up the necessary knowledge to design future generations of catalysts, and provide models to understand the chemistry taking place in manganese and non-heme iron-dependent oxygenases. Our recent advances in the design of iron and manganese based catalysts will be discussed.

EXHAUST EMISSION CONTROL CATALYSTS

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This talk will focus on the catalytic technologies for controlling the exhaust emissions originating from internal combustion engines used in modern automotive applications. A particular emphasis of the talk will be the next generation *“lean-burn”* engine emission control systems utilizing the “NO_x Storage Reduction” (NSR) technology which has been recently innovated by the Toyota Motor Company in Japan. Implications of the recent environmental regulations in the EU and the US on the automotive sector and the exhaust emission control technologies will be also discussed. Finally, design of *“atomically fine-tuned”* novel automotive catalysts using modern tools of nanotechnology and surface science in the Ozensoy research labs will be described.

LIQUID PHASE SELECTIVE OXIDATION via HETEROGENEOUS CATALYSIS

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Boreskov Institute of Catalysis

Catalytic oxidation in the liquid phase finds widespread application in the chemical industry for the manufacture of a wide variety of chemicals ranging from commodities to fine chemical specialties. Heterogeneous catalysts have the clear advantage, compared to their homogeneous counterparts, of facile recovering and recycling and thus meet the requirements of sustainable chemistry, which has become one of the greatest challenges of our time [1]. Furthermore, confinement of catalytically active species in porous matrices may potentially endow them with unique selectivities as well as preclude their deactivation. In the last decades, the area of heterogeneous catalysis related to liquid phase selective oxidations has experienced an impressive progress [2]. The revolution in this field occurred at the beginning of the 1980s when Enichem researchers developed Titanium Silicalite-1 (TS-1), the catalyst which is now employed in three H_2O_2-based industrial processes. Since that time, other families of solid catalysts, namely framework-substituted mesoporous molecular sieves, supported transition metal complexes and noble metal nanoparticles, as well as a novel class of functional materials, metal-organic frameworks, have received significant attention. This lecture has the aim to give a brief overview of the main achievements and challenges in the field of heterogeneous liquid phase selective oxidation. A selection of the most relevant results reported thus far in the literature is provided, with particular attention paid to the critical issues of the operational stability and reusability of the catalysts. Protocols for establishing the nature of catalysis (truly heterogeneous versus homogeneous caused by active species leached into solution) are addressed. Different approaches elaborated in recent years to create leaching-tolerant solid catalysts are compared, and the scope and limitations of the existing catalyst systems are discussed.

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NANO-CATALYTIC PROCESSES for ENERGY APPLICATIONS

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Nowadays the development of new catalytic systems on the basis of metal-containing nanoparticles is one of the most important and actively developing fields of chemistry and chemical technology. Huge surface area and small size are responsible for high activity that allows synthesizing effective catalysts with low metal content. However, the main issue of metals nanoparticle synthesis is the necessity of control over their shape, size and monodispersity. We proposed the method of catalyst synthesis, which is based on the idea of nanoparticle formation in nanoporous matrix of hypercrosslinked polystyrene (HPS). Synthesized HPS-based catalysts revealed high performance in the processes of synthesis of biomass-based fuel components.

Biomass has received considerable attention as a sustainable feedstock that can replace diminishing fossil fuels for the production of energy, especially for the transportation sector, which is strongly dependent on petroleum, a non-renewable fossil source of carbon. HPS-based catalysts were shown to be promising for such processes as hydrodeoxygenation (the way of biofuel obtaining in the form of saturated hydrocarbons from the oxygen-containing compounds); hydrolytic hydrogenation of cellulose (for production of polyols); liquid-phase methanol synthesis. For example, catalytic hydrodeoxygenation of stearic acid, which is potential feedstock to produce the second generation of biodiesel, was investigated using Pd/HPS catalysts. It was revealed, that the main product of the reaction was n-heptadecane. The selectivity of the process (regarding to n-heptadecane) reached up to 98.8% at 100% of substrate conversion. Ru/HPS catalysts were studied in hydrolytic hydrogenation of cellulose at variation of metal loading, type of HPS, reaction conditions, substrate pretreatment, etc. We demonstrated that the use of Ru/HPS allows achieving the total sorbitol and mannitol yield about 50% at the ~85% conversion that is comparable with the results obtained with more complex and expensive catalytic systems. For liquid-phase methanol synthesis the series of Cu, Zn, Cr, Cu/Zn oxide catalysts on the base of HPS were synthesized at variation of metal loading. Besides, the influence of reactor type was investigated. It was demonstrated that the developed catalysts allow decreasing the reaction temperature and pressure without loss in process rate and selectivity (methanol productivity was found to be up to 16 g/(kg(Cat)*h)).

All the synthesized catalysts were characterized by the method of low-temperature nitrogen physisorption, transmission electron microscopy, elemental analysis, X-ray photoelectron spectroscopy, etc. It is noteworthy that the physicochemical characterization of developed catalysts showed formation of nanoparticles (in many cases mean diameter of nanoparticles was about 1-3 nm) in HPS matrix.

ELECTROCATALYSIS for ENERGY CONVERSION SYSTEMS: INSIGHTS FROM NEAR-AMBIENT PRESSURE XPS

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Global pursuit of clean and sustainable energy is guiding the development of electrochemical energy conversion and storage technologies, including fuel cells, batteries, and electrolyzers, where the interface between an electronic and an ionic conductor (solid, liquid or polymer) plays a central role. The development of efficient energy conversion systems not only requires potent, durable and cost-effective materials, but also asks for precise engineering of electrochemical interfaces where molecular, ionic and electronic flows merge. Future progress in the field thus heavily relies on the availability of in situ techniques to probe structure and composition of the dynamic electrode/electrolyte interfacial region. While various spectroscopic and microscopic methods are nowadays available for the investigation of such interfaces, methods which allow probing of the chemical state of the interface under operation conditions are still limited.

X-ray Photoelectron spectroscopy (XPS) is one of the most powerful techniques for studies of the chemical composition and the oxidation state of components located within the near-surface region. Recent advances in vacuum and analyzer technologies have resulted in the development of specialized instruments which allow performing the so-called Near Ambient Pressure Photoelectron Spectroscopy (NAP-XPS) measurements in the pressure range of millibars [1,2].

In this presentation we will discuss recent insights into the structure and dynamics of electrode/electrolyte interfaces from NAP-XPS measurements of model membrane-electrode assemblies of a proton-exchange fuel cell/electrolyser. We will see that XPS not only provides information on red-ox transitions and segregation/dissolution phenomena of the electrode constituents, but also offers insights into reversible and irreversible electrolyte transformations under polarization.

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CATALYTIC TRANSFORMATIONS for PRODUCTION of BIOFUELS, SPECIALTY CHEMICALS and PHARMACEUTICALS from WOODY BIOMASS

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Biomass as a source of renewable energy and chemicals is attracting more and more attention. Woody biomass utilization in particular can lead, besides a range of such biobased products as lumber, paper and pulp, furniture, housing components and ethanol, also to chemicals and fuels.

Chemical treatment of wood can have several targets. One option is delignification of the biomass leading to cellulose and some residual hemicelluloses, which are further applied in production of paper or board, or the derivatives of cellulose. Thermal (or catalytic) treatment of biomass, e.g. thermal or catalytic pyrolysis, is a route to bio-based synthesis gas and biofuels. Depolymerization of wood components (cellulose, hemicelluloses and lignin), which can be done with an aid of heterogeneous catalysts, results in the formation of low-molecular-mass components (sugars or sugar alcohols, phenols, furfural, various aromatic and aliphatic hydrocarbons, etc.), e.g. unique building blocks for further chemical synthesis.

In addition wood biomass contains many valuable raw materials for producing fine and specialty chemicals. The catalytic derivatization methods for these chemical compounds will be reviewed in the lecture.

RESEARCH in CATALYSIS at KAZAN NATIONAL RESEARCH TECHNOLOGICAL UNIVERSITY

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Kazan National Research Technological University (KNRTU) is one of the leading universities in Russia in Chemical Engineering. KNRTU priority areas are Chemistry and Technology of Polymers, Chemistry and Technology of Energy Efficient Materials, Integrated Hydrocarbon Processing, Nanomaterials and Nanotechnologies, Energy and Resource Efficient Technologies. Each of the these areas involve various catalysts. This presentation is dedicated to the overview of research carried out by various departments of KNRTU. The majority of research activities are experimental and practically-oriented. There are, however, theoretical studies dedicated to the modeling of chemical reactions and technological processes.

Professor Kharlampii Kharlampidi developed various catalytic systems at the department of General Chemical Engineering for oxidation of ethylbenzene, solid paraffins and petroleum sulfides. The department is carrying our research both in homogeneous catalysts based on molybdenum compounds and various heterogeneous catalysts. The results of research in ethylbenzene oxidation formed the basis for technological regulations for the development of joint propylene oxide and styrene production process. These results have been implemented at OJSC “Nizhnekamskneftekhim”.

Several departments of the Institute of Polymers are carrying out research in new catalysts for hydrogenation/dehydrogenation of hydrocarbons and polymerization processes. The major focus is given to titanium-magnesium catalysts.

Academician Oleg Sinyashin (Department of Organic Chemistry) is the supervisor of the research activities in the development of nanoheterogeneous catalysts for electrochemical processes including systems containing phosphorus-organic compounds.

The role of formation of supramolecular structures in the mechanisms of homogeneous and enzyme catalysis is studied at the Department of Plastics Processing Technology.

Heat Engineering Department (chaired by professor Farid Gumerov) is studying processes of catalyst synthesis and recovery with the use of supercritical fluids such as carbon oxide. Another research area is the application of such fluids for the production of biodiesel fuel.

Research in nanocatalysts and conversion of super heavy oils in the conditions of aquathermolysis and application of catalysts is carried out at the Department of Chemistry and Technology of Oil and Gas Processing.

Chemical Industry Equipment Department is developing a technology for purification of cellulose nitrate production exhaust gases. Engineering Ecology Department is developing catalysts for purification of waste waters from hydrocarbons.

At the Department of Chemical Process Engineering, under the supervision of professor German Dyakonov, mathematical models have been developed for catalytic polymerization of various grades of synthetic rubber. The models were tested for their adequacy at OJSC "Nizhnekamskneftekhim".

The research group headed by professor Grigoriy Khrapkovsky at the Department of Catalysis uses quantum chemistry methods for the study of thermal decomposition mechanisms of C-, N- and O-nitrocompounds. It has been proved that the major role in the thermal decomposition of these compounds (especially in the liquid phase) belongs to autocatalytic and catalytic processes. The department is currently carrying out calculations for the mechanisms of aquathermolysis of aliphatic and aromatic ethers and sulfides. Aquathermolysis is the process when water is simultaneously a medium, a reactant and a process catalyst, that is confirmed by the calculations. In addition, acidic aquathermolysis calculations have been carried out for various acids (from carbonic acid to phosphoric acid) which are definitely more efficient as catalysts than water molecules. It is planned in the future to move from the calculations of model compounds to the calculations of asphaltenes which are the main components of many heavy oils.

Interesting results have been obtained from the calculations of methane conversion to butadiene and then to benzene with the use of platinum nanoparticles (from Pt_4 to Pt_{14}) with various spin conditions, various structures, either deposited or not deposited on an aluminum oxide support. The results demonstrated that the limiting stage of the process is the release of the target product from a molecular cluster. The activation energy is, however, small (especially for benzene). All the process intermediates have less energy than the total energy of the respective number of methane molecules and a catalyst cluster.

NANOREACTORS IN CATALYSIS

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One of the most ambitious targets in catalyst preparation is to design and produce catalysts with well defined catalytic properties through the development of multi-site catalysts involving single isolated sites for the different desired catalytic activities. Considerable efforts have been devoted to the fabrication of nanomaterials with well-defined morphologies for specific applications. This is the case of nanocapsules that simultaneously provide the advantages of hollow and porous systems. Particular interest in the performance of chemical reactions in these confined environments has led to catalyst-containing hollow nanocapsules, so that a diffusional product/substrate exchange between the inner cavity and the bulk solution takes place in an efficient way. Thus, the design and synthesis of hollow/yolk-shell mesoporous structures (nanoreactors) with catalytically active ordered mesoporous shells can infuse new vitality into the applications of these attractive structures [1].

The nanoreactor is the “confined space of nano level” (1-100 nm) where catalytic process including transport of reactants, reaction and transport of products could be performed. The nanoreactors are characterized with some nanoscale advantages common for nanoscale materials such as elevated surface/volume ratio, unique electronic properties, huge amount of low-coordinated sites and high homogeneity (Figure 1).

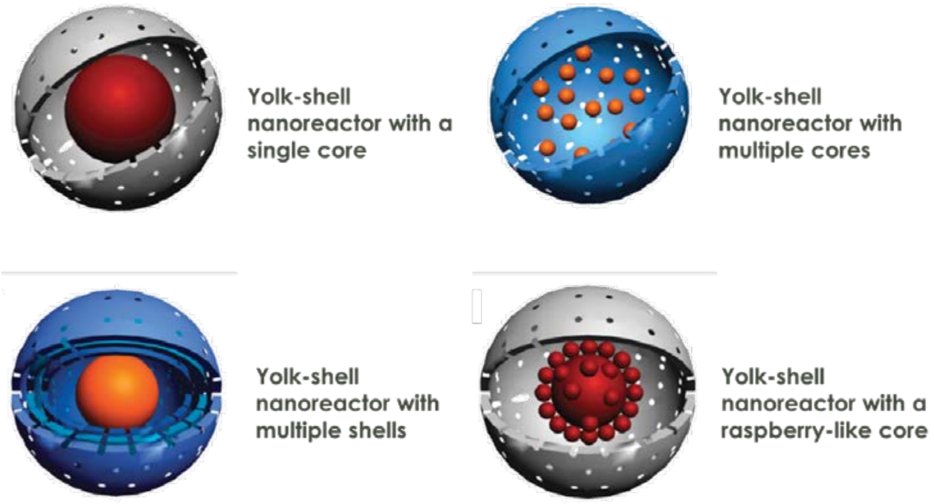

Figure 1. Main types of nanoreactors with a spherical shape and yolk-shell structure.

The current presentation is dedicated to the classification of the nanoreactors, methods of their fabrication and catalytic applications.

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TIME-of-FLIGHT SECONDARY ION MASS SPECTROMETRY (ToF-SIMS): TECHNIQUES and APPLICATIONS for the CHARACTERIZATION of CATALYSTS

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Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is one of the surface characterisation techniques that have been developed significantly during last decades. Together with traditional surface characterisation technique such as X-ray photoelectron spectroscopy (XPS) ToF-SIMS can provide surface analysis with a very high degree of chemical precision. Such analysis undoubtedly can facilitate the detailed characterisation of solid heterogeneous catalysts.

The main strength of ToF-SIMS is its ability to provide high sensitivity and detailed surface chemical structure information. In some cases, ToF-SIMS is able to provide unique molecular information that is not available with other surface characterisation techniques. Together with the detailed chemical information ToF-SIMS routinely provide spatial distribution of signal on the surface of a sample. Together with many advantages ToF-SIMS have also some drawbacks such as difficulties in the interpretation of mass spectra and quantification problems.

There are different areas of catalysts characterisation where ToF-SIMS can be applied. The SIMS studies of the adsorption and surface reaction on single crystals were conducted on the early stage of SIMS development. Modern ToF-SIMS instruments were used in the study of supported mixed oxide catalysts. These catalysts are usually multicomponent and multiphasic, their surface chemistry is very complex that requires the application of different techniques for characterisation. The transformation of organometallic clusters used as precursors for the preparation of heterogeneous catalysts is another area where ToF-SIMS was successfully applied.

ORAL PRESENTATIONS

DEVELOPMENT of ACID CARBON MATERIALS: PREPARATION and USE as ACID CATALYSTS

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A lot of industrial esterification processes are carried out in the presence of strong Bronsted acid catalysts such as sulfuric or *p*-toluenesulfonic acids. However, such homogeneous acids are not environmentally benign and require special processing in the form of neutralization involving costly and inefficient catalyst separation from homogeneous reaction mixtures. This results in substantial energy wastage and the production of large amounts of chemical waste. Recently, standard acid catalytic systems were replaced by carbon materials prepared from D-glucose or other saccharides (e.g. [1]).

In this study we have developed synthetic methods for preparation acid carbon materials from available precursors such as heavy oil fraction, sulfuric acid and different templates (for example rice husk). The main advantage of our way of preparation is cheap precursors and easy variation of acid content in material and value of specific surface. Obtained composites were characterized by BET, SAXS, TEM and they are also tested in catalytic activity (esterification fatty acids reaction).

The catalytic properties and durability of the obtained materials studied in the esterification reaction. Esterification of higher fatty acid was carried out at 80 °C in an ethanol–oleic acid ($C_{17}H_{33}COOH$) mixture (ethanol, 0.10 mol; oleic acid, 0.010 mol) under Ar atmosphere. Total density of the composite acid sites can be estimated via sulfur element analysis, because each sulfonic acid group constitutes a potential acid site. Elemental analysis data are well consistent with results on irreversible titration by pyridine solution.

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SYNTHESIS and CATALYTIC ACTIVITY of the POLYMER-STABILIZED PALLADIUM NANOPARTICLES

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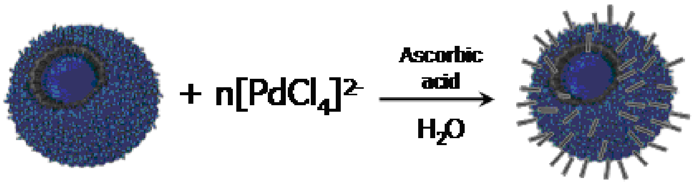
The results of last years show that the nanosized metal particles demonstrate higher catalytic activity compare to bulk metal due to larger surface to volume ratio. It involves many researches to create new catalytic nanosystems with different shape and properties. [1] The most promising systems showing high stability and catalytic activity are nanocomposites on base of polymer and metal nanoparticles. [2]

In this presentation, we will demonstrate our last results concerning the creation of new catalytic hybrid nanocomposites of palladium nanoparticles stabilized on the surface of polymeric nanocapsules.

Polymeric nanoparticles was synthesized as described in [3]. The nanocomposite Pd@p(MVCA8+-co-St) was obtained using the modified method [4]. Pd@p(MVCA8+-co-St) was characterized by the physical and chemical method of IR-, NMR- spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), dynamic light scattering DLS.

NMR spectroscopic experiments were carried out with an Avance 600 spectrometer (Bruker, Germany) equipped with a pulsed gradient unit capable of producing magnetic-field pulse gradients in the z direction of about 56 Gcm1. D2O was used as a solvent in all experiments. Chemical shifts were reported relative to HDO (d= 4.7 ppm) as an internal standard. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 25 UV/Vis spectrometer. Fluorescence emission spectra were recorded with a Cary Eclipse fluorescence spectrophotometer (USA). Imaging of the polymer nanocapsules with and out palladium nanoparticles probe microscope (Veeco). The morphology of the implanted structured silicon surfaces were characterized in plan-view by scanning electron microscopy (SEM) using high-resolution microscope Merlin Carl Zeiss combined with ASB (Angle Selective Backscattering) and SE InLens (Secondary Electrons Energy selective Backscattering) detectors, which was also equipped for energydispersive X-ray spectroscopy (EDX) analysis with AZTEC X-MAX energy-dispersion 5 spectrometer from Oxford Instruments.

For the creation of new catalytic nanocomposite, the polymeric nanoparticles decorated with viologen groups (p(MVCA8+-co-St)) were chosen. p(MVCA8+-co-St) effectively binds with negative charged metal complexes PdCl42- due to electrostatic forces. The soft reduction of PdCl42- leads to the formation of Pd nanoparticles stabilized with p(MVCA8+-co-St) (Pd@p(MVCA8+-co-St)) (Scheme 1). The TEM image (Fig. 1A) show that Pd nanoparticles with the size about 10 nm decorate the surface of the polymer nanoparticles p(MVCA8+-co-St) to form the flower like nanocomposite Pd@p(MVCA8+-co-St).



Scheme 1. Synthesis of p(Pd@MVCA8+-co-St).

The catalytic properties the nanocomposites were examined on the reaction of reduction of p-nitrophenol by NaBH4 in water. The reduction of p-nitrophenol is a conventional reaction for the evaluation of catalytic activity. [5] The results show that Pd@p(MVCA8+-co-St) shows very high catalytic activity. Six nanomoles of palladium in Pd@p(MVCA8+-co-St) is enough for the completely reduction of nitrophenol during 10-15 minutes.

The synthesis, characterization and catalytic properties of Pd@p(MVCA8+-co-St) nanocomposited will be discussed in the presentation.

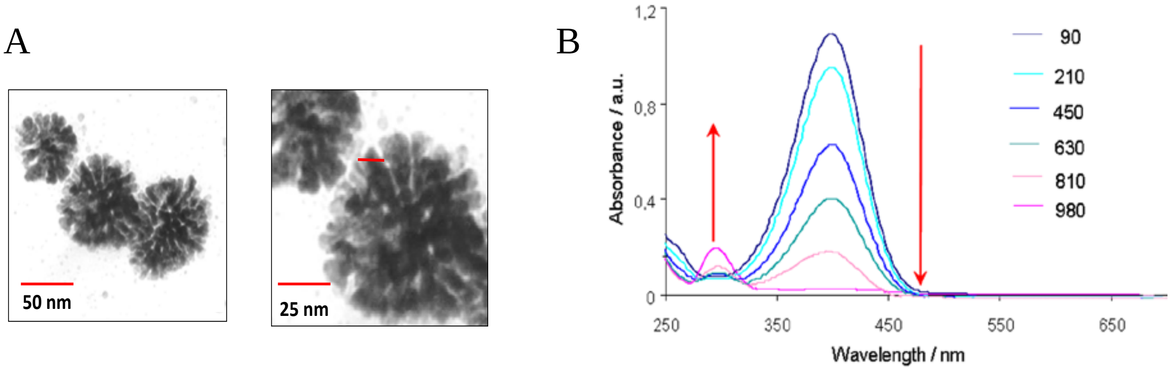


Fig. 1. A) TEM images of Pd@p(MVCA8+-co-St). B) UV−vis spectra of Pd@p(MVCA8+-co-St) at various reaction times.

We demonstrated a new method to prepare new hybrid nanomaterials. The Pd@p(MVCA8+-co-St) obtained, exhibits a high catalytic activity. In the future, we plan to investigate this catalyst in other reactions.

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PREPARATION of PELLETIZED COMPOSITE FISCHER–TROPSCH CATALYST with RANEY COBALT as an ACTIVE COMPONENT

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Fischer–Tropsch synthesis (FTS) is the main stage of the technology of synthetic oil production from carbon containing feedstock. This technology attracts increasing attention as an alternative to the exploitation of dwindling oil reserves. Cobalt catalysts are considered as the most promising ones, because they prevent formation of undesirable aromatics and oxygenates [1–2]. At the present time the supported cobalt systems are the most common in industry and laboratory practice. However Raney cobalt catalysts represent a possible alternative for the FTS. The purpose of this work was the preparation of composite FTS catalyst with Raney cobalt, its characterization and investigation of catalytic properties.

The catalyst was prepared from a mixture comprising 50 wt. % of highly dispersed aluminum metal powder, 20 wt. % of binder (boehmite), 10 wt. % of zeolite Beta in H-form (SiO_2/Al_2O_3 = 38) and 20 wt. % of highly dispersed Raney cobalt as described in patent [3]. Particle size was below 45 µm for aluminum powder, 4–5 µm for boehmite, 1–2 µm for zeolite HB and about 3×1–12×7 µm for Raney cobalt. The catalyst was prepared by mixing the powders with the liquid phase (a mixture of 9.4% HNO_3, $C_6H_{14}O_4$ and C_2H_5OH). As the homogeneity was obtained the paste was formed by piston extruder through the 2.5 mm diameter die. Then extrudates were dried, calcined and cut to 2.5–3 mm long pellets.

Exposition to air, drying and calcinations lead gradually to the boehmite transformation into alumina, which bound all the other components into one composite. As a result, aluminum powder and Raney cobalt were organized as a uniform heat-conductive system. It can be seen from Fig. 1 that all the components are homogeneously mixed in the composite. One can also observe transportation pores and shiny pieces of aluminum metal evenly distributed across the field (Fig. 1a, 1b). The function of aluminum metal in this composite is to provide heat removal from active sites, while the function of Raney cobalt is to serve as an active component and to provide additional thermal interface. Fig. 1c represents polycristallic Raney cobalt particle consisting of cobalt cristallites of size below 20 nm.

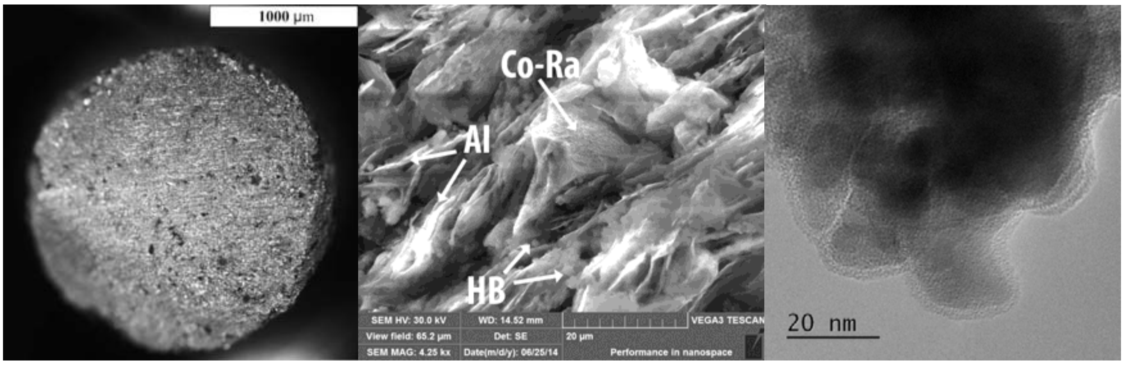

Fig. 1: Optical (a), SEM (b) and TEM (c) images of the catalyst

The structural parameters of the porous system of prepared catalyst were studied by physical adsorption of nitrogen and by helium pycnometry. BET specific surface was 114 m^2/g, pore volume was 0.6 cm^3/g and porosity was 67%.

The synthesis was carried out in a fixed-bed tubular reactor with 10 mm inner diameter, catalyst loading was 2.5 cm^3. The catalyst was activated in pure hydrogen before synthesis, gas was supplied at gas-hour space velocity (GHSV) of 3000 hr^{-1} at 400˚C and 0.1 MPa for 1 hr. After activation the catalyst was heated in synthesis gas stream (molar ratio $H_2/CO = 2$ with 5 vol.% of N_2 as balance and internal reference) at 2MPa, 170–240°C, 1000–5000 hr^{-1}.

The investigated catalyst was active in FTS: CO conversion reached 86%, C_{5+} hydrocarbons selectivity reached 62% while maximum productivity was registered 493 g/kg/hr at 5000 hr^{-1}. Produced C_{5+} hydrocarbons contained 25–37% of olefins, 42–48% of n-parafins and 19–27% of iso-parafins; chain growth probability was 0.72–0.76 depending on GHSV.

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SYNTHESIS and ACTIVATION of COPPER–CONTAINING CATALYSTS BASED on ZIRCONIUM OXIDE for ETHANOL DEHYDROGENATION

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Conversion of alcohols (bio – alcohols) into valuable products and intermediates for fine chemistry is well-known processes. In recent years, it can be noted that interest in the use of environmentally friendly catalytic reactions, had been growing. These processes, for example, could replace the main method of acetaldehyde production via oxidation of ethylene, to avoid environmental pollution and a large number of wastewater [1–3].

The aim of this work was to study the physicochemical properties and catalytic activity of copper-containing catalysts based on zirconium dioxide. Zirconium dioxide was obtained via sol-gel method and stabilized with PVP (polyvinylpyrrolidone) [4]. After calcination procedures tetragonal ceramic ZrO_2 was obtained (DTA, XPA) and it was impregnated with copper chloride (II) with copper content 1, 3, 5 wt.%. All copper containing samples were reduced by H_2 at 400°C. Catalytic experiments were performed on a flow-type setup with the chromatographic analysis of substances.

It is shown that the activity and selectivity of ethanol conversion depends on the pretreatments conditions, surface area, as well as on the loading of the catalysts. Activity of based ceramic zirconia dioxide was low [5]. Prereduction of copper-containing samples in a stream of hydrogen allows to produce acetaldehyde with 100% selectivity. Activity of reduced copper-containing samples depends on the copper content in the sample and correlated with the number of active surface sites. Moreover bond strength of alcohol with the surface decreases with increasing content of copper. Maximum conversion of ethanol in a dehydrogenation reaction reaches 60% at 380°C on reduced by H_2 copper-containing samples.

It has been investigated the possibility of activation of copper-containing nanocomposites based on zirconia dioxide using preliminary critical low-temperature treatments. Modifying the preparation process by adding low temperature quenching stage (T = –195°C) allows to achieve the most active catalyst with the 80% conversion of ethanol to acetaldehyde. Increased activity is connected with the formation of large number of active sites by creating additional defects of zirconia oxide and redistribution of copper ions on the surface before the reduction treatment.

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EXPERIMENTAL DETECTION of MOBILTY of HYDROCARBONS in ZEOLITE-BASED CATALYSTS by MEANS of SOLID STATE ^{2}H NMR

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The microporous solids are the key element for a more effective and environment-friendly chemicals production. Especially wide attention have received zeolites-based catalyst due to their stability, catalytic properties and tunability. The tunability can be achieved, either by simply varying the zeolite structure, or by tuning the already chosen pore topology by changing the Al/Si ratio or surface enhancement by metals, oxides, etc. These modifications may have a huge impact of the reaction as they directly change the catalyst active site, however this change is not the only one. The other side of the zeolite framework is the ordered porous network of channels and intersections that constitute the active surface of the zeolite-based catalyst. For most zeolites these channels do not exceed 1-2 nm, i.e. their dimensions are comparable with the size of the adsorbed molecules. As a consequence the transport phenomena plays a crucial role in the reaction pathway: some reagents are able to access only certain sites, while some products are not able to leave the channels. In such situation the knowledge of molecular mobility is essential for a molecular-level understanding and design of new zeolite-based catalysts.

In the current work we focus on several specific examples of hydrocarbons mobility in different zeolite systems probed by solid state ^{2}H NMR.

On the example of linear alkanes trapped inside 5A zeolite, tert-Butyl alcohol adsorbed into MFI structure (silicalite and H-ZSM5) and ethylene/methane mixture in Ag-enhanced H-ZSM5 zeolites we demonstrate that molecular mobility can be a crucial aspect of the reactions occurring inside zeolite catalysts and how these dynamical phenomena can be tracked down by means of solid state ^{2}H NMR technique. We demostrate that be considering the temperature evolution of ^{2}H NMR spectra line shapes and T_1, T_2 relaxations of the deuterated hydrocarbons confined inside the zeolite pores we are able to understand both the mechanism of the reorientation and give the characteristic rates and barriers of the motions.

Acknowledgements

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DIVALENT DOPED CERIA: A TOOL for DESIGN of HIGH THERMOSTABLE CATALYSTS of LOW-THEMPERATURE CO OXIDATION

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Ceria is well known catalytic material with unique properties. It is characterized by ability to dissolve a foreign metal cations in ceria lattice and reversible Ce^{3+}/Ce^{4+} transitions which is accompanied by oxygen release and storage. These properties allow btaining Pd/CeO_2 catalysts which are active in CO oxidation reaction below 0°C.

In our previous work it was shown that $Pd_xCe_{1-x}O_{1-x-\delta}$ solid solution is active phase in CO oxidation [1]. In this phase Pd^{2+} ions locate in a near-square-planar coordination in ceria lattice (fig.1) that leads to increase of thermostability of the catalyst. It was revealed by DFT calculatuions and Raman spectroscopy that Ni^{2+} ions have the same near-square-planar coordination in the lattice of $Ni_xCe_{1-x}O_{2-x-\delta}$ fluotite-type solid solution. The succesful attempt for substitution of a part of palladium by nickel in ceria lattice was made. Obtained $Pd_xNi_yCe_{1-x-y}O_{2-x-y-\delta}$ catalysts were craracterized by enchanced activity in CO oxidation compared with single metal doped ceria (fig.1). The catalysts retained low-themperature activity in CO oxidation even after calcination at 900°C.

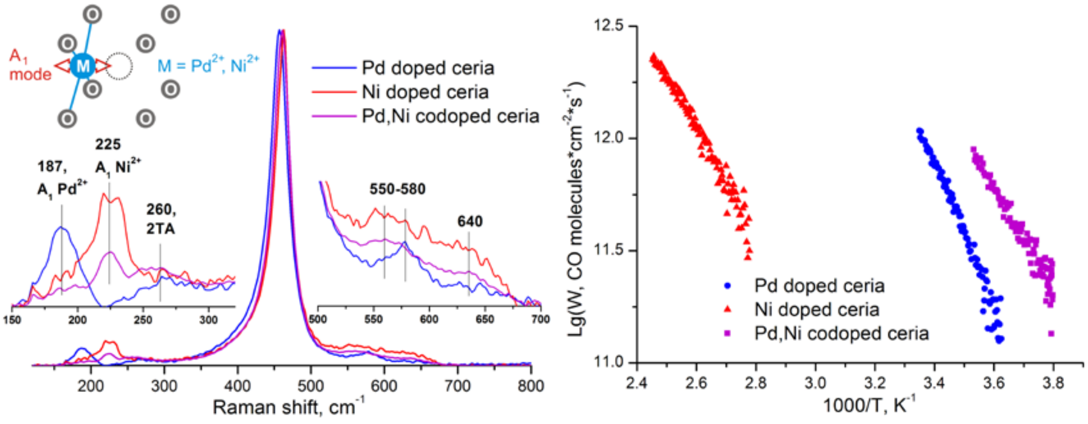

Figure 1. Raman spectra obtained for Pd and Ni doped ceria as well as for Pd,Ni codoped ceria calcined at 600°C. In inset M^{2+} coordination sphere in fluorite lattice with A_1 vibrational mode eigenvector is shown. In right part Arrhenius plots of $CO+O_2$ reaction rates obtained for given catalysts calcined at 800°C are presented.

High thermostability was reached due to both cation and anion ceria sublattice distortions produced by Ni^{2+} and Pd^{2+} ions, that strongly hindered the sintering processes at high calcination temperatures and prevented the decomposition of solid solution into individual oxides.

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STUDY and CHARACTERIZATION of NANOSCALE RUTILE TiO_2 SYNTHESIZED by SOL-GEL METHOD

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Nanoscale titanium dioxide has been stadied extensively because of its wide applications in pigments, catalysit supports, fillers, coatings, ceramics, cosmetics, gas sensors, inorganic membranes, dielectrics, nanobiomedicine and so on [1]. A key requirement to improving its functionality is to increase the specific surface area and decrease the primary particle size of titania. Generally, titania is obtained either from a solution of titania salts or alkoxides. Depending on the preparation route and experimental conditions it is formed usually as anatase or rutile. In most cases, TiO_2 with the anatase structure is the preferable modification. However, rutile TiO_2 has some advantages over anatase in some catalytic processes like oxidation of hydrogen chloride (the Deacon process) on the RuO_2/TiO_2 catalyst, rutile is important for raising the reaction efficiency and selectivity [2,3]. To our knowledge, most synthesis methods of nanoscale TiO_2 with the rutile structure reported in the literature produce mainly a mixture of two or three TiO_2 modifications with the rutile phase yield not higher than 60%. Our work is devoted to developing well reproducible methods for synthesis of nanoscale TiO_2 (rutile) with a high specific surface area and 100% yield of the target phase. It was found that structural, textural and morphological properties of nanorutile depend on the balance of interacting parameters of the synthesis.

Titanium dioxide was synthesized by thermolysis of titanium tetrachloride $TiCl_4$ in water and in an aqueous solution of HCl upon variation of the main synthesis parameters: the synthesis temperature was 60 and 90 °C at a constant value of $[H_2O]/[Ti] = 39$ and varied molar ratio $[Cl]/[Ti] = 4.0, 4.4, 4.8$. The effect of synthesis conditions on the structural features of nanoscale titanium dioxide and its physicochemical properties was studied. At the low-temperature synthesis (60 ºC) and deacidification, a mechanism of reaction has been found to move to formation of the rutile phase and attains 93.8, 34.3, 3.4% at [Cl]/[Ti] indicated above. Carrying out the thermolysis at 90 °C has provided a high quantity of rutile phase independ on acidity. The tendency of increasing rutile yield from 88 to 95% has been noted at raising the molar ratio [Cl]/[Ti], i.e. inverse effect as compared to low temperature conditions. Effect of synthesis parameters on structural (crystallite size) and textural parameters (specific surface area and pore volume) of the rutile samples has been found.

The rutile phase in the products was identified by XRD and Raman spectroscopy methods. The XRD studies showed that crystallite size of the rutile samples was 55-70 Å along plane 1.1.0, and 140-200 Å along plane 0.0.2. According to TEM data, the crystallites formed long filaments constituting fan-shaped agglomerates (Fig. 1). SEM images clearly demonstrate that the samples have a multilevel packing system: consisting of conglomerates of half-formed spheres comprising of the radially jointed fan-like agglomerates or autonomous spheres.

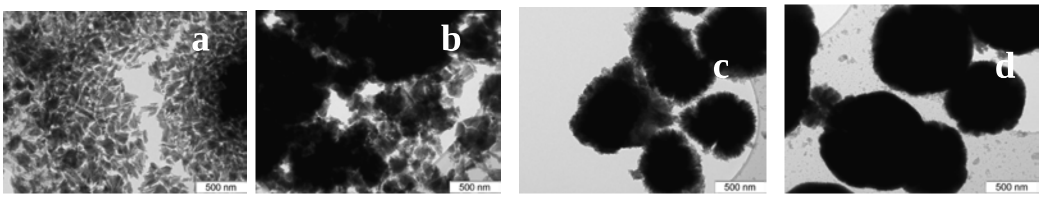

Fig. 1. TEM images of dry rutile powders obtained from $TiCl_4$ at: a - 60°C, [Cl]/[Ti] = 4; b - 60°C, [Cl]/[Ti] = 4,8; c - 90°C, [Cl]/[Ti] = 4; d - 90°C, [Cl]/[Ti] = 4,8.

It has been shown that all samples of nanorutile are characterized by a high specific surface area. The highest results have been obtained for the samples synthesized at a ratio of [Cl]/[Ti] = 4: A_{BET} = 160 m^2/g, V_{Σ} = 0,2 cm^3/g at 60 °C and A_{BET} = 190 m^2/g, V_{Σ}=0.18 cm^3/g at 90 °C. The crystallite size of rutile increases with the medium acidity in the both cases a low temperature and a high-temperature synthesis. Heterogeneous pore structure of rutile powders including micro-, meso- and macropores was established.

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OP-8

PREPARATION and CHARACTERIZATION of PALLADIUM-ZIRCONIUM and COPPER-ZIRCONIA UHV MODEL CATALYSTS for C_1-SURFACE REACTIONS

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Abstract

To prepare an active "inverse" methanol-reforming Zr^0-(pre)-catalyst on Pd- and Cu-metal substrates, a novel ALD/CVD approach was followed and compared to results of previous experiments using a self-developed sputter device [1]. The latter, sputter-based experimental series already showed that H_2O activation sites exist in the Zr(ox)-Cu system, combining Zr redox activity ($ZrO_2 \leftrightarrow ZrO_{2-x}$) with water activation [2]. The ALD/CVD technique using organometallic Zr precursors was originally used to prepare thin insulating layers of ZrO_2, aiming to scale down microelectronic devices. This ALD/CVD system was now adopted for inverse model catalyst synthesis. However, different kinds of interaction between precursor, Zr and catalytically active substrate have been observed for different metals leading to various active sites for MSR.

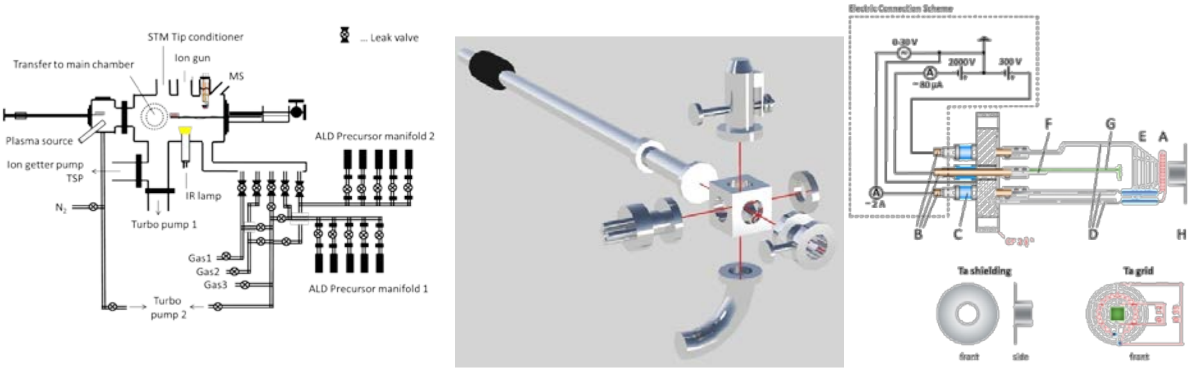

Figure1: UHV ALD/CVD cell scheme (left), model of a portable ALD/CVD cell (middle) and a scheme of our self-developed UHV compatible mini sputter source (right)

General

ALD/CVD preparation of Zirconium-t-butoxide (ZTB) was investigated on Cu(111) and Pd(111) single crystals using in-situ and ex-situ XPS, STM, HREELS and LEED. The aim was to prepare a metallic Zr (sub-) monolayer film on a metal substrate as an inverse pre-catalyst to maximize potential bi-functional sites induced by ZrO_x segregation under reaction conditions. Alternatively, a ZrO_2/ZrOH layer with a high number of active interface sites can already be formed via organic precursor hydrolysis and/or oxidation. The Zr results were compared with Al on Pd(111), using tri-methyl-aluminum (TMA) as a precursor. Differences in particle topography and size result in significant differences in redox activity of Al and Zr.

Palladium-Zirconium

Temperatures between 300°C and 550°C are required for Zr^0 deposition via decomposition of the volatile ZTB compound on Pd(111). The organic moieties of the precursor can easily be removed by heating in vacuum, leading to subnanometer Zr^0 clusters of a few atoms. These clusters behave very different as bulk Zr^0 with respect to redox activity. The subnano-Zr can be oxidized or hydroxylated reversibly and, by annealing in vacuum at 400°C, it can be very easily reduced to Zr^0 again. This highly redox active state has been characterized with in-situ XPS and was also found to be active for methanol decomposition. The unusual Zr-redox behavior on Pd was not observed for Al, according to STM, because no sub-nano Al-clusters but rather big particles were formed on Pd(111).

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WATER-GAS-SHIFT and METHANE REACTIVITY on REDUCIBLE PEROVSKITE-TYPE OXIDES

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A current trend in catalysis sees a re-focus on the catalytic action of the individual parts of a more complex catalyst entity. As many catalyst systems represent a combination of (noble) metals and (oxidic) supporting materials, the latter are increasingly studied with respect to their intrinsic surface reactivity. However, due to the inherent structural and electronic complexity of oxides, the identification of e.g. a catalytically active site is not straightforward. These challenges are far higher if more complex oxide systems are studied. Such complex systems may also come as a single phase binary oxide adopting a distinct crystallographic structure. A well-known example are perovskitic materials. Uses as ferroelectrica or solid oxide fuel cell (SOFC) cathodes are well-known. Catalytic applications are reported for environmentally relevant de-NO_x processes, diesel exhaust catalysis, total oxidation of hydrocarbons or dry reforming of methane. Specifically, also the water-gas shift reactivity on perovskite systems has been in the focus of research1. However, direct correlations of catalytic properties and associated structural changes still remain scarce. This is a particular pity, since e.g. hydrocarbon conversion is usually carried out at high temperatures (T > 600°C), eventually giving rise to an array of structural changes, including surface reconstruction or chemical segregation of individual atom species. Especially the surface structure and chemistry (e.g. the cation or oxygen vacancy concentration) are in a dynamical state depending on the experimental conditions (e.g. hydroxylation degree of the surface or oxygen partial pressure). Thus, surface and bulk structure and composition might significantly deviate from one another and need to be separately assessed.

To clarify this issue, a comparative study of activity for hydrogen oxidation, water-gas shift and methane reforming was performed on the two perovskitic materials $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) and $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$ (STF) with the aim of directly linking surface and bulk reactivity to catalytic properties. Impedance measurements on LSF thin film model electrodes revealed a comparatively high surface activity of the material in oxidizing as well as reducing atmospheres. On powder samples the (inverse) water-gas shift reactivity starting at about 450°C was observed on both LSF and STF. Only total oxidation of methane to CO_2 with reactive lattice oxygen on initially fully oxidized powder samples was observed. The catalytic activity of both perovskite-type oxides is strongly dependent on the degree of reduction and the associated reactivity of the remaining lattice oxygen. Structure-wise, high-resolution high-angle annular dark-field electron microscopy images (Figure 1, right) show that after a catalytic reaction both perovskites still appear SrO-terminated (Figure 1, left). However, Raman measurements on STF reveal a reversible modification of the Fe/Ti-O structural entity upon treatment in the water-gas shift reaction mixture at 600°C. Generally, by combining XRD and Raman measurements, a clear difference in the surface and bulk reactivity of the two perovskite-type oxides results.

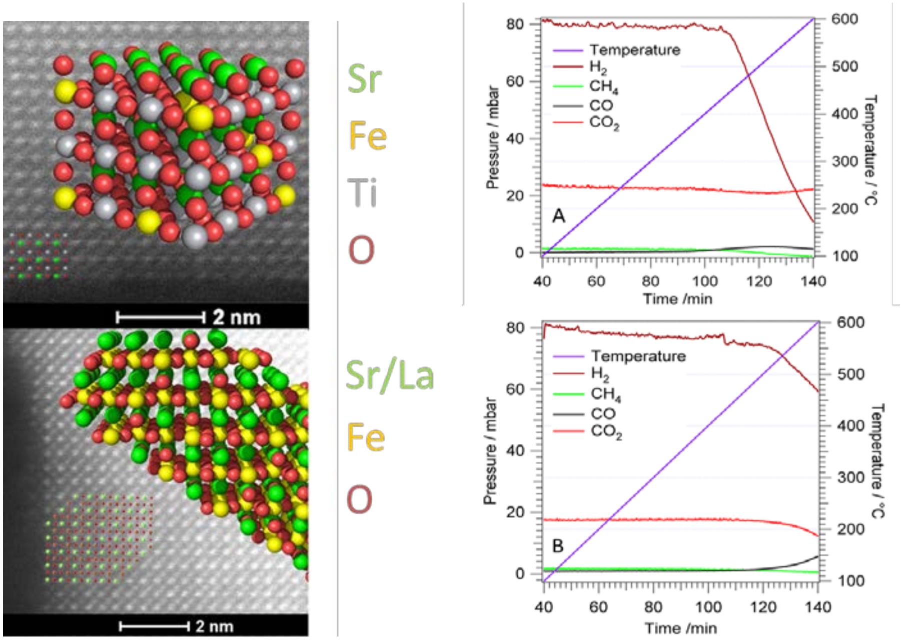

Fig. 1. Left: High-resolution STEM-HAADF images of STF (above) and LSF (below) after an inverse water-gas shift reaction (iWGSR) cycle up to 600°C with overlaid crystallographic structures showing the exact position of each atom in the structure and at the surface. Right: Reaction profiles of the iWGSR on STF without (panel A) and with (panel B) pre-reduction in hydrogen at 600°C (1 h, 1 bar).

As the most important parameter highly influencing the reactivity, the reduction degree controls the oxygen reactivity and the specific oxidation and reduction capability of the active sites in the working state of the perovskitic catalysts. The presented results in turn allow for the first time the direct correlation of a catalytic profile measured on a perovskite system to bulk and surface structural changes occurring during each step of catalytic pre-treatments and catalytic reaction.

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A MODEL for the ACTIVATION of METALLIC CATALYSTS for MULTI-WALLED CARBON NANOTUBE GROWTH

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Due to their unique mechanical, optical properties, high electrical and thermal conductivity multi-walled carbon nanotubes (MWCNTs) are of great interest to be applied in such industries as aerospace, constructions, electronics, medicine etc. Extensive attention to MWCNTs in past two decades has allowed developing of the techniques for nanotube largescale production, for tunable surface functionalization, quality characterization. However, an amount MWCNT-based aplications is still limited. This can be attributed to lack in understanding mechanism and processes to take place during MWCNT growth. Therefore, one fails to fully conrol tailor characterstics of MWCNTs. Such properties of carbon nanotubes as diameter distribution, number and structure of walls, and morphology are determined during the activation of the MWCNT grwoth catalyst.

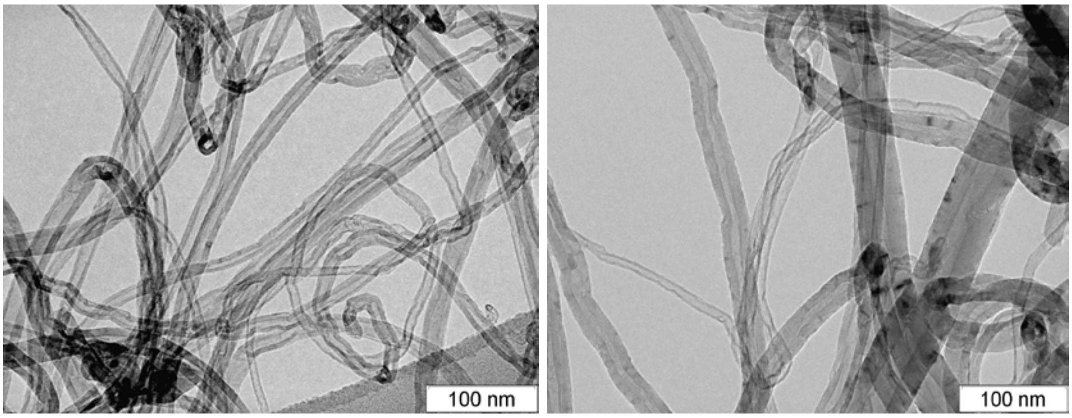

Figure 1: HRTEM images of MWCNTs produced at 650ºC (left image, d_{aver}=17.5 nm) and 730 ºC (right image, d_{aver}=38 nm)

In the present work, a kinetic aspects of the catalyst activation have been studied using in situ [1-3] and ex situ methods (fig. 1). Special attention have been paid to mechanism of the activation of the MWCNT growth catalyst. At least for elementary steps during the activation have been distinguished. There are reduction of the active metals, their sintering accompanied with saturation with carbon with the following nucleation of carbon nanotube [4]. It was found that sintering of the metallic particles is the rate-determining step of the catalyst activation. On the basis of this mechanism a kinetic model for the activation has been developed. The results obtained with this model are in good agreement with expreiment.

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MONTE CARLO SIMULATIONS OF NiCu NANOPARTICLES

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Although segregation phenomena in NiCu alloys are in focus of a number of theoretical studies, segragation in NiCu nanoparticles (NP) is still poorly understood. Only a few attempts were made previously to describe the structure of such systems with the help of Monte Carlo (MC) and molecular dynamics simulations [1, 2], which prompts to gain a deeper insight into the structure of NiCu nanoparticles used in electrocatalytic processes. In this work atomistic MC simulations (NVT-ensemble) were performed to investigate the structure of binary NiCu nanoparticles. In the simulations the geometry of nanoparticles is fixed, while the lattice positions of Ni and Cu atoms are changed. Atomic interactions are described by a set pair Morse potentials [3]. According to our results the segregation takes place at any composition of the NPs. If the Ni fraction prevails, the Cu atoms tend to assemble in the surface region. In contrast, when the Ni is solute, the Ni atoms prefer to segregate on the particle surface. This agrees qualitatively with experimental data collected in literature for the NiCu alloys. The effect of the shape, size and surface steps of NPs on the segregation is investigated in detail.

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MATHEMATICAL ANALYSIS OPTIONS to UPGRADE DEHYDROGENATION ISOAMYLENES to ISOPRENE PLANTS and CONDUCT PILOT TESTS

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As a result, the flow of the endothermic dehydrogenation reaction (heat of reaction of 550 to 650 ºC is 121,2 ÷ 110,7 kJ/mol, respectively) in the adiabatic reactor temperature drop occurs in the upper layer of the catalyst, the value of which depends on the amount of steam, fed are inert cooled, which leads to lower conversions of the isoamylenes. Thus, dilution of feedstock with steam in a molar ratio isoamylene:steam equal to 1:10 and reduces the temperature by 83 °C, an increase in the ratio 1:30 temperature drop decreases in the catalyst bed to 36-37 °C with a steam dilution to 1:40 temperature gradient of 20 °C. The yield of isoprene is 40 %, with a selectivity of 88 %. An amount of steam consumption increases the cost of the product and reduces the efficiency of the process. It is known, the same catalyst under isothermal conditions in the long-term provides performance at a level activity = 50 %, selectivity = 90 %, on an industrial adiabatic reactors are respectively 28 and 88 %. Thus, the use of an adiabatic reactor capacitive contact type in this case is unprofitable and proposed variant "pseudo-isothermal" mode when the temperature drops after the reaction gas was supplied to the pin an additional amount of heat.

In this paper, we consider three possible options for the implementation of the dehydrogenation process with additional heat input: 1) two consecutive heated reactor with an intermediate track of gas; 2) a reactor with an additional introduction of superheated steam into the catalytic bed; 3) two consecutive reactor with addition of further superheated steam in space between reactors.

For the approximation to the isothermal dehydrogenation process takes into account the condition that all three schemes temperature steam feed mixture after the additional heating or steam becomes the same as it was at the reactor inlet of the catalyst in the upper layer.

The use of these circuits provides a dehydrogenation activity growth up to ~ 5 %, but the greatest increase in selectivity (1,1 %) is observed for a system of two successive reactors supplemented with additional superheated steam into the second reactor.

One of the schemes, namely the two-reactor with an intermediate supply additional steam has been tested in practice by means of a pilot plant with two reactors connected in series. Thus, sampling and analysis was carried out of the contact gas, after the first and after the second reactor, which allowed to carry out a comparative analysis of the results using the conventional circuit and an intermediate circuit with two reactor feed vapor.

Based on the results conducted by pilot test shows that carrying out the process for the dehydrogenation of isoamylenes to a two-reactor circuit further supplying steam into the second reactor compared with the conventional activity allows to increase 16,6-29,3 %. The results obtained during pilot tests are in good agreement with the mathematical modeling of the process of dehydrogenation of isoamylenes in isoprene by two-reactor scheme.

Thus, carrying out the dehydrogenation process with an intermediate supply steam to the reactor is promising, and may be used in the present dehydrogenation process cycle plant. On the basis of pilot tests, it was proposed to test the scheme in terms of operating the dehydrogenation reactors. Industrial test plant them in “Nizhnekamskneftekhim” are under way.

COLLOIDAL CRYSTAL TEMPLATING of THREE-DIMENSIONALLY ORDERED MACROPOROUS PEROVSKIT: APPROACHES to CATALYST with HIERARCHICAL POROSITY

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Activity and stability of a catalyst are strongly related to its properties, such as particle size distribution, morphology, and crystallinity, which are determined by the preparation method adopted. Unfortunately, the traditional methods (e.g., sol–gel, citrate, solid-state reaction, co-precipitation, and polymerizable complexing) involve in high-temperature solid-state reactions, leading to the destruction of pore structures and hence to low surface areas (<10 m_2/g), unfavorable for enhancement in the catalytic performance of the obtained perovskite (ABO_3) materials [1]. Therefore, it is highly desirable to develop an effective strategy for the controlled preparation of porous ABO_3 that are high in surface area. Recently, this problem has been solved using the colloidal crystal templating method, by which one can create a Three-dimensionally Ordered Macroporous (3DOM) structure [1,2]. The colloidal crystal template is fabricated by ordering monodispersed microspheres (e.g., polystyrene (PS), poly(methyl methacrylate) (PMMA), or silica) into a face-centered close-packed array. The concept of preparing 3DOM materials is simple: close-packed colloidal crystal templates (CCT) are infiltrated with solution or vapor-phase chemical precursors, followed by the removal of templates by thermal processing, solvent extraction, or chemical etching (Fig. 1). Improved syntheses have not only added to the variety and complexity of inverse opal compositions, but have also permitted greater control over structural morphology from the nanometer length scale of the wall skeletons to the micrometer-to-centimeter dimensions of the overall macroporous solids. New methods to functionalize the internal surfaces of 3DOM materials have resulted in the development of unique composite structures [3].

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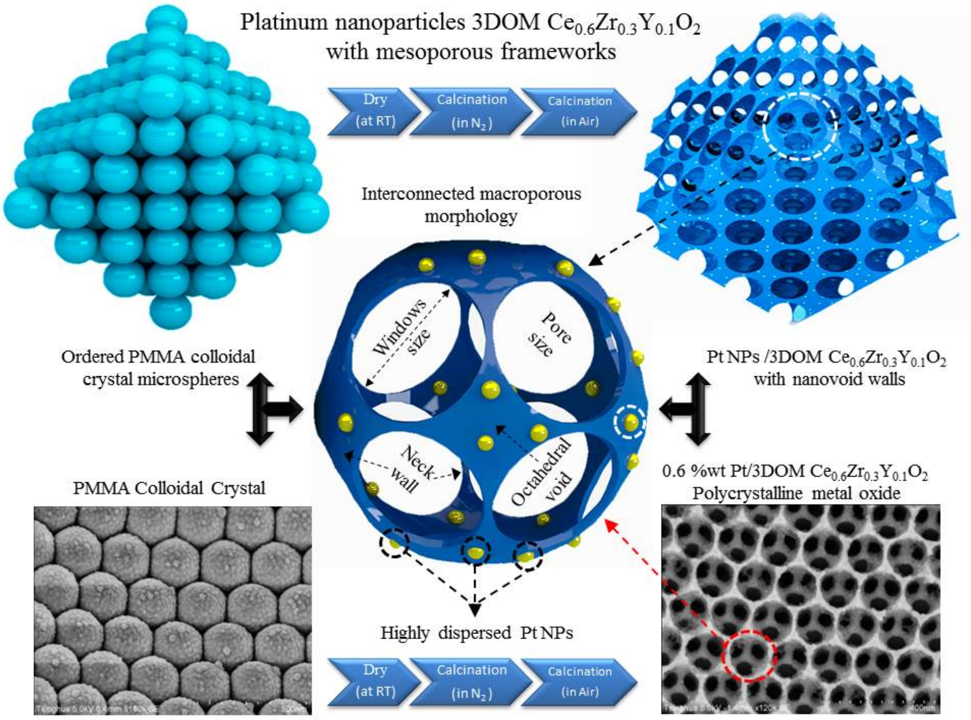

Figure 1:3DOM CZY supported platinum samples were denoted as xwt% Pt/3DOM CZY.

Oxygen vacancies are often present in ABO_3 as point defects, and their effect on the complex oxide properties is typically uniform and isotropic. Controlling the oxidation state of B-site metal cations within ABO_3 oxides is very important for the oxidation of hydrocarbons at low temperatures due to their high thermal stability, number of oxygen vacancies and the redox properties of B-site element. The catalytic performance is significantly influenced by the redox properties of the B-site metal cation, whereas oxygen vacancies provide the sites for substrate adsorption and activation [1-3]. The study conducted using new porous nanohybrid ABO_3 materials to design template sizes, precursors and supports as well as metal NPs by templating with self-assembly methods. This allowed for greater control over the skeleton of porous and nanohybrid materials and formation of novel ABO_3 materials as well as reveal the underlying engineering.

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IMPACT of ALUMINUM FLAKES SIZE on PERFORMANCE of Co-BASED CATALYST in FISCHER–TROPSCH SYNTHESIS

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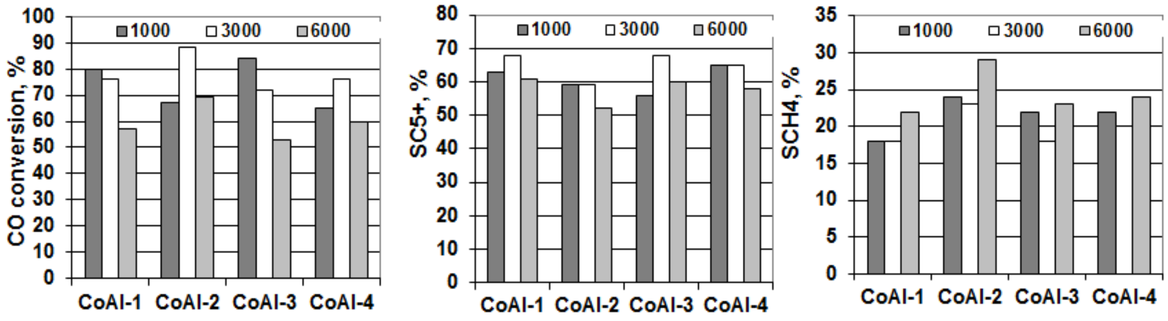
Fischer–Tropsch process is the main stage of so-called XTL (anything-to-liquids) technology that allows converting natural gas, coal and biomass into liquid hydrocarbons [1, 2]. The products produced by Fischer–Tropsch synthesis (FTS) are sulfur and nitrogen-free synthetic fuel, naphtha, lubricants and chemical feedstocks. Cobalt catalysts have been widly used for FTS because they prevent formation of oxygenates and aromatics. In presence of cobalt catalyst syngas (a mixture of CO and H_2) can be converted into sythetic liquid hydrocarbons, mostly linear paraffins. The combination of FTS traditional catalyst with zeolites in a composite material leads to formation of bifunctional catalyst producing high-quality synthetic oil in one step by eliminating the hydrotreating stage [1].

Since the nature of FT reaction is strongly exothermic, efficient heat removal is of crucial importance because a catalyst of low thermal conductivity may lead to loss in selectivity and rapid deactivation of the catalyst [2]. Metallic additives in FTS catalyst tend to form the effective heat removal network, which provides higher thermal conductivity.

The aim of this work was to study the influence of Al flakes size in Co-based bifunctional catalyst on peformance in FTS.

The investigated catalysts were produced by the extrusion of pastes. All samples were produced from 50 wt.% of Al with different flakes size, 20 wt.% of binder and 30 wt.% of zeolite HBeta. Aluminum flakes chracteristic size in catalysts increases in the following order: CoAl-1 < CoAl-2 ≤ CoAl-3 < CoAl-4. The introduction of cobalt (20%) as an active component into the samples was conducted by two-step impregnation with a $Co(NO_3)_2{\cdot}6H_2O$ aqueous solution.

All catalysts were active in FTS. Al flakes size, presumably, influences both pore volume of catalyst and thermal conductivity of the pellet: smaller size of Al flakes provides better thermal conductivity due to closer contact between flakes, which leads to higher C_{5+} selectivity at higher GHSV (Fig.1a).



a) b) c)

Fig.1. Influence of aluminum flakes size on (a) CO conversion, (b) selectivity of C_{5+} hydrocarbons formation and (c) selectivity of CH_4

Thus, the highest C_{5+} selectivity at 1000 h^{-1} was registered for CoAl-4 and at 6000 h^{-1} — for CoAl-1 (Fig.1b). CoAl-1 characterized by the highest pore volume (0.84 cm^3/g), showed the best methane selectivity (Fig.1c).

Group composition depended on flakes size significantly at 1000 h^{-1} only (Fig.2).

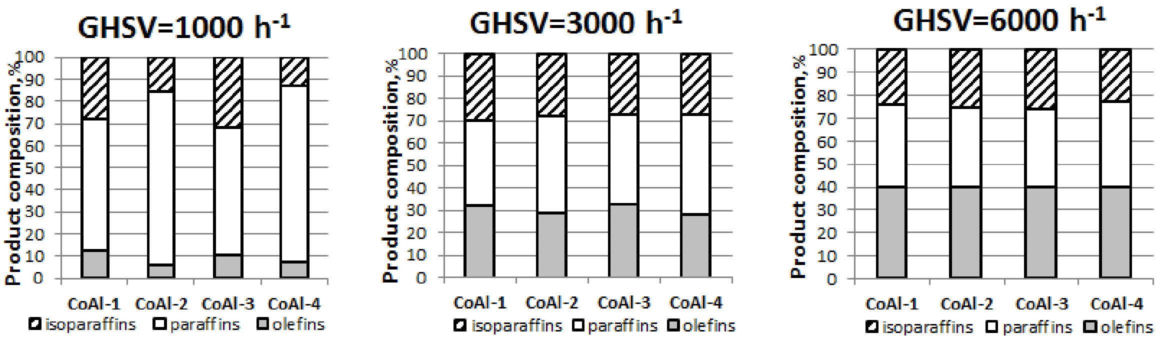


Fig.2. Influence of aluminum flakes size on the C_{5+} hydrocarbons composition

Thus, the Al flakes form the effective heat-conducting network, which helps to remove heat of exothermic reaction, however pore volume in catalyst pellet is more important for mass-transfer in FT process.

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ZIRCONIUM PHENOLATE BASED CATALYSTS for ETHYLENE OLIGOMERIZATION: SYNTHESIS, COMPOSITION, STRUCTURE and ACTIVITY

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It is well-known that the zirconium complexes when activated by an appropriate alkylaluminium co-catalyst form the efficient catalyst systems for conversion of ethylene into low-carbon linear alpha-olefins [1-3]. In the present paper catalytic systems based on zirconium phenolate complexes with aminohydrochloride substituents and alkylaluminium compounds are studied for ethylene oligomerization. The main object of this work is the study of the electronic and geometrical influence of phenolate ligands on the activity of catalyst and product distribution and preparation of catalyst composition based on zirconium phenolate and organoaluminium compounds with improved activity and selectivity for getting of linier low molecular weight alpha-olefins preferably, with improved C_4-C_{18} fraction.

Zirconium phenolates of the general formula $LZrCl_2$, where L = 2-piperidinylmethyl -4-methylphenol **(1),** 2- morfolilmetil-4-methylphenol **(2)**, 2- dietilaminometil-4-methylphenol **(3)** and 2 (2,6-diizobutilfenilimino) phenol **(4),** were synthesized by reacting of $ZrCl_4$ with these phenols in tetrahydrofuran at 323-343K. These catalysts are tested in the oligomerization of ethylene into higher linear olefins at 363-373 K and 2,5 MPa pressure. The effect of composition of the Zr-based catalysts on the activity and distribution of products of ethylene oligomerization are given in table 1. As can be seen from the table the interaction of the synthesized phenolate compounds of zirconium with alkyaluminiumchlorides in a molar ratio Zr:Al = 1:(25-30) leads to the formation of the heterogenized catalyst systems active in the oligomerization of ethylene. The process results in a high yield of C_4-C_{18}, (C_4, C_6) linear alpha-olefins in the case of complex 1 in toluene when Et_2AlCl is used as a co-catalyst. The most active catalyst is obtained for complex 1 especially, in the case when the amount of coordinated Et2AlCl to LZrCl2 is increased. More stronger bonding of the organoaluminum compound leads to an increase in the electron density at the Zr atom and weakened the strength of the Zr-alkyl bond and as a result the insertion of ethylene into the Zr-alkyl bond is enhanced.

Table 1. Composition of products of ethylene oligomerization by Zr-complexes (T=363K, solvent-50ml, reaction time 5h, pressure of ethylene 2,5 MPa)

Zr-complex	Reaction medium	$(C_2H_5)_n$ $AlCl_{3-n}$	Ratio Al/Zr	Catalyst activety,	Reaction products, mas. %			
					C_4	C_6	C_8-C_{18}	C_{20+}
1	Heptane	$C_2H_5AlCl_2$	25:1	156	3,5	9,8	26,7	60,0
	Chlorbenzene	$C_2H_5AlCl_2$	25:1	273	5,0	26,5	18,5	50,0
	Toluene	$(C_2H_5)_3Al_2Cl_3$	25:1	420	41,3	15,8	35,8	7,1
	Toluene	$(C_2H_5)_2AlCl$	30:1	1210	2,7	63,2	34,1	traces
	Toluene	$(C_2H_5)_3$ Al	25:1		Polyethylene	Polyethylene	Polyethylene	
	Heptane	MAO	200:1					
2	Heptane	$C_2H_5AlCl_2$	25:1	185	18,2	15,3	20,5	46,0
3	Heptane	$C_2H_5AlCl_2$	25:1	1150	15,2	40,0	30,8	14,0
4	Heptane	$C_2H_5AlCl_2$	25:1	1100	5,0	62,9	25,5	6,0

The synthesized complexes and products of their interaction with the alkylaluminium compounds before and after oligomerization were isolated and characterized by atomic absorption spectroscopy, X-ray fluorescence microscopy, infrared spectroscopy. Dynamic light scattering method was used for description of dimethylsulfoxide dispersion of solids obtained in the reactions of initial compounds with alkylaluminium compounds before and after oligomerization of ethylene. The estimated values of particle size in dispersions are in the range 110 ÷ 350 nm. The nature of the supramolecular complexes, their composition and structure as a function of medium composition is discussed.

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CARBIDE and GRAPHENE GROWTH, SUPPRESSION and DISSOLUTION in Ni MODEL SYSTEMS STUDIED by in-situ XPS and SXRD

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Carbon chemistry represents one of the fastest evolving and expanding research areas primarily due to the extraordinary physicochemical properties of its modifications, especially graphene and carbon nanotube materials [1]. In catalysis, the activity and selectivity of the entire catalytic entity can be modified by carbon in connection with metal-support interaction [2]. Furthermore, the stability of Ni-based anode materials in Solid Oxide Fuel Cells (SOFC) can be enhanced by carbon management, when they are exposed to hydrocarbon rich fuel gas. Carbon managment requires the understanding of the adsorption, migration, dissolution and resegregation of carbon on the catalyst, as well as of the structural and electronical properties of different scenarios of C-distribution. In particular, the role of the clock-reconstructed Ni(111) surface carbide regarding further C-growth and dissolution is tested and experimental data are compared to the structural models proposed in the literature[3].

In our work, we focus on the behavior of Carbon on different Nickel systems in the temperature region of 300K to 800 K. The samples were exposed to methane and ethylene under different pressure and temperature condition to observe carbide and graphen/ite formation and dissolution.

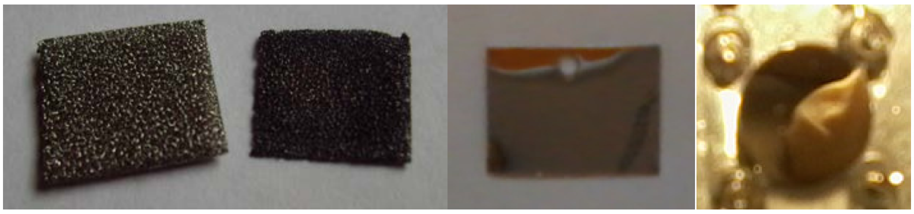

Fig. 1. Ni-Foam(left), -foil(middle) and Ni(111) single crystal(right) used to investigate carbon chemistry.

Experiments were performed at the following beamlines and UHV-systems:

I. In-situ XPS at the beamline ISISS-PGM of BESSY II, Berlin
II. SXRD at the ID03 beamline of ESRF, Grenoble
III. Additional ex-situ experiments in UHV system, Innsbruck [4]

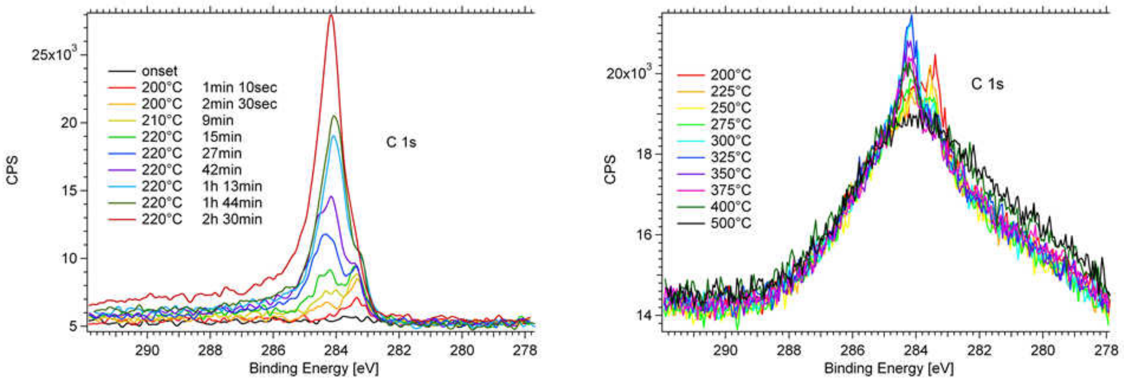

Fig. 2. In-situ XPS spectra of carbide and graphene/ite growth on Ni-foam(left) and Ni-foil(right)

As shown in Fig 2, sequential formation of carbide and graphene/ite could be observed both on Ni foam and Ni foil, whereby more amorphous carbon was observed on the latter. In addition, the coexistence of surface carbide and graphene/ite in a certain temperature region was observed as well as the preferential dissolution of the surface carbide at >= 670 K.

Carbide was moreover grown on Ni(111) and the subsequent graphene/ite formation was observed, using similar experimental conditions as on foam/ foil. After thermal dissolution of the carbidic clock-reconstructed $(39)^{1/2}$R16.1°x$(39)^{1/2}$R16.1°phase at 700 K, as indicated by the loss of the related diffraction intensities, the presence of epitaxial and unrotated graphene domains is indicated by the absence of rotated graphene reflections, together with a strong alteration of the specular reflectivity of the surface. These results complement recent structural investigations by STM [5, 6]. Structure modelling of SXRD data to confirm the most plausible configurations of unrotated graphene on Ni(111) will be presented.

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SELECTIVE CO METHANATION OVER Ni-, Co- and Fe/CeO_2 CATALYSTS

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The selective CO methanation in hydrogen-rich gas mixtures in the presence of CO_2 is a promising way for deep CO removal designed for low-temperature proton-exchanged membrane fuel cell feeding applications, as well as a challenging fundamental problem of substrate-selective hydrogenation. Besides the target CO methanation reaction (1), undesirable CO_2 methanation (2) and reverse water-gas shift (3) reactions may occur, causing considerable hydrogen losses and increasing CO outlet concentration.

In spite of extensive research efforts Ru- and Ni-based systems remain the most active catalysts for CO and CO_2 methanation [1]. At the same time, metals such as Co and Fe are known to be active in carbon oxides hydrogenation reactions, including Fischer-Tropsch synthesis and RWGS, but the properties of Fe and Co-based systems in the selective CO methanation are not studied.

This work reports the results of comparative study of Ni-, Co- and Fe/CeO_2 catalysts, prepared from nitrate and chloride precursors, in the selective CO methanation.

Catalysts with metal loading of 10 wt.% were prepared by incipient wetness impregnation of CeO_2 by the water solutions of metal's nitrate and chloride salts. They were characterized by BET, XRD, TEM, EDX, XPS, FTIR and CO chemisorption techniques. Selective CO methanation was studied in a flow reactor at atmospheric pressure in the temperature interval 180 − 360 °C, at WHSV = 29 000 $cm^3g^{-1}h^{-1}$ and feed gas composition (vol.%): 1.0 CO, 20 CO_2, 10 H_2O, 65 H_2 and He-balance.

It was shown, that Fe-based and Co(Cl)/CeO_2 catalysts were inactive in CO and CO_2 methanation reactions. Ni/CeO_2 and Co/CeO_2 catalysts were active in both CO and CO_2 methanation, but showed low selectivity. Ni(Cl)/CeO_2 catalyst showed the best performance in selective CO methanation, being less active than Ni/CeO_2 and Co/CeO_2, but considerably more selective.

XRD, TEM and EDX analysis showed the presence of chlorine on the surface of Ni(Cl)/CeO_2, even the CeOCl particles. Thus the observed differences in catalytic behavior of Ni-based catalysts could be associated with chlorine influence.

The TOFs calculated for Ni/CeO_2 and Ni(Cl)/CeO_2 catalysts at 210 °C (at this temperature S_{CO} = 100 % and CO conversion < 15 % for both catalysts) were similar: $5.0 \cdot 10^{-3}$ s^{-1} and $4.0 \cdot 10^{-3}$ s^{-1}, respectively. These data mean, that Ni/CeO_2 and Ni(Cl)/CeO_2 catalysts exhibited similar activity in CO methanation. In other words, the presence of chlorine does not significantly influence on the CO methanation activity, but it dramatically inhibits the CO_2 hydrogenation activity, thereby promoting catalyst selectivity.

Based on the data obtained, the nature of the active centers, origin of the observed activity order and probable mechanisms of CO and CO_2 methanation over Ni/CeO_2 and Ni(Cl)/CeO_2 catalysts are discussed.

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METALS (Ni, Rh, Co) on PEROVSKITES (LSF, STF) for SOFC USAGE

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Perovskites are currently the most popular material for SOFC cathodes [1-2]. Our approach is to use them as anode materials. In this respect perovskites can act as mixed ionic and electronic conductors (MIECs), transporting both oxygen ions and electrons effectively to and from the triple phase boundary, where the following reaction takes place:

$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$$

Two different perovskites, LSF ($La_{0.6}Sr_{0.4}FeO_{3-d}$) and STF ($SrTi_{0.7}Fe_{0.3}O_{3-d}$), have been selected as promising materials regarding methane chemistry and water gas shift activity. For improvement of catalytic activity and selectivity they were subsequently impregnated with various metals (Ni, Rh and Co) and investigated concerning their methanation and methane reforming activity.

For the pure perovskites no methanation or methane reforming activity could be observed. The fully oxidized perovskites can be reduced with methane and CO, producing CO_2. Water gas shift reaction starts for both STF and LSF at 300°C, the inverse reaction was observed above 500 °C.

For Ni-STF the methanation reaction starts at 250 °C. The methane is formed up to 400 °C. Above this temperature methane reforming yields increasing amount of carbon monoxide. Also for Ni-LSF, methanation activity can be monitored, starting at 300 °C. At 370 °C methanation competes with the inverse water- gas shift reaction and carbon monoxide is formed. Above 550 °C the methane is reformed.

Conclusion

Both perovskites show water gas shift reactivity. Methanation / methane reforming reactivity on perovskites can only be achieved after impregnation with metals whereby STF shows better performance regarding methane production.

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HYDROGEN PRODUCTION via STEAM REFORMING of BIO-OIL'S LIGHT COMPONENTS – ETHANOL AND GLYCEROL - over SUPPORTED NIKELATES

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Catalytic steam reforming (SR) of bio-oils to produce hydrogen and synthesis gas can be the most promising process for the clean and renewable fuel generation. The main problem in the bio-oil catalytic transformation is high coking ability of oxygenates leading to fast deactivation of cheap traditional Ni catalysts [1]. In the previous work, catalysts based on Ln ferrites-nickelates were shown to provide a high activity, stability and selectivity in SR of ethanol [2]. However, they have a low specific surface area (SSA) and cannot provide required performance being supported on structured substrates. The perspective approach to get over these difficulties is loading perovskites on the supports of a high SSA such as γ-Al_2O_3 with additives of alkali-earth elements to prevent formation of coke.

In the present work, the catalysts mLnNi$_{0.9}$Ru$_{0.1}$O$_3$/nMg-γ-Al_2O_3 (Ln = La, Pr, m=10-20%wt, n=6-15%wt) were synthesized and tested in the steam reforming of ethanol (ESR), steam and oxy-steam reforming of glycerol (GSR and GOSR) in a plug-flow reactor at the atmospheric pressure and temperature range of 500-800°C.

The catalysts were characterized by XRD, BET, TEM with EDX, UV-vis, XPS and H_2 - TPR, FTIRS of CO test molecule. It was shown that in terms of catalysts stablity to coking the most important parameters are the Mg content, Ln nature and preparation method.

The study of the catalysts performance in ESR and GSR shows that they provide high values of oxygenates conversion, hydrogen yield and coking stability. The optimal composition of the catalyst with high activity and coking stability has been revealed. It was found that the addition of oxygen in the reaction mixture (GOSR) increases the stability of catalyst to coking, without compromising a high hydrogen yield.

The optimal catalyst supported on Ni-Al foam substrate shows a high and stable performance in ESR in a pilot reactor in a realistic reaction mixture during 50 hours.

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MOLYBDENUM CLUSTER SULPHIDES as CATALYSTS FOR PHOTOREDUCTION of WATER

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Molybdenum sulfide materials have emerged recently as low-cost alternatives to Pt and other precious metals for the photo- and electrocatalytic reduction of water.[1] Molybdenum disulfide, MoS_2, was not considered as an active catalyst for H_2 evolution until MoS_2 nanoparticles were employed instead of bulk materials.[2] After the catalytically active sites in MoS_2 nanocrystals were identified to have a triangular geometry, molecular clusters that feature similar topologies have been investigated. Jaramillo et al. have shown that incomplete cubane-type $Mo_3S_4^{4+}$ aqua clusters supported on highly oriented pyrolytic graphite possess high electrocatalytic activity for H_2 evolution, comparable to that identified for MoS_2 edge surface sites.[3] Recently, these authors have also reported that supported sub-monolayers of the $Mo_3S_{13}^{2-}$ clusters over graphite surfaces exhibit excellent H_2 evolution activity and stability in an acid medium.[4] The enhanced catalytic activity of the $Mo_3S_{13}^{2-}$ cluster complex versus that of the $Mo_3S_4^{4+}$ aqua ion is attributed to the presence of three bridging and three side-on bonded disulfide ligands in the former, which mimics the proposed electroactive MoS_2 edge structure.

Our groups have developed a series of molecular molybdenum(IV) trinuclear Mo_3S_7 and Mo_3S_4 clusters that only differ in the nature of the bridging ligands, disulfides, and sulfides, respectively. In the case of the Mo_3S_7 cluster unit, the metal atoms define a triangle with a capping sulfur and three bridging S_2^{2-} ligands, an ideal topology to mimic the active sites in MoS_2.

In our recent work,[5] the potential of diimine trinuclear Mo_3S_7 molecular clusters as co-catalysts was evaluated. We reported on the synthesis of two new Mo_3S_7 clusters coordinated to 4,4'-dimethyldicarboxylate-2,2'-bipyridine and 4,4'-dinonyl-2,2'-dipyridyl. The molecular diimino trinuclear clusters were adsorbed homogeneously on TiO_2 P25 nanoparticles, and the photocatalytic activity toward H_2 evolution from water was investigated using Na_2S and

Na_2SO_3 as sacrificial agents. The diimino cluster complexes evolve to yield the catalytically active species as revealed by changes in the UV/Vis and X-ray photoelectron spectra. A series of electrochemical measurements confirm that these active species are generated by the reduction of the diimino Mo_3S_7 clusters. In addition, these reduced diimino Mo_3S_7 clusters enhance the photocatalytic H_2 evolution greatly if they are deposited on TiO_2 nanoparticles. The fact that the diimino Mo_3S_7 clusters can be distributed over the TiO_2 surface in a homogeneous and controlled manner paves the way for their integration in other materials and thus for the design of new photocathodes for H_2 generation.

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NEW NANODIAMOND/TiO_2 COMPOSITE MATERIALS FOR THE SOLAR ENERGY CONVERSION INTO HYDROGEN BY WATER SPLITTING

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Natural resources of energy present on Earth are decreasing year by year. That is why it is necessary to find new ways of producing energy to solve the problem of global consumption. Production of hydrogen using solar energy is one of the key solutions that are envisaged to solve this problem. The process which allows to convert the photons from the sunlight into chemical energy, electrons, is called photocatalysis. In our study we are using the titanium dioxide (TiO_2), a cheap and common semi conductor material, as a photocatalyst in order to chemically split the H_2O molecule. This is called the water-splitting **[1]**. The hydrogen produced by this process could be used in the future as a source of energy more efficient that gasoline.

The production of hydrogen by titanium dioxide could be improved by adding other materials. The aim of the study is to add nanodiamonds to titanium dioxide and to observe the different interactions between the two materials.

Thus, concerning photocatalytic water-splitting production, the influence of (i) the way of synthesis of the Nanodiamonds/TiO_2 composites, (ii) the composition of the composites, *i.e.* the relative amount of nanodiamonds, (iii) the nature of nanodiamonds (as synthetized or hydrogenated), (iv) the presence or absence of Pt nanoparticules and (v) the addition of methanol acting as sacrificial agent will be discussed.

Titanium dioxide is synthesised by a sol-gel process **[2]** and its activity toward H_2 production by water-splitting is compared to that of the TiO_2 reference (P25). The precursor used is titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$). The nanodiamonds are synthesized by a detonation of high explosives method **[3]**. The Nanodiamonds /TiO_2 composite are synthesized from previously described TiO_2 and detonation nanodiamonds. Different strategies of synthesis have been carried out in order to obtain the composite material. (1) The first one is based on the addition of nanodiamonds during the sol gel process in order to get TiOH gel with nanodiamonds inside the gel. After a calcination step at 400°C, the Nanodiamond/TiO_2 composite is finally obtained. (2) Another way of elaboration is based on the impregnation of already synthesized and crystallized TiO_2 with a suspension of nanodiamonds by mechanical mixing in an aqueous medium under inert gas.

Another catalyst, the platinum will be added by impregnation of H_2PtCl_6 to these composite materials; the results observed with and without platinum will be compared. The platinum is a material which increases drastically the yield of the photocatalysis reaction.

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SYNTHESIS and REACTIVITY of Au/g-C_3N_4/TiO_2 NANOCOMPOSITES for WATER_SPLITTING under SOLAR LIGHT ILLUMINATION

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Nowadays, the major challenge is to find new environmentally friendly ways to produce energy that may cover the global consumption. The direct conversion of solar energy though an energy carrier (fuel), storable and usable upon request, appears as an interesting alternative [1]. Photocatalysis is an innovative and promising way to produce pure hydrogen from renewable energy sources. Indeed, the water dissociation (water-splitting) highlighted by Fujishima and Honda in a photoelectrocatalytic cell opened a promising way to produce hydrogen from light energy [2]. Hydrogen (H_2) is a selective energy carrier due to its high specific energy density [3].

In our study, we will focus on a photocatalytic titanium dioxide-based system (TiO_2) associated with graphitic carbon nitride (g-C_3N_4). With a band gap of 2.7 eV, g-C_3N_4 allows the valorization of an important part of the visible light spectra in the context of water splitting [4].

Titanium dioxide (TiO_2) powder is obtained via a standard “sol-gel” process [5] and graphitic-carbon nitride (g-C_3N_4) was obtained via a thermal polycondensation reaction of specific nitrogen-containing precursors [6]. g-C_3N_4/TiO_2 nanocomposites were obtained by introducing g-C_3N_4 (as synthesized) during the sol-gel synthesis of TiO_2. Gold nanoparticles were synthesized - directly onto the TiO_2, the g-C_3N_4 and the g-C_3N_4/TiO_2 support – by chemical reduction of the $HAuCl_4$ precursor in an excess of $NaBH_4$.

Water-Splitting tests were carried out into a quartz reactor containing 900mL of ultra-pure water and 250mg of sample under flowing N_2 at 100cc/min and irradiated with a 150 W halide lamp. Methanol (from 0.1 to 1 vol. %) was used as a sacrificial agent in order to increase yields of hydrogen production. The sample activity was measured by a gas phase µGC. The first set of measurements of the activity of Au/g-C_3N_4 samples showed optimal gold concentration around 0.3wt.% with a hydrogen production yield of 25µmol/h after stabilization. The first test on 0.3wt.%Au/50wt.%g-C_3N_4/TiO_2 composite showed a significant production of hydrogen. Compared to 0.3wt.% Au/TiO_2, a higher H_2 production is obtained (above 30 µmol/h) with 2 times less TiO_2.

The synthesis of new nanostructured composites allowed us to achieve better hydrogen production yield than the reference Au/TiO_2 and Au/g-C_3N_4 samples. Furthermore best hydrogen production was obtained with a gold loading of 0.3 wt. %. Future goals are to find the optimal amount of Au on the Au/g-C_3N_4/TiO_2 composites but also the optimal amount of g-C_3N_4.

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FLASH – PRESENTATIONS

MoVTeNb CATALYST in the SELECTIVE OXIDATIVE TRANSFORMATIONS of PROPANE

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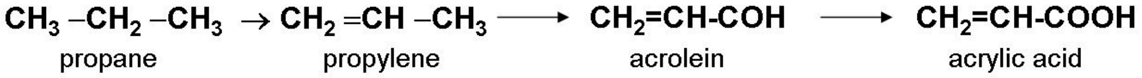
To date, the problem of oil gas utilization and industrial processing of its components (methane, ethane and propane) is very actual. This issue is closely connected with the need to develop new power saving technologies in petrochemical industry. Selective catalytic transformation of propane is economically attractive for the production of acrylic acid and acrilonitrile as compared with conventional process from propylene due to inexpensive and abundant raw materials. MoVTeNbO catalysts are reported [1, 2] to be the most efficient catalysts for the oxidation of propane to these processes. Orthorhombic M1, hexagonal M2 and tetragonal $Mo_{5-x}(V/Nb)_xO_{14}$ phases were shown to form in MoVTeNbO system depending on the synthesis conditions [3, 4]. The intrinsic activity and the role of each of these phases in the propane selective transformation are still under debate. The work object is elucidation of the phases function in selective oxidation of propane. The catalyst was synthesized from aqueous slurry using ammonium heptamolybdate, ammonium metavanadate, telluric acid and niobium oxalate. The prepared slurry was spray-dried at 220°C and heated in an air flow at 320°C during a short period and in He at 600°C for 2h. XRD, IR-spectroscopy and HRTEM have been used for characterization of final catalysts. The propane, propylene and acrolein oxidation was performed at 380°C temperature using a reaction mixture of 4%C_3H_8, C_3H_6 or C_3H_4O, 30% H_2O, 66% air. Propane transformation to acrylic acid at MoVTeNb oxide catalyst runs by successive mechanism through intermediate propylene and acrolein:



$$CH_3-CH_2-CH_3 \rightarrow CH_2=CH-CH_3 \longrightarrow CH_2=CH\text{-}COH \longrightarrow CH_2=CH\text{-}COOH$$

Such reaction mechanism makes it necessary to create active component for each step and combine these components optimally in a single polyfunctional catalyst. To clear up the role of the phases in selective oxidation of propane, the samples containing mainly (more than 95%) M1, M2, $TeMo_5O_{16}$ or $Mo_{5-x}(V/Nb)_xO_{14}$ phase were prepared and tested in propane, propylene and acrolein oxidation. Fig. 1 presents a summary picture of the catalytic action of the phases in the oxidation of propane, propylene and acrolein.

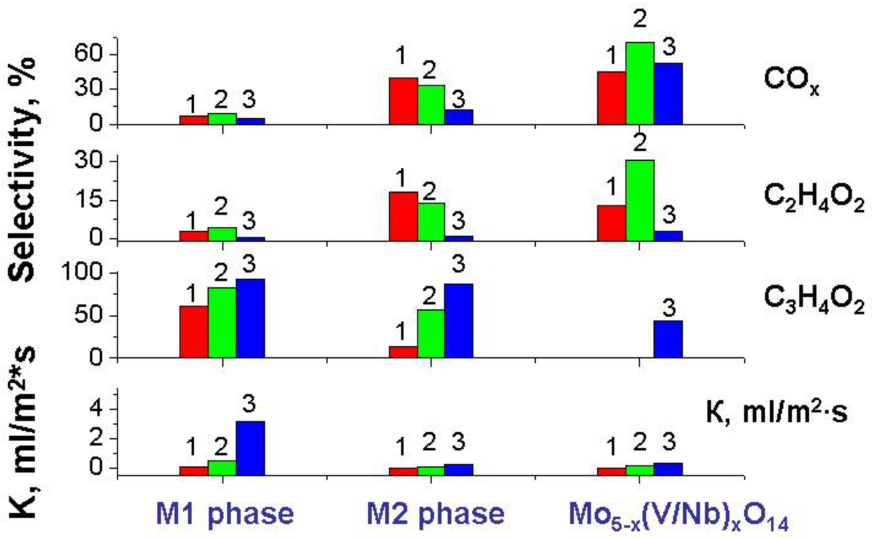


Fig 1. The rate constant (K, ml /s * m^2) and selectivity (S) to acrylic acid ($C_3H_4O_2$), acetic acid ($C_2H_4O_2$) and carbon monoxide (CO_x) to "single-phase" samples during the oxidation of propane (1), propylene (2) and acrolein (3). Propane conversion of about 5%, of propylene - 40%, acrolein -75%.

On $Mo_{5-x}(V/Nb)_xO_{14}$ phase, acrylic acid forms from neither propane nor propylene. For all the reactants, main direction of transformation is destructive, which leads to the formation of acetic acid and deep oxidation products. M2 phase shows the lowest activity in the oxidation of propane, propylene and acrolein. The absence of niobium in the structure weakens the ability of this phase to activate the reactants. The main direction of propane oxidation on the M2 phase is deep oxidation, which proceeds by three routes: directly from propane, via overoxidation of propylene and overoxidation of acrylic acid. M1 phase shows the maximum activity and selectivity toward the direct oxidation of propane and individual steps of the consecutive reaction – oxidation of propylene and acrolein. Note, phase $TeMo_5O_{16}$ is non active in all studied reactions. Taking into account the consecutive mechanism of propane transformation, it is reasonable to attribute MoTe active sites to the oxidation of propylene to acrolein, and VMo sites to the oxidation of acrolein to acrylic acid. The role of Nb is to stabilize the structure of M1 phase and modify the site of propane activation. Such compositions of the active sites can be distinguished in the structure of M1 phase. M1 phase is sufficient for efficient proceeding of the reaction, whereas M2, $TeMo_5O_{16}$, $Mo_{5-x}(V/Nb)_xO_{14}$ phase phase is less active and selective in all the reactions, so its presence in the catalyst is undesirable. Propane is activated on the vanadium sites, propylene is oxidized to acrolein on the MoTe sites, and acrolein is oxidized to acrylic acid on the VMo sites. Such compositions are present in M1 phase probably in the optimal combination.

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DEVELOPMENT and OPTIMIZATION of Ni_2P/SiO_2 CATALYSTS for METHYL PALMITATE HYDRODEOXYGENATION

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Transition metal phosphides are considered as promising materials for hydrodeoxygenation (HDO) of fatty acid based feedstocks such as vegetable oil, tall oil or waste-cooking oil [1,2]. HDO of these crudes leads to the mixture of hydrocarbons frequently called “green diesel” or “second generation biodiesel”. Preparation of phosphide catalysts includes temperature treatments that can influence on the physicochemical and catalytic properties [3].

The aim of the present work is the investigation of the Ni_2P/SiO_2 temperature pretreatment conditions (calcination and reduction) for HDO of vegetable oil model compound – methyl palmitate ($C_{15}H_{31}COOCH_3$ – MP).

The catalysts were prepared by impregnation of silica with aqueous solutions of $Ni(OAc)_2$ and $(NH_4)_2HPO_4$. Ni:P molar ratio was maintained 1:2. Impregnation followed by drying at 110°C, calcination at 500, 600, 700, 800 or 900°C and reduction *in situ* in hydrogen flow at 550, 600 or 650°C. The catalytic tests were carried out using fixed-bed continuous-flow stainless steel reactor at 290°C and p_{H2}=3.0 MPa. Reaction mixtures were analyzed by GC-MS and GC-FID. The catalysts were characterized by elemental analysis, N_2 physisorption, H_2-TPR, XRD, HR-TEM, XPS.

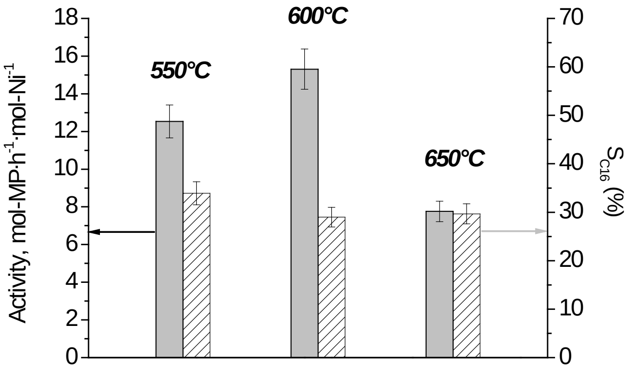

Fig. 1. Activity and S_{C16} dependence on reduction temperature of Ni_2P/SiO_2

According to H_2-TPR experiments reduction of calcinated precursors occurs in a similar way. XRD analysis confirmed for precursors calcinated at 500-800°C the presence of the Ni_2P phase after reduction. Calcination at 900°C resulted in SiO_2 sintering and crystallization. According to XRD and HR-TEM data phosphide particles sizes increase with icreasing of calcination temperature but remains almost the same with increasing of reduction temperature from 550 to 650^{o}C. The main products of MP HDO on Ni_2P/SiO_2 are *n*-pentadecane and *n*-hexadecane. The sample reduced at 600°C showed the highest catalytic activity (Fig. 1), but selectivity toward *n*-hexadecane (S_{C16}) is slightly higher for samples reduced at 550°C. The optimal conditions for Ni_2P/SiO_2 catalysts activation were found.

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SYNTHESIS of CARBON-CARBON COMPOSITES via CATALYTIC PROCESSING of HYDROCARBONS

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Associated petroleum gases (APG) combustion is well known problem of today's oil and gas industry due to economical, ecological and social disadvantages and risks [1]. Recent advances in catalytic vapor deposition (CVD) technique have proved it to be useful tool for hydrocarbon processing [2]. Natural gas and associated petroleum gases could be decomposed to carbon nanofibers (CNf) and hydrogen using CVD. The iron subgroup metals (Fe, Co, Ni) and their alloys are common catalysts for this process. CNf are characterized via low density, high surface area, electrical and thermal conductivity. This material has a great potential in a wide range of applications including polymer reinforcements, electronic devices and membrane technologies.

Using CVD approach for hydrocarbon processing, we have obtained carbon-carbon composites presented itself CNf layer anchored to carbon macrofiber (Mf) surface. Such modification of Mf allows producing carbon-carbon composites with increased surface area (SA). Treatment mentioned seems to be perspective for polymer reinforcement as it solves the problem with low SA of pristine macrofibers.

In terms of research, composite samples x%CNf/Mf were synthesized (x – wt.% of CNF ranged from 1 to 200%). Firstly, catalytic particles of nickel and Ni-Cu alloy were deposited via impregnation technique with the following drying and reduction in hydrogen flow. Then growth of CNf layer on carbon microfiber surface was carried out by catalytic chemical vapor deposition of various hydrocarbons in reactor with MacBain balances which allowed us to monitor kinetics of the process. Ethylene, propane-butane mixture (model components of APG) and natural gas were used as a hydrocarbon source.

It was found that maximum of CNf yield can be obtained in the case of ethylene decomposition. Extended data regarding kinetics of the process will be given and discussed during the presentation.

Scanning and transmission electron microscopy investigations revealed that methane decomposition resulted in root type of CNf growth (when catalyst particle remains anchored to substrate surface; fig. 1, *left*). Tip type of carbon nanofiber growth was observed for all other hydrocarbons used (fig.1, *right*).

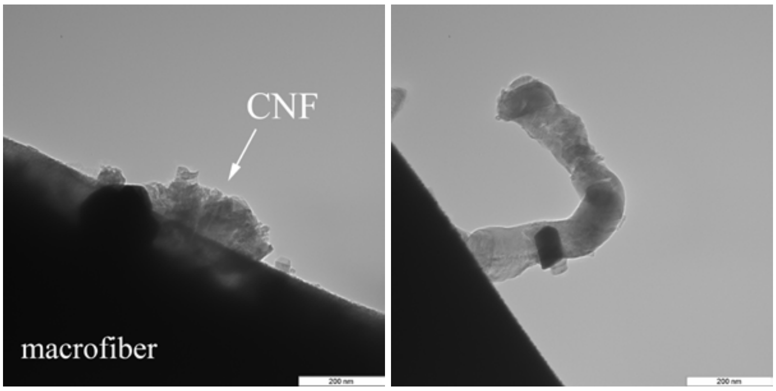

Figure 1. SEM images of carbon-carbon composites CNf/Mf obtained from methane (*left*) and ethylene (*right*) decomposition on nickel catalyst.

Using the BET method it was shown that surface area increased up to ten times (from 1.8 m^2/g to 6-20 m^2/g) after modification.

Preliminary tests indicated that method suggested permits one to provide noticeable improvement of physicomechanical properties of materials reinforced with carbon Nf/Mf composite.

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FP-4

CATALYTIC OXIDATIVE DEALKYLATION of N-ISOPROPYL PHOSPHONOMETHYL GLYCINE

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One of the environment friendly methods of glyphosate (highly efficient broad-spectrum systemic herbicide) production is the atom efficient route based on the N-alkyl substituted glyphosates (**1**) synthesis followed by oxidative dealkylation and returning of the formed alkylcarbonyl to the first step of the process. Oxidative dealkylation was carried out in the liquid phase in the presence of heterogeneous platinum catalysts using oxygen as the oxidant [1].

We decided to study the possibility of gold catalysts application for the oxidative dealkylation of N-isopropyl glyphosate with hydrogen peroxide as an environmentally benign oxidant (Fig. 1). We have studied the oxidation with 30 % hydrogen peroxide water solution in the presence of nanosized Au/C catalyst (2 % Au) prepared by gold deposition on mesoporous carbon support using cationic adsorption method [2].

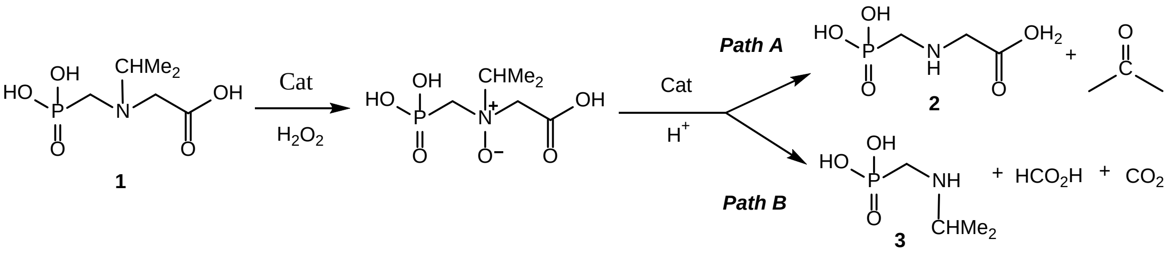
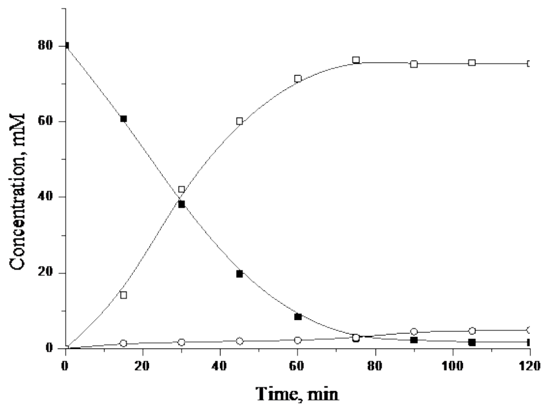


Fig.1. The major products of N-isopropyl glyphosate oxidation.

It was found that in the studied conditions in 75 min conversion of the substrate (**1**) reaches the level of 97%, at the same time the content of the by-product (**3**) in the reaction mixture does not exceed 4% when the content of the target product (**2**) is at least 90% (Fig. 2).

In the range from 0.16 to 1.64mM Au and at initial substrate concentration of 82 mM the initial rate of glyphosate accumulation is directly proportional to the mole number of supported gold being in the reaction mixture, and order of reaction with respect to catalyst is the first. The optimum concentration of catalyst can be considered as the minimum one at which after 75 minutes reaction time yield of glyphosate is not less than 90%, i.e. M 0.082-0.041 (based on Au)



■ – N-isopropyl glyphosate (**1**)

□ - glyphosate (**2**)

○ - N-isopropyl aminomethylphosphonic acid (**3**).

Conditions: $[Sub]_0$=0.082 M, $[H_2O_2]_0$=0.25 M, [Sub]/[Cat]=100, T=70 ˚C, ω=1000 rpm.

Fig. 2. Changes in the concentrations of reaction mixture components during the reaction time.

It was determined that at the substrate concentrations in the range 41 mM - 82 mM and catalyst concentrations (based on gold) 0.16 mM - 1.6 mM the order of reaction with respect to both the substrate and the catalyst is the first.The obtained results allow us to conclude that for the glyphosate synthesis the maximum possible substrate concentration determined by the solubility of the product in the aqueous medium of the reaction mixture is optimum.

Thus, it have been found that in the studied conditions catalytic oxidative dealkylation of N-isopropyl glyphosate with hydrogen peroxide aqueous solution in the presence of the nanosized Au/C catalyst (2 % Au) proceeds with high yield (90%) of the target product - glyphosate.

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INFLUENCE of the NATURE of SULFUR-ORGANIC MOLECULES on ODS CATALYTIC ACTIVITY of MODIFIED CuZnAl-O CATALYST

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New specifications for sulfur in diesel fuel have been established in many countries [1]. In hydrodesulfurized diesel with 350-500 ppmw S, sulfur is contained mainly in compounds of the dibenzothiophene family. One of alternative methods of sulfur removal from diesel is selective oxidation of sulfur-organic compounds over catalysts with oxygen (ODS). During this process sulfide and heterocyclic sulfur-compound transform to sulfur dioxide; hydrocarbon fragments do not change or are oxidized to carbon dioxide and water [1]. The efficiency and selectivity of the oxidation of sulfur-organic molecules depend on their reactivity.

The aim of this work is to study the catalytic behavior of a modified CuZnAl-O catalyst in the ODS of different sulfur-organic molecules (like thiophene, DBT, 4,6-DMDBT) in toluene. We selected CuZnAl-O catalyst due to its high catalytic peformance in ODS [2]. The ODS tests were conducted in the temperature range 250-430°C at a ratio of $O_2/S=120$, GHSW=3000 h^{-1} and WHSW=6 h^{-1}. Physico-chemical properties of the modified CuZnAl-O catalyst before and after ODS reaction were studied by XRD, AAS-ICP, CSH-analysis, H_2-TPR, DTA-MS, and others to find correlation between sulfur reactivity.

Figures 1 and 2 show that oxidation of the sulfur-containing molecules in the presence of a modified CuZnAl-O catalyst increases in a sequence: thiophene<DBT<4,6-DMDBT. The main ODS products are sulfur dioxide, carbon dioxide, water and desulfurized model fuel. As follows from the results of GC-MS study, sulfoxide, sulfones and H_2S are absent in liquid reaction products. However certain amounts of benzaldehyde and 3-phenyltoluene in the products were detected.

Sulfur-organic molecules was shown to inhibit the toluene oxidation insignificantly. The lowest toluene conversion was observed in the presence of thiophene.

According DTA-TG data, ODS proceeds via the stage of adsorption of sulfur containing molecules, followed by their destruction and evolution of SO_2 into the gas phase. In case of strong interaction of sulfur-containing molecules with the catalyst active sites, the accumulation of sulfur on the catalyst surface takes place, in the form of metal sulfides, polysulfides and sulfates. Stronger interaction with catalyst surface is observed for thiopnene.

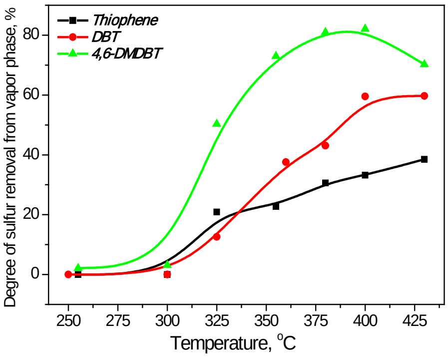

Fig. 1 – Removal of sulfur from vapor phase

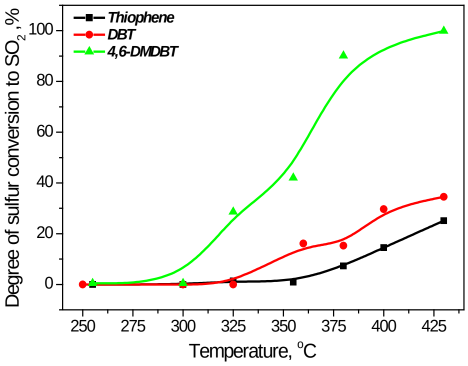

Fig. 2 – SO_2 formation in the gas phase

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DEVELOPMENT of SOLID ACID CATALYSTS BASED on CARBON and METAL OXIEDS for CONVERSION of CELLULOSE into 5-HYDROXYMETHYLFURFURAL

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5-Hydroxymethylfurfural (5-HMF) is one of the most promising bio-based chemicals so-called "platform molecules". The aim of the study was a development of non-corrosive solid acid catalysts for 5-HMF production from an inedible cellulose in the hydrothermal one-pot process. In this work the investigation proposed solid catalysts based on graphite-like carbon Sibunit and niobium oxide supported on zirconia and studied of mechanism their catalytic action.

The carbon catalysts were prepared via sulfonation of graphite-like carbon Sibunit in fuming H_2SO_4 at 80-250 °C; oxidation by HNO_3 or wet air; and additional sulfonation of oxidized carbons at 200 °C. Nb/ZrO_2 were made by presipitation and following calcination of Nb precursor on the 3D-stuctured ZrO_2 which was prepared by template method.

Investigation of the carbon catalysts by N_2 absorption showed that formation of the acidic species on the surface leads to simultaneous partial destruction of the carbon structure. The total amounts of acidic species determined by titration for the sulfonated, oxidized and oxidized-sulfonated carbons were 3-15 (sulfonated, oxidized) and 20-30 (oxidized-sulfonated) times higher than for the initial Sibunit. The XRD of Nb/ZrO_2 catalysts showed that Nb oxide was amorfus. All the Nb catalysts were stable under hydrothermal conditions.

HPLC analysis of solutions after catalytic experiments revealed glucose and 5-HMF as the main products. Moreover an accumulation of small amounts of cellobiose, mannose, fructose, levulinic and formic acids was detected. Catalytic tests showed high activity of sulfonated carbon catalysts in the investigated process. Oxidized and oxidized-sulfonated samples possessed the activity comparable to the activity of the catalysts sulfonated at 150 and 200 °C. The maximum glucose and 5-HMF yields were reached over Sibunit sulfonated at 200 °C (46.0% and 21.5%, respectively). The Nb/ZrO_2 catalysts were also active in the reaction. The highest yields of 5-HMF and glucose 16.5 and 21% respectively were achieved in the presens of 0.5%Nb supported on the ZrO_2 without macropores.

For elucidation of the mechanism of catalytic action and the role of catalysts the experiments with such intermediates as cellobiose, glucose, fructose and 5-HMF were carried out. Beside, a kinetics of substrate, intermediates and products in the presence of diluted H_2SO_4 as a catalyst and lower loading of the catalysts were registered. The heterogeneous mechanism of the cellulose depolymerization was supposed base on the results of these experiments. The dissolving cellulose appeared to be a limiting step of the process while hydrolysis is the fast reaction. Rearrangement of glucose to fructose was also slow reaction. The irreversible dehydration of fructose was the most rapid step. Moreover there were different ways of glucose transformations (except glucose↔fructose→5-HMF).

Acknowledgements

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SELECTIVE OXIDATION of PSEUDOCUMENE with HYDROGEN PEROXIDE CATALYZED by DIVANADIUM-SUBSTITUTED γ-KEGGIN POLYOXOMETALATE

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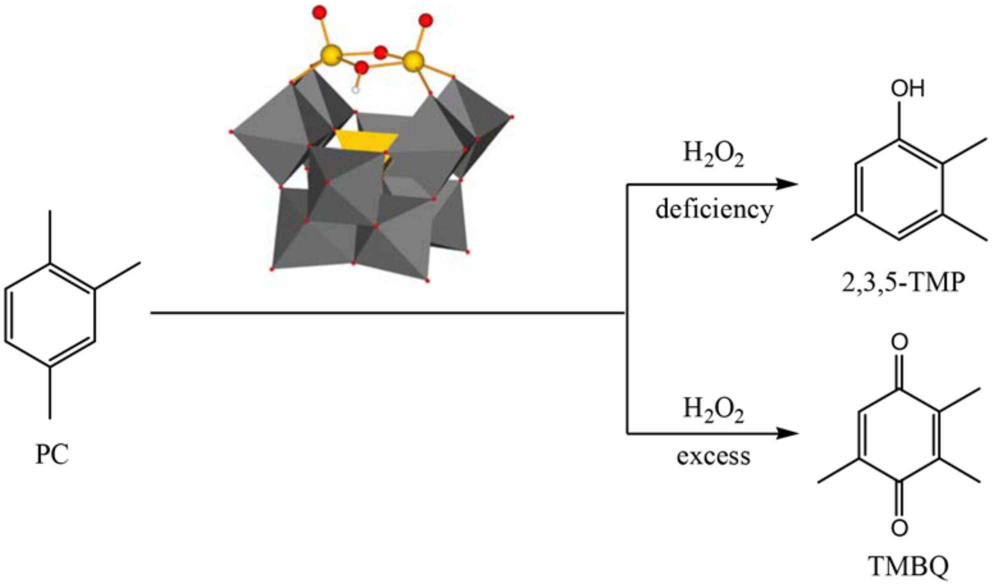
The direct hydroxylation of aromatic rings of alkylsubstituted arenes with atom efficient and green oxidants such as aqueous H_2O_2 is a demanding task of organic synthesis. Hydroxylation and further oxidation of 1,2,4-trimethylbenzene (pseudocumene, PC) lead to industrially important 2,3,5-trimethyl-1,4-benzoquinone (TMBQ, vitamin E key intermediate). Recently, Mizuno and co-workers reported oxidation of some alkylarenes with hydrogen peroxide catalyzed by a divanadium-substituted polyoxometalate (POM) $(Bu_4N)_4H[\gamma\text{-}PW_{10}V_2O_{40}]$

(γ-$PW_{10}V_2$) [1]. In this work, we attempted to apply of this POM as a homogeneous catalyst for the selective oxidation of PC and to get insights into the oxidation mechanism.

In case of H_2O_2 deficiency, PC hydroxylation proceeds with unusually high chemo- and regioselectivity to produce 2,3,5-trimethylphenol (TMP) as the sole isomer. It occurs effectively in a solvent mixture MeCN/*t*-BuOH (1:1 v/v) in the presence of γ-$PW_{10}V_2$ and 1 equiv. of $HClO_4$ in the temperature range of 30–80ºC. The presence of $HClO_4$ and *t*-BuOH is vital for the catalytic activity. Optimization of the reaction conditions has led to a 2,3,5-TMP yield of 73% based on H_2O_2 [2]. When an excess of H_2O_2 was used ($[H_2O_2]:[PC] = 8$), the initially formed 2,3,5-TMP oxidized further to give TMBQ and other overoxidation products. TMBQ selectivity attained 41% at PC conversion of 41%.



The kinetic regularities and estimated rate constants acquired from the kinetic study on PC oxidation with H_2O_2 in the presence of γ-$PW_{10}V_2$ are in good agreement with the theoretically predicted reaction mechanism where peroxo complex [γ-$PW_{10}O_{38}V_2(O_2)]^{3-}$ is the main active species responsible for the aromatic ring hydroxylation.

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EFFECT of COPPER OXIDE SINTERING on CATALYTIC CO OXIDATION

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Copper-containing systems are widely used catalysts in various processes such as water-gas shift reaction (WGS), preferential oxidation (PROX), alcohol oxidation etc. Copper oxide nanoparticles are usually considered as active component of such catalysts. In this work CuO particles with different specific surface area (SSA) were tested in catalytic CO oxidation and investigated by the complex of physicochemical methods including XPS, XRD, TEM, DRIFTS.

Initial CuO nanopowder was synthesized by precipitation of Cu(II) salt in alkali solution. Series of CuO was prepared by air calcination of initial sample at temperature from 350 to 850°C. Catalytic properties were tested in flow reactor under 0.2%CO/1%O_2/He reaction mixture with contact time equal 0.015 sec. Catalytic activity of initial CuO nanoparticles was found to be high at low temperatures (below 150°C), while sintering of particles above 550°C resulted in the shift of CO conversion curve towards high temperatures up to full disappearence of low-temperature activity.

Based on XRD data it was found that initial nanopowder in contrast to sintered CuO sample was characterized by large number of microstrains and enhanced volume of unit cell. Otherwords, the crystal structure of CuO nanoparticles was found to be more defective than those of sintered samples. Similar finding was revealed during XPS analysis of CuO surface. The deficiency of 10-15% of surface oxygen for CuO nanoparticles was found that explain efficient reduction of CuO nanoparticles at low temperatures. During the first step of its reduction the thin surface layer of metastable Cu_4O_3 was found by HRTEM [1].

Prepared series of CuO samples was studied by DRIFTS using *in situ* reaction cell. For CuO nanoparticles carbonyls Cu^{1+}-CO with vibration frequency ~2100 cm^{-1} were found during CO reduction and under catalytic CO+O_2 conditions at low temperatures, while vibration frequency of Cu^{1+}-CO complexes at the surface of sintered CuO was found to be equal ~2120 cm^{-1}. Such behaviour can be explained by different nature of Cu^{1+}- surface sites for nanosized and bulk particles. Probably, in case of nanoparticles carbonyls Cu^{1+}-CO with vibration frequency ~2100 cm^{-1} can be attributed to Cu_4O_3 oxide layer on CuO surface [1], while Cu_2O/CuO structure can be realized for partially reduced bulk CuO .

On the base of presented work it is proposed that unique electronic/structural properties of Cu_4O_3 surface layers with high oxygen deficiency and low-valence Cu^{1+} sites can provide the formation of O_2 and CO adsorbed species with high reactivity and the implementation of the CO oxidation at low temperatures.

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This work was partially supported by the Russian Foundation for Basic Research (project №14-33-50322) and by the Ministry of Education and Science of the Russian Federation.

STUDYING of the MOBILITY of METHANE in MFI-TYPE ZEOLITES: H-ZSM-5, Ag/H-ZSM-5 and SILICALITE-1 by MEANS of SOLID STATE ^{2}H NMR

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Zeolites are microporous aluminosillicate materials that are widely used as adsorbents and catalysts. One of the most important representatives of this class of materials is ZSM-5 zeolite. Due to its regular structure and acidity ZSM-5 is eidely used for such reaction types as hydrocarbon izomerization, the alcylation of hydrocarbons and ethylene polymerization. Another good example of ZSM-5 catalytic propeties is given by the reaction of methane dehydro-aromatization on a Mo-modified zeolite [1]. This example underline another useful feature of the zeolites - the possibility to vary the catalytic properties by introduction of the different metal ion sites on the internal surface of the zeolites pores.

One of the most challenging problem in hydrocarbon chemistry is the catalytic transformation of methane. Some of these transformations have been performed on metal enhanced zeolites, particularly on In-ZSM-5. However, the mechanism is still debated. One of the reasons it due to the complex molecular diffusion on methane in zeolites porous network: it is well known that molecular mobility has a crucial meaning for the heterogeneous catalysis since it governs transport of the reagents to the catalytic sites. On common acidic zeolites like H-ZSM-5 the translational mobility of methane was studied by quasi-elastic neutron scattering and NMR pulsed field gradient technique at different loadings[2]. However, the influence of different modifications of the zeolites inner surface on molecular diffusion of methane remains unknown.

In this work molecular mobility of methane has been studied as a function of ZSM-5 zeolite’s modifications: Silicalite-1, H-ZSM-5, Ag-modified H-ZSM-5 and Ag-modified H-ZSM-5 in presence of ethylene molecules with loading equal to concentration of Ag ions. The main goal is to show how gradual complication of the structure leads to the changes of the motion mechanism.

Studying of dynamics was performed by means of the solid state ^{2}H NMR technique. By considering T_1, T_2 relaxations of the deuterated methane confined in zeolite, we managed to elucidate the mechanism of the reorientation and the characteristic rates and barriers of the motions.

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INFLUENCE of NICKEL OXIDE ADDITIVES on the PHYSICO-CHEMICAL and CATALYTIC PROPERTIES of Pt/(NiO-TiO$_2$) CATALYSTS in CO OXIDATION

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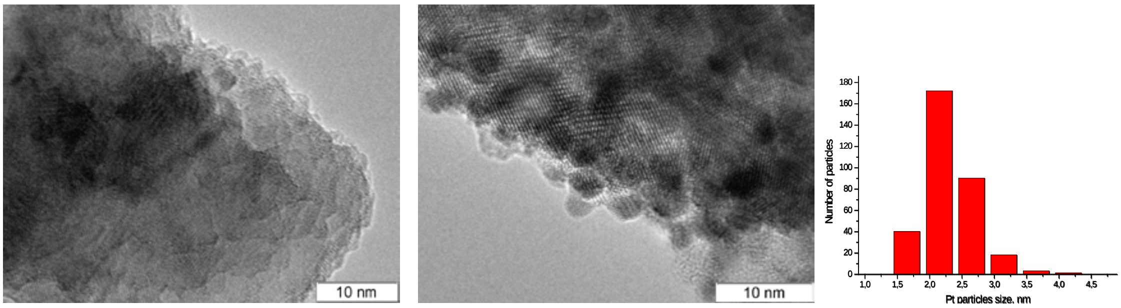
Pt supported on TiO$_2$, modified by transition metal additives, exhibit higher activity in CO oxidation compared to Pt/TiO$_2$. It is due to the strong interaction Pt with support which plays critical role in determening the size and electronic state of platinum particles. In this work we investigated the influence nickel oxide addeitievs on the physico-chemical an catalytic properties of Pt/(NiO-TiO$_2$) catalys in CO oxidation.

The support of NiO-TiO$_2$ was prepared by impregnation of anatase with Ni(NO$_3$)$_2$ solution followed by drying at 110 °C and thermal treatment at 500 °C in air. The obtaned support was impregnated with an appropriated amount of a platinum nitrate solution. The resulting material were dryed at room temperature, than at 110 °C and calcined in air at 500 °C. Catalysts were investigated with HRD, HRTEM, XPS and adsorption methods. Activity measurements in CO oxidation were studied in flow-circulation reactor. The heating rate was 1,7°C/min . The measurements were made with 0.25-0.50 mm grane size. The reaction mixture containing 1 vol % CO, 11 vol % O$_2$, and He balance was fed at a rate of 4.46×10^{-3} mol/min, and the catalyst weight was 0.36 g.

According to XRD data the sample 1% NiO/99% TiO$_2$ is anatase structure. TEM data fig.1(a) showed that the anatase structure is nanocristalline and consists of anatase particles 6-8 nm in size. The crystal cell parametres of anatase phase is not changed. Obviously the structure of support contaning interblock boundaries between anatse crystals were Ni ions are localized. Fig.1(b) demostrated the typical mirostructure of supported Pt/(1% NiO-99% TiO$_2$) catalyst. For example for the catalyst 1% Pt/(1% NiO-99% TiO$_2$) high dispersed Pt particles of 1.5-3.5 nm in size are observed on the catalyst surface (Fig.1(c)).



a b c

Fig. 1 Electron micrograph of the crystal structure of 1% NiO/99% TiO_2 support (500 °C) (a), 1% Pt/(1% NiO-99% TiO_2) catalyst (b) and size distribution of Pt (c).

The catalytic properties of catalysts contaning 0.5-2 wt.% Pt/(1% NiO-99% TiO_2) compare to 1 wt.% Pt/TiO_2 are presented in Fig. 2. Increasing the Pt content from 0.5 to 2% wt. lead to the increasing the catalytic activity. One can see that at thr same Pt content 1% wt. Pt (1% NiO-99% TiO_2) catalysts is much more active than 1% wt. Pt/TiO_2 in CO oxidation.

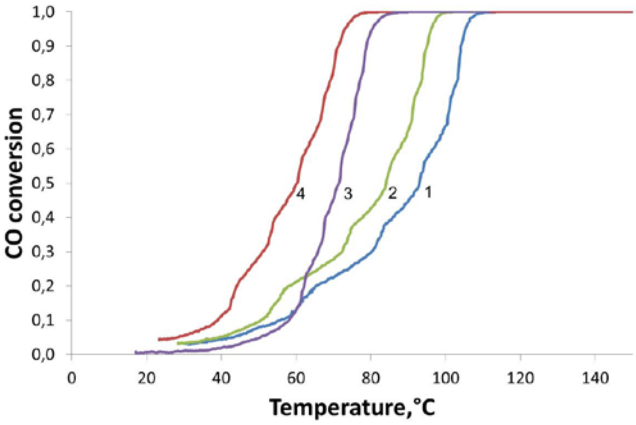


Fig. 2. Catalytic perfomance of Pt/TiO_2 (1) and Pt/(1% NiO-99% TiO_2) catalysts with different Pt content (2-4).

XPS data showed incresing of $Pt^{\delta+}$ electronic state in Pt/(1% NiO-99% TiO_2) catalysts. It is due to the more strong interaction Pt with support in Pt/(1% NiO-99% TiO_2) compare to Pt/TiO_2.

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Cu-SUBSTITUTED ZSM-5 ZEOLITE as CATALYSTS for WET PEROXIDE OXIDATION of RHODAMIN 6G

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Catalytic wet peroxide oxidation (CWPO) is one of the most economical and environment-friendly advanced oxidation processes. It makes a promising technology for the treatment of refractory organic pollutants in industrial wastewaters. Our previous works showed the best catalytic performance of Fe/ZSM-5 among other zeolites (Fe/Y, Fe/USY) in CWPO of Rhodamin 6G dye[1]. Moreover the modification of the Fe/ZSM-5 by Cu cations improves its catalytic properties [2]. Copper-containing zeolites Cu-ZSM-5 prepared by ion-exchange methods showed high efficiency and stability in CWPO of formic acid [3] and phenol [4].

Here, we report our systematic study of ion-exchanged Cu-ZSM-5 catalysts in the CWPO of more complex organic substrate (Rhodamin 6G).

Screening of the catalytic properties of Cu-containing zeolites was performed in CWPO of Rhodamin 6G in semi-batch reactor at folloiwing reaction conditions: 0.1 g L^{-1} R6G, 0.18 M H_2O_2, 1.3 g L^{-1} solid catalysts, pH 2-10, 50ºC. We varied Cu-content (0.3-3 wt. %) and Si/Al ratio (17, 30, 45). Cu-containing zeolites with the atomic ratio Si/Al equal 30 and the content of Cu from 0.5 to 1.5 % appeared to be the most active catalysts. The acceptable stability of catalyst Cu-ZSM-5-30 (0.5% Cu) was demonstrated in 3 cycles of CWPO of model substrate. The leaching of copper from these catalysts during the process does not exceed 2.5 %. Leaching test showed that the activity of Cu-containing zeolites to the CWPO of Rhodamin 6G is accounted for by heterogeneous copper in the composition of the zeolite but not copper ions leached to the solution.

The characterization of fresh and spend catalysts using UV-Vis DR and ESR spectroscopic techniques allowed us to suppose that the high efficiency of Cu-ZSM-5 to redox reactions in aqueous media is provided by nanostructured square-planar clusters of copper oxide localized in the channels of zeolite.

The study of adsoption of Rhodamine 6G and intermediates adsoption UV-Vis DR and ESR spectroscopic techniques on the catalyst in the course of the reaction showed the difference in the reaction mechanizm at different pH value (2-5 and 10). Free radical (Fenton-like) mechanizm was postulated for in the acidic and molecular mechanizm was suggested for the alkaline media.

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Acknowledgements

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Cu/ZSM-5 PREPARATION with CuO_x SPECIES of DIFFERENT STRUCTURE and THERE CATALYTIC PROPERTIES in SCR NO with PROPANE

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One of the most common methods of removing nitric oxide from gaseous emissions is the selective catalytic reduction (SCR) of NO to N_2 with propane, over Cu/ZSM-5 catalysts. Is spite of the extensive investigations of the physicochemical and catalytic properties of Cu/ZSM-5 catalysts for a long time, the optimal characteristics of these catalysts have not been determined. Significant factors in the catalytic properties of Cu/ZSM-5 catalysts are the state of copper ions and their location in the zeolite structure. A promising line of investigation of the Cu/ZSM-5 catalysts in order to improve their catalytic properties is to successively study and optimize the main catalyst formation stages with various copper containing precursors. Here, we report the state of copper in the Cu/ZSM-5 supported catalysts prepared with ammonia solutions of copper nitrate of different structure and the catalytic properties of these catalysts in the SCR of NO with propane.

Cu/ZSM-5 catalysts were prepared by ion exchange of the HZSM-5 with Si/Al =17 with aqueous ammonia solution of copper nitrate with $NH_4OH/Cu = 23$ and 2, which were prepared by dissolving of $Cu(NO_3)_2\ 3H_2O$ (Aldrich) in aqueous ammonia with a preset ammonia concentration. The zeolite was immersed into a solution with a given NH_4OH/Cu ratio and stirred at room temperature for 24 h. The copper concentration in all cases was 10 g/L, the ratio of solution volume to zeolite weight was 10. Catalysts were investigated with UV-Vis (DRS), IR, ESR, H_2-TPR. Activity measurements in SCR of NO with propane were carried out in fixed-bed quartz flow reactor under steady state conditions. Temperature was measured in the 200–500°C range, GHSV was 42000 h^{-1}. The reaction mixture was 340 ppm NO, 0.15 vol % C_3H_8, and Ar as the balance. The NO conversion rates at reaction temperatures of 275 °C were calculated.

It was shown in [1] that at $NH_4OH/Cu = 23$ in aqueous ammonia solutions of copper nitrate tetraammine copper association species axially bonded by hydroxyl groups and a weak exchange interaction between Cu^{2+} ions (CC I) are formed. At $NH_4OH/Cu = 2–3$, Cu^{2+} association yields species with hydroxyl groups in the equatorial plane, water and ammonia molecules in the axial positions, and a strong exchange interaction (CC III). The amount of sorbed copper on zeolite under equilibrium conditions was much larger for CC III than for CC I (3.15 wt % against 1.72 wt. %). Investigation of the distribution of copper in the pore space of zeolite by sorption methods and IR spectroscopy of adsorbed CO demonstrated the location copper species mainly on the surface of mesopores formed by the packing of zeolite nanocrystallites. In the Cu/ZSM-5 sample prepared using CC I, the total copper concentration determined by IR spectroscopy is close to the concentration determined by chemical analysis (97%), in the catalyst obtained using CC III copper concentration determined by IRS is 59% of the concentration determined by chemical analysis. This distinction due to CC III yielding larger clusters in which only part of the copper ions is accessible to CO being chemisorbed [2]. The activity of Cu/ZSM-5 obtained using CC I increase with an increasing copper content from 0.5 to 1.72 wt %. The catalyst with 3.15 wt % Cu/ZSM-5 prepared using the CC III is more active than the best of the sample based on CC I (Tabl. 1). The reaction rate per gram of Cu for the catalysts prepared using CC I changes only slightly as the copper content increased. For the catalyst prepared using CC III, the reaction rate is lower than the W values for the catalysts obtained using CC I [3].

Tabl. 1 Catalytic properties of the Cu/ZSM-5 prepared with CC I and CC III solutions (reaction rates W_m and W were calculated for 275°C)

Cu, wt. %	Type of CC	$T_{X=50\%}$, °C	W_m, 10^{-7} mol NO $g_{cat}^{-1}min^{-1}$	W, 10^{-5} mol NO $g_{Cu}^{-1}min^{-1}$
0.5	CC I	368	2.0	3.9
1.05	CC I	310	3.3	3.6
1.72	CC I	284	6.5	3.8
3.15	CC III	267	9.5	2.9

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PHOTOCATALYTIC HYDROGEN PRODUCTION on $Cd_{1-X}Zn_XS$ and $Cd_{0.4}Zn_{0.6}S/TiO_2$ CATALYSTS under VISIBLE LIGHT

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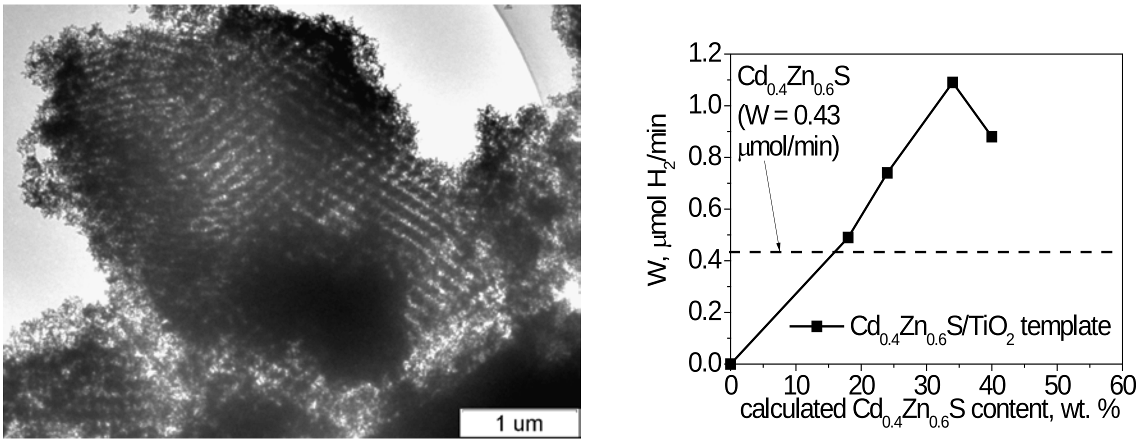
Hydrogen seems to be an attractive alternative to traditional energy sources, but it exists in nature in the form of compounds with other elements. Water is an ideal hydrogen source. One of the most effective ways of water splitting is photocatalysis on semiconductors, but catalytic activity in this process is quite low due to the recombination of photogenerated charge carriers on the semiconductor surface. The addition of sacrificial agents in the system reduces the rate of charge recombination and increases the rate of hydrogen evolution. CdS is considered to be one of the most well-known semiconductor photocatalyst . The photocatalytic properties of CdS could be modified by mixing with wide band gap chalcogenide semiconductors s such as ZnS [1] and by depositing CdS on the mesoporous materials with large surface area such as TiO_2 [2]. Titanium dioxide (TiO_2) is the most popular photocatalyst used in heterogeneous photocatalysis for its excellent properties, such as high stability and low cost. TiO_2 can only respond to UV light because of its wide bandgaps, while $Zn_{1-x}Cu_xS$ can produce H_2 under visible light irradiation.

In this study a series of $Cd_{1-x}Zn_xS$ ($x = 0.2, 0.4, 0.6, 0.8$) photocatalysts were prepared by the coprecipitation method. $Cd_{0.4}Zn_{0.6}S$ catalysts show the highest activities of hydrogen production under visible light irradiation. Further, cadmium and zinc sulfide solid solution $Cd_{0.4}Zn_{0.6}S$ was deposited on the surface of TiO_2 samples with different porous structure. Four samples of titania obtained by the template and temaplate-free synthesis technique and commercial TiO_2 Degussa P25 were used for the synthesis of the composite photocatalysts $Cd_{0.4}Zn_{0.6}S/TiO_2$. The best photocatalytic activity was possessed by $Cd_{0.4}Zn_{0.6}S$ deposited on the mesoporous TiO_2 which was prepared by the template synthesis with polystyrene spheres as a template. This sample has a regular porous structure (Fig. 1a). Fig. 1b shows the dependence of hydrogen evolution rate on the $Cd_{0.4}Zn_{0.6}S$ content in the composite photocatalyst.



a) b)

Fig. 1. The dependence of hydrogen evolution rate on $Cd_{0.4}Zn_{0.6}S$ content in the composite photocatalyst.

Fig. 1b represents that the rate grows with the $Cd_{0.4}Zn_{0.6}S$ content until 40 wt% and then slightly falls at the wt% of cadmium and zinc sulfide solid solution equal to 50%. The sample with the active component content of 40 wt.% possesses the highest activity in thehydrogen production equal to 1308 mmol h^{-1} g^{-1}. This is a quite high value for the noble metal free photocatalysts. An increase in the photocatalytic activity is likely caused by the heterojunction formation between titania and cadmium sulfide nanoparticles; moreover, the regular porous structure of titania can benefit the reaction rate as well.

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ENHANCEMENT of the OZONATION PROCESS of WASTEWATER by USING the ADDITIVES

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Highly polluted wastewaters from the production of styrene and propylene oxide of the enterprise "Nizhnekamskneftekhim" are characterized by a high organic loading (the COD – chemical oxygen demand varies from 30,000 to 450,000 mg O_2/l) and alkalinity (pH ranges from 12 to 13). The rate of oil-contamination formation in aquatic ecosystems is much higher than the rate of their natural biodegradation.

In this work we studied the effect of additives on the ozonation process. Each experiment was performed for 60 minutes, wherein $MnSO_4$ and H_2O_2 at different concentrations were used as additives. The COD conversion of the non-catalytic ozonation was 50.2 %, while the purification degree in the presence of additives was much higher. Using 0.1 wt. % of $MnSO_4$ allowed the cleaning efficiency to be reached by 80.1%. The high efficiency was obtained due to the fact that in the presence of manganese, ozone decomposes very rapidly in aqueous solutions and the hydroxyl radical ($^{\bullet}OH$) is formed [1-5].

The best result of ozonization process (90.5%) was observed when using 0.075 wt. % of H_2O_2. This can be explained that the use of H_2O_2 as a catalyst in the ozonation process increases the amount of formed hydroxyl radicals [6]. The removal rate of 1-phenyl ethanol was 99 %, whereas ethylbenzene, acetophenone and alkylphenols were completely removed from the wastewater after 60 minutes of ozonation. The COD decreased to 3420 mg O_2/l, which allowed the treated water to be suitable for final treatment by biological method.

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DEEP OXIDATION of PROPANE-BUTANE MIXTURE on Pt-WO_3/Al_2O_3/METAL GAUZE CATALYST

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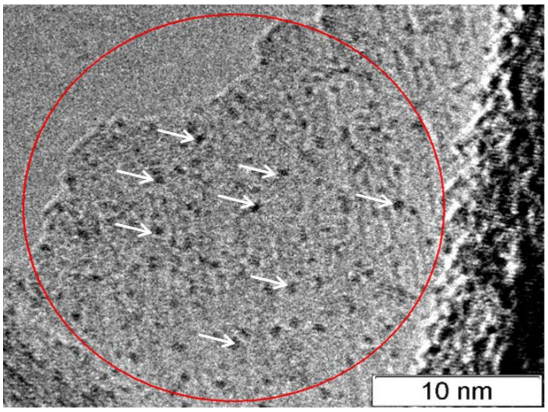
Unburned or unreacted hydrocarbons are constituent of exhaust gases of many technological processes and harmful for health and environmental. Catalytic oxidation of hydrocarbons to CO_2 and H_2O could become the effective way to solve this problem. Metal gauze catalysts are promising for designing the catalytic reactors. Such catalysts possess excellent heat- and mass-transfer characteristics. Metal gauzes can be used to create structures with a higher surface area per unit volume and a lower heat capacity as compared with honeycomb structures, thus providing a 20–40-fold increase in the mass transfer efficiency.

Platinum deposited on alumina was used as a catalyst. A heat-resistant aluminum-containing steel gauze was used as the catalyst support. The alumina layer was obtained using the Bayer process (precipitation of aluminum hydroxide from sodium aluminate solutions). Platinum and tungsten were deposited on alumina by incipient wetness impregnation from solutions of precursors. The efficiency of catalysts were measured for reactors with a length of 45 mm and a diameter of 14 mm inside of which circle metal gauze patterns of catalyst were packed. A honeycomb catalyst produced from the heat-resistant steel was tested as reference.

TEM data show that size of Pt particles of fresh catalyst is ca. 1-2 nanometers. Temperature increase results in strong sintering of the metal particles. Average size becomes 50-100 nanometers at 850 ^{O}C. Particles of WO_3 are highly dispersed and located on the alumina (Fig. 1). The addition of tungsten decreases the temperature of 50 (T_{50}) present of hydrocarbons conversion significantly for reduced and non-reduced catalysts (Fig. 2, compare lines 1 and 2, lines 3 and 4). This effect is connected with the increasing of acidity of alumina surface when tungsten is added [1]. Pre-reduction of Pt/Al_2O_3 и Pt-WO_3/Al_2O_3 catalysts by hydrogen decreases T_{50} for both cases as well because reduced Pt is more active in oxidation of hydrocarbons [2].



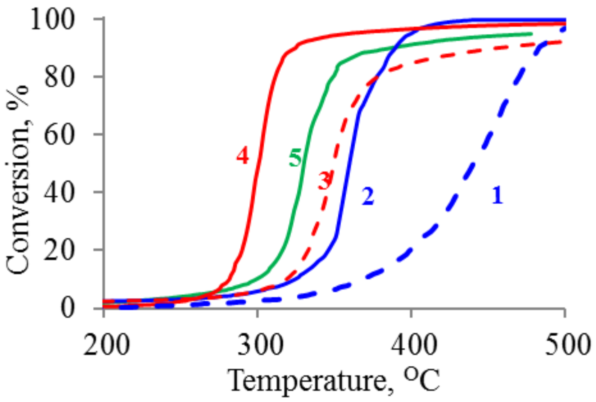


Fig. 1 (left). TEM image of WO_3 particles on the surface of Al_2O_3. Fig. 2 (right). Hydrocarbons conversion on the catalysts: 1,2 – Pt/Al_2O_3; 3,4,5 – $Pt\text{-}WO_3/Al_2O_3$; 1,3 – non-reduced catalysts; 2,4,5 – catalysts after reduction by hydrogen; 1-4 – catalysts on metal gauze support; 5 – catalysts on honeycomb support; 1-5 – Pt content 0,19 g/l.

$Pt\text{-}WO_3/Al_2O_3$ catalyst on the metal gauze has better light-off characteristic than on the honeycomb catalyst (lines 4, 5 accordingly, Fig. 2). This is due the fact that the turbulent gas flow is formed and maintained inside the gauze structure. While laminar flow is established in the honeycomb structure. As consequence the process of mass exchange is more effective inside the metal gauze structure then inside the honeycomb structure [3]. A catalyst on metal gauze structure has potential for creation catalytic reactor and practical using.

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GETTING EFFECTIVE METHYLENEBIS PHENOLIC STABILIZERS USING CATION EXCHANGE RESINS

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The most essential contribution to process of aging of polymers is made by the reactions proceeding under the influence of oxygen and the increased temperatures. For delay of process of thermooxidizing aging enter antioxidants into polymers. As antioxidants the increasing value is gained by the replaced phenolic connections [1]. The high stabilizing ability the metilenbisfenol having in situation 2 and 6 in relation to hydroxyl group alkilny deputies possess. The industrial method of receiving metilenbisfenol of such structure consists in reaction of di - the replaced phenols with formaldehyde in the conditions of a homogeneous catalysis mineral and organic acids [2]. Such technology demands inclusion in the technological scheme of production of a stage of washing and neutralization of the catalyst. It leads to formation of a large number of water and organic waste. Besides, use of the formaldehyde which is let out in the form of 36% water solution considerably increases volumes of water and organic sewage.

Objective of this research is creation of a way of receiving the metilenbisfenoly stabilizer on the basis of 2,6-di-tert-butylphenol and the waterless predecessor of formaldehyde (dioksolane) who in the sour environment breaks up with formation of formaldehyde with use of heterogeneous catalysts.

During work problems of optimization of conditions of interaction of 2,6-di-tert-butylphenol with with dioxolane and trioxane were solved. The ratio of reagents, reaction time, temperature varied. Used as the catalyst cation exchange resin Amberlist 36Wet, Resinex KP 533028, Lewatit K 2420 pitches were used.

It is revealed that interaction 2,6-DTBF and a dioxolane with the maximum exit proceeds at a temperature of 100-105 °C at a ratio of reagents 2,6-DTBF: dioxolane = 1:1,5 (mol), respectively, lasting reaction 3,5 hour.

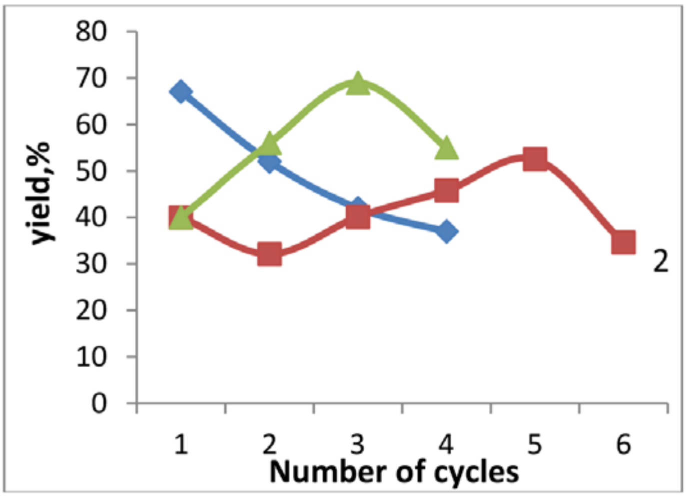

Fig. 1 Effect of the number of cycles of use of the catalyst (3.5 hour reaction time, temperature 105 C, the catalyst quantity 10% by weight.) To yield 4,4'-methylene-bis (2,6-di-tertbutylphenol)

1 – Amberlist 36Wet
2 – Resinex KP 533028
3 – Lewatit K 2420

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INFLUENCE of OXYGEN BULK DIFFUSION on OSCILLATORY REGIMES in METHANE OXIDATION over NICKEL: MATHEMATICAL MODELLING

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This study is devoted to theoretical analysis of the influence of the diffusion of oxygen atoms in subsurface layers of nickel on the self-sustained rate oscillations in the catalytic oxidation of methane. The microkinetic scheme for the oxidation of methane over nickel was published elsewhere [1]. Parameters of elementary reactions, such as enthalpies and activation energies, were determined using a phenomenological approach suggested by Shustorovich [2]. Pre-exponential factors of elementary steps were evaluated in the framework of the transition state theory [3]. The diffusion coefficients of oxygen atoms in nickel were determined on the basis of experimental data. The mathematical model of the reaction consists of a system of ordinary differential equations and takes into account concentrations of surface intermediates, an oxygen concentration in the subsurface layers, and the heat balance.

The model of the catalytic oxidation of methane over nickel was amended with a step of the diffusion of oxygen atoms from the nickel surface into the subsurface layers. It allows us to study the influence of this step on the characteristics of the oscillatory behavior. In full agreement with previous study [1], the model without the oxygen diffusion under certain parameters has oscillatory solution. In this case the oscillations starts without any delay. In contrast in the model with the oxygen diffusion we found a long induction period before arising the self-sustained oscillations. Similar effect was observed experimentally. Also we found that the concentration of oxygen in the subsurface layers of nickel oscillates synchronously with the concentrations of reaction products in the gas phase.

The addition of the oxygen diffusion into the model leads to the appearance of an induction period before the self-sustained rate oscillations. The concentration of oxygen in the subsurface layers of nickel oscillates synchronously with the concentrations of reaction products in the gas phase.

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POSTER PRESENTATIONS

STRUCTURE and PROPERTIES of CATALYSTS CONTANING Mo

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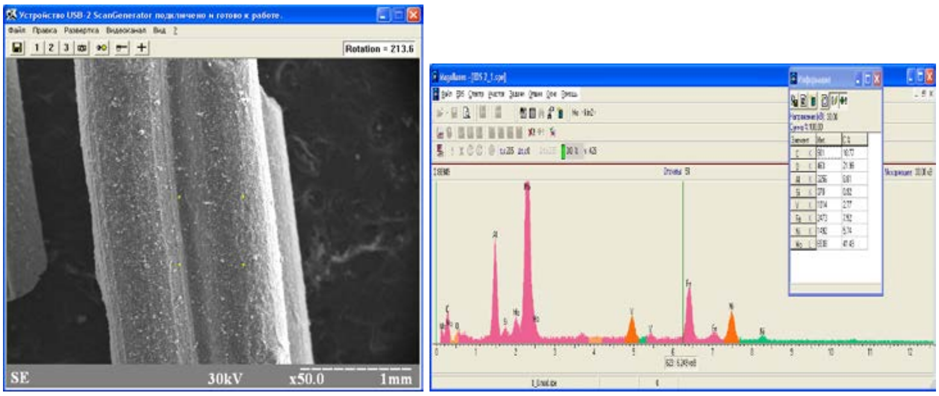
Nowadays catalysts containing Mo are widely used in chemical industry, for example, as hydrotreating catalysts. Every year the volume of their use increases. Compounds of molybdenum are rather expensive and therefore the problem of extraction of molybdenum from the worked-out catalysts is particularly actual. In this work the structure and properties of the separated molybdencontaining catalysts are studied for the subsequent consideration of them for utilization technology.

The structure of these catalysts is given in the table. The element analysis was carried out at Federal State Unitary Enterprise Tsniigeolnerud by method of the scanning electronic microscopy (SEM), the microprobe element analysis. Tests have been finished by making an image with higher magnification (47-550 times) – only 28 pictures and are presented in figure. Surfaces of prepared samples exhibit heterogeneity at the level of 10-20 microns and linear longitudinal grooves. Chips of samples are characterized by a rakovisty surface, with numerous cavities of diameter 10 - 50 microns. Structure is cryptocrystalline with size of distinguishable grains of 5 microns [1]. Element composition of catalysts is in the table.

Table 1. Element composition of catalysts

Elements *%*	***Cat 1***	***Cat 2***	***Cat 3***
C	3.7	9.8	10.6
O	33.2	24.5	32.1
Al	27.5	13.6	20.1
Si	–	0.9	1.9
V	–	2.9	–
Fe	–	10.9	24.6
Ni	–	4.3	2.5
Co	3.8	–	1.8
Mo	31.8	39	35.8
Ca	–	0.87	–



Устройство USB-2 ScanGenerator подключено и готово к работе.

Figure 1. The Range of the element analysis on the Market place of cat. №1, SW. 47

Power dispersive ranges reflect the maintenance of elements both on the area of a preparation, and in certain sites. higher content of molybdenum on chips is detected. The spectral line of carbon is registered for sample prepared with a carbon dusting. Average concentrations of the defined elements (percentage) are presented in the table [2]. The similar analysis was carried out for the catalyst (the modified GO-70), having the following chemical composition, %:

- molybdenum oxide (MoO_3) - 15,0-18,0;
- cobalt oxide (CoO) - 4,0 - 5,0;
- sodium oxide (Na_2O) no more than 0.08;
- iron oxide (Fe_2O_3) no more than 0.08;
- aluminum oxide (Al_2O_3) all the rest

Physical properties of the catalyst:

- diameter of granules, mm 1.5-2.5;
- bulk density, kg/m^3 670-810;
- durability index not less than 2.1;
- specific surface, m^2/g 250

These catalysts contain about 30-40% of Mo. The technological scheme is developed for utilization of any Mo containing catalysts with release of molybdenum oxides .

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THE NEW METHODS of OBTAINING and ACTIVATION ORGANONICKEL CATALYSTS for OLIGOMERIZATION and POLYMERIZATION of ETHYLENE

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This report is devoted to the development of new types of catalytic systems based on organonickel σ-complexes, which can be used as catalysts in the production technologies of polymeric and oligomeric materials [1]. The main advantages of development lies in the fact that the waste of many industries, for example, hydrocarbon halides may be used as raw material. Generation of organonickel complexes is carried out halides exactly. Catalysts based on σ-nickel complexes are formed in a "green chemistry", so this leads to a reduction of anthropogenic impact on the environment of industrial areas. The combination methods of metalocomplex catalysis and organic electrosynthesis attracts more and more attention because of the high selectivity and efficiency of this approach in the process of obtaining various chemical compounds with bonds of carbon-carbon and carbon-element. The mild process conditions, single-stage and cyclic regeneration of the catalyst, and the use of a convenient and relatively inexpensive type of energy as electricity is an advantage of electrochemical methods. The aim of this report lies in develop environmentally safe methods of obtaining organonicel σ-complexes, research of their properties and the catalytic activity of the processes of polymerization and oligomerization of ethylene.We have developed a new high efficient and environmentally safe methods of obtaining and stabilization of organonickel σ-complexes, which are key intermediates in the catalytic oligomerization of ethylene. The developed process includes the use of an unseparated (without diaphragm) electrolyzer, which is provided with an electrochemically soluble nickel anode and proceeds in a "green chemistry" in the complete absence of side products. The obtained organonicel σ-complexes showed high activity in the processes of polymerization and oligomerization of ethylene. It leads to the formation linear alpha-olefins, which are demand in modern industry.

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SOLVENT INFLUENCE on DIALKYLPHOPHITES' INTERACTION with HEXACARBONYLMETALS(0)

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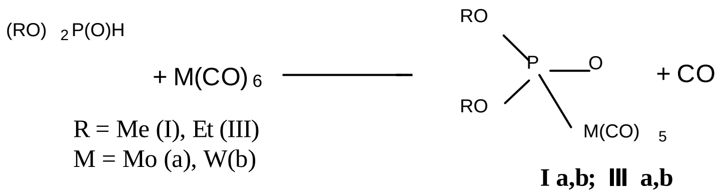
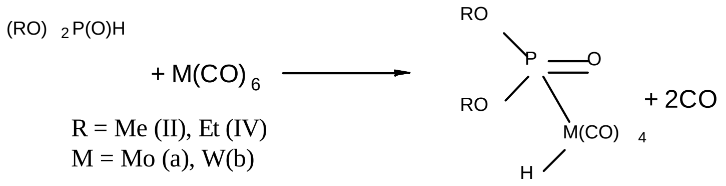
The products of interaction of transition metals’ complexes with dialkylphosphites can act as the reactive intermediates of catalytic phosphonate synthesis.

In order for getting the necessary information needed for the guided design of olefines hydrophosphorylation catalysed by organometallic and coordination compounds we have studied the reactions of dialkylphosphites with tungsten and molybdenum(0) hexacarbonyl complexes. The study revealed that the product structure depends on the reaction media.



I a,b; III a,b

Thus, the reaction in the benzene solution containing 5-10% dialkylphoshite allows to obtain phosphaorganometallic compounds having the hydroxy-tautomeric form of the H-phosphonate in the metal’s coordination sphere linked with the molybdenum or tungsten via the P–M bond. The structure of the products obtained was confirmed by the means of NMR атв IR studies.



II a, b, IV a, b

Quite different results were obtained when we have studied the reactions of $W(CO)_6$ and $Mo(CO)_6$ with dialkylphosphites in pure H-phosphonate.

In this case the reaction products are the phosphahydride derivatives of tungsten and molybden, also according with IR and NMR data. The experimental results obtained are in good accordance with quantum-chemical modelling of the reactions studied (B3LYP/LANL2DZ).

ENERGY and RESOURCE-SAVING METHOD of PRODUCING MOLYBDENUM CATALYST for the EPOXIDATION of OLEFINS

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Complex molybdenum catalyst (KMC) is the basis of the production of propylene oxide hydroperoxide epoxidation. It is prepared by dissolving metal molybdenum powder in a mixture of ethylbenzene hydroperoxide (GPEB) and ethanol. This catalyst is quite active in the process of epoxidation of propylene. However, it has a number of disadvantages. One of the main drawbacks is a significant flow of ethylbenzene hydroperoxide required to transfer metallic molybdenum in a soluble state.

The purpose of this study was to develop a method for producing molybdenum epoxidation catalyst reduce energy demands and consumption of ethylbenzene hydroperoxide in the preparation of the catalyst epoxidation of propylene.

Ethylbenzene hydroperoxide obtained by oxidation of ethylbenzene with oxygen in the cascade of airlift type reactors. From the last reactor is withdrawn 10% solution of GPEB in ethylbenzene (oxidate), which is further concentrated to 25-29% hydroperoxide content.

Concentrated oxidate is used in two ways: the synthesis of the catalyst and the epoxidation of propylene. In order to reduce the cost of ethylbenzene hydroperoxide synthesis catalyst we investigated the possibility of using oxidate with 10% hydroperoxide content.

The patent literature contains many examples of the use of hydrogen peroxide for the synthesis of molybdenum epoxidation catalyst.

Therefore, we replaced stage of strengthening oxidate by distillation introducing hydrogen peroxide in the composition of catalyst preparation.

In experiments we use 30% hydrogen peroxide. Table 1 shows composition of preparation of a commercial catalyst and proposed catalyst.

Table 1. Composition of epoxidation catalyst

The composition of the reagents for the synthesis of industrial catalyst	The composition of reagents for the synthesis of the developed catalyst
1. Strengthening the oxidate (26% GPEB)	1. ethylbenzene oxidate (10% GPEB)
2. Ethanol	2. Ethanol
3. Molybdenum powder	3. Hydrogen peroxide (30% solution)
	4. Molybdenum powder

The study will identify the amount of hydrogen peroxide required for the preparation of the catalyst for a new recipe and the optimal concentration of dissolved molybdenum in the catalyst.

Testing of activity of the molybdenum catalyst, obtained in the hydroperoxide epoxidation reaction of kinetic analogue propylene -octene-1 showed that this catalyst provides a comparable with commercial catalyst results in the epoxidation of 1-octene.

Thus, the molybdenum catalyst is not inferior in the catalytic activity of Industrial CMC can be obtained from the ethylbenzene oxidate GPEB containing 10% with the addition of hydrogen peroxide. It reduces the consumption of thermal energy to strengthen that part of oxidate, which is the synthesis of CMC. Also significantly reduces the consumption of hydroperoxide to obtain a catalyst.

PP-5

APPLICATION of SODIUM OCTACARBOXYLATE RESORCINARENES in SYNTHESIS of SILVER NANOPARTICLES

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1 Introduction

Metallic nanoparticles (Au, Ag, Pd, Pt) show unique optical, electric and catalytic properties [1,2] and, therefore, are of a great interest for researchers. Silver nanoparticles have been applied in electronics, optoelectronic [3] and in medicine [4]. We have used amphiphilic derivatives of resorcinarenes with decyle ($C_{10}H_{19}$-CA), decynyl ($C_{10}H_{21}$-CA), methyl (CH_3-CA) and ferrocene (Fc-CA) groups at the lower rim as stabilizers in the synthesis of the monodisperse silver nanoparticles (AgNPs). The resorcinarenes prevent the aggregation of AgNPs and influence the size and shape of the silver nanoparticles produced.

2 Experimental/methodology

Stable colloidal silver nanoparticles have been obtained in aqueous media using common methods in the presence of $C_{10}H_{19}$-CA, $C_{10}H_{21}$-CA, CH_3-CA as stabilizers and sodium borohydride as a reducing agent. In the case of Fc-CA, the reducing agent was not used, the ferrocene groups act as reducing agents.

AgNP were characterized by the data of UV-vis and IR spectroscopies, static and dynamic light scattering (SLS and DLS), atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and thermogravimetry (TG).

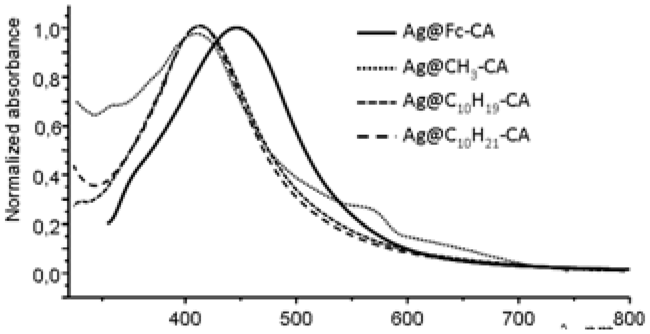

Fig.1. UV-Vis spectra of hybrid nanoparicles Ag@Fc-CA, Ag@$C_{10}H_{19}$-CA, Ag@$C_{10}H_{21}$-CA and Ag@CH3-CA.

3 Results and discussion

The influence of the length of the hydrophobic tail of the size and shape of AgNPs is investigated. The silver particles of different sizes are formed using of methyl-resorcinarene CH_3-CA. while the assembled resorcinarenes $(C_{10}H_{19}\text{-CA})_n$ and $(C_{10}H_{21}\text{-CA})_n$ produce monodispersed AgNPs of about

30 nm. The average size of hybrid systems Ag@$C_{10}H_{21}$-CA and Ag@$C_{10}H_{19}$-CA is about 85 nm, and the hydrodynamic diameter is about 90 nm. Hybrid nanosystems stable in water for a long time, and turbidity of the solutions is observed only after several months of storage.

In the synthesis of silver nanoparticles was also used ferrocene-resorcinarene. It acts not only as a template and stabilizer, but also as a reductant. Formation of Ag(0) is due to the reduction of silver ions ferrocene groups resorcinarene by followed the organization in hybrid nanoparticles Ag@Fc-CA.

In the case of Ag@Fc-CA the average size of AgNPs is slightly larger and it is about 35-40 nm. The diameter of the hybrid nanoparticle Ag@Fc-CA is slightly smaller than Ag@$C_{10}H_{19}$-CA and Ag@$C_{10}H_{21}$-CA. At the data of AFM and SEM mean diameter of Ag@Fc-CA is about 60 nm, and the hydrodynamic diameter is about 80 nm. Evidently, the ferrocene-resorcinarene forms thinner organic cover in Ag@Fc-CA, as compared with the Ag@$C_{10}H_{19}$-CA and Ag@$C_{10}H_{21}$-CA.

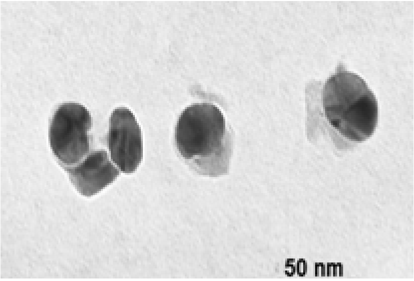

Fig. 2. TEM image of Ag@Fc-CA.

Catalytic properties of the hybride nanosystems Ag@CA were studied in the common used reaction of reduction of p-nitrophenol with sodium borohydride in water. The results shows that sodium borohydride does not reduce nitrophenol in pure water. The addition of 40 nanomole of Ag@CA rapidly accelerates the reaction, and it is finished in a few minutes. The highest catalytic activity is observed for Ag@$C_{10}H_{19}$-CA. The lowest activity is detected for Ag@Fc-CA due to the lower surface area of metal nanoparticles or formation of dense packing of Fc-Ca molecules on the silver surface.

The synthesis and characteristics of Ag@CA will be discussed in the presentation.

Table 1. Observed rate constants and normalized rate constant of reduction reaction p-nitrophenol using hybrid nanoparticles Ag@CA.*

Catalyst	Rate constants, k, s^{-1}	Normalized rate constant, k_{cat}, Ag-$mol^{-1}s^{-1}$
Ag@Fc-CA,	0,0029	72500
Ag@$C_{10}H_{21}$-CA	0,0045	112500
Ag@$C_{19}H_{19}$-CA	0,0128	320000

*n(Ag@CA) = 40 × 10^{-9} M, C(p-nitrophenol) = 0,113 mM, C($NaBH_4$) = 5 mM, H_2O, 25 °C.

4 Conclusions

Thus, amphiphilic resorcinarenes with carboxylic groups on the upper rim were used as templates for the creation of silver-containing hybrid organic-inorganic nanoparticles Ag@CA. The hybrid nanoparticles exhibit high catalytic activity, which was demonstrated by the reduction reaction of nitrophenol in water.

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SYNTHESIS and APPLICATION of ARYLOXYISOBUTYLALUMINUM COMPOUNDS as EFFECTIVE ACTIVATORS of METALLOCENE COMPLEXES in OLEFIN POLYMERIZATION

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The metallocene-based catalytic systems are effective catalysts for homo- and copolymerization of olefins. The most common and effective activator is methylalumoxane (MAO). However, the disadvantages of MAO associated with high cost at the necessity of high molar excess to metallocene, uncertainty of MAO composition and activating species structure, as well as variability of activating ability inder storage set the actual task of creating of new low-cost and effective activators of metallocene catalyst. In the works [1-4], it was found that higher alumoxanes and aluminum trialkyls modified with phenols bearing bulky and electron withdrawing substituents may work as effective activators. Such activators provide greater activating ability than unmodified analogs and show high chemical stability [5].

Here we report the new class of effective activators. We have synthesised the set of isobutylaluminium aryloxides with tert-butyl group in the 2,4 and 6 positions of aryloxy group. It was shown that such compounds are very effective activators of metallocenes in homo- and copolymerization of ethylene and propylene.

The hydrolysis of diisobutylaluminum aryloxides has been studied. It was found that hydrolysis proceeds not on Al–C bonds of the compounds but selectively on Al-OAr bond leading to formation of phenols, isobutane and polyisobutylalumoxane. It was shown that only trace amount of aryloxyisobutylalumoxanes are formed in the course of hydrolysis.

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THE STRUCTURE of Mn-La MONOLITHIC CATALYSTS SYNTHESIZED by the “SOLUTION COMBUSTION” METHOD

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Properties of the fuel combustion catalysts are determined mostly by the structure of their supports and particle size of the active component. High dispersion of the active component is obtained using unconventional methods, in particular, the surface self-propagating thermal synthesis (SSTS) [1, 2] or the so-called “solution combustion” (SC) technique [3]. The essence of SC is that the exothermic reactions of a mixture of fuel additive and precursors of the active component with air oxygen are carried out directly on the surface of supports having different properties and geometric shape.

The structural, textural, morphological and redox properties of the Mn-La catalysts with monolithic aluminosilicate ceramic supports, which were synthesized by “solution combustion” and conventional incipient wetness impregnation were investigated. The effect exerted by the synthesis method on the catalyst activity in the deep oxidation of butane was elucidated.

The XRD study demonstrated that, irrespective of the synthesis method, the diffraction patterns of the catalysts are characterized by the phase of support and amorphous state of the active components. According to HRTEM, the active component of all the tested catalysts is represented by the compound of variable composition $Mn_aLa_bAl_cSi_dO_x$. Particles of the active component with different depths of penetration into support matrix were found in subsurface layers of the support (Fig. 1). The “solution combustion” method was found to facilitate a deeper penetration and stabilization of the particles (Fig.1 b, c). As shown by H_2-TPR, the sample synthesized by conventional method contains a mixture of highly dispersed MnO_2 and Mn_3O_4 phases, which strongly interact with the support, and the interaction phase $MnLaO_3$. The TPR curves of the catalysts synthesized by “solution combustion” have the peaks of Mn_3O_4 and $MnLaO_3$ reduction, the amount of Mn_3O_4 phase being much greater as compared to the catalyst prepared by conventional method. The catalysts synthesized by “solution combustion” are more active in the deep oxidation of butane.

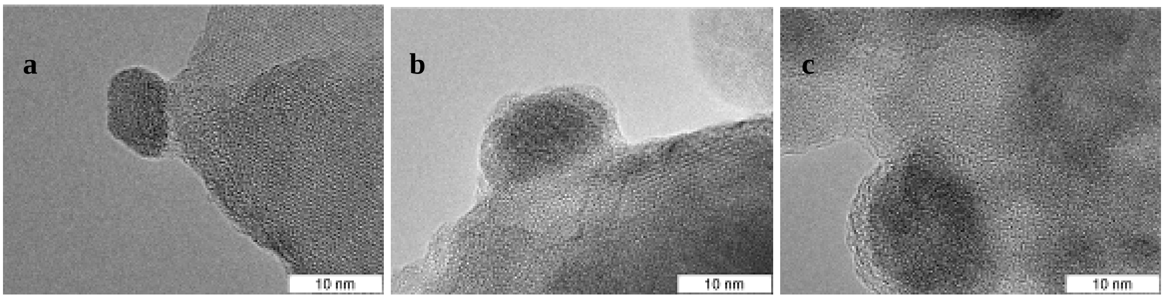

Fig. 1. TEM images of the active component particles in subsurface layers of the support: a – (MnO_2+La_2O_3)/AlSi, b – (MnO_2+La_2O_3)/AlSi-gl, c – (MnO_2+La_2O_3)/AlSi-5gl

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RESEARCH and DESIGN of HZSM -5 ZEOLITECONTAINING CATALYST on Al - PILLARED MONTMORILLONITE for VACUUM GAS OIL CRACKING

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Catalytic cracking is a major process for high oil refining and production of highoctane gasoline. As the active components of catalysts in processes of cracking the petroleum feedstock weighted widely used type zeolites ZSM-5, providing a high gasoline yield and thermostability of certain catalyst composition in the matrices.

This work is devoted to the development and research of HZSM-5 catalyst in a matrix of aluminum pillared montmorillonite for cracking of weighted vacuum gas oil. Catalytic cracking experiments were carried out in a laboratory setup with a fixed catalyst bed. The catalysts were tested before and after steam treating for cracking of Shymkent refinery "PetroKazakhstan Oil Products" vacuum gas oil with the end of boiling point 610^0C.

For the catalyst preparation we used zeolite ZSM-5 (15%) with a ratio SiO_2 / Al_2O_3=29 and Al-pillared natural montmorillonite in Na-form. The optimum concentration pillarization agent equal to 5 mmol Al^{3+} / g NaMM was determined in advance. The catalyst was prepared by mixing aqueous suspensions of zeolite and AlNaMM, molded, dried and calcined.

The resulting catalysts were investigated by BET, XRD, TPD of ammonia. The reaction products were analyzed by chromatography. According to the XRD basal reflex catalyst equal to 14,9Å, higher than that for non pillared NaMM (14.0Å), which testifies the expansion layers of AlNaMM after the introduction of the zeolite.

It has been shown that steam treatment of HZSM- 5- containing catalyst leads to a reduction of specific surface area from 146.8 to 30.6 m^2 / g, pores volume and number of mesopores from 90.8 to 87.5%. The catalysts activity somewhat increases. For example, at 500 and 550^0C gasoline yields (boiling point beginning-205^0 S) on samples without steam treatment (s.t.) are 21.0 and 21.6%, light gas oils-42.2 and 40.8%, gases- 7.6 and 16.3 %. After s/t at 550^0C gasoline yield increases to 27.5%, light gas oil to 45.3% at 500^0C. The process is accompanied by considerable formation of gases, especially noticeable after s/t (20.2 -24.4%). The assumption was made about the influence of catalyst acidity on the formation of gases.

The acidity of the catalyst is defined before and after steam treating. It is shown that the original Al (5,0) NaMM + HZSM catalyst has high acidity equal to 274.0 mmol NH_3 / g. This 28% of a.s. accounted for the strong a.s. and 32% for the middle a.s. Steam treatment did not significantly change the total acidity -266.0 mmol NH_3/g and leads to a significant increase in the number of strong a.s. (53.2%). Thus the formation of gases in the cracking VG in the presence of a HZSM - zeolite determined by large total acidity and by high strengths acid sites.

Activation energies of ammonia desorption for two maxima termodersorbtion curves (218 and 444^0C) were calculated after s/t as described in [1]. The first maximum corresponds E_{des}= 130 kJ / mol, the second maximum-190.4 kJ / mol, which corresponds to the presence of middle and strong a.s. at these temperatures. The presence of such strong a.s leads apparently to the localization of adsorbed molecules near the strong acid sites, difficulty of hydrogen transfer and as a consequence – aromatization of the cracked raw. In the composition of the cracking products was found aromatic hydrocarbons (39-22,8%) before and after steam treatment. The content of isoparaffins was 36.5 and 22.8%.

Constant the catalyst activity after s/t indicates a high thermal stability of catalyst in a matrix of aluminum pillared NaMM. Easiness of preparation of the catalyst, high yields of light gas oil, the yields of light products and high conversion of VG allow us to consider the composite as a component of catalyst cracking of vacuum gas oil. The presence in gasoline of a large amount of isomers makes it an attractive component of commercial gasoline. The high value of the cetane number of light gas oil (63 units) suggests the possibility of using the resulting product as a component of diesel fuel.

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EFFECT of LIGAND OF CATALYST on the DECAY of CUMENE HYDROPEROXIDE

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Liquid-phase oxidation process of alkyl aromatics considered the most promising for the synthesis of hydroperoxides in present time. Compounds of transition and non-transition metals have a catalyzing effect on the stage of degenerate chain branching in the oxidation of hydrocarbons. The catalytic activities of these compounds is determined by their ability to co-ordinate and activate the hydroperoxide [1].

The aim of this work is to study the influence of the ligand environment of the metal to its catalytic activity on the example of calcium 2-ethylhexanoate ($Ca(EG)_2$) and calcium naphthenate ($Ca (Nf)_2$) in the decomposition reaction of cumene hydroperoxide (CHP) in the environment of chlorobenzene.

Laws of catalytic decomposition of CHP studied by ampoule method under a nitrogen atmosphere in the temperature range 120-130°C, $[CHP]_0 = 0 \div 1.5$ mol/l, $[CaL_2]_0 = 0.5 \div 7 \times 10^{-3}$ mol/l. In the result of researches were identified following regularities:

1. Introduction $Ca(EG)_2$ causes a noticeable decomposition hydroperoxide. The decay rate depends linearly on the concentration of the catalyst, that indicating the first order reaction.

2. Relation between the decomposition rate and the concentration of hydroperoxide is linear only up to a concentration of 1×10^{-3} mol/l. Further increases in the catalyst concentration leads to slight increase cleavage rate of the hydroperoxide. Calcium naphthenate has low catalytic activity because at concentrations more than 1×10^{-3} mol/l of alkali metal naphthenates in solution is strongly associated and exist in the form of colloidal solutions[2,3]. Prior to this concentration of activity of the two catalysts are practically identical, indicating the absence influence of ligand on the decomposition of cumene hydroperoxide.

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CATALYTIC PROPERTIES of CATIONIC SURFACTANTS

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Cationic surfactants find diverse application in solving scientific and practical problems, used in various branches of industry, medicine and agriculture. They have strong surface and aggregation properties have a significant influence on the mechanism and the rate of chemical processes. The aim of the present work was to identify the relationship between the aggregation behavior and catalytic activity in the process of nucleophilic substitution of cationic surfactants containing aromatic fragment in the molecule structure. We used a number of physico-chemical methods of research: tensiometry, conductivity, dynamic light scattering, chemical kinetics. The critical micellization concentration (CMC) of Miramistin an order of magnitude higher than that of Benzo-16-bromine (1.4*10-3 and 5*10-4, respectively), probably this is based on the binding of protivoionov in solution and due to the length of the "tail". Hence, Miramistin more complicated forms micelles. It was further revealed that the surface potential of Benzo-16-bromine higher than that of Miramistin. This is reflected in the catalytic activity of the investigated surfactants: the maximum effect in the process of alkaline hydrolysis of esters has a cationic surfactant - Benzo-16-bromine.

Acknowledgements

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DECOMPOSITION OF CUMENE HYDROPEROXIDE under the ACTION of MAGNESIUM and CALCIUM 2-ETHYLHEXANOATES

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One of the ways to improve the oxidation process of hydrocarbons by molecular oxygen is a selection of new efficient catalysts. The most promising is the use of homogeneous oxidation catalysts and, particularly, the compounds of transition metals. The purpose of this research is the determination of the catalytic activity of calcium and magnesium compounds in the liquid-phase oxidation processes of alkylaromatic hydrocarbons with oxygen. It was studied the decomposition of cumene hydroperoxide (CHP), in chlorobenzene in the presence of calcium 2-ethylhexanoate and magnesium 2-ethylhexanoate. Laws of catalytic decomposition of cumene hydroperoxide studied by ampoule method under a nitrogen atmosphere in the temperature range 120-130 °C, $[CHP]_0 = 0 - 1.5$ mol/l, $[Ca\ (EH)_2]_0 = 0 – 5*10^{-3}$ mol/l, $[Mg\ (EH)_2]_0 = 0 – 5*10^{-3}$ mol/l. CHP concentration was determined by iodometric method. It was found that the organic magnesium and calcium salts initiate decay of alkyl aromatic hydroperoxides. Kinetically proved that the decay is preceded by formation of intermediate activated complex hydroperoxide-catalyst. Kinetic parameters of gross-decay of the complex were determined by Lineweaver-Burke's method [1].

The rate of decomposition is described by the Michaelis-Menten equation. Investigated salts depending on the catalytic activity are arranged in the following sequence: $Mg(ЭГ)_2 > Ca(ЭГ)_2$.

Thereby, compounds of transition metals initiate decomposition of hydroperoxides, nature of the metal affects the catalytic activity of the salts.

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ETHYLBENZENE HYDROPEROXIDE DECOMPOSITION in the PRESENCE of VANADYL ACETYLACETONATE

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It is known that hydroperoxides under the influence of catalyst, they decompose with production of radicals and by that they realize degenerated branching of the chains. The ways of hydroperoxide decomposition usually determine velocity and selectivity of the process as a whole. Moreover the study of degenerated branching of the chains, on the one hand, allows to get fundamentally new scientific data in the sphere of homogeneous catalysis theory of oxidizing reaction. On the other hand, it allows to offer a number of new patterns of catalytically system to chemical engineering.

The objects of study of research are organic vanadium derivatives.

Experimental procedure

Catalytic decomposition of ethylbenzene hydroperoxide was led in twin compartment reactor with working volume 7 ml., bathed in ultra thermostat. Ethylbenzene hydroperoxideand catalyst were introduced in separate sections. Agitator was turned on after achieving necessary heating temperature. In a given time, we thieve and put it into the retort immediately for analysis. We used iodometric analysis.

Solvent- chlorbenzen (line «ch») was rectified according to acid-based method and was sublimated.

Ethylbenzene hydroperoxidewas dried above warmed up Al_2O_3 and was distillated under vacuum twice. Boiling point – 35 °C (2.27KPa).

Acetylacetonate of vanadyl $VO(acac)_2$ was obtained by interreaction of vanadyl sulphate with acetylaceton, which was recrystallized from trichloromethane.

In this research we studied decomposition of ethylbenzene hydroperoxide with acetylacetonate of vanadium with 20, 40, 60 °C, $[PEH]0=0$, 0.08 mole/l, $[VO(acac)_2]_0=0$, 0.015 mole/l.

With the help of the definite experiments it was stated that ethylbenzene hydroperoxide doesn’t thermally decompose in the given temperature band.

Results and discussions

While mixing both chlorbenzen of preparations of ethylbenzene hydroperoxide and acetylacetonate of vanadium, mixture obtains dark-red color, which in some minutes turns into yellow-green. We were interested in the beginning stage of the reaction-first 5-10 minutes.

There are 2 ways to determine initial velocities of reactions: graphic method and approximation. In case if there are few points and they are scattered, then the kinetic curve is approximated with suitable polynomial.

We have chosen polynomial of 3d degree as approximate function, by virtue of the fact that it fits to the process. Moreover all of experimental data was processed with cubic polynomial.

Type of W and reagent concentration relationship points out the middle complexing of hydroperoxide with catalysts.

According to Michaelis-Menten equation, disintegration rate changes according to hyperbolic law and while $K[ROOH]_0 >> 1$ and approaches to its maximum. $W_{max} = [VO(acac)_2]_0$.

Thus, velocity and concentration of ethylbenzene hydroperoxide relationship achieves plateau, if the concentration is high; which clearly shows the middle complexing between ethylbenzene hydroperoxide and vanadyl acetylacetonate.

EFFECT of PREPARATION CONDITIONS on HYDROGENATION of PHENYLACETYLENE over the Pd-Fe/SiO_2 CATALYSTS

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Selective hydrogenation of phenylacetylene possesses considerable importance because phenylacetylene is regarded as a harmful component in feedstocks for the industrial manufacture of polystyrene [1]. Pd-based catalysts are generally used in the selective hydrogenation of phenylacetylene. Modifications of the Pd-based catalysts by alloying with other metals resulted in active and selective catalysts [2,3]. The Pd-Fe_3O_4/SiO_2 catalyst shows the reasonably high conversion and selectivity [3], yet alloyed Pd-Fe NPs exhibit a decrease in TOF as compared with Pd NPs [4]. Therefore, it seems of particular interest to evaluate the effect of preparation procedure of Pd-Fe/SiO_2 catalysts on the catalytic activity in the hydrogenation of phenylacetylene (PhA) to styrene.

The Fe-Pd catalysts were prepared by simultaneous (SD) or consecutive (CD) incipient wetness impregnation of the silica carriers with aquoes solutions of the metal precursors. The specific surface area of the carriers was 340 m^2g^{-1} (HS) or 30 m^2g^{-1} (LS). The chemicals $(NH_4)_3[Fe(C_2O_4)_3]$ and $[Pd(NH_3)_4]Cl_2$ were used as precursors. The impregnated carriers were dried at 60ºC. Then a different thermal treatment was applied. The catalytic activity of prepared samples was tested in the selective hydrogenation of PhA to styrene at the following reaction conditions: 0.130 M PhA in the solvent, 30 mg of a catalyst, 1 atm H_2, 20-60ºC, molar ratio PhA : Pd = 200-1000. The influence of solvents such as ethanol and isopropanol on the activity and selectivity to styrene was investigated.

After decomposition of precursors at 250 ºC in air, all samples prepared (Table 1) exhibitted catalytic activity in the PhA hydrogenation. At the same reaction conditions the activity of catalyst was higher if ethanol was used as a solvent (Fig.1).

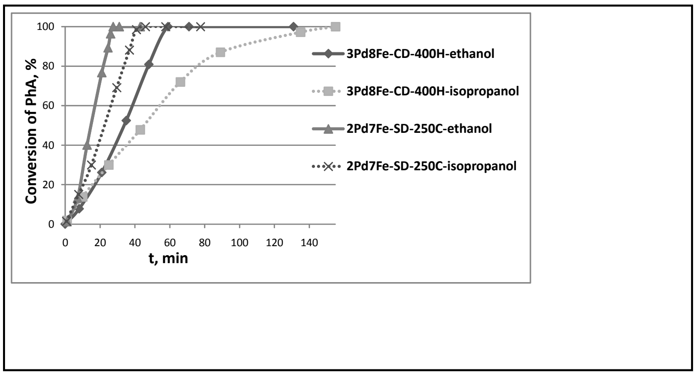

Fig.1. The influence of solvents on the activity Fe-Pd catalysts

The catalytic activity, initial rate of hydrogenation and selectivity of catalysts depends on the preparation procedure and especially on the conditions of thermal treatment. The simultaneous deposition of the Fe and Pd precursor resulted in more active and stable samples than consecutive deposition. The initial rate of hydrogenation on the calcined samples at 350 ºC (Table 1, lines 4, 5) was higher than on the calcined samples at 250 ºC (Table 1, line 2). Further reduction of the dried or calcined samples in a hydrogen flow at 400ºC resulted in a decrease in the initial rate of hydrogenation and selectivity.

Table 1. The initial rate, selectivity to styrene and its yield at the complete PhA conversion.

Sample[a]	Fe, %	Pd, %	t, min[b]	S^{100}styrene,%	r_0, mol$_{PhA}$ mol$_{Pd}^{-1}$ s^{-1}	r_0, mol$_{H2}$ mol$_{Pd}^{-1}$ s^{-1}	Yield, g g$_{ct}^{-1}$ h^{-1}
3Pd8Fe-CD-R	3.2	7.8	59	82	0.06	0.07	8
3Pd8Fe-SD-250C	3.0	7.6	15	77	0.35	0.34	16
3Pd8Fe-SD-R	3.0	7.6	25	90	0.18	0.13	17
3Pd8Fe-SD-350C	3.0	7.6	6	60	0.88	0.45	46
1Pd7Fe-SD-350C	1.1	6.7	16	80	0.80	0.46	25

[a] The prepared samples are denoted as xPdyFe/A-B, where x and y are referred to the Pd and Fe loading (mass %), A was the method of preparation, and B denotes the sample treatment (C - calcined, R - reduced at 400ºC).

[b] Time of 100% conversion of phenylacetylene

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Pd LOCALIZATION in $Ce_{1-x}Pd_xO_{2-\delta}$ SOLID SOLUTIONS by ANOMALOUS X-ray PDF

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Pd supported on CeO_2 is widely used as an active component of various heterogeneous catalysts [1]. For instance, it is an important part of automotive there-way catalysts [2], catalysts for total [3] and partial [4] hydrocarbon oxidation and low-temperature CO oxidation [5]. This system is characterized by strong metal-support interaction that could be the reason for unique properties of this system, e.g. high catalytic activity and thermal stability. $Pd_xCe_{1-x}O_{2-x-\delta}$ solid solutions have been observed in many cases of Pd/CeO_2 studies. However, there is no common agreement in the literature on its structure. In the number of experimental [16] and theoretical [36] works Pd ions have been shown to stay in a regular fluorite positions in the solid solutions. Other studies argue that Pd ions preserve characteristic square-planar local environment by shifting from fluorite positions after dissolution in ceria.

The difficulty of locating Pd inside the CeO_2 lattice may be overcome by employing resonance X-ray diffraction. The method requires measurements of two diffraction data sets at two energies close to the absorption edge of atomic species. In our study powder diffraction patterns have been measured close to the Pd-K adsorption edge. After Fourier transformation the difference of between these two normalized diffraction data sets gives Differential Pair Distribution Function (DPFD) that shows only Pd-O, Pd-Ce and Pd-Pd correlations within the fluorite structure. The similar information on a very local scale can be obtained by Extended X-ray Absorption Fine Structure (EXFAFS) spectroscopy. However, in the case of $Pd_xCe_{1-x}O_{2-x-\delta}$ solid solution the study of long interatomic distances of Pd that show DPDF data is of crucial importance in order to obtain the experimental evidence of Pd dissolution in the bulk of ceria.

Anomalous diffraction experinemts at the Pd K edge have been performed at the Materials Science beam line X04SA Swiss light Sourse (Villigen, Switzerland). The measurements have been performed at energies of 24.00 and 24.35 keV, since its energy spectrum is ideally suited for anomalous powder diffraction. Three samples with composition of 10, 5 and 1 wt % Pd in CeO_2, calcined at 600°C have been analized. Detailed analysis of DPDFs showed that Pd ionic species are introduced into the bulk of fluorite phase due to exhsistance of expended Pd-Ce interatomic distances. Pd is shifted from the center of the oxygen cube – ideal fliorite position - along [100] almost into the oxygen plane with C_{4v} local symmetry.

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Acknowledgements

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CONFORMATION ANALYSIS of the SILVER(1)-P-TOLUENESULFONATE MOLECULE by USING QUANTUM CHEMICAL METHODS

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The compaund of the tosylate ($CH_3C_6H_4SO_3^-$) anion and Ag could be used as a catalyst in the electrochemical industry. This is due to their electrochemical, chemical and thermal stability. The silver(1)-p-toluenesulfonate manage to create complex with p-aminobenzoic acid in ethanol [1]. The crystal structure of this complex shows a two-dimensional sheet structure based upon a distorted tetrahedral AgO_3N center involving three oxygens from independent sulfonate residues and an amine nitrogen.

That was reason for the investigation and making conformation analysis of the silver(1)-p-toluenesulfonate molecule by using quantum chemical HF and B3LYP methods of theory using the 3-21g and CEP-31g basis sets. The optimized geometries of silver complex are shown in Fig. 1.

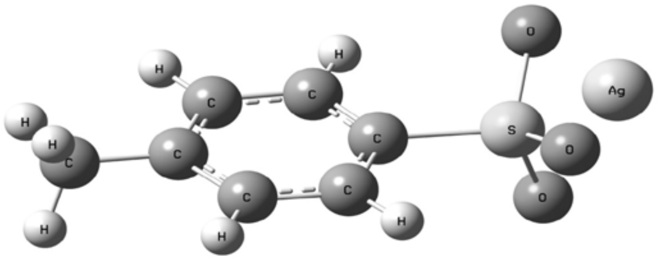

Fig. 1 Optimized geometries of silver(1)-p-toluenesulfonate (B3LYP/CEP-31g)

The silver atom is located between two atoms of the oxygenium and about 4 Å from the third one. Unfavorable conformation of this molecule which atoms of the oxygenium and the silver is not located in cyclic plane of the phenyl ring.

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PP-16

THEORETICAL STUDY of the PLATINUM (0)-1,3-DIVINYL-1,1,3,3-TETRAMETHYLDISILOXANE COMPLEX STRUCTURE

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Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex is used for the metal catalyst phase in the electrochemical system of Pt/SnO_2. The article [1] considers the metallic phase of this complex does not tend to agglomerate and therefore maintain a high electrochemical activity, so we analyzed the structure of this complex using quantum chemical methods. The calculations were carried out with the Gaussian 09 program. Zero-point energy (ZPE), the optimized geometries and harmonic vibrational frequencies were calculated with the B3LYP methods of theory using the LanL2dz basis sets. The optimized geometries of the local minima platinum complex are shown in Fig. 1.

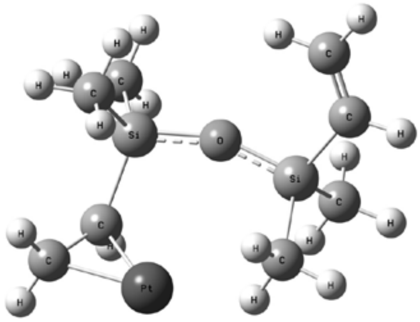

Fig. 1 Optimized geometries of platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex at the B3LYP/LanL2dz level.

As shown in Fig. 1, after calculating atom of the platinum were connected to the ethylene fragment. The distanse between Pt and C is 2.09 Å. The angle Si-O-Si is 157.33^o. It should be announced that each Pt(0) center is surrounded by three alkene ligands in Karstedt's catalyst [2]. The Pt center and six coordinated carbon atoms are approximately coplanar, as found for simpler complexes such as $Pt(C_2H_4)_3$.

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THEORETICAL STUDY of the STRUCTURE of DICHLOROBIS (4-METHYLPYRIMIDINE)-BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

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Complexes of ruthenium(II) with different ligands are very important in promoting catalytic reactions. Theoretical study of the structural characterization of these complexes, carried out with the quantum-chemical methods, is of interest.

Dichlorobis(4-methylpyrimidine)bis(triphenylphosphine)ruthenium(II) can be prepared from 4-methylpyridine and $[RuCl_2(PPh_3)_3]$ in the solution of absolute ethanol [1].

The structure of six-coordinate ruthenium(II) complex was optimized using B3LYP and PBE1PBE with Lanl2dz basis set. All calculations were carried out using Gaussian 09W package [2]. The geometric structure of the dichlorobis(4-methylpyrimidine)-bis(triphenylphosphine)ruthenium(II) is represented in figure 1.

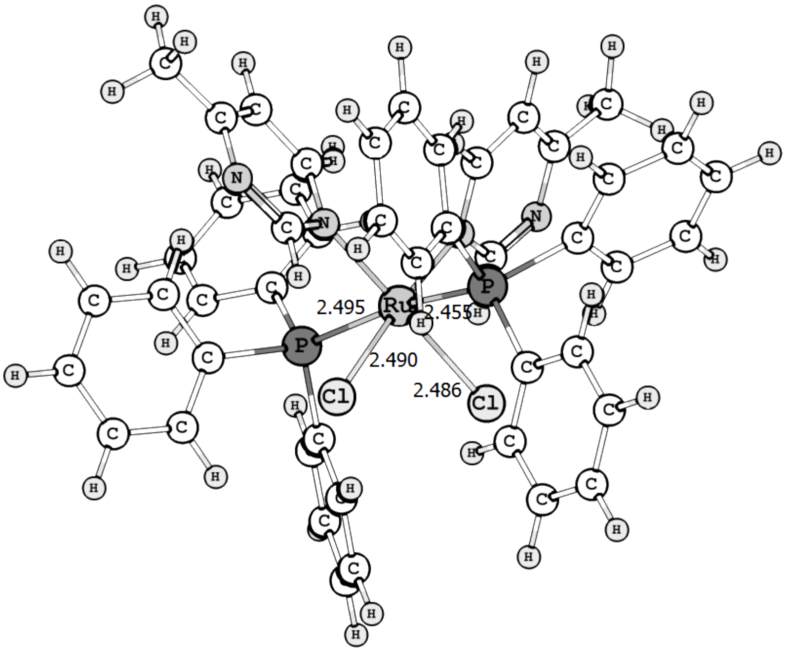

Fig. 1. Optimized structure of the dichlorobis(4-methylpyrimidine)-bis(triphenylphosphine)-ruthenium(II) at the PBE1PBE/Lanl2dz (bond lengths are given in Å)

The Ru-P1 distance is 2.495 Å and Ru-P2 distance is 2.455 Å at the PBE1PBE/Lanl2dz method, the Ru-P2 bond distance is shorter than Ru-P1 distance by 0.051 Å at the

B3LYP/Lanl2dz method. The bond lengths Ru-Cl1 and Ru-Cl2 are close. The Ru-N1 bond lengths average 2.113 Å and the Ru-N2 - 2.123 Å; the angle Ru-P1-N1 is 90.7°, the angle Ru-P2-N2 is 87.3° at the PBE1PBE/Lanl2dz.

The results of the theoretical study of the geometric structure of the dichlorobis(4-methylpyrimidine)-bis(triphenylphosphine)ruthenium(II) did not show any inter-molecular stacking interaction involving phenyl rings and 4-methylpyrimidine ligands.

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PP-18

DESIGN CONFORMATION of the ((2-METHOXYPENTAN-3-YL)-OXY)DIOXOOSMIUM with QUANTUM CHEMICAL METHODS

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The catalytic reaction oxidation of olefins to glycols with OsO4 works through a concerted process whereby two oxygens from the osmium of the form double bond [1]. Design of structure ((2-methoxypentan-3-yl)oxy)dioxoosmium (1), molecular conformation, and conformational calculations was carried with quantum chemical methods. Conformational analysis this molecule is the study of the different energy levels associated with the different conformations. Fig. 1 is a plot of the energy rotation of the angle of the ethyl group. Barriers to internal rotation were calculated.

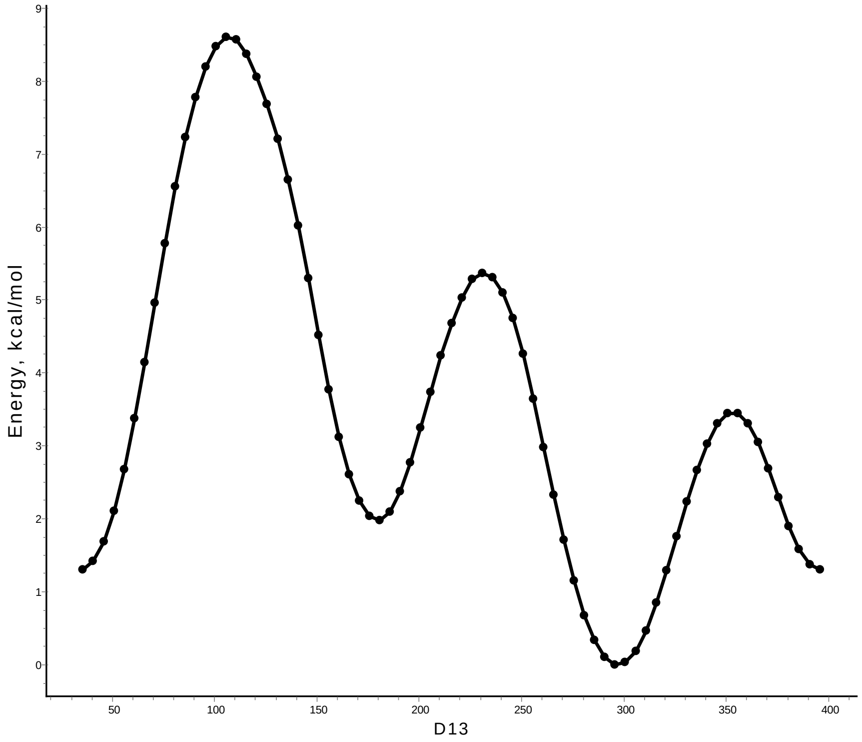

Fig.1 Rotation of the dihedral angle H-C4-C1-C2 in the molecule 1 (by using B3LYP/LANL2DZ method)

The most favorable conformation is shown in Figure 2. The dihedral angle C2-C3-C4-C5 is 175.4°. A bond between Os-O1 and Os-O2 have the same lengths.

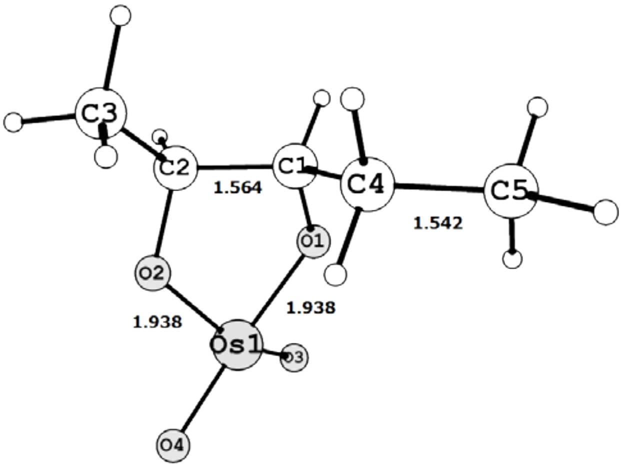

Fig.2 Structure ((2-methoxypentan-3-yl)oxy)dioxoosmium (bond lengths in angstroms)

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The XPS STUDY of HIGHLY OXIDIZED RHODIUM NANOPARTICLES: CHARGING STATES, THERMAL STABILITY and REACTIVITY

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The highly oxidized rhodium species are considered to be very promising materials for application as supercapacitors, electrode materials for memory applications etc. Moreover, rhodium based catalysts are widely used in many industrially important reactions. However, there is little information about catalytic properties of highly oxidized Rh species. In our work the photoemission study of highly oxidized rhodium nanoparticles was performed to analyze the charging states of rhodium species and to establish their thermal stability and reactivity towards CO oxidation reaction.

The RF-discharge in an oxygen atmosphere was applied for synthesis of the oxidized Rh nanoparticles. The X-ray photoelectron spectroscopy (XPS) and Transmission electron microscopy (TEM) were used for the characterization of nanoparticles properties.

The TEM data indicated that the RF-sputtering of Rh electrode for 3 minutes resulted in the formation of particles with irregular shape and dendrite-like structure (Figure 1a). The particles comprise smaller crystallites about 2 nm in size connected by the intergrain boundaries. The rhodium spectra Rh3d showed single doublet at binding energy (E_b) of $Rh3d_{5/2}$ 308.4 eV (Figure 1b). Such binding energy value is typical for Rh^{3+} species, however Rh^{4+} forms seem to have very similar E_b [1,2]. The O1s spectra gave two main peaks at 529.5 eV and 531.4 eV. The former peak is close to the oxygen in Rh_2O_3 oxide, while the latter might be related to the hydroxyl species, chemisorbed oxygen or oxygen in RhO_2 oxide [1,2]. The O1s/Rh3d peaks intensity ratio gave ~2.5, allowing us to propose the formation of RhOOH or RhO_2 species together with Rh_2O_3 oxide. The annealing of the oxidized Rh nanoparticles in the vacuum resulted in the substantial depletion of the O1s peak at 531.4 eV at 150^0C pointing to the decomposition of RhO_2/RhOOH structures. The decrease of the intensity of the O1s peak corresponded to Rh_2O_3 oxide occurred at temperatures higher 225^0C. According to the literature data the thermal stability of bulk Rh_2O_3 oxide is higher

800^{0}C. The observed in our work lower thermal stability of Rh_2O_3 oxide might be caused by the small particles size and their defect structure. The reaction probability of the oxidized Rh species was tested by a step-by-step CO exposure. The partial titration of oxygen species with E_b(O1s)=531.4 eV proceeded at temperature higher 75^{0}C followed by the reduction of Rh_2O_3 oxide to Rh^0 at 125^{0}C. The reoxidation of the obtained metallic system by the molecular oxygen at 125^{0}C resulted in the formation of Rh_2O_3 species only. The RhO_2/RhOOH (E_b(O1s)=531.4 eV) species were not recovered.

Thus, the RF-sputtering of the rhodium electrode in the oxygen atmosphere resulted in the formation of highly oxidized Rh species RhO_2/RhOOH. In comparison with Rh_2O_3 these species have lower thermal stability and higher reactivity towards CO oxidation. However, as opposed to Rh^{3+} oxide, they could not be recovered by the molecular oxygen exposure.

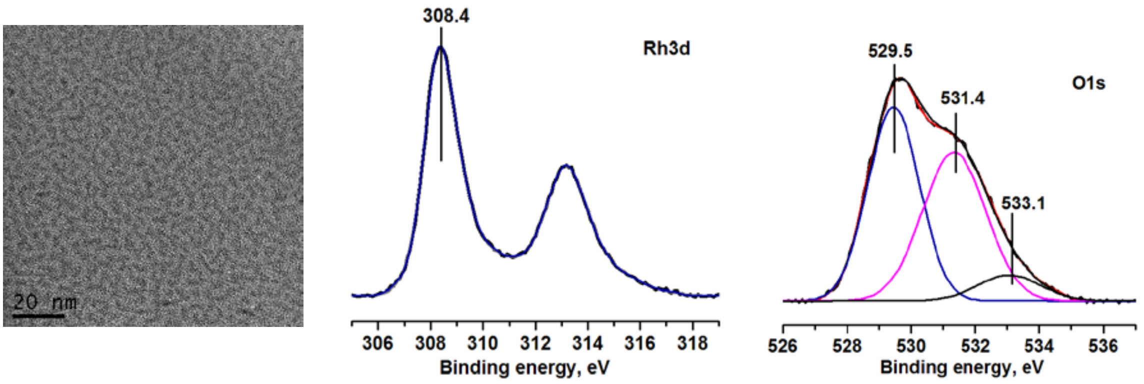

Figure 1. The (a) TEM and (b,c) XPS data for the oxidized rhodium nanoparticles.

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Acknowledgements

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PP-20

MODELING of the STRUCTURE (2,6-BIS((DICHLOROPHOSPHINO)METHYL)-PHENYL)(2,2,2-TRIFLUOROACETOXY)PALLADIUM

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Modified mesoporous materials containing the complex palladium demonstrated a high catalytic activity, both in solution and on support. Pd solution is slowly released from the complex Pd, where it is resistant to degradation [1]. A direct correlation exists between it contained soluble Pd and reaction conversion. Quantum-chemical calculations were performed on the basis of density-functional theory (DFT), using the B3LYP along with the CEP-31g basis set. The optimized structure for (2,6-bis((dichlorophosphino)methyl)-phenyl)(2,2,2-trifluoroacetoxy)palladium is shown in figure 1.

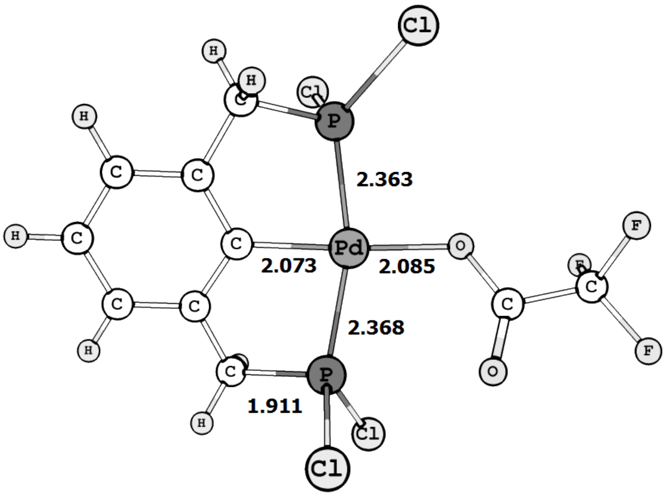

Fig. 1. Structural models for (2,6-bis((dichlorophosphino)methyl)phenyl) (2,2,2-trifluoroacetoxy)palladium (distances in angstroms)

The angle P-Pd-P is 163.3°; the angle C-Pd-O is 176.6°. It should be noted that the Pd-catalyst containing two fragments -$OCOCF_3$ can be used in the selective asymmetric hydrogenation of C=C bond [2].

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AB INITIO MODELING of COMPLEX RUTHENIUM (II)

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Ruthenium complex is applied as an olefin metathesis catalyst [1]. In this theoretical study was employed Hartree-Fock level of theory with 3-21g basis set. In fig. 1 show the optimized structure of dichloro(cycloocta-1,5-diene)ruthenium(II). The Ru-Cl bond length was calculated to be 2.40 Ǻ. The distance Ru-C16 was 2.47 Ǻ. Angle Cl-Ru-Cl is 102.36°.

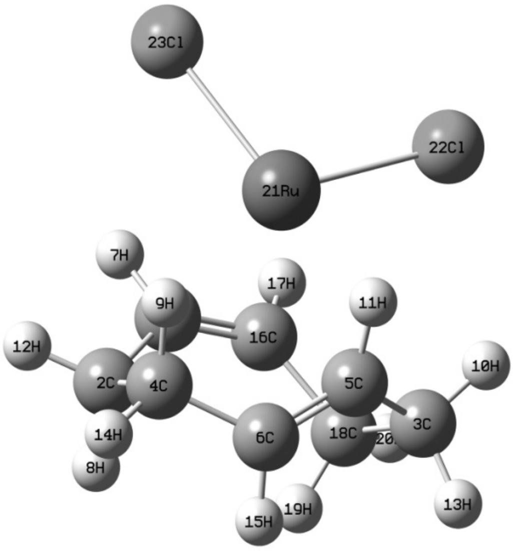

Fig. 1. Geometric structure of dichloro(cycloocta-1,5-diene)ruthenium(II) optimized using the HF/3-21g calculations

Atomic charges were obtained from ab initio molecular orbital calculations. It was investigated scans of the potential surface for the C−Ru bond in this molecule.

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PP-22

ANALYSIS of the GAS PHASE DURING OXIDATION METHANOL at PRESENCE of the CATALYST on BASE of $Fe_2(MoO_4)_3$

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The analysis of the gas phase in the Formox process is carried out in a continuous mode with a gazanalyser Test-200 and periodically with GC Krystal 5000.2 [1]. This allows the possibility of keeping track of operating regime $Fe_2(MoO_4)_3$ based catalyst. Thus, an increase of content of CO_2 measured prior and after the reactor of oxidation for manufacturing plant of urea-formaldehyde concentrate (UFC) shows the catalyst in this process is more impuried with Fe compare the catalyst for manufacturing plant of formaldehyde (Fig. 1,2).

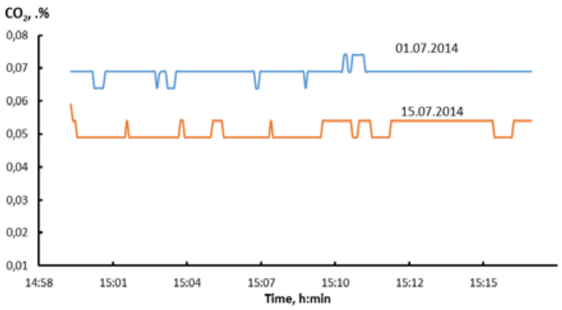

Fig. 1 C_{CO2} on plant of UFC

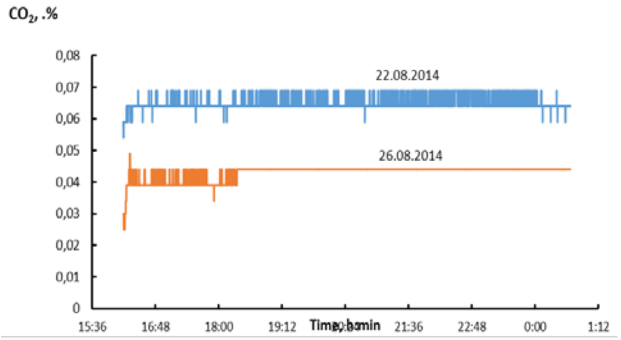

Fig. 2 C_{CO2} on plant of formaldehyde

Another example of the qualitative analysis of methanol, water and dimethyl ether is the gas chromatographic analysis on the thermal conductivity detector of GC with the faucet for the input gaseous sample. The measurement was carried out by means of metal column filled with phase "Chromosorb" in the isothermal regime at temperature 110ºC (gas-carrier – hydrogen; 20 ml/min). Fig 3 presents the chromatogram of the abgase of UFC manufacturing plant.

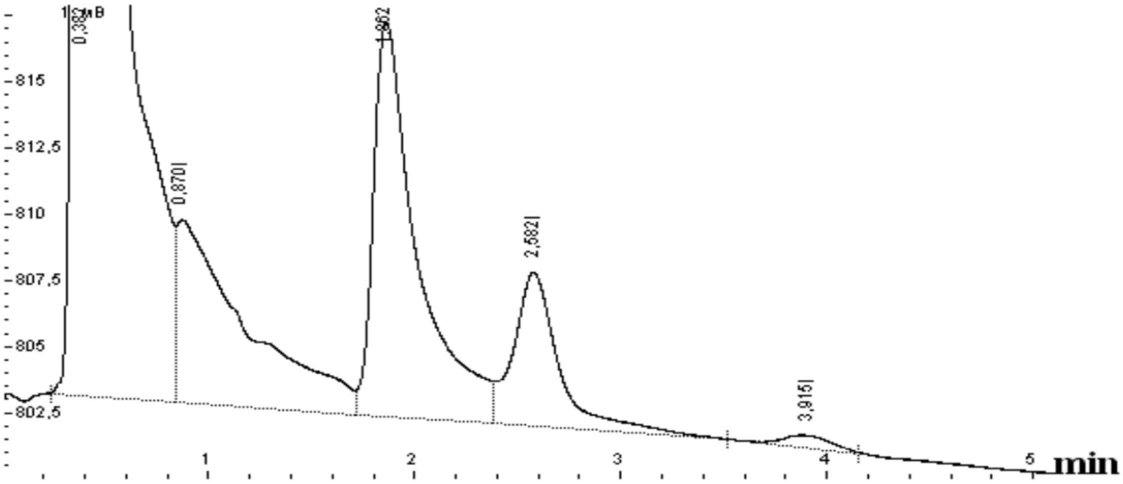

Fig. 3 Chromatogram of the abgase of UFC manufacturing plant after the oxidation

The peak (on the chromatogram has a retention time 1,862 min and it is greatly reduced when pre-release sample through the dryer) refers to the water retention time. The Peak 2,682 min is the peak of the dimethyl ether retention time. This peak was also identified using the mass spectroscopy detector of the gas chromatograph located in the IOS of Ural Branch of the RAS. The peak at 3,915 min on the chromatogram refers to methanol. In our opinion this procedure can be applied for the quantitative analysis of methanol in gases, using the gas mixture (dimethyl ether:air=99,5:0,5) as a calibration gas mixture

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INFLUENCE of PLASMA-CHEMICAL TREATMENT on the PILLARED MATERIALS CATALYTIC ACTIVITY

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A lot of organic xenobiotics which constantly pollute the water and soil cannot be removed by using conventional biotechnological, physical and chemical processes owing to high purification cost and/or formation of waste-water having difficult recycling [1]. As alternative methods are considered Advanced Oxidation Techniques (AOT), based on action hydroxyl radicals (OH •) [2]. One of the most important AOT processes for generation hydroxyl radicals is based on both action of Fe^{2+}, H_2O_2 and UV radiation in so-called homogeneous photo-Fenton process [3]. In addition using nanoparticles of metal iron for effective decomposition various organic pollutants in cleaning environment technologies [4] actively develop and introduce.

Today actively developing area is design solid catalysts for heterogeneous photo-Fenton processes [5]. Recently a perspective direction is modification layered aluminosilicates into so-called pillared layered materials which characterised unique layered-columnar structure [6-8]. Using various techniques, polymeric or oligomeric hydroxy metal cations can be intercalated into interlayer spaces. It lead to obtain materials with a high specific surface and constant porosity. By present time a lot of publications cover catalytic activity researches of smectites, intercalated by the combined mixes (Al-Cu, Al-Fe, Ce-Al, Al-Ce-Fe) and mono hydroxy metals. In the book [9] effective ways of production, property and use of similar catalysts are considered.

Authors [10] describe characteristics and synthesis pillared materials, intercalated Ti, Zr and Fe polycations with increase d-spacing (001) to 4.0, 4.6 and 6.3 nm respectively from 1.2 nm for smectite in Na^+-form. These pillared structures are characterised by constant porosity and a specific surface to 281 m2/g, when smectite in Na^+-form shows values at level 26 m2/g. In work [11] the most rational way of production pillared materials with use of high reagents concentration and minimum water consuption is offered.

The application of plasmochemical technologies as one of stages for production pillared materials based on layered silicates and metals compounds is being studied by European research teams because realization of this approach gives the chance to design pillared materials with set oxidation levels of metal compounds introduced in silicates structure at lower temperature conditions.

In this investigation the lowered pressure radio-frequency hydrogen plasma for Fe and Al pillared materials treatment was used. Prior experiments with goethite reduction (α-FeOOH) in plasma showed that the initial goethite powder was reduced to metal iron (Fe^0) and magnetite (Fe_3O_4) in the ratio of 25% and 75% respectively.

Catalytic activity of pillared materials before and after plasmochemical treatment was estimated by chlorine-containing organic dyes decolouration. Results showed the increase of catalytic activity for pillared materials after plasmochemical treatment.

The results are considered as the initial stage of original synthesis of pillared materials based on iron compounds, layered silicates and RF plasma.

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^{1}H NMR STUDY of COMPLEXATION REACTION of THF with SEVERAL ORGANOALUMINIUM COMPOUNDS OPERATING as ACTIVATORS of IVB METALLOCENE COMPLEXES

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The metallocene-based catalytic systems are effective catalysts for homo- and copolymerization of olefins. The most common and effective activator is methylalumoxane (MAO). Recently we have shown [1] that isobutylalumoxanes obtained by controlled hydrolysis of triisobutylaluminum (TIBA) with water show activating ability comparable with that of MAO. Most recently it has been also shown that another class of organoaluminium compounds (OAC), i.e. isobutylaluminium aryloxides which are individual compounds containing 3-coordinating aluminum atom also effectively activate metallocene precursors in homo- and copolymerization of olefins. So, these OACs similarly to MAO form cationic intermediates with transition metal species, therefore acting as Lewis acids. To achieve better understanding of how the OAC nature affects the properties of catalytic systems, it is important to compare Lewis acidity of OAC of different structures.

The work describes ^{1}H NMR study of complexation of isobutyl-based OAC with THF (as model Lewis base), followed by the comparison of their acceptor properties, based on evaluation of complexation constants and comparison of the values of electonegativity of aluminum atom in these compounds. The OAC under investigation were triisobutylaluminum, isobutylalumoxanes, obtained via hydrolysis of triisobutylaluminium, and different isobutylaluminium aryloxides. Conceptually experiments included titration of OAC with THF with reagents molar ratio varied in the range 0.1 – 5 mol/mol. The difference between ^{1}H chemical shifts of OCH_2 and CH_2 protons of THF has been monitored, and accumulated data were further used for evaluation of complexation constants. The general correlation between the Al/THF molar ratio and relative chemical shifts ($\Delta\delta$) of OCH_2 and CH_2 groups of THF used for analysis is shown on Fig.1.

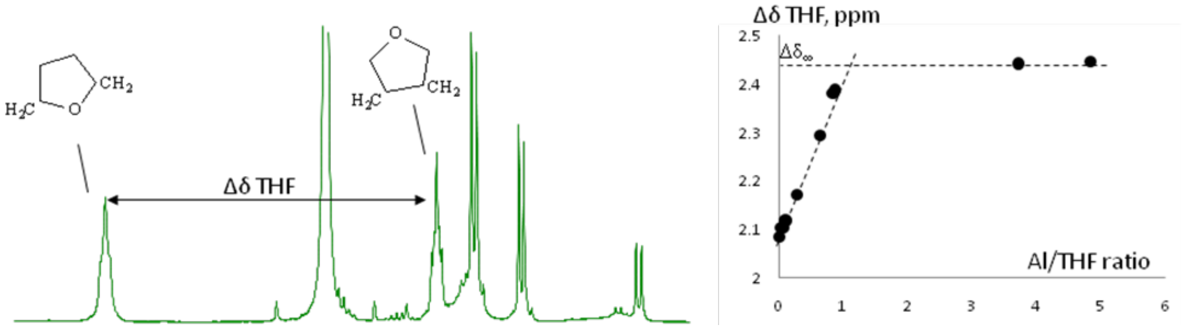

Figure 1. Left: ^{1}H NMR spectrum of THF/OAC mixture, with Δδ marked as relative chemical shift of OCH_2 and CH_2 signals. Right: correlation between Δδ and Al/THF ratio with marked linear and saturation areas.

The said correlation had been proved to include the initial linear area, where Δδ increases proportionally to Al/THF ratio, and saturation area, where Δδ rests at the same level ($\Delta\delta_\infty$). The dependencies, along with precise data on concentration of reagents, allowed determination of complexation constants. The relative chemical shift of CH_2 and CH_3 protons of isobutyl groups has been used for estimation of aluminum atom electronegativity in both pure OACs and their complexes with THF.

The resulting electron acceptor potency of the compounds is discussed.

The complimentary information was also obtained from IR study of binary OAC/THF mixtures.

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KINETIC STUDY OF ONE-POT PROCESS OF VALERIC ACID INTO N-NONANE

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Carboxylic acids play a predominant role in biomass transformations into fuels and chemicals when lignocellulose is considered as a raw material. Carboxylic acid such as levulinic acid is generally considered as a biomass-based building block for conversions into chemicals and fuels. For both, fuels and chemicals, the reduction of the oxygen content is an important issue. Hereby, the reduction of levulinic acid into valeric acid is straightforward via γ-valerolactone (GVL). The ketonic decarboxylation is a very suitable and environmentally benign reaction for further reducing the oxygen content, and increasing the molecular weight at the same time which is also highly desired in biomass transformations [1]. ketones are reported to be used as key precursors for producing fuel components via their consecutive reduction into alkanes. One-pot mode of carboxylic acid decarboxylation coupling followed by ketone hydrogenation into alkane over Pt(Pd)/ M_xO_y bifunctional catalyst can be considered as a more attractive way to produce green diesel components.

In the present work we study the one-pot mode of valeric acid ketonization followed by hydrogenation of obtained 5-nonanone into n-nonane over bifunctional catalysts Pd/ZrO_2.This reaction was carried out in the gas-phase at elevated temperatures (543–628◦K) under hydrogen stream at ~ 6 atm. The main attention is focused on the kinetic investigation of the process with the aim to optimize the chemical process.

Calculation (estimation) of energy activation, pre-exponential factor and kinetic modeling of the one-pot mode of valeric acid conversion into 5-nonanone were performed. Futhermore, the value obtained were compared with the same ones for separate stages, valeric acid ketonization and 5-nonanone hydrogenation.

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MATHEMATICAL MODELING of SOOT TRAPPING both INSIDE and above POROUS MATERIALS of CATALYTIC FILTERS

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Diesel particulate filters (wall-flow monolith) are successfully used for soot removal from engine exhausts. The exhaust gas flows through the porous walls from the inlet channel into the outlet ones. Soot particulates either are trapped in the pores of the wall or deposit on its surface in the inlet channels. The efficiency of the further oxidation of accumulated soot depends on the ratio of soot captured inside the wall to one collected on the wall surface, because soot inside the pores has more close contact with catalyst and for the beginning of the soot oxidation the more low temperatures will be needed. The usual size of soot particulates ranges from 0.01 to 0.7 μm.

Many theoretical and experimental studies have devoted to investigation of the soot capturing and its oxidation in diesel particulate filters. Either soot trapping inside the porous material of filters and oxidation of accumulated soot or only regeneration of the filters with soot been deposited as a layer on the wall surface is studied in theoretical papers. Usually a constant particulate dimension equal to the mass-based average of the particulate size distribution measured is assumed in mathematical models.

The paper is devoted to the development of the unsteady-state mathematical model which takes into account the simultaneous soot accumulation both inside of the wall pores and on its surface. It is assumed that the soot particulates are captured in the pores by inertial impaction, interception, Brownian diffusion and interactions between interception and Brownian diffusion. We consider also particulate size distributions in the model. Besides it is assumed in the model that soot collects on the solid part of the wall surface firstly by inertial impaction, after the soot amount near the inlet of the wall exceeds a certain level, the pores are bridged by soot and all soot deposits on wall surface. The accumulation of soot in the wall and on its surface increases the flow resistance and decreases the flow rate through the porous wall. The results of mathematical modeling and simulation are presented.

NEW NANOCOMPOSITE MATERIALS BASED on ETHYLENE - PROPYLENE COPOLYMER and MODIFIED NAFEN^{TM}

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A known method for improving physico-chemical characteristics and performance of polyolefin materials is the introduction of inorganic fillers into the polymer matrix, nowdays, mainly of nanofillers having at least one dimension from 1 to 100 nm. Nanofillers have very much higher ratio of surface area to volume than bulk materials. So, relatively much higher part of nanofiller will interact with polymer matrix than those of bulk fillers and improvement of nanocomposite properties (servicing characteristics, thermal-oxidative, gas permeation barrier, etc.) may be reached even at low degrees of filling (0.5-5 wt. %). Of particular interest is the development of methods of preparation and study of properties of new polyolefin nanocomposites with nanofibers of aluminum oxide. Surprisingly these nanofillers are not yet markedly used for modification of polyolefins according to the literature. Unique high quality and cheap commercially available nanomaterial Nafen^{TM} is good candidate for the purpose. Nafen^{TM} used in this study is γ-phase nanofibers of Al_2O_3 with monodispersed diameter of 7-9 nm and length about 100 nm. A variety of methods of surface modification of Al_2O_3 opens the possibility to provide the compatibility of this nanofiller with the polyolefin matrix.

Our main aim is to create a new class of polyolefin hybrid materials with modified Nafen^{TM} as nanofiller with the properties improved compared to pristine polymers. As have been shown by SEM data stable nanodispersion of Nafen in toluene can be obtained by ultrasonic technique under established conditions. To ensure compatibility of polar nanofiller with nonpolar polymer matrix, Nafen^{TM} was modified by vinyltrimethoxysilane. The resulting samples were analyzed by IR and solid NMR (^{1}H, ^{13}C, ^{27}Al, ^{29}Si). The analysis showed the presence of C=C double bonds of anchored vinyl silane and allowed conclude that silanol and silane groups are predominant groups of bound modifier. The synthesis of nanocomposites has been carried out by copolymerization of ethylene with propylene on homogeneous catalytic system $Et(2\text{-}MeInd)_2ZrMe_2$/alumoxane in the presence of a nano suspension of modified Nafen^{TM}. It has been shown (TEM, SEM) that modified Nafen is distributed in copolymer matrix as individual or low aggregated nanoparticles. Copolymers with Nafen^{TM} content of 0.005, 0.13, 0.3, and 3 wt. % have been obtained. Nanocomposites have been characterized by different techniques (FTIR, GPC, physico-mecanical measurements, DMA, DSC, TGA, etc.). The most interesting observation is rather high increase in temperature of thermal oxidative destruction of ethylene/propylene copolymers up to 20-30 °C at nanofiller content of 0.3-3 wt. %. The presence of Nafen nanoparticles does not change physico mechanical characteristics of obtained nanofilled elastomers in comparison with copolymers without filler.

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HYDROGEN and OXYGEN INTERACTION with SINGLE SUPPORTED GOLD NANOPARTICLES

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In recent years, scanning tunnelling microscopy (STM), which ensures resolution at the atomic level, has been widely used for the study of supported metallic nanoparticles. It was found that surface structures and adsorption properties of supported metallic nanoparticles are determined by their shapes which in turn strongly depend on the nature of the support. At the same time, such low coordinated sites as edges and kinks strongly affect the interaction of a surface with adsorbed species. The use of STM for the analysis of surface structures of metallic nanoparticles seems promising, in that this method allows *in situ* analysis of surface structures, i.e., in the course of a reaction.

Scince demonstrating by Haruto their catalytic activity three decades ago gold nanoparticles retains attention of many scientists. Gold nanoparticles which, in contrast with the bulk metal, manifest catalytic activity in certain reactions. In this study we demonstrated dependence of adsorption properties of single gold nanoparticles on the nature of the substrate. High ordered pyrolytic graphite (HOPG) and silicon covered oxide (SiO_2/Si) were used as substrate.

Morphology and electronic structure of gold nanoparticles were determined by scanning tunneling microscopic technique by Omicron. The residual gas pressure in the setup chamber didn’t exceed $P = 2 \times 10^{-8}$ mbar. Local changing of the surface state of gold nanoparticles was defined by current-voltage dependence of tunneling contact including single gold nanoparticle (*I(V)*-curves).

Gold nanoparticles were prepared by a deposition method. Chloroauric acid with a gold loading of 5 wt % was first dissolved in distilled water and after deposited on the surface of substrate (HOPG and SiO_2/Si). Substrate with acid was dried and then calcined in ultrahigh vacuum (10^{-10} mbar) at 500 K for 6 h.

Single gold nanoparticles supported on HOPG (Au/HOPG)

The formation of gold nanoparticles occurs near the lattice defects of graphite surface. Both isolated nanoparticles of 4-5 nm and large agglomerates with lateral sizes of 40-100 nm consisting of individual 5 nm particles on the graphite surface were observed. The current-voltage dependence of tunneling contact consisting gold nanoparticles corresponds to the metallic conduction.

To study the interaction of hydrogen with gold nanoparticles at room temperature sample was kept over 500 seconds at room temperature in molecular hydrogen at a pressure of

$P = 2 \times 10^{-6}$ mbar (exposure 1000 L). The hydrogen exposure doesn't lead to shape and sizes changing of gold nanoparticles. The band gap with width of 0.8 V on the *I(V)*-curves was observed after hydrogen exposure. Hydrogen-gold binding energy lower limit was measured by thermodesorption method and is equal to 1.7 eV. Based on the results of quantum-chemical calculation made by us the hydrogen adsorption on Au_{13}-H_{12} clusters is characterized by breaking of H-H bond and formation of Au-H bond with binding energy of 3 eV.

The oxygen adsorption can be determined only after the preliminary exposure of gold nanoparticles in hydrogen. Current-voltage dependence of tunneling contact of Au/HOPG with adsorbed oxygen and hydrogen doesn't differ from these of gold nanoparticles coated by hydrogen only. Perhaps oxygen adsorption occurs without breaking of O-O bond.

Au/HOPG sample, coated firstly by hydrogen and then by oxygen, were exposed into the hydrogen for evaluation of Au/HOPG reactivity. The measured current-voltage dependence exhibit multiple local maxima located almost symmetrically with respect to the coordinate origin. The voltage differences corresponding to the position of peaks on the experimental curves was 0.41 and 0.25 V between adjacent peaks which is accurate within a dimensional factor corresponds to quanta of electron-vibration excitation of the O-H bond and the deformation vibration of the water molecule.

Single gold nanoparticles supported on SiO_2 (Au/ SiO_2)

The lateral diameter of single gold nanoparticles supported on SiO_2 is 4-5 nm. The comparison of gold nanoparticles diameters into SiO_2 and HOPG allows making a conclusion that type of substrate doesn't have a significant influence on the morphology of gold nanoparticles.

Au/HOPG and Au/Sio_2 equally interact with hydrogen. Hydrogen is chemisorbed on gold nanoparticles supported on SiO_2 at room temperature as well as on gold nanoparticles supported on HOPG. However at the following puffing of oxygen the formation of water molecules on the surface of gold nanoparticles was observed. Thus, it was found that water is formed at the gases puffing by H-O-H scheme on Au/HOPG and by H-O scheme on Au/SiO_2.

The conditions of hydrogen and oxygen adsorption on Au/HOPG and Au/Sio_2 were determined by methods of scanning tunneling microscopy and spectroscopy. Production of water molecules on gold nanoparticles was observed. It was shown that, application of semiconductor as a substrate dramatically increases the reactivity of gold nanoparticles.

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PLASMA CHEMICAL TREATMENT as METHOD of MODIFICATION of the CATALYTIC PROPERTIES of CONDUCTORS TYPE of NASICON and BIMEVOX

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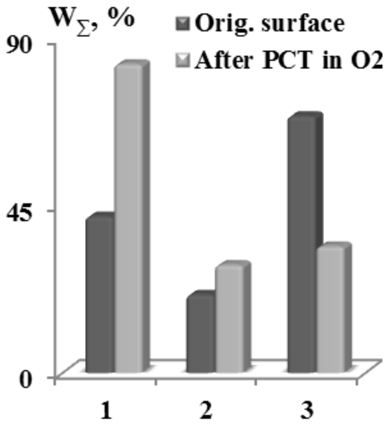
Chemistry of solid electrolytes (SELs) is actively developing at present. SELs with lamellar framework structure of considerable interest complex Na-Zr-phosphate (**NASICON**) with cationic conductivity type [1] and complex perovskite structure (**BIMEVOX**) the anionic conductivity type [2]. The possibility of modification in the structure of NASICON and BIMEVOX by 3d-metal ions allows their usage as heterogeneous catalysts in the acide-base and redox reactions. 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. The purpose of this work was to determine the influence plasma chemical treatments in oxygen on the catalytic activity of complex sodium-zirconium phosphates $Na_3CuZr(PO_4)_3$ and bismuth vanadate $Bi_4V_{2-2x}Cu_xO_{11-\delta}$ (with x=0.06, 0.16) in reactions of butanol-2 and isobutanol.

Catalysts $\mathbf{Na_3CuZr(PO_4)_3}$ were prepared by the sol-gel method. Complex oxides $\mathbf{Bi_4V_{2-2x}Cu_xO_{11-\delta}}$ were obtained by solid-phase synthesis [3]. All samples were studied in detail by means of DTA, XPA, and IR spectroscopy. Plasma chemical treatment (PCT) was performed in the zone of oxygen glow discharge burning in a vacuum flow alternating current unit. The catalytic properties of the modified compounds were studied on a flow unit. The products were analyzed by chromatographing with helium as a carrier gas and a flame ionization detector at 200-400°C.

All initial samples catalyzed the dehydration and the dehydrogenation of alcohols. It was shown that modification of the catalyst structure influence on the rate and selectivity of the conversion of alcohol (tabl., fig.). This indicates that the copper ion is included in the active site. Dehydrogenation reaction centers are different, as can be seen from the various values of $E_a^{C=O}$ for NASICON and BICUVOX. The most active catalyst was sample bismuth vanadate with x=0.16 (fig.). The high activitie of the sample ***3*** in this reaction were caused by a multiple decrease in the activation energy, as is seen from the data of the table. After the plasma chemical treatment of catalysts, the dehydrogenation reaction only occurred. We see that the activation energies of dehydrogenation on the samples ***1*** and ***2*** retained. Increased activity is associated with an increase the active site.

To summarize, we showed that plasma chemical treatment caused deactivation of the centers of dehydration of alcohols and increased the yield on $\mathbf{Na_3CuZr(PO_4)_3}$ by a factor of 2.

	$Na_3CuZr(PO_4)_3$	$Bi_4V_{2-2x}Cu_xO_{11-\delta}$	
	1. *x=1.00*	**2.** *x=0.06*	**3.** *x=0.16*
Original surface			
$S^{C=O}$, %	89	95	81
$E_a^{C=O}$, kJ/mol	20	58	8
lnN_0	−14.2	−11.9	−19.2
After PCT in O_2			
$S^{C=O}$, %	100	100	100
$E_a^{C=O}$, kJ/mol	27	50	62
lnN_0	− 11.4	−11.2	−8.5



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TITANIUM (+4) POLYMETALLIC COMPOUNDS with OO-TYPE LIGANDS as CATALYSTS for ETHYLENE POLYMERIZATION

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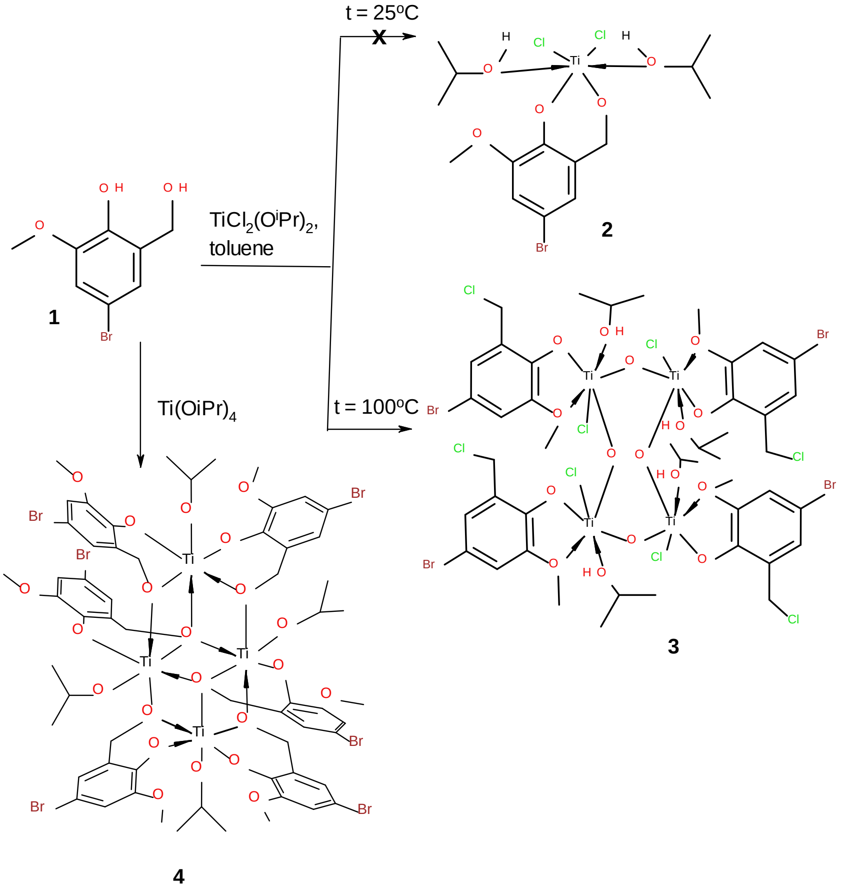
Synthesis of titanium monometallic complexes, stabilized by 6-metoxy saligenin derivatives, has been studied. Interaction between ligand **1** and $TiCl_2(OiPr)_2$ under mild conditions the formation of the expected product **2** of $LTiCl_2(iPrOH)_2$ apparently doesn't occur. Single crystals, suitable for X-ray structure analyses, failed to grow; NMR spectra are complex, reflecting the formation of a set of complexes. Carrying out the reaction under more severe conditions is accompanied by chemical modification of the ligand – hydroxyl group substitution by chlorine, and yields compound **3** (scheme 1).

By the reaction of the same ligand **1** with titanium tetraisopropoxide compound **4** has been obtained.

Catalytic properties of synthesized catalysts in the ethylene polymerization reaction have been studied. It has been shown that the catalytic activity of compounds (activated by Et_2AlCl / Bu_2Mg = 3/1) varied between 1825-3200 kg [PE] / (mol [Ti] h atm).

All samples of polyethylene had a molecular weight more than 1500000, as evidenced by their insolubility in trichlorobenzene at 130 °C.



Scheme 1. Synthesis of titanium (+4) complexes based on ligand 1.

Acknowledgements

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CATALYST for COMPLETE OXIDATION of NITROGEN CONTAINING SAMPLES

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High temperature catalytic oxidation of nitrogen containing compounds has great importance for the analysis of environmental and industrial samples and the control of emissions of waste incineration facilities. The complete oxidation of nitrogen in different functional groups to NO and NO_2 is a crucial step for the determination of nitrogen in samples and NO_x abatement [1,2]. Altough platinum group metals have excellent oxidation activity, they are expensive and easily poisoned by the presence of S, Cl and P containing organic substances. Therefore, there is a great interest to develop new active, selective and resistant catalyst to treat waste oxidation gases. In this study, the activities of CuO/ Al_2O_3, $CuO-CeO_2$ / Al_2O_3 and Pt/ Al_2O_3 catalysts for total oxidation of nitrogen containing compounds were analyzed. The catalyst samples were prepared to obtain a loading of 10% Cu, 3%Cu-7%Ce, 1% Pt over the Al_2O_3 as a suppport by impregnation method. Characterization of the catalyst samples was performed by X-ray powder diffraction (XRD) and BET. EDTA, urea, potassium nitrate, ammonium chloride, thiourea, pyridine, glycine, yeast extract, metylamine were selected as model components representing various nitrogen containing functional groups. The experiments were performed in a quartz tubular reactor in two zone furnace and the sample first oxidized at 700-850 ^{o}C under air flow of 200 ml/min and the cataytic oxidation was performed at 500^{o}C in second zone, gas stream passed over catalytic bed. The catalytic activities of the samples were investigated with mass spectrometry by analyzing combustion products. In table 1, BET surface area values of the catalysts samples are given. It is seen that the surface area changes significantly when impregnating cerium and copper on Al_2O_3.

Table 1: BET Surface area of the catalyst

Sample	**BET Surface Area (m^2/g)**
Al_2O_3	314.8
1%Pt/Al_2O_3	309.6
10%Cu/Al_2O_3	244.3
3%Cu- 7%Ce/Al_2O_3	261.0

NO (m/z=30) signals observed in mass spectrometry for urea and EDTA samples having equivalent mass of nitrogen (7.52 mg), over 10%Cu/Al_2O_3 catalyst sample are shown in figure 1. As it is seen from the figure, EDTA oxidation follows at least two step mechanism compared with the simple structure of urea.

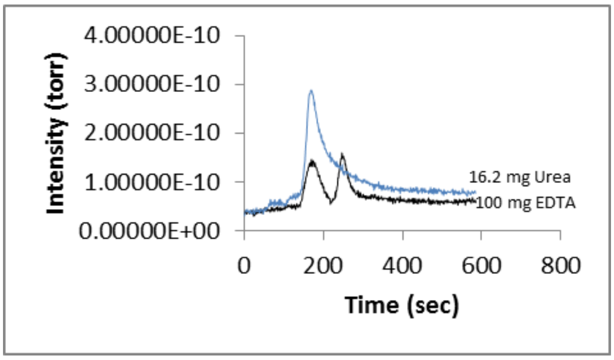

Figure 1: Change in amount of NO in the combustion gases

Acknowledgements

We would like to thank KOSGEB due to their support and founding this research.

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PP-32

THE SYNTHESIS of CATALYSTS BASED on Ni- and Cu-DOPED $Cd_{0.3}Zn_{0.7}S$ for PHOTOCATALYTIC HYDROGEN PRODUCTION under VISIBLE LIGHT

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Hydrogen is known to be a promising energy carrier. One of the most interesting way of hydrogen evolution is photocatalytic water splitting on semiconductors [1]. Unfortunately, catalytic activity in this process is quite low due to short lifetime of photogenerated charge carriers on the semiconductor surface. In order to increase the lifetime of charge carriers sacrificial agents such as aqueous solutions of Na_2S + Na_2SO_3 should be added in reaction solution. Earlier it was shown that the most active photocatalyst for hydrogen production from Na_2S + Na_2SO_3 is $Cd_{0.3}Zn_{0.7}S$ [2]. In order to increase its photocatalytic activity, it is doped by transition metalls species such as copper and nickel [3]. The influence CuS, NiS, $Cu(OH)_2$, and $Ni(OH)_2$, on the photocatalytic properties of $Cd_{0.3}Zn_{0.7}S$ was invesistigated. The activity of $CuS/Cd_{0.3}Zn_{0.7}S$ was shown to exceed that of $NiS/Cd_{0.3}Zn_{0.7}S$ photocatalysts likely because of the more favorable heterojunctions. Also hydrogen can be produced by catalytic cycle realized on $CuS/Cd_{0.3}Zn_{0.7}S$ photocatalysts. The highest photocatalytic activity (3.52 $mmol*g^{-1}*\ h^{-1}$) was possessed by 1 mol % $CuS/Cd_{0.3}Zn_{0.7}S$ [3]. Fig. 1a represents dependence of the rate reacion on photocatalyst composition $M(OH)_2/Cd_{0.3}Zn_{0.7}S$, M = Cu or Ni. $Ni(OH)_2$ is known to be reduced to Ni^0 which can produce hydrogen from protons under visible light irradiation.

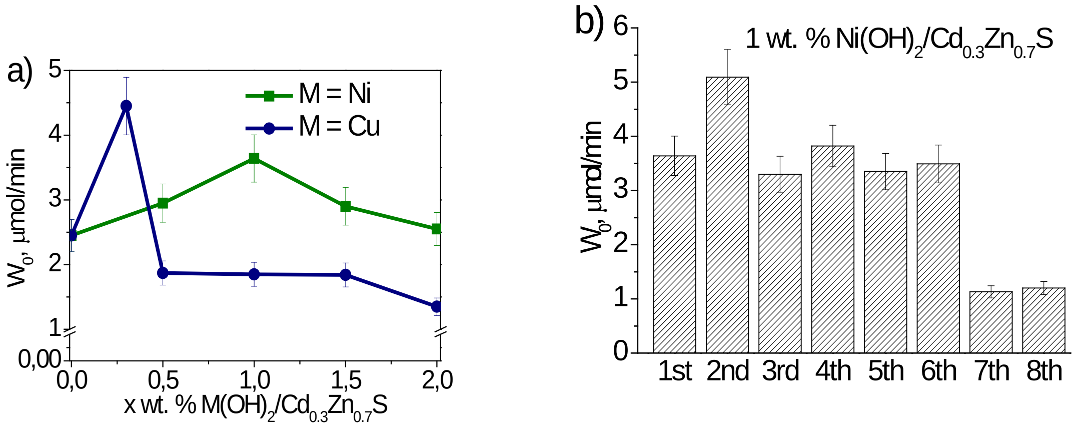

Fig. 1. The photocatalytic activity of $Cu(OH)_2/Cd_{0.3}Zn_{0.7}S$ and $Ni(OH)_2/Cd_{0.3}Zn_{0.7}S$ (a) and reusability of 1% $Ni(OH)_2/Cd_{0.3}Zn_{0.7}S$ (b).

Also $Cu(OH)_2$ can be reduced to Cu or Cu_2O. The last one is semiconductor, so this system may be active because of heterojunctions between Cu_2O and $Cd_{0.3}Zn_{0.7}S$. The most active sample are 1 wt.% $Ni(OH)_2/Cd_{0.3}Zn_{0.7}S$ (4.04 mmol*g^{-1}* h^{-1}) and 0.3 wt.% $Cu(OH)_2/Cd_{0.3}Zn_{0.7}S$ (5.34 mmol*g^{-1}* h^{-1}). As shown in Fig. 1b, 1 wt.% $Ni(OH)_2/Cd_{0.3}Zn_{0.7}S$ photocatalyst does not show obvious loss of activity after 9 h (6 cycles) of photocatalytic reaction. Some activation is observed in the first cycle. To sum up, 1 wt. % $Ni(OH)_2/Cd_{0.3}Zn_{0.7}S$ photocatalyst is stable and has good reusability.

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PP-33

ASYMMETRIC EPOXIDATION of OLEFINS with H_2O_2 CATALYZED by NON-HAEM AMINOPYRIDINE MANGANESE COMPLEXES: INFLUENCE of STERIC and ELECTRONIC PROPERTIES of LIGANDS on ENANTIOSELECTIVITY

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The catalytic asymmetric epoxidation of olefins is a highly important chemical transformation since the resulting epoxides are useful strucrural motifs or versatile intermediates for organic synthesis. Non-haem manganese complexes with tetradentate aminopyridine complexes were shown to be efficient and selective catalysts of olefins epoxidations with H_2O_2 exhibiting moderate to good enantioselectivities [1]. Herein we report a systematic study of bipyrrolidine-based manganese catalysts focusing on influence of sterically and electronically different substituents in pyridyl fragments of aminopyridine ligands. The following manganese complexes were synthesized and characterized by RSA:

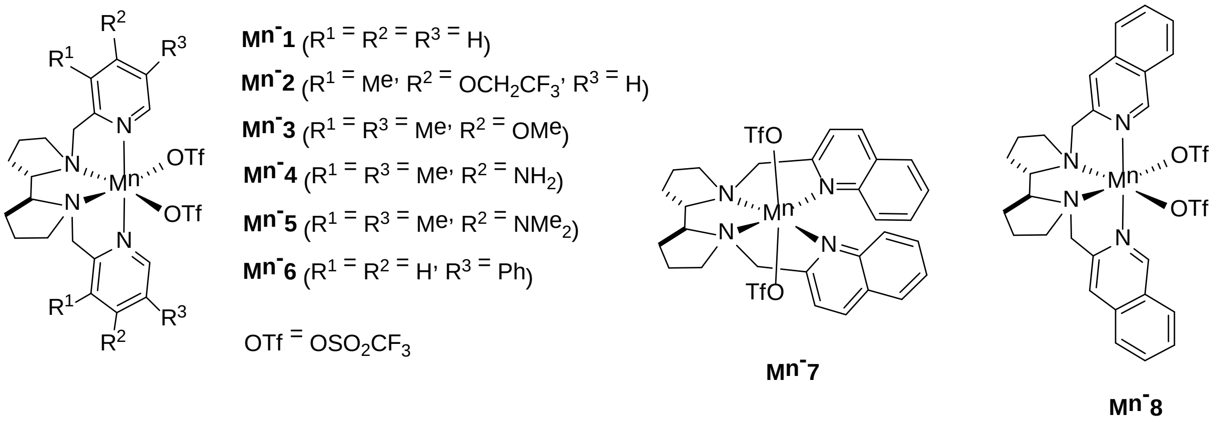

Fig. 1. Non-haem Mn complexes.

Catalytic epoxidations of chalcone or styrene with H_2O_2 in the presence of complexes **Mn-6**, **Mn-7** and **Mn-8** (having ligands with enhanced steric crowd) demonstrated only slight increase in enantioselectivities compared to parent complex **Mn-1** (+3 %). On the other hand, the influence of electronic properties of substituents in pyridyl moietes appears to be more significant. The presence of electron-donating groups in complexes **Mn-3**, **Mn-4** and **Mn-5** notably improved enantioselectivities with respect to parent complex **Mn-1**. For example, epoxides of chalcone and 2,2-dimethyl-2*H*-1-benzopyran-6-carbonitrile were obtained with 98 and 99 % *ee* respectively in the presence of 0.1 mol % of catalyst **Mn-4**. A number of *α*,*β*-unsaturated ketones, *α*,*β*-unsaturated esters and unfunctionalized olefins were epoxidized with *ee*'s from 70 to 96 % using complexes **Mn-4** and **Mn-5** as catalysts. All reactions were carried out at –30 °C in the presence of 2-ethylhexanoic acid as an additive, the role of the latter were studied earlier [1].

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Acknowledgements

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SELF-ORGANIZING CATALUSIS FOR DECOMPOSITION OF INDUSTRIAL ORGANOCHLORINE WASTES

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Chlorinated compounds are still among the most important solvents used in chemical industry as well as in smaller-scale laboratories throughout the world. Nevertheless, they exert hazards to the environment, mainly because of the lack of natural self-governing processes for their destruction. [1]. Several methods have been employed to destruct or convert these environmental hazards to value added compounds [2].

The authors of this work have focused on the development of catalytic method to utilize the multi-component mixtures of chlorinated hydrocarbons (CHCs). Such wastes are produced in large volume as the by-product of industrial processes of organochlorine synthesis and known to represent rather complicated ecological problem for Russian Federation. According to proposed method, decomposition of CHCs results in formation of nanostructured carbon material with unique properties thus extracting the carbon from the composition of waste [3].

The suggested approach for catalyst preparation is based on the phenomenon of metal dusting (MD) of the standardized bulk Ni-M alloys used as precursors [4]. During the MD process, Ni nanoparticles which catalyse the growth of carbon nanomaterials (CNMs), are produced spontaneously from the bulk metal precursors. Thus prepared self-organized catalytic system was found to be characterized by very high activity in decomposition of 1,2-dichloroethane (superior to that known for analogous supported catalysts), extreme resistance to deactivation and huge productivity towards carbon nanomaterial exceeding 500 g/g_{Ni} [5].

In the presented study, the bimetallic alloys Ni_{1-x}-M_x (M=Co, Cu, Cr; x=0.01÷0.5) have been synthesized by coprecipitation method [6]. The catalysts formed from the bimetallic alloy Ni_{1-x}-M_x were tested in real processing organochlorine synthesis wastes to give CNMs (fig. 1).

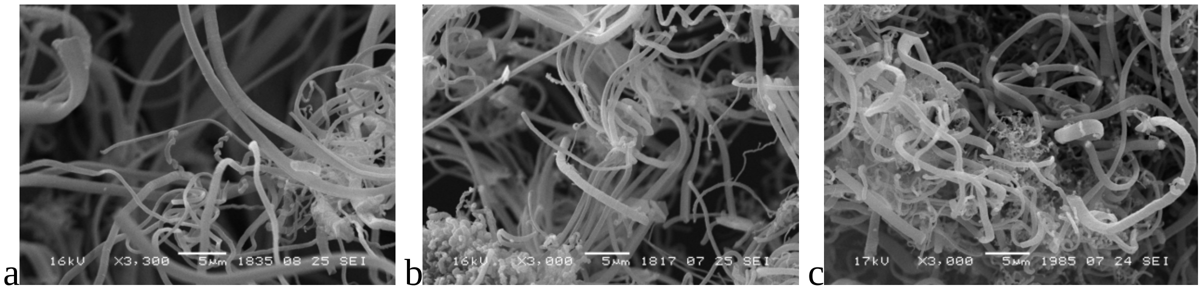

Fig. 1 SEM images of carbon fibers derived from decomposition (550°C) of waste (industrial production of chloromethanes, Volgograd, Russia) over self-organized catalysts obtained from following bimetallic alloys:
$Ni_{0.99}$-$Cu_{0.01}$ (a), $Ni_{0.99}$-$Co_{0.01}$ (b) and $Ni_{0.95}$-$Cr_{0.05}$ (c).

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2-IMINOPYRIDYL NICKEL(II) COMPLEXES BEARING ELECTRON-WITHDRAWING GROUPS in the LIGAND CORE: ETHYLENE OLIGOMERIZATION and POLYMERIZATION BEHAVIOR

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During the last two decades nickel(II) complexes with bidentate *N*,*N*-donor ligands have been attracting considerable attention as catalysts for polymerization of ethylene and linear α-olefins yielding polymeric products with various types of branching [1]. Up to date, the post-metallocene catalysts based on nickel complexes providing branched and hyperbranched polyethylene are of great importance due to the unprecedented chain architectures and unique physical properties of these polymers [2].

Nickel(II) complexes with 2-[(arylimino)alkyl]pyridine ligands are of special interest due to the simplicity of ligands syntheses, rich opportunities for fine tuning of their steric and electronic properties by the introduction of different substituents into the phenyl rings, and the ability to give low-molecular-weight polyethylene with different content of branches. However, only ethylene polymerizations over 2-iminopyridine catalysts with electron-donating (alkyl) substituents at the aryl rings have been reported previously [3]. It is challenging to probe the effect of electron acceptors on the performance of nickel catalysts. Previously, introduction of electron-withdrawing groups was reported to increase the activity of analogous iron, cobalt and nickel tridentate bis(imino)pyridine catalysts for ethylene and norbornene polymerization [4].

In the present work a series of 2-iminopyridine nickel(II) dichloride (or dibromide) complexes containing electron-withdrawing substituents (R_2-R_5 = F, Cl, Br, CF_3) in aryl moieties have been examined in ethylene polymerization and oligomerization using methylaluminoxane as a co-catalyst.

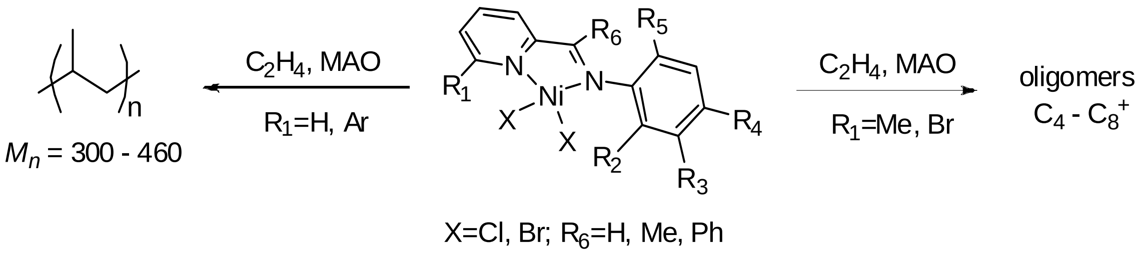

Fig. 1. 2-iminopyridine nickel(II) complexes

All complexes containing substituted 6-position of pyridine ring (R_1 = Me, Br) and fluoro-substituted phenyl ring (R_2, R_4, R_5 = F, CF_3) displayed high activities (up to $9.6\cdot10^6$ g·(mol Ni)$^{-1}\cdot$h$^{-1}\cdot$bar^{-1}) towards ethylene oligomerization yielding a wide variety of ethylene oligomers (1-butene, (*Z*)-2-butene, (*E*)-2-butene, 2-ethylbutene-1, etc.).

Catalysts with unsubstituted or aryl-substituted 6-position of pyridine ring (R_1 = H, Ar) and *o*-trifluoromethyl group in phenyl ring turned out to be highly active towards ethylene polymerization (up to $6.6\cdot10^6$ g·(mol·Ni)$^{-1}\cdot$h$^{-1}\cdot$bar^{-1}) yielding low-molecular-weight branched polyethylenes (20-85 branches per 1000 C determined by NMR spectroscopy), with *sec*-butyl branches being identified. To the best of our knowledge, this is the highest reported activity for ethylene polymerizations and oligomerizations over 2-iminopyridine nickel catalysts.

New 2-iminopyridine nickel complexes have been found to be highly active catalysts of ethylene polymerization and oligomerization upon the activation with methylaluminoxane. The catalytic activity as well as the product morphology has been found to correlate with the number and position of electron-withdrawing substituents.

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EPR SPECTROSCOPIC STUDY of the ACTIVE SPECIES of CATALYTIC ALKENE EPOXIDATION MEDIATED by BIOMIMETIC FERRIC COMPLEXES

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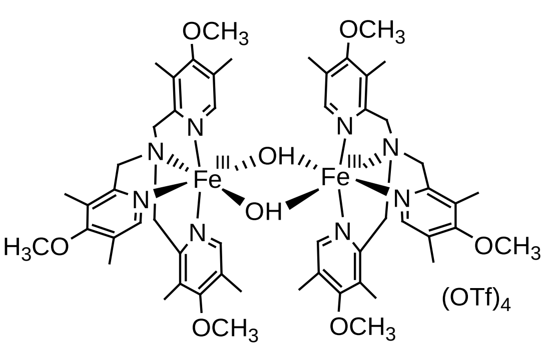
Catalyst systems based on iron complexes with tetradentate *N*$_4$-donor, mainly, aminopyridine ligands, H_2O_2, and carboxylic acid as an additive have attracted particular attention in the last decade due to high efficiency and selectivity in the preparative oxidations of C–H and C=C groups of various organic molecules.[1a] Although the mechanistic landscape of aminopyridine iron catalysts has been discussed in a series of elegant experimental works, the problem of direct experimental detection and identification of the elusive oxygen-transferring species in these catalysts is far from being solved.[1b] In the present study we have undertaken an EPR spectroscopic study of the active species of the highly effective and enantioselective catalyst systems (epoxidizing olefins with up to 99% *ee*)[2] based on aminopyridine iron complexes **1** and **2** with electron-donating substituents at the pyridine rings.



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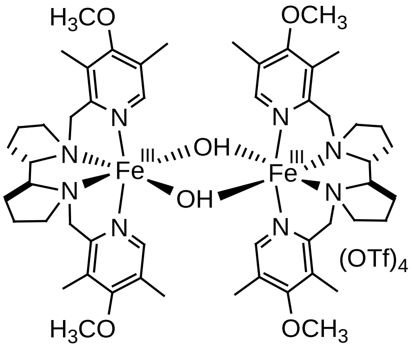

2

Mixing complex **1** (or **2**) with CH_3COOH (10 equiv) and H_2O_2 (3 equiv) at −80…−75 °C led to the formation of new low-spin (S = 1/2) iron-oxygen intermediates **1a** (g_1 = 2.070, g_2 = 2.005, g_3 = 1.956) and **2a** (g_1 = 2.071, g_2 = 2.008, g_3 = 1.960) extremely unstable even at −85 °C ($\tau_{1/2}$(**1a**) = 5 min, $\tau_{1/2}$(**2a**) = 4 min). The evaluated maximum concentration of **1a** and **2a** did not exceed 1-2% of the total iron concentration.

To directly assess the reactivity of **1a** and **2a** towards alkene epoxidation, the rates of decay of **1a** and **2a** in the absence and in the presence of various alkenes were compared. It was found that the addition of relatively small amounts of cyclohexene or *cis*-*β*-methylstyrene ([alkene]/[Fe] = 0.5) to the samples containing **1a** or **2a** results in the decrease of the half-life time of **1a** and **2a** from $\tau_{1/2}$ = 4-5 min to $\tau_{1/2}$ < 0.5 min at −85 °C, whereas electron-deficient alkenes (1-acetyl-1-cyclohexene and cyclohexene-1-carbonitrile with an [alkene]/[Fe] ratio up to 10) do not visibly affect the decay rates of **1a** and **2a**. Hence, **1a** and **2a** are highly reactive towards electron-rich alkenes even at −85 °C. To quantify the products of interaction of **1a** and **2a** with cyclohexene, catalytic oxidation experiments at −85 °C were performed. 4.5 and 5.3 TN cyclohexene oxide were obtained 15 min after the reaction onset with catalysts **1** and **2**, respectively (TN = moles of product per mole of Fe, $[Fe]:[H_2O_2]:[CH_3COOH]:[C_6H_{10}]$ = 1:10:20:30, [Fe] = 0.02 M). The total amount of other cyclohexene oxidation products was <1% with respect to the epoxide. Thus, the active species **1a** and **2a** oxidize cyclohexene at −85 °C with >99% selectivity towards the epoxide.

The *g*-values and line widths of intermediates **1a** and **2a** are very similar to those of spectroscopically well characterized model oxoiron complex $[(TMC)Fe^{V}{=}O(NC(O)CH_3)]^{+}$ (TMC = tetramethylcyclam).[3] On the basis of this similarity and reactivity data, we have assigned intermediates **1a** and **2a** to the oxoiron(V) $[(L)Fe^{V}{=}O(OC(O)CH_3)]^{2+}$ active species of selective alkene epoxidation by the studied catalyst systems studied.

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SIMULATION of ETHANOL to ETHYLENE DEHYDRATION on ALUMINA CATALYST IN MULTITUBULAR REACTOR

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Ethylene is one of the largest chemical products in the world, and one of the most important raw materials for petrochemical industry [1]. At present, the main technical trend to produce ethylene is hydrocarbon-cracking, that is recognized unsafe for environment. Because of the rising interest in a chemicals production from renewable non-food plant sources, the bioethanol to bioethylene dehydration technology received much attention in last decades. Alumina and zeolite catalysts have been investigated extensively in this catalytic process. Due to the higher stability and productivity at high ethanol concentration, the alumina-based catalysts are regarded as more perspective for industrial application. The ethylene yield reported for alumina catalysts was not less than 97% [2]. The ethanol dehydration process is strongly endothermic; the selectivity to the target product is highly sensitive to the temperature. Thus, the proper temperature control is a key operation factor for this process.

In the recent paper [2] kinetic studies, pilot reactor testing, and process simulation on alumina-based catalyst have been elaborated; ethylene yield was found to be ca. 96% for industrial multi-tubular reactor. However, these data were obtained on catalyst with a relatively low activity. The kinetic model developed in [2] assumed that ethylene was formed both directly from ethanol and via intermediate formation of diethyl ether; while by-products acetaldehyde and butylenes were formed from ethanol and ethylene, respectively. Reaction scheme is presented in Figure. Experimental results obtained in the pilot-scale tubular reactor were in good agreement with simulation data.

In the present paper, kinetic model [2] was used for theoretical study of the ethanol dehydration process on alumina catalyst under wider variation of catalysts activity and process parameters.

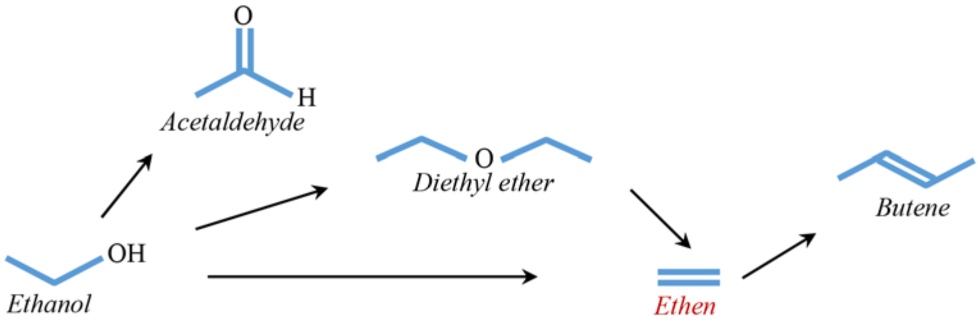

Figure. Network of ethanol to ethylene dehydration on alumina catalyst

To simulate the process, 2D pseudo-homogeneous model of tubular fixed bed reactor [3] was used. Results of mathematical modeling of ethanol dehydration in a multi-tubular reactor showed that 2-fold increase of the catalyst activity promotes formation of ethylene as high as 97.5% and 1-1.5% decrease of by-products yield. The effect of catalyst activity and selectivity on the process productivity and parametric sensitivity was analyzed; optimized operating conditions that favor the high yield of ethylene in multi-tubular reactor were determined.

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CATALYSTS BASED on FOAM MATERIALS for STEAM REFORMING of NATURAL GAS to SYNTHESIS GAS

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The development of the catalysts for hydrocarbon fuel reforming to synthesis gas is becoming increasingly important in view of the potential application of synthesis gas as an additive to the engine fuel for achieving Euro-4 standards. Available experimental data [1] indicate that the use of synthesis gas generator on-board an internal combustion engine reduces harmful emissions (including carbon black), decreases considerably the diesel glow dose and improves ICE efficiency. The use of traditional granular catalysts in such systems is unpromising due to their low mechanical strength and negligible thermal conductivity. Alternative decision is to create the new catalysts based on new materials: highly porous metals and metal foams.

In this work, the 7% NiO/7-9% MgO catalysts deposited on porous nickel and nickel foams with PPI 60-80 were developed and tested under the following experimental conditions: T = 300-660˚C, P = 1 atm, GHSV = 6400-16500h^{-1}. Fig.1 presents the temperature dependencies of methane conversion over the developed catalysts in comparison with those over industrial catalyst NIAP-18 (10.0-12.0% NiO).

It is seen that the reaction on the nickel foam-supported catalyst is closer to the thermodynamic equilibrium than the reaction on NIAP-18.

In view of possibility to create regular structures, the catalysts supported on foam materials show obvious promises for using in steam reforming of natural gas to synthesis gas.

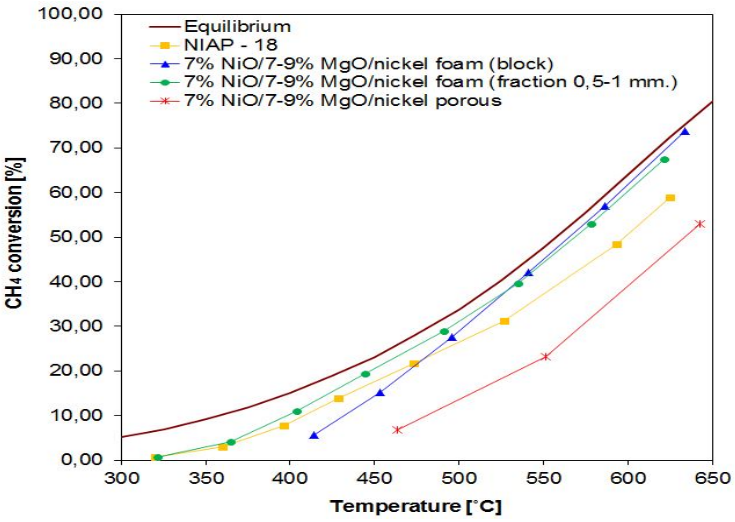

Fig. 1 Influence of temperature on methane conversion at GHSV=10200 h^{-1}

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Acknowledgement

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DEVELOPMENT of TECHNOLOGY for PVC RECYCLING by CATALYTIC THERMOLYSIS to OBTAIN STRUCTURED CARBON and IRON CHLORIDES

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Today plastics are the very popular materials used for many applications. As a result, the volume of wastes containing large amounts of polymers constantly grows. Many methods have been developed for processing and utilization of waste polymers. However, they are not widely used due to their inefficiency and high cost. Plastics, such as polyethylene and polyvinylchloride, can be used as feedstock for synthesis of valuable products with useful properties. For instance, they contain carbon. So, they can be used in technologies for production of structured carbon materials. In this study we propose a technologically simple method for processing of polyvinylchloride based on the method developed by Gedanken et al. [1] leading to the formation of iron chloride and carbon structures in the form of fibers.

The process is carried out in a sealed reactor without access of oxygen. Bulk iron metal or iron-containing alloy are used as catalysts. The redox reaction on the metal surface results in the formation of dispersed metal particles acting as the active sites for growth of carbon structures.

We have studied products formed during pyrolysis of polyvinylchloride under catalytic conditions using iron metal as the catalyst. Chlorine atoms present in the polymer macromolecule acted as the oxidizer. SEM images revealed structures on the metal surface composed from carbon atoms according to the results of chemical analysis (Fig. 1). The formation of such products is related to catalytic corrosion of bulk metal due to redox transformations on its surface. Note that such products are not observed for polyethylene, which does not contain an oxidizer (e.g. halogen atoms).

The approach to thermolysis of polymers used in this study can be implemented in new technologies for processing of plastics.

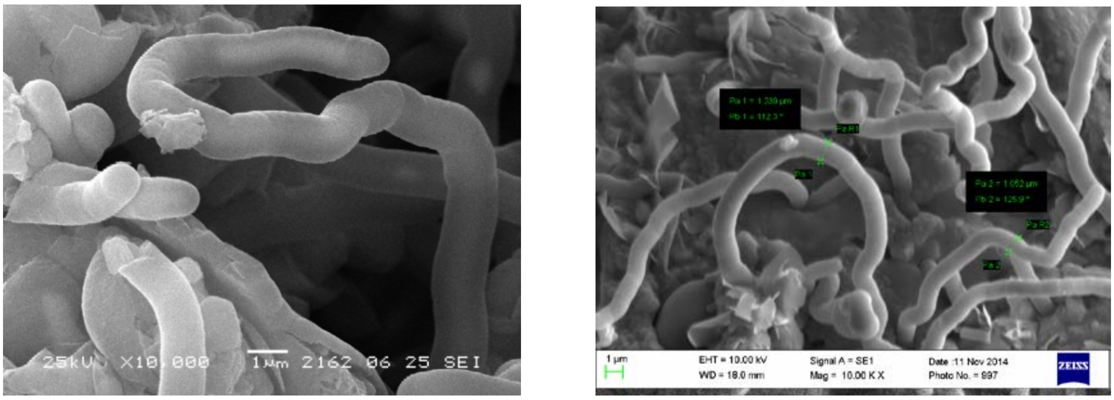

Fig. 1. Carbon structures formed on the surface of iron metal

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Acknowledgements

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MICROCHANNEL REACTOR for METHANOL to FORMALDEHYDE OXIDATION: EXPERIMENTAL STUDIES and PROCESS SIMULATION

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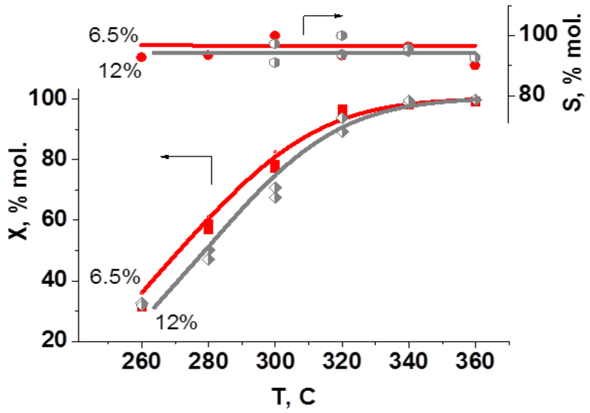
Modern challenges of industrial development require that key technological processes should be optimized and significantly intensified. Micro-channel reactor (MCR) technologies can be one of the promising innovative solutions to perform chemical processes [1] under conditions that sometimes are far from the conventional ones.

In this paper, specific features of highly exothermic catalytic process in MCR were studied on the example of methanol to formaldehyde oxidation. Commercial formaldehyde processes are realized in multi-tubular reactors, or in adiabatic reactors. However, due to the explosion safety reasons and limitation of the heat removal, conventional processes are conducted at rather low initial methanol concentration; ca. 6-8 % vol. Design and material of MCR allow avoiding these difficulties due to sub-millimeter sizes of the channels and separate feed of reactants, thus securing uniform flow distribution over the cross-section of MCR [2].

Experimental studies were executed on a lab-scale MCR setup under varying parameters as follows: volume rate GHSV=17100-65600 h^{-1}, inlet methanol concentration $[CH_3OH]_0$ = 6% vol. and 12 % vol., temperature T=240-380°C. The major operating unit of setup was the brass plate 10 mm thick perforated by 499 through channels 1 mm diameter [2]. All channels were filled with particles of commercial Fe-Mo catalyst crushed and sieved to 0.25-0.50 mm, total load was 4 ml.

During the experiments conversion at the temperatures 340-380°C was not less than 95%, while selectivity to formaldehyde was 94-96%. In order to simulate the process, a 2D-continuum model of the tubular reactor [3] was used. This model describes catalytic process in one channel, in assumption that uniform flow distribution secures similar behavior of all other channels. Each MCR channel is considered as a separate tube with heat transport conducted through the wall. This model adequately describes methanol-to-formaldehyde catalytic process in MCR. Discrepancies between the experimental and the predicted values of conversion and selectivity did not exceed 5-10% over the entire studies, see Figure.



$[CH_3OH]_0$=6.5 and 12% vol.,
$[O_2]/[CH_3OH]$=1.5; U= 0.15m/s;
GHSV= 52500 h^{-1}.
Points- experiment.
Lines - simulation.

Fig. Conversion and selectivity to formaldehyde vs. temperature in MCR.

Operation conditions in MCR for methanol-to-formaldehyde process allow ca. 10-fold increasing the specific productivity of the catalyst compared to conventional technology; the process is safety at increased methanol content within the explosion range of methanol-oxygen mixture. The catalyst stability at extreme conditions should be thoroughly investigated; the search for special catalyst for MCR potential application may be required.

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STUDY of TITANIUM COMPOUNDS and THEIR TRANSFORMATION into the ACTIVE SITES of SUPERACTIVE 'LOW-PERCENTAGE' TITANIUM-MAGNESIUM CATALYSTS FOR ETHYLENE POLYMERIZATION

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The state of titanium ions and the formation of active component in supported $TiCl_4/MgCl_2$ catalysts with different titanium content were studied using ESR, gas chromatography and chromatography-mass spectrometry. A high fraction of isolated Ti(III) compounds (up to 70 mol.%) was observed for superactive catalysts with a low titanium content (≤ 0.1 wt.%) after their interaction with aluminum trialkyls [1, 2]. These catalysts substantially differed from conventional TMCs with titanium content of 1-3 wt.%, in which a set of isolated and associated Ti(II) and Ti(III) compounds was formed after the interaction with AlR_3. A linear correlation was found between the activity of TMCs and the content of isolated Ti(III) compounds observed by ESR [1, 2].

Organic products of the TMC interaction with AlR_3 were identified by gas chromatography and chromatography-mass spectrometry. The data obtained allowed us to suggest the formation schemes of active sites in the catalysts with high and low titanium contents. For the 'low-percentage' catalysts, active sites are formed via a homolytic cleavage of the titanium-alkyl bond in isolated $TiCl_3R$ compounds leading to the formation of isolated Ti(III) compounds. In the case of catalysts with a high titanium content (≥ 1 wt.%), Ti(III) and Ti(II) compounds are formed by both the homolytic decomposition of isolated $TiCl_3R$ compounds and the decomposition of $TiCl_4 \cdot TiCl_3R$ binuclear complexes.

The interaction of carbon monoxide (CO) with the 'low-percentage' TMCs activated by $AlMe_3$ in the presence and in the absence of α-olefins was studied by ESR. In both cases, ESR spectra of the catalysts before their interaction with CO showed signals with high g-values. In addition, the catalysts containing Ti(III) compounds only with the chlorine ligands were studied. In ESR spectra of such a catalyst, g-values were lower as compared to activated TMCs. After the activation of such $AlMe_3$ catalyst, the g-values shifted toward greater values and the ESR spectrum was close to the spectrum of activated catalyst $TiCl_4/MgCl_2 + AlMe_3$. The interaction of CO with the catalytic system activated by $AlMe_3$ produced changes in ESR spectra. Parameters of the spectra had values lying between the parameters for activated and non-activated TMCs; a change in the signal waveform ($g_{\parallel} > g_{\perp}$) was observed. This may indicate the incorporation of CO via the titanium-alkyl bond and changes in titanium ligand environment.

ESR method was shown to identify Ti(III) compounds in the environment of chlorine atoms and Ti(III) compounds with the titanium-alkyl bond in titanium-magnesium catalysts. The data obtained testify that the treatment of $TiCl_4/MgCl_2$ catalysts with aluminum trialkyl results in the formation of Ti(III) compounds containing the alkyl bond.

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THE BEHAVIOR of a CATALYST SYSTEM DEPENDING on the NATURES of the STARTING CHROMIUM(III) COMPLEX COMPOUND

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The hexene-1 formation was observed for the first time in small quantities in the preparation of PE in the presence of chromium catalysts [1]. Later polycomponent homo- and heterogeneous catalyst systems (CS) based on compounds of chromium(III)–pyrrole-derivatives and organoaluminum compounds for the selective oligomerization of ethylene to hexene-1 were found [2-4].

Analyzing the obtained earlier experimental data [5], it can be said that the CS behavior depends not only on the molar ratios of the components, reaction conditions, the nature of cocatalyst, modifier and stabilizing ligand, but on the complex nature of the starting compound used as a basis for CS formation.

The aim of the present study was to investigate the CS type $Cr^{III}/AlEt_3/PyH/CCl_4$, where Cr^{III} – tris(atsetilatsetonat)chromium(III) and tris(2-ethylhexanoate)chromium(III) within wide range of temperatures from 60 to 80 °C and a pressure of 2 to 3 MPa in the presence and absence of the modifier. The experimental data is presented in Table 1.

Comparing the results for CS1 and CS3 one could take notice of a considerable increase in hexene-1 quantity (by 44 wt.%) and a significant decrease in PE quantity (by 51 wt.%). In the case of CS2 and CS4 the observed dependencies are similar.

It should be noted that despite the different nature of the initial complex compounds, the modifier administration to CS leads in both cases to the increase of PE quantity.

Table 1. The experimental data.

№	Molar ratio Cr : Al : L : M	*T*, °C	*P*, MPa	PE	Butene-1	Hexene-1	Activity CS, $g_{hexene\text{-}1}\cdot(g_{Cr}\cdot t)^{-1}$
				wt.%			
CS1 $Cr(acac)_3/AlEt_3/PyH$							
1	1 : 20 : 3	80	3	54	сл.	43	75
CS2 $Cr(acac)_3/AlEt_3/PyH/CCl_4$							
2	1 : 20 : 3 : 2	80	3	91	-	8	45
CS3 $Cr(EH)_3/AlEt_3/PyH$							
3	1 : 20 : 3	60	2	3	<1	87	2470
CS4 $Cr(EH)_3/AlEt_3/PyH/CCl_4$							
4	1 : 20 : 3 : 2	60	2	14	<1	72	1523

The CS3 demonstrated the best selectivity to hexene-1 among the studied systems.

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PP-43

LIQUID-PHASE AEROBIC OXIDATION of PETROLEUM HYDROCARBONS ın the PRESENCE of PENTANUCLEAR CR-COMPLEXES

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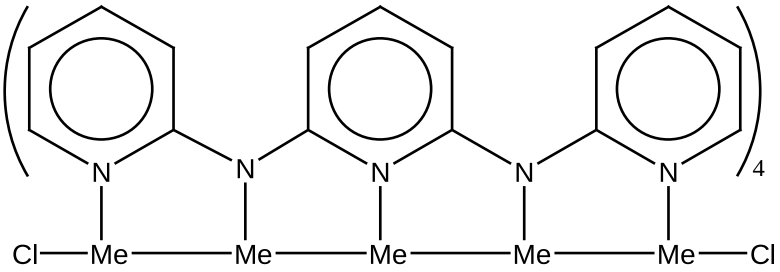
In the present paper pentanuclear Cr-complex is characterized as catalyst in the aeroobic oxidation of petroleum hydrocarbons into naphtenic and oxicarbon acids.

The used petroleum hydrocarbons are represented the dearomatized fraction of Azerbaijan oils boiled in the range 217-349°C. As a catalyst for oxidation of petroleum hydrocarbons in liquid phase pentanuclear $[Cr_5(tpda)_4Cl_2]$ (tpda = tripiridildiamin) complex is studied. This complex is synthezed in the Tayvan National University and is presented courtesy to investigate its catalytic properties [1,2]:



The oxidation process is carried out in the bubble type installation and the air flow rate was 300 *l*/kg·hour during the 6 hours at 135-140°C. The content of catalyst in ratio to liquid phase was 0,1 mas.%. After the reaction the oxidation products was separated and characterized by GC/MS, FTIR-spectroscopy [3].

The results of catalytic oxidation of the used petroleum hydrocarbons are given in the table 1.

Table. 1. The yield and composition of reaction products.

Liquid phase without(1) and in the presence (2) of catalyst	Conversion, %	Yield of the carbon acids,%	Reaction products,%	
			Petroleum Acids	Oxy-carbon acids
1	14,6	4,2	3,2	0,5
2	67,2	24,7	15,0	7,1

As can be seen from the table 1 the presence of catalyst essentialy increase the conversion of hydrocarbons and the yield of the petroleum and oxy-carbon acids.

The synthesized complexes and solid products of catalytic reactions before and after oxidation of petroleum hydrocarbons were isolated and characterized by atomic absorption spectroscopy, X-ray fluorescence microscopy, infrared spectroscopy. Dynamic light scattering method was used for determining of ”hydrodynamic radius” and diffusion coefficient of catalyst particles in liquid phase before and after oxidation process. The estimated values of particle size in dispersions are in the range 10 ÷ 50 nm (Table 2).

Table 2. Physical-Chemical Parameters of Cr-complexes before and after oxidation reaction in liquid phase

Samples, before(1) and after(2) reaction	Content of Cr in liquid phase, mas. % масс, (by AAS)	Electron Absorption Spectra, λ(max.), nm	Parameters of Dynamic Light Scattering (DLS)	
			Particles size (average) in liquid, nm	Diffusion coefficient, E^{-11} m^2/sec
1	0,022	420, 740	9,8	4.5879
2	0,019	405, 750, 910	10.5, 35,0	4.1890

The effect of the reaction medium on the nature of the complexes, their composition and structure is discussed.

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FERROMAGNETIC ^{59}Co NMR STUDY of Co NANOPARTICLES SUPPORTED on MULTI-WALL CARBON NANOTUBES for CATALYTIC APPLICATIONS

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Over the last few years, the interest to carbon nanostructures has grown enormously that mostly relates to the numerous searches of possible industrial applications. Among large variety of carbon nanomaterials, carbon nanotubes (CNTs) attract a special attention. Due to unique mechanical properties, large specific surface area, high electrical and thermal conductivity, and chemical stability, CNTs can be considered as a key component in different composites, in various electrochemical devices (lithium-ion batteries, supercapacitors) and for different applications in catalysis as supports. CNTs could be utilized as supports for various catalytic processes. For instance, one of the promising directions is Fischer-Tropsch synthesis (FTS) in the form of cobalt catalysts supported on CNTs [1]. High thermal conductivity of MWCNTs makes them also attracting as supports for the development of new catalysts of FTS avoiding overheating of the catalyst bed. In the present work, the structure of cobalt systems based on the perspective carbon supports, functionalized multi-wall carbon nanotubes (MWCNTs), has been investigated. The special attention has been applied to characterize Co species fixed on the surface of MWCNTs by ferromagnetic ^{59}Co NMR.

MWNTs were synthesized by CVD of ethylene decomposition over the bimetallic Fe-Co catalysts at 680°C. We have used functionalized MWCNTs containing surface carboxylic groups (0.76 groups per 1 nm^2) produced via boiling concentrated nitric acid (denoted as MWNT-Ox-NA) [2]. Co-containing samples were prepared by impregnation of MWCNTs (surface area of 305 m^2/g, average particle diameter of 9.4 nm) with the aqua solutions of Co (II) salts followed by calcination under an inert atmosphere and reduction in a stream of hydrogen at the temperature of 350°C. The samples with Co concentrations: 3.5, 7.3, 11.7 and 14.1wt.% were obtained. The structure of the cobalt metal in the catalyst after the reduction was investigated by ferromafnetic ^{59}Co NMR providing information about the structural

(FCC, HCP, and stacking faults - sfs) and magnetic (magnetic domains and domain walls) features [3].

Ferromagnetic ^{59}Co NMR probes five different types of metallic Co particles. The increase of Co concentration leads to the decrease in the relative content of Co in a cubic stacking, resulting the increase of the HCP/FCC ratio from 1.0 to 1.7.

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Acknowledgements

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ENHANCED PHOTOCATALYTIC OXIDATION of CO on TITANIA DEPOSITED with Ag NANOPARTICLES

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TiO_2 photocatalyst is a widely used material for oxidation of organic compounds under UV irradiation for environmental protection. In numerous photocatalytic oxidation (PCO) processes of volatile organic compounds, carbon monoxide is often one of the main oxidation byproducts and is not easily eliminated by the PCO, especially in humidified conditions. It is known that modification of TiO_2 catalysts by transition or noble metal improves its efficiency in photocatalytic oxidation. Practically, deposition of Pt on TiO_2 greatly enhanced the CO photooxidation rate [1]. However, due to the high cost of such catalysts they are not widely available. In this study, the influence of Ag deposits on TiO_2, a less expensive noble metals dopants alternative, on CO photooxidation rate at room temperature was investigated.

Ag/TiO_2 samples (1-10wt.% of Ag) were prepared following standart incipient wetness impregnation method using $AgNO_3$ water solution and TiO_2 anatase powder (Hombifine N, ~300 m^2/g). Two different pretreatment of Ag/TiO_2 samples were compared: 1) heating in O_2 at 450°C for 1 h and then reduction in H_2 at 400°C for 1 h and 2) reduction in H_2 at 100°C for 1 h. After cooling to room temperature samples were kept in atmospheric air. Before catalytic experiments the samples were evacuated at room temperature for 20 min to partially remove physically adsorbed water.

Naked TiO_2 and 5% Ag/TiO_2 after different pretreatments were compared for their photocatalytic activity of CO oxidation at room temperature. The results showed that when Ag nanoparticles were deposited on TiO_2, it exhibits great photocatalytic activity of CO oxidation under UV light irradiation. The optimum pretreatment for photocatalytic oxidation of CO on Ag/TiO_2 was heating in O_2 and subsequent reduction in H_2.

The influence of Ag content on CO oxidation was investigated for Ag/TiO_2 samples after optimum pretreatment in the dark and under UV light irradiation (Fig. 1). Oxidation activity raises with the increase of Ag contents within 1–10 wt.%. Simultaneously UV-irradiation significantly increases the oxidation rate on Ag/TiO_2 samples comparatively to the dark reaction. Thus, Ag nanoparticles deposited on titania enhance UV-induced CO photocatalytic oxidation at room temperature. The comparision of the activities of Ag/TiO_2 and Pt/TiO_2

samples shows that 1%wt Ag/TiO_2 and 0.2%wt Pt/TiO_2 have almost the same photocatalytic activity under identical condition used in this study, while the former is noticeably cost-effective.

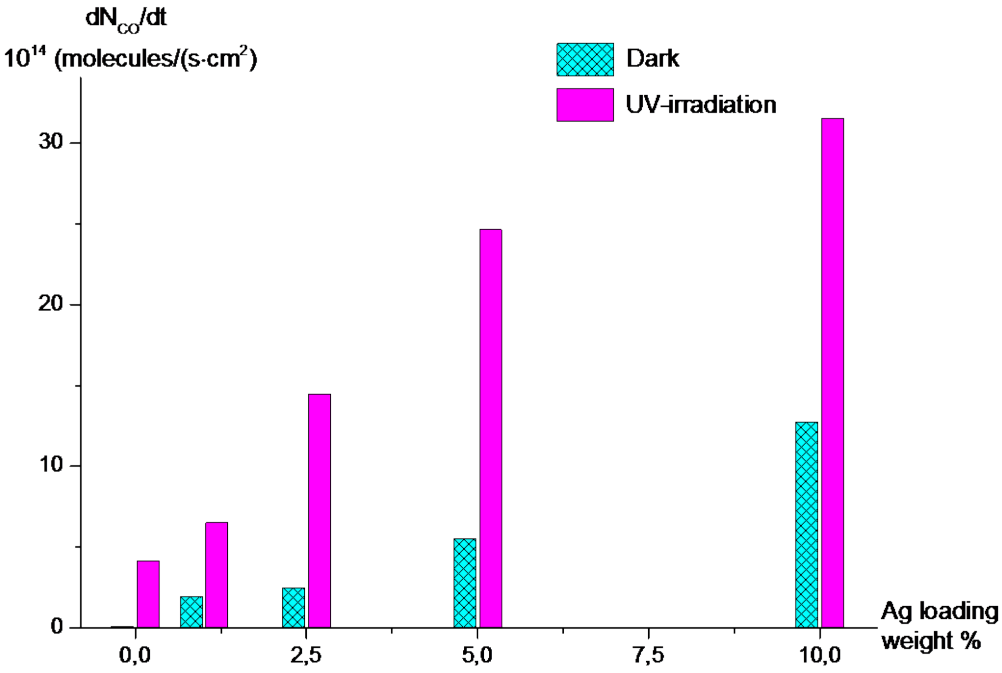

Fig. 1. The effect of different Ag loadings on the catalytic activity of CO oxidation on Ag/TiO_2 in the dark and under UV light irradiation.

It was concluded that the Ag enhancement effect in CO photooxidation is ascribed not only to the Schottky-barrier electron trapping in metal deposits because of insignificance of this value for Ag (in comparison, for example, with Pt). More possible explanation is the plasmonic enhancement of photocatalytic activity in semiconductor-metal nanocomposite materials because of Ag nanoparticles have strong surface plasmon resonances in the the near-UV region. This can leads to enhancement of the electric near-field in the vicinity of the Ag nanoparticles. This enhanced near-field could boost the excitation of electron-hole pairs in TiO_2 and therefore increase the efficiency of the photocatalysis.

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ANALYSIS of COKE DEPOSITS on DIESEL DEWAXING LABORATORY CATALYSTS SAMPLES

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Diesel hydrodewaxing processes take place on bifunctional catalysts. The acid component of these catalysts is zeolites and zeolite-like structures, size of channels which provides passing n-alkanes only. Conversion of branched alkanes, naphthenes and aromatic structures remains low. Component providing hydrogenation-dehydrogenation function is usually metals are Ni, Co, Mo, W, Pt and Pd. Also catalyst composition includes promoters, modifiers and binder.

Formation of coke on the catalyst causes a significant change in their activity for two reasons. Firstly, catalyst active sites are involved in the formation of coke. This sometimes leads to a very strong physical and even chemical degradation of catalyst system. Second, coked of catalyst necessitates regeneration, which is associated with multiple cyclic change of reducing and oxidizing environments and extreme temperature changes. This research allows to study features of coking and regeneration of different composition catalysts, suggest methods of studying catalyst properties and optimizing the conditions of its operation.

The object of investigation were taken 7 samples of catalytic dewaxing and isodewaxing catalysts ("fresh" samples) and the same samples after testing in hydrogenation processes (coked samples). Investigated catalyst samples had the following functional composition:

– acid component: zeolites of different structural types are in amount of 40-70% wt;

– hydrogenating component: in the samples 1, 2, 4, 6 – transition metals: Ni, Mo, W; samples 3, 5 – transition and noble (Pt and Pd) metals; the total metal content – 6-20% wt;

– binder component and promoters are in amount of 1-5% wt.

As a method of study was used simultaneous thermal analysis (STA): combination of thermogravimetry and differential scanning calorimetry. Registration test sample mass change and comparison its temperature with temperature an inert sample are being gone simultaneously under identical conditions.

Dryed fresh catalysts samples was pre-analyzed. Results are identical for all samples.

Results of STA-analysis for coked catalyst samples are presented in the Table below.

Catalyst sample	Parameter	Regenereation stage			
		I	II	III	IV
1	Temperature, ˚C	23-220	220-325		>325
	Mass loss, %	2,65	1,64		5,56
2	Temperature, ˚C	23-280	280-445		>445
	Mass loss, %	10,49	3,15		1,64
3	Temperature, ˚C	23-260	260-310		310-600
	Mass loss, %	21,42	3,08		4,38
4	Temperature, ˚C	23-275	275-310	310-490	>490
	Mass loss, %	8,09	0,67	3,98	1,35
5	Temperature, ˚C	23-280	280-520		>520
	Mass loss, %	7,46	3,01		0,71
6	Temperature, ˚C	23-260	260-620		>620
	Mass loss, %	7,57	7,35		1,6
7	Temperature, ˚C	23-275	275-360	360-395	>395
	Mass loss, %	7,76	2,21	1,15	4,16

Results for coked samples zeolite catalysts containing transition metals Ni, Mo, W are similar, regeneration goes in four stages. At first, combustion of liquid hydrocarbons adsorbed catalyst take place (stage I). Subsequently burning less dense surface coke occurs (stage II), then dense coke on the external surface and inside pores of the catalyst is removed (stage III). Finally, at the highest temperatures complete combustion of the coke located mainly inside catalyst pores is occured (stage IV).

It was established that Pt and Pd containing zeolite catalysts were characterized by less coking. Their regeneration can be conducted at low temperatures; coke are formed mainly on catalyst surface and has a lower degree of compaction.

Thus, simultaneous thermal analysis allows investigate location of coke on catalyst grain depending on the composition and type of catalyst. This method can be used as a rapid analysis of coke amount, temperature and heat of its combustion, as well as to optimize conditions of catalyst regeneration. This ensured that the financial losses associated with duration of industrial unit repair period can be reduced.

HOMOGENOUS CATALYTIC VINYLATION of AROMATIC ACETYLENE ALCOHOLS in the HIGHER SYSTEM

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The reaction of homogenous catalytic vinylation of aromatic acetylene alcohols (AAA) in MeOH-DMSO (MeOH- LiOH, NaOH and KOH) solutions has been carried. It has been observed that target vinyl ethers (VE) are synthesized in the yield range of 40-60% [1, 2].

The obtained results show that, when LiOH, NaOH and KOH are used as MOH in the system of CsF-MOH-DMSO, the yield of product goes through maximum while the temperature is raised. It has been determined the increase of AAA on the series LiOH·CsF < KOH·CsF < NaOH·CsF in the selected catalytic systems. As temperature rose from 80 to 120 ^{o}C, the yield raised appreciably.

It can be explained that catalytic activity of presented system is determined by the formation of CsOH and NaF, particularly by less solubility and stronger basic properties of CsOH. In LiOH and KOH systems, the solubility of the formed LiF and NaF is higher, and they exist in ionic form. Hence, CsOH does not show high activity. Owing to this, LiOH+CsOH+LiF+CsF system has been used as catalyst.

It has been observed, vynilation process on the AAA higher base-system, reaction undergoes under top level along with the formation of polycomponent mixtures on the some stages. Herein, moving hydrogen of acetylene goes on base of stereo-regioselectivity, also its exchanging process does easily. Although investigations on the vinylation process of organic compounds including members of various classes hydroxyl group containing in their molecules have been carried out for years, reaction mechanism hasn't enough researched scientifically yet. At present having formed catalytic active center, reactions being carried out in the system MeO-CsF-DMSO, formation of metal solvates and having become interval metal complex possessing active center, counterbalances the function of catalyst.

As the result of the investigation, it has been determined that the duration of the reaction appreciably effects on the product yield. When the reaction process lasted for 6 hours, it was observed vinyl ethers was formed with the highest yield.

We can explain higher yield of VE formed in NaOH/CsF system comparing to KOH/CsF system by following:

– exchanging reaction with CsF goes to the end, as the result of injection of sodium hydroxide in DMSO solution, forming CsOH in relatively higher quantity, thus metal complex possessed active catalytic center and it just reacts with acetylene easily;

– Due to higher solubility of KF comparing to NaF, having formed intermediate compound with DMSO, KF causes quantity of CsOH to be less.

Conclusion, in order to synthesize AAA VE with higher yield 6 hour's process at 100 ^oC temperature in the system of NaOH–CsF–DMSO has been chosen. In this case, the yield of product has been determined to be the highest.

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RECEIVING of ZINCATE (1-HYDROXY-1-PHOSPHONOETHYL) PHOSPHONIC ACID and SCALE INHIBITOR COMPOSITION

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The analysis of patent works [1,2] shows that when receiving zn-hedp the significant role is played by sequence of operations: to hedp solution add a metal oxide, give endurance during 0,5 – 1,5 h and the ambassador add alkali in the form of finely crushed powder or solution. As it is noted by authors, violation of an order of introduction of reagents leads to pollution of a target product or to impossibility of receiving them in a crystal form. For example, addition of alkali to hedp solution leads to formation of the hedp disubstituted salt which drops out in a look a deposit of the sticky lumps incapable fully to interact further with powdery oxides of metals which envelop lumps from a surface. Need of endurance after addition of oxides of metals to hedp is explained by that right after metal oxide addition to hedp the metastable complex is formed, and at alkali solution introduction to this complex, at the expense of increase рн environments, it partially turns into the insoluble tetrareplaced metal complex in water polluting a target product.

Problem of this work is modification of process of synthesis zn-hedp, and on its basis receiving cheap compositions of inhibitor of adjournment of mineral salts with high efficiency.

The way of receiving zn-hedp in the presence of the initiator is offered. As the initiator used lemon acid. The way is carried out in the following sequence: in the reactor supplied with a mechanical mixer and a shirt pour water in number of 50 ml and add 0,2-2,0 g polyatomic alcohol, then add the calculated amount of (1-hydroxy-1-phosphonoethyl) phosphonic acid (10,6 g). After that add a zinc oxide in number of 4,2 g and mix before full dissolution and receiving transparent liquid. Then in reactionary mix add (4,3 g) the calculated quantity of a finely ground hydroxyl of sodium and intensively mix. Thus, control temperature within 23 – 25oC. The ready-made product is stored in the refrigerator at a temperature of 0-10°c. Exit not less than 98%.

Next added earlier prepared mix of the distillation residue of monoethanol amine (du-x product) to reactionary mix or a polyamine croton (pci-3) (du-xx product) with extraction phosphoric acid in the ratio 1:1. There are a lot of publications in which it is described about use of these products as a component of the inhibitor increasing efficiency.

Comparative results of the inhibiting activity of hedp (1), zn-hedp (2), ekf+pci (3), du-h (4) and du-xx (5) are given in fig. 1, 2.

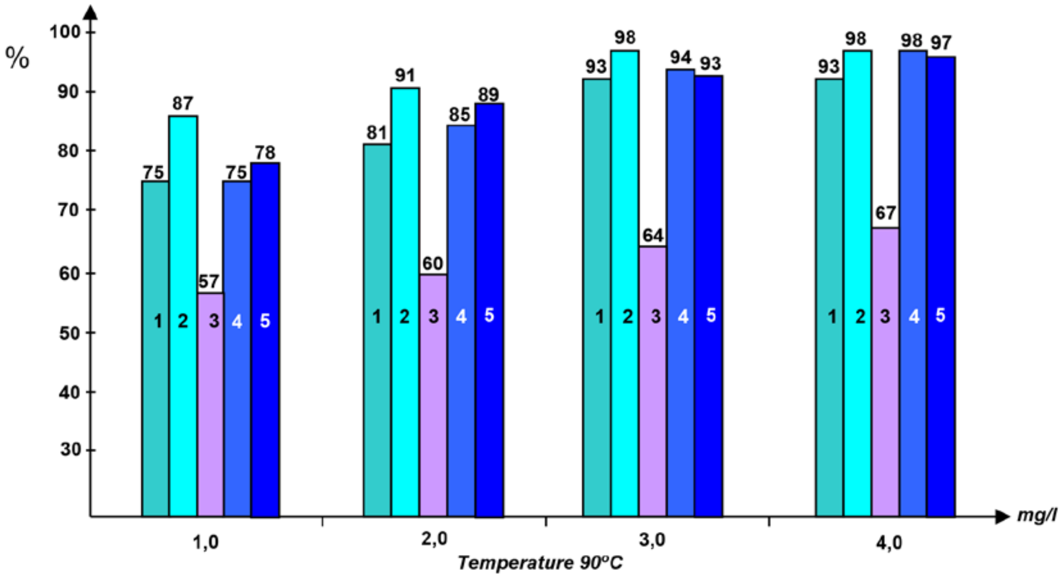

Figure 1. Extent of protection against salt sedimentation in water of rigidity of 4-6 mg/l for the received inhibitors

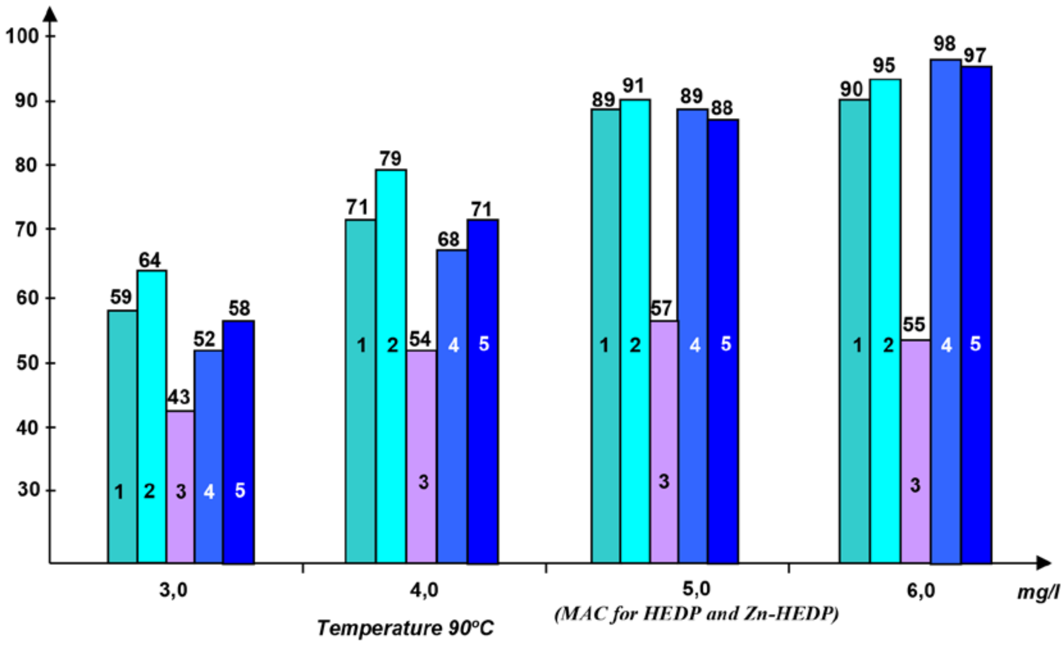

Figure 2. Extent of protection against salt sedimentation in water of rigidity of 12-14 mg/l for the received inhibitors

Apparently from data of drawing, the received compositions on the inhibiting properties don't concede to Zn-HEDP, thus the account quantity of such valuable product is twice less.

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INFLUENCE of CHARGING due SUBSTRATE on the CATALYTIC PROPERTIES of ORGANOBORON NANOPARTICLES in the AMMONIA DECOMPOSITION REACTION

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Currently, there is not enough information to fully describe the effect of the substrate on the heterogeneous catalytic processes involving nanoparticles. In general, the substrate can prevent coalescence of the nanoparticles or contribute in opposite process, modify the shape, structure and charge of the nanoparticles, bring in the nanoparticle-padded catalytic system additional active sites (which can be for example, oxygen vacancies or nanoparticle-substrate interface in oxide substrates), stabilize the intermediate reaction products [1]. As a result of the interaction effects described above the nanoparticle chemical properties may vary within wide limits. Our purpose was to compare the catalytic properties of organoboron nanoparticles (OBN) deposited on substrates of various nature (conductors and semiconductors), on the example of the ammonia decomposition.

OBN formed individual clusters of on the substrates surfaces. Clusters size varied from 4-5 micron laterally with 140 nm altitude which is about 10 nanoparticles layers down to single nanoparticles. Mass spectra of the gaseous medium components in the vacuum chamber exhibit a number of lines corresponding to the starting substances and their decomposition products. Lines with M/e = 2 and 28 correspond to H_2^+ and N_2^+, ions formed from NH3 decomposition products, M/e = 17 – mainly correspond to NH_3^+ ions, formed from NH_3 reactant. The degree of ammonia decomposition achieved by OBN coverage was determined by comparing NH_3 conversion in the OBN-on-substrate experiment with the control experiment on substrate without OBN. Thus obtained ammonia conversions due OBN are 2.8%, 2.3% and 1.2% for HOPG, Al_2O_3 and SiO_2 substrates respectively.

State of the OBN coverage before and after reaction was determined by scanning tunneling microscopy and spectroscopy. These data showed that the OBN physical characteristics do not undergo changes during the interaction with NH_3. At the same time, shape of the CVC curves for OBN on substrates of various natures varies considerably. OBN/HOPG sample CVC matches CVC formed by conductors (S-shaped relationship), while CVC for OBN/Al_2O_3 and OBN/ SiO_2 samples are both diode-like as they demonstrate sharp asymmetry of positive and negative voltage branches. Wherein the CVC measured on OBN coverage are shifted relative to CVC measured on pure substrates in 0.2 V and 0.6 V for Al_2O_3 and SiO_2. Such a shift indicates potential difference between OBN and the substrate due to the transition of electrons in OBN.

Thus, it can be argued that there is a correlation between the catalytic ability of OBN and their potential against the substrate. This result can be explained as follows. The NH_3 decomposition is a straight-chain process with radicals generated by the ammonia decay $NH_3 \rightarrow NH_2\bullet + H\bullet$, which occurs under pretty high activation energy (750 K). Carborane easily transforms into a diradical $C_2B_{10}H_{12}\bullet\bullet$. The two-stage formation of radicals in the $NH_3/C_2B_{10}H_{12}$ system $C_2B_{10}H_{12}\bullet\bullet + NH_3 \rightarrow C_2B_{10}H_{12}H\bullet + NH_2\bullet$, $C_2B_{10}H_{12}H\bullet \rightarrow C_2B_{10}H_{12} + H\bullet$ should occur at a higher rate than single-stage $NH_3 \rightarrow NH_2\bullet + H\bullet$. OBN consist of interconnected partially dehydrated $C_2B_{10}H_{12}$ molecules, so diradicals can be easily generated on the surface of OBN, accelerating the $NH_2\bullet$ and $H\bullet$ radicals emergence, which explains the catalytic properties of OBN in the decay of ammonia. The presence of relative to the substrate negative potential on the OBN causes OBN negative charging. Surplus electrons fill upper energy orbitals of OBN and prevent the formation of diradicals as their presence implies an OBN valence electron transition to higher free energy level. Thus, the higher the OBN potential, the smaller will be the OBN surface diradicals concentration and, accordingly, less catalytic effect, as is observed experimentally.

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Acknowledgements

The research group would like to thank RFBR for grants 14-03-31068, 14-03-00156, 14-03-90012, 13-03-00391, 15-03-00515.

SCANNING ELECTRON MICROSCOPY OBSERVATION of PLATINUM SURFACE TRANSFORMATION in OXYGEN ATMOSPHERE

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Platinum catalysts are widely used in the chemical industry to produce different substances, in ecology to protect the environment from harmful emissions as well as in transport and industrial enterprises [1]. Platinum metals are active catalysts in oxidation reactions of hydrogen, carbon monoxide, hydrocarbons and others. Platinum is also used in the oxidation process of ammonia to be used for production of nitric acid. It is known that chemical composition and structure of the catalyst determine its activity. Therefore, nowadays composition and structure of catalysts are being actively studied by means of modern physico-chemical methods. The aim of this work is to study microstructural transformations on the surface of the polycrystalline foil by scanning electron microscopy in an oxygen atmosphere at temperatures between 600-1400 K.

Processing of platinum foil as thick as 50 μm was carried out in a quartz flowing reactor at the pressure of 1 atm and the flow rate of 1.5 l / hr, the temperature of 1400 K for 3 and 50 hours. Investigation of the microstructure and surface morphology of the sample were carried out with a scanning electron microscope JSM-6460 LV (Jeol) at a spatial resolution of 3 nm and the interval magnifications from 10 to 300,000. To investigate the microstructure of the surface of the samples micrographs of secondary electrons (SEI) and backscattering electron (BEC) allowing to analyze the surface morphology and phase composition, respectively, were obtained. In order to determine the chemical composition of these samples X-rays spectroscopy was used.

Investigation of the microstructure specimens of platinum by scanning electron microscopy (SEM) shows that in the first 3 hours grains grow, with their surface presented by smooth fragments. The average size of a forming grain is ~ 40 μm. Local chemical analysis indicated the contents of carbon (21.2% at.) and oxygen (4.4% at.). It is known that carbon and oxygen are not dissolved in the bulk of Pt. Carbon also forms graphite-like films on the surface of Pt, and oxygen can be contained as impurities on the surface of the graphite film. After 50 hours of sample processing the size of grains doesn't change significantly, on average up to about 60 μm, however, the grains acquire crystalline facets on the surface. The micrographs obtained with small increases clearly display that the surface of grains is covered with a continuous layer of crystalline facets of various form and orientations. The chemical composition of the surface of the grains covered with the crystalline facets, doesn't change considerably, so the carbon content is 30.2%, and the oxygen content is 5.5% . The obtained data allows us to allocate the basic processes occurring in the interaction oxygen with the polycrystalline platinum at 1400 K. At the beginning when $t \leq 3$ hours the process of interaction of oxygen with carbon film on the surface and recrystallization that involves annealing of surface and bulk defects and grains growing occurs intensively. Owing to absorption of defective and small grains (≤ 1,0 μm), they grow to an average size of ~ 40 μm with carbon (21.2% at.) and oxygen (4.4% at.) detected on the surface. This could be residual carbon film containing oxygen impurity. During the interaction of oxygen with platinum ($t \geq 50$ hours) the surface faceting occurs gradually, as a result of which the surface is fully covered in crystalline grains facets. The facets are formed due to the release of the Pt atoms from intergrain boundaries on the surface of grains. These atoms migrate on the surface and gradually get incorporated into energetically advantageous locations. As a result of prolonged processing these processes lead to the formation of continuous layer of crystalline facets polished by surfaces with lower surface energy. The chemical composition of developing facets is close to the composition of the samples treated for $t \leq 3$ hours. It is likely that together with the residual carbon films, carbon is also deposited on the surface of platinum under electron probe.

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FEATURES OF THE CO-HYDROTREATING OF DIESEL CUTS AND VEGETABLE OILS OVER Co(Ni)$_6$-PMo$_{12}$S/Al$_2$O$_3$ CATALYSTS

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In recent years, the transport sector of the world economy has faced the significant problems. Over 92% of the energy used is produced by fossil resources, particularly oil [1]. Moreover, with each year consumption of fuels is steadily increasing. Today researches on the development of technologies for the production of motor fuels from renewable hydrocarbons are actively conducted. One of solution to this problem is to develop a collaborative process of hydroprocessing of renewable raw materials (vegetable oils, animal fats, bio-oil, etc.) and petroleum fractions. The use of the mixture of raw materials adversely affects the operation of the traditional sulfide hydrotreating catalysts Ni(Co)MoS/Al$_2$O$_3$. This is caused by increased coking as well as inhibition of the target reactions. The aim of this work was to study the process of joint hydrotreating of diesel fractions (DF) and vegetable oil (VO) on Co(Ni)$_6$-PMo$_{12}$S/Al$_2$O$_3$ catalysts prepared on the basis of 12-molybdophosphoric heteropolyacid (PMo$_{12}$ HPA) and cobalt citrate.

γ-Al$_2$O$_3$ with a specific surface area of 205 m^2/g, pore volume 0.63 cm^3/g, average pore radius 48 Å, obtained from aluminum hydroxide of SASOL (Germany) was used as a carrier. Co(Ni)$_6$-PMo$_{12}$S/Al$_2$O$_3$ catalysts were prepared by impregnating the carrier single wetness solution of precursors of the active components: $H_3PMo_{12}O_{40}\times 18H_2O$, $CoCO_3\cdot mCo(OH)_2\cdot nH_2O$ or $NiCO_3\cdot mNi(OH)_2\cdot nH_2O$, citric acid qualification "A.C.S.". After impregnation, the samples were dried at temperatures of 60 to 80 °C for 2 h and 110 °C for 6 h. The content of the metals in the catalysts was monitored using X-ray fluorescence analyzer EDX800HS Shimadzu.

Textural properties were measured on the catalyst adsorption porosimeter Quantochrome Autosorb-1 by low-temperature nitrogen adsorption. The specific surface area was calculated by Brunauer–Emmett–Teller model at relative partial pressure $P/P_0 = 0.05 - 0.3$. The total pore volume and distribution of the radii calculated from the desorption curve using the model of Barrett-Joyner-Halendy. Study of hydrotreating process carried out under hydrogen pressure at a flow installation, consisting of a feed preparation and hydrogen, reactor unit and the stabilization unit. 15 cm^3 of catalyst volume in the form of 3-5 mm granules (diameter

1.3 mm, trefoil) diluted with SiC (fraction 0.25-0.5 mm) in 1: 1 ratio and charged into a tubular reactor.

It has been found that conversion of triglycerides of fatty acids was 100% during co-hydrotreating the feeds with 15 wt. % of VO on $Co(Ni)_6$-$PMo_{12}S/Al_2O_3$ catalysts. Obtained hydrogenates had a greater cetane number (on 5 points) and pour point (+ 5°C) compared to ones obtained from DF. The depth of hydrodesulfurization of the feed containing 15% wt. of VO decreased more significantly on Co_6-$PMo_{12}S/Al_2O_3$ catalyst than Ni_6-$PMo_{12}S/Al_2O_3$. $Co(Ni)_6$-$PMo_{12}S/Al_2O_3$ catalysts were more susceptible to deactivation feed containing VO than secondary diesel fractions. At the same time, Co_6-$PMo_{12}S/Al_2O_3$ catalyst was less stable than Ni_6-$PMo_{12}S/Al_2O_3$.

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EFFECT of CARBON PROPERTIES on ADSORPTION-CATALYTIC PURIFICATION of WATER from 1,2-DICHLOROBENZENE

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Environmental contamination by chloroaromatic wastes is a global environmental problem. Chloroaromatic compounds find application as solvents, transformer oils, pesticides and repellents. The use of chloroaromatic compounds is accompanied by their emissions into the environment. Adsorption technologies are the major methods for extracting the highly toxic compounds. Traditionally, spent carbon based adsorbents are regenerated at high temperature. During this regeneration step not only adsorbed compounds but also carbon adsorbent are oxidized. So, the adsorbent losses are not economically favorable.

In this work, a method for purification of aqueous emulsions of 1,2-dichlorobenzene (1,2-DCB) is discussed which includes: (1) adsorption from the aqueous medium and (2) a single-stage liquid-phase regeneration of the adsorbent catalysts (1% Pd/MeKS, 1% Pd/FAS, 1% Pd/Sibunit – 6, 1% Pd/AG-2000) by hydrodechlorination at low temperatures. The resulting products can be recycled as valuable chemicals.

It was shown that the deposition of palladium changes the distribution of surface functional groups on the carbon support. It leads to changing the adsorption capacity of adsorbent-catalysts.

It was found that the adsorption of 1,2-DCB from aqueous emulsion proceeds by pore volume filling mechanism. Where the 1,2-DCB adsorption in the pores of the carbon materials is proceeded by condensation of drops 1,2-DCB on the carbon surface where they coalesce.

It was shown that the regeneration rate of adsorbent-catalysts correlates with the palladium particles size. The smaller are the particles the more active is the catalyst. The concentration and nature of the oxygen-containing surface functional groups on the carbon materials affect the dispersion of palladium.

Thus, the specific surface and porous structure of the carbon material, the nature and the concentration of surface functional groups define the adsorptive and catalytic properties of adsorbent-catalyst. The regeneration rate increases with the decrease of palladium particles size.

AN INVESTIGATION of CuO/γ-Al_2O_3 CATALYST for CHLOROBENZENE TOTAL OXIDATION

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One of the most important ecological problems nowadays is the chemical pollution of environment. Halogenated organic wastes cause strong toxic influence on nature. By this reason chemical industry requires to clean emissions that contains halogenated organic wastes. That is often achieving through some form of thermal process such as controlled high-temperature incineration, fume incineration and regenerative thermal oxidation. These processes require very high-temperatures, usually on the order of 1000 – 1200 °C. An alternative approach is to utilize catalytic oxidation. High efficiency of catalytic oxidation can be obtained at much lower thermal conditions — typically, in the range of 300 – 500 °C.

It is known that that copper based catalyst is used either for the oxidation of CO to CO_2, for methane or ethylene oxidation and total oxidation of hydrocarbons.

This paper examines the influence of CuO/γ- Al_2O_3 based catalyst in the total oxidation of chlorobenzene. Alumina was prepared according to the scheme bayerite – boehmite - gamma alumina. CuO/γ- Al_2O_3 (1wt.% of copper oxide) based catalyst was prepared by impregnating of γ-Al_2O_3 with 1% solution of $Cu(NO_3)_2$ till the color of solution disappears. Deliquefaction of the catalyst was carried out by the slowly heating to 120 ^{0}C on air for 3 hours. The calcination was carried out at temperature of 400 °C for 5 hours. The content of Cu in the catalyst was defined by the method of atomic absorption spectrometry.

Catalytic oxidation was performed in a flow-through tubular quartz reactor. Experimental conditions: temperature interval 250-600 °C, the catalyst volume 5 cm^3, chlorobenzene concentration in the feed of 0.7 vol.%, feed space velocity of 2000 h^{-1}, and fourfold excess of oxygen.

The composition of the oxidation products and the chlorobenzene content in the starting mixture was determined with an LKhM-8MD and a Kristall-2000M gas-liquid chromatographs and with an Agilent Technologies 6890N/5975 gas chromatograph-mass spectrometer.

The total oxidation of chlorobenzene starts at the temperature above 300 ^{o}C, whereas thermal decomposition of chlorobenzene under the above-indicated experimental conditions on γ-Al_2O_3, as well as in the reactor without catalyst, is observed only at temperatures exceeding 450 ^{o}C. The degree of conversion of chlorobenzene at the catalyst was almost 90% at 500 ^{o}C, selectivity with respect to CO_2 was 45%.

In chlorobenzene transformation products, along with CO_2, we identified by gas chromatography-mass spectrometry 1,2- (or 1,3-, or 1,4-) – di-chlorobenzene, 1,3,5- (or 1,2,3- or 1,3,4-) –tri-chlorobenzene, 1,2,3,4- (or 1,2,3,5-, or 1,2,4,5-) – tetrachlorobenzenes, pentachlorobenzene, and hexachlorobenzene in trace amounts. Perhaps these products originate from chlorobenzene disproportionation.

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AMINATION of ETHANOL by AMMONIA at NEW Cu(Zn)-CONTAINING CATALYSTS

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Acetonitrile (I) is an important product of fine chemicals. According to forecasts its demand will grow annually by 3-4%. The basic amount of (I) is obtained as a byproduct in the industrial synthesis of acrylonitrile by ammoxidation of propylene. In recent years an alternative method for the synthesis of (I) by catalytic hydroamination of ethanol with ammonia was extensively investigated:

$$C_2H_5OH + NH_3 \rightarrow CH_3CN + H_2O + 2\ H_2$$

The advantages of the latter process is the possibility of using bioethanol and carrying out the process under the milder conditions.

The purpose of this work is to create the highly selective and stable catalysts on the basis of CuO, CuO-ZnO and oxide compounds of aluminum, vanadium, chromium subgroups for the direct synthesis of (I) from ethanol.

Copper-containing compositions were prepared by LLC "NIAP-CATALIZATOR" (Novomoskovsk, Russia). Experiments were performed in a flow-type reactor at a temperature 220-300°C, load of 93.5% ethanol equal to 1.14 $g/(g_{kat} \times h)$, and the molar ratio $EtOH : NH_3 : H_2 = 1{,}0 : 5{,}0 : 1.2$. At 280°C in reaction mixtures besides acetonitrile a mono-, di-, and tri-ethylamines were also identified.

The influence of the qualitative and quantitative content of the individual components of the catalysts on the process has been investigated. The promising bifunctional catalyst compositions, which are comparable to foreign analogues, have been identified.

INFLUENCE of MIXED HETEROPOLYACIDS KEGGIN STRUCTURE H_4 [$SiW_{12}Mo_{12-n}O_{40}$] on THEIR ACTIVITY in the OXIDATIVE DESULFURIZATION of DIBENZOTHIOPHENE

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Currently, much stricter environmental requirements for motor fuel sulfur content. Process of oxidative desulphurization of petroleum fractions attracts more attention in view of the fact that it can be carried out under mild conditions (room temperature and atmospheric pressure) to obtain valuable sulfur compounds and ultra low sulfur fuel.

The aim of the work was to study the catalytic behavior of Keggin structure heteropoly H_4 [$SiW_{12}Mo_{12-n}O_{40}$] in the oxidative desulfurization of model feed containing dibenzothiophene.

Synthesis geteropolyacids H_4 [$SiW_{12}Mo_{12-n}O_{40}$], where n = 1 to 3 was carried out in several stages by preparing salts distorted Keggin structure (lacunary) W heteropolyanions, followed by selective introduction and separation of Mo geteropolyacids ether extraction. Composition and structure of the synthesized compounds was studied by IR, Raman spectroscopy and X-ray analysis.

Was studied using H_4 [$SiW_{12}Mo_{12-n}O_{40}$] as catalysts of oxidative desulfurization of DBT hydrogen peroxide. The results showed that trimetallic compounds exhibit high activity in the preparation of sulfones and sulfoxides.

PLASMA ELECTROLYTIC FORMATION of Zn-CONTAINING OXIDE COATINGS on TITANIUM and the STUDY of THEIR STRUCTURE and PHOTOCATALYTIC ACTIVITY

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Plasma electrolytic oxidation (PEO) is one of the modern and advanced methods of complex oxide layers formation on metals. Nowadays the titanium oxide coatings obtained by PEO are widely tested as the photocatalysts of various organic pollutants degradation process. The photocatalytic activity of titanium oxide can be improved by the incorporation of transition metal oxides among which zinc oxide is of prominent importance.

The formation of oxide layers on titanium by PEO method in electrolytes containing zinc compounds and the study of their composition, surface morphology and photocatalytic activity were the aims of the work.

The oxide coatings were obtained in electrolytes containing 0.1 mol/l Na_3PO_4 and various concentrations of ZnF_2 or Zn $(CH_3COO)_2$ under galvanostatic conditions at an effective current density i = 0,1-0,2 A/cm^2 during 5-10 minutes. The photocatalytic activity of coatings was estimated by the degradation degree of the methylene blue dye when subjected to UV radiation. The change in dye concentration of the solution was observed on the intensity variation of the dye absorption peak by a spectrophotometer. The spectrophotometric measurements were performed by the spectrophotometer Unicom 1201. To calculate the degradation degree of a dye α, % the following formula was used:

$$\alpha = (A_0 - A)/A_0 \cdot 100\ \%,$$

where A_0 – optical density of feed (initial) solution, A - optical density of the solution after the exposure to UV radiation for 2 hours.

As the Table 1 shows the coatings formed in phosphate electrolyte with zinc fluoride addition include titanium oxide of the rutile and anatase modifications, the ratio of which increases with the increase of zinc fluoride concentration and with increase of oxidation time. The highest methyl blue degradation degree is observed when using coatings formed in the phosphate electrolyte and contain phosphorus in the smallest amount, phosphorus can be included in compounds without photoactivity.

Table 1. Phase composition and photocatalytic activity of the coatings formed in 0,1 M Na_3PO_4 with addition of zinc fluoride.

№	$C(ZnF_2)$, g/l	t, min	Ia/Ip	Elemental composition, at.%					α, %
				C	O	Zn	P	Ti	
1	0	5	5,9	12,8	56,0	-	2,7	28,9	32,1
2		10	27	7,7	59,9	-	2,8	29,5	25,2
3	2	10	7	-	62,0	-	3,6	31,9	13,3
4	5	5	20	13,1	59,6	2,3	4,0	20,6	13
5		10	72,5	-	62,7	3,3	4,9	29,1	10,9

As the phosphate electrolyte $Zn(CH_3COO)_2$ is added, there is the coating formation on titanium containing titanium oxide anatase modification only, the relative content I_a of which decreases with the increase of both the oxidation time and with the increase of zinc acetate concentration in the electrolyte Table 2. The degradation degree of methylene blue increases with the increase of zinc concentration in the surface layer composition, which in turn increases with the increase of zinc acetate concentration in the electrolyte.

Table 2. Phase composition and photocatalytic activity of the coatings formed in 0,1 M Na_3PO_4 with addition of zinc acetate.

№	C $(Zn(CH_3COO)_2)$, g/l	t, min	Ia, relative units	Elemental composition, at.%				α, %
				O	Zn	P	Ti	
1	2	5	155	69,8	1,1	6,6	22,4	17,2
2		10	100	70,8	1,2	5,2	22,9	12,9
3	5	5	150	70,0	1,7	5,8	22,3	24,6
4		10	82	70,4	1,5	5,3	22,7	24,7
5	10	5	100	67, 6	2,6	8,1	19,3	25,9
6		10	80	69,9	3,1	6,7	20,2	27,3

Thus, the study shows that the elemental and phase compositions of the coatings depend on the zinc salts added to the phosphate electrolyte. All obtained coatings exhibit a certain degree of photocatalytic activity in the degradation reaction of methylene blue. The most active phosphate coatings were formed in the phosphatic electrolyte without zinc salts addition.

CATALITIC OXIDATION of FERULIC ACID by PEROXIDE COMPOUNDS with HPA-5-Mn

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Research process of catalytic oxidation of phenolic compounds by peroxide compounds is significant for elaboration theoretic basis of environmentally friendly processes of refining of herbal feedstock to prepare a wide range of product with predefined properties. For this purpose we studied catalytic oxidation ferulic acid (FA), which simulates the structural unit of lignin, with hydrogen peroxide (H_2O_2) and peracetic acid (PAA) in acidic medium. Polyoxometalate (HPA-5-Mn), a manganese-containing sodium vanadomolybdophosphate, was used as a homogeneous catalyst. Process of oxidation was monitored by change of oxidizable substance concentration by specrtophotometric analysis (Specord 200 Analitic Yena). Products of oxidation were identified by using gas chromatography with mass-spectrometry detector QP-2010 Plus (Shimadzu). Derivatization of products was performed before to the analysis by N,O-bis(thimetilsilil)trifluoroacetamide with pyridine. Influence of pH, nature and concentration of oxidizer were researched on the kinetics of the process, composition and yield of oxidation products. On the basis of studies it is established that ferulic acid was not oxidized by peroxide compounds in absence of the catalyst in acidic medium. It was also discovered, that pH has a significant impact on process of oxidation. The best results of oxidation were obtained when using the PAA as an oxidizer at pH 3. Hydrogen peroxide showed much less activity within pH 3, but H_2O_2 revealed itself as a strong oxidizing agent in a more acidic range. It was found that the major monomeric product of oxidation in all experiments, regardless of composition of oxidizer, was vanillin, the output of which may reach 14%.

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HOMOGENEOUS CATALYTIC VINYLATION of AROMATIC ACETYLENE ALCOHOLS

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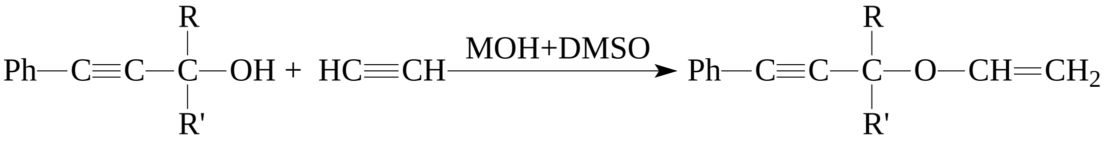
As initial reagents, vinyl ethers are commonly used in chemical industry to produce acetals, corotinoida, oligonucleotides, citrals, herbal preparations, polymers, heteropolymers, glue, lacquer, emulsion, paint, alkyd resins, artificial leather, plasticizers, oil additives [1, 2].

The reaction of vinylation of aromatic acetylene alcohols (AAA) containing phenyl group in the presence of acetylene has been investigated and vinyl ethers (VE) have been synthesized.



$$Ph-C\equiv C-\underset{R'}{\overset{R}{C}}-OH + HC\equiv CH \xrightarrow{MOH+DMSO} Ph-C\equiv C-\underset{R'}{\overset{R}{C}}-O-CH=CH_2$$

$R= -CH_3, R^I= -C_2H_5; R= -CH_3, R^I=$ *izo* $-C_3H_7, R= -CH_3, R^I= -C(CH_3)_3;$

$R= -CH_3, R^I= -C_6H_3, Ph= -C_6H_5,$

MOH- LiOH, NaOH and KOH.

The influence of temperature, catalyst and solvents on the yield of target products has been studied and analyzed systematically. On the basis of received results, the highest yield of VE has been observed for DMSO solution in the presence of KOH catalyst, when acetylene was reacting with AAA at temperature 120 °C for 6 hours.

Orientational polarity of positively charged hydrogen in AAA hydroxyl group towards triple bond of acetylene depends on the exchange between metal cation of the catalyst and active hydrogen of acetylene. It is known that orientational polarity, alongside with high temperatures, which intensify acetylene molecule motions resulting in the distortion of molecular arrangement, determine the product yield . It has been determined the decrease of solubility of alcoholates correlates with the increase of their molecular weight, and low solubility prevents acetylene attachment that results in the decrease of VE yield. Acetylene and other reagents were used in high concentrations to increase the amount of product formed. High initial concentration of the reagents increase the duration of the reaction and recycling demands to implement complicated technological processes.

To sum up, it has been observed that the decrease in vinyl ethers yield depends on the reaction between acetylenes and metals followed by hydrolysis, the stability of alcoholates formed by joining AAA containing ethyl, isopropyl and triple radicals with metals.

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