

"Catalysis is not a branch of chemistry but a general concept without which one can not state and understand the regularities of chemical conversion"

Sapich

The 20th of April, 2007 is the centenary of birth of academician Georgii K. Boreskov, an eminent Russian scientist in physical chemistry, catalysis and chemical engineering, teacher and science manager.

In his scientific activity, Georgii Boreskov preserved the best traditions of classicists of the Russian chemistry – D.I. Mendeleev, A.E. Favorsky, N.D. Zelinsky – who combined the profound basic research and solution of important practical problems.

The contribution of Georgii Boreskov to catalytic science can hardly be overestimated.

His formulation of the concept of catalysis as an exceptionally chemical phenomenon mediated by the interaction between reactants and the catalyst was of particular importance to establishing the modern physicochemical basis of catalysis science.

The generalized comparative analysis of energetic profiles of catalytic and non-catalytic reactions led him to demonstrate for any type of catalytic reactions – homogeneous, heterogeneous, enzymatic – that the reaction acceleration upon addition of a catalyst is caused by compensation of the bond cleavage energy in the reactants with the energy of formation of new bonds in the reaction products owing to the intermediate chemical interaction between the reactants and catalyst.

Of principal importance for the theory and technology of catalytic processes appeared the Boreskov's idea on the mutual influence of the reaction medium and the catalyst in the course of the catalytic reaction. In practice, that led to the formulation of the *Boreskov rule*: specific catalytic activities of substances of identical chemical compositions are approximately equal irrespectively of their preparation procedures.

The Boreskov's works in the field of kinetics of reversible reactions were fundamental for the theory of the complex reaction kinetics and disclosed a general relationship between activation energies of the direct and reverse reactions, the concept of *apparent* molecularity of a complex chemical reaction and the methods for their finding.

Of extreme importance to Georgii Boreskov was his education activity. He created an actively functioning scientific school with numerous disciples who are now professors and PhD graduated people. For many years he gave courses catalysis and chemical engineering in leading Russian universities and established the Chair of Catalysis and Adsorption in the Novosibirsk State University.

Georgii Boreskov was the main founder of the Institute of Catalysis of the Siberian Branch of the USSR Academy of Sciences in 1958. The principles of the creation of the Institute were comprehensive coverage of all catalytic problems – from scientific basis of prediction of catalytic action and catalyst preparation to calculations on contact apparatuses and industrial implementation of catalytic processes.

The activities of Georgii Boreskov were exceptionally fruitful. He was a man of huge positive and attractive magnetism who could share his knowledge, experience and enthusiasm to young scientists and make the creative medium around him. His fidelity to principles, self-exactingness, working capacity and self-discipline in combination with goodwill and tolerance allowed him to earn prestige and respect of all people around him and also in the world.

Siberian Branch of Russian Academy of Sciences
Boreskov Institute of Catalysis

III International Conference
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Application”

dedicated to the 100th anniversary
of Academician Georgii K. Boreskov

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ABSTRACTS

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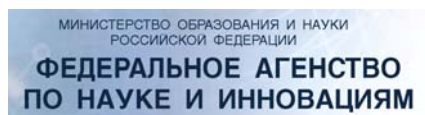
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POSTER PRESENTATIONS

SECTION I MECHANISMS OF HETEROGENEOUS AND HOMOGENEOUS CATALYSIS AT MOLECULAR LEVEL



OSCILLATORY BEHAVIOUR DURING METHANE OXIDATION OVER Co CATALYSTS

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Oscillatory behaviour during methane oxidation over a cobalt foil has been studied using on-line mass-spectrometry and video recording of the colour of the catalyst surface. It was demonstrated that during oscillatory behaviour, periodic transitions of the catalyst surface from an oxidised state (dark colour) to a reduced state (light colour) occurred together with the variation of the catalyst temperature. The comparison of the observed oscillatory behaviour with thermokinetic oscillations during methane oxidation over Ni catalysts is presented.

Oscillatory behaviour during methane oxidation over a cobalt foil has been detected at temperatures 860-950 °C in a reaction mixture comprising CH₄:O₂:Ar=25:5:1. The oscillations have been studied using on-line mass-spectrometry and video recording of the colour of the catalyst surface. Fig.1 shows regular oscillations at 925 °C.

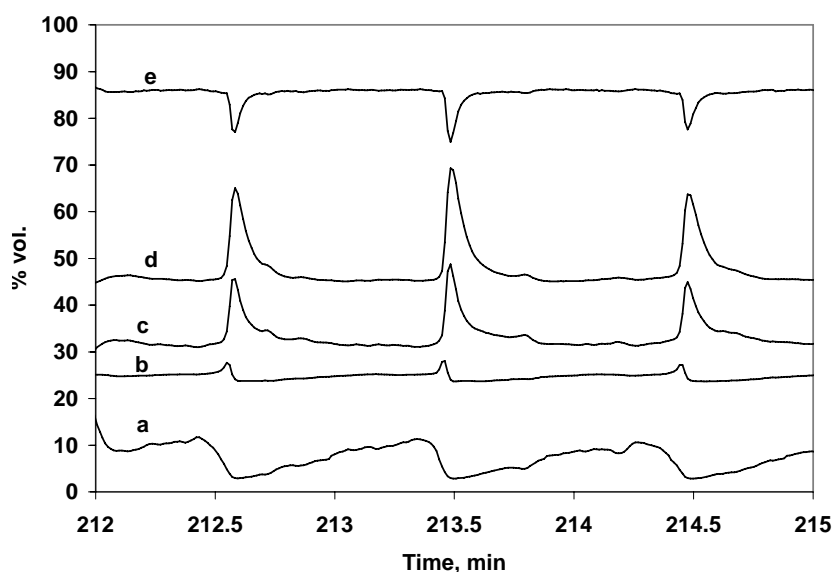


Fig.1. Regular autonomous oscillations at 925°C, flow rate 15 ml/min (a) O₂ × 10, (b) CO₂ + 20 (c) CO + 20, (d) H₂ + 40, (e) CH₄ + 20.

The mass-spectrometer signals of the CH₄, CO, CO₂ and H₂ species have been vertically offset by the factors indicated in figure caption.

It was demonstrated that during oscillatory behaviour, periodic transitions of the catalyst surface from an oxidised state (dark colour) to a reduced state (light colour) occurred together with the variation of the catalyst temperature. It could also be noted that the catalyst spent

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more time in the oxidised state than in the reduced state. Simultaneous measurements of concentrations in the gas phase revealed that the oxidised state was characterised by lower activity of methane oxidation, while the extent of methane conversion was much greater on the reduced surface. CO and H₂ concentrations reached their maxima over the completely reduced surface. These thermokinetic oscillations have much in common with oscillatory behaviour which was observed earlier over a nickel foil [1]. It can be supposed that similar to Ni catalysts thermokinetic oscillations over Co catalysts could arise from periodic oxidation and reduction of the catalyst surface, the variation of the selectivity of the process and the competition of reactants for free active sites [2]. However there are also some differences between oscillatory behaviour over Ni and Co catalysts. Oscillations over the cobalt foil appeared at higher temperatures (860-950 °C), and had longer periods, in comparison with oscillatory behaviour which was observed earlier over a nickel foil (650-860 °C) [1]. The application of TGA in combination with TPR experiments revealed the differences in nickel and cobalt redox properties which are responsible for the variation in the properties of the oscillations. It was demonstrated that metallic cobalt oxidised much more extensively than nickel, and pre-oxidised Co needed much more time for reduction by H₂ or CH₄.

Forced oscillations could be obtained in a low temperature region (700-860 °C), if bare chromel and alumel wires were spot-welded separately to the cobalt foil. It was shown that in this case the chromel wire induced oscillatory behaviour of the whole cobalt foil. Complicated mixed mode oscillations detected at higher temperatures were shown to be the result of the coupling of high frequency oscillations produced by the unshielded chromel–alumel thermocouple and low frequency oscillations originating over the cobalt foil.

The coupling of oscillations from two various foils has been studied in a quartz cross-shaped reactor. The antiphase temperature oscillations were the result of the coupling of the Ni and the Co foils, while in the case of two Ni foils completely synchronous oscillations have been observed indicating that the strength of coupling via the gas phase was very strong.

Acknowledgement

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APPLICATION OF ULTRASONIC RADIATION IN HETEROGENEOUS CATALYSIS

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Under consideration is mechanism and kinetics of heterogeneous catalysts preparation and regeneration in ultrasonic field.

Economic efficiency of application of ultrasonic radiation in catalysis has been demonstrated.

Despite the fact that ultrasonic radiation (US) is currently used in various industries, its application in heterogeneous catalysis has not been addressed in the literature so far.

It can be attributed to the fact that mechanism and kinetics of the catalytic action of substance in various chemical processes is at the research stage. Existing catalysis theories are based on various assumptions with regard to catalytic action nature. At that, the conceptual issue is still view of the catalyst and the reactant as a single system in which the catalyst undergoes change under chemical action.

Use of ultrasonic radiation in preparation and regeneration of heterogeneous catalysts is noted for significant complexities considering that when describing mechanism and kinetics of an active catalytic structure formation in ultrasonic field it is necessary to take into consideration a complex of chemical, thermal, diffusion, acoustic-hydrodynamic processes occurring in "liquid – solid" system.

Currently the following trends can be identified in research on application of ultrasonic radiation in heterogeneous catalysis:

- preparation of substrate based catalysts by ultrasonic impregnation method;
- synthesis of mixed catalytic contacts in ultrasonic field;
- spent catalyst regeneration under the influence of ultrasonic radiation;
- research of catalytic processes in presence of catalysts and ultrasonic field;
- purely ultrasonic catalytic processes without catalyst.

Character of the selected research direction is influenced by the mechanism and kinetics of the catalytic action in presence of ultrasonic radiation. For reactions, which occur at high temperatures, phase mechanism plays the dominant role while in transfer to low temperatures combined mechanisms start to dominate.

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Study of chemical reactions proceeding by phase mechanism allows to determine effects of composition on individual phase rate and catalyst surface stationary condition discovering at that general regularities in controlling catalytic properties.

Study of chemical reactions proceeding through formation of compound activated complexes, determination of compounds of those complexes and of nature of catalyst surface local chemical changes allow to identify mechanism of ultrasonic catalytic action and to find out pre-conditions for studying kinetics of ultrasonic catalytic reactions.

The obtained solutions of sonar equation in quasiclassical approximation allow to suggest new process solutions for synthesis of new generation heterogeneous catalysts for various chemical processes.

PHOTOCATALYSIS OF OXIDATION REACTIONS AS NATURAL PHENOMENON

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An analysis of own and literary data was made to understand nature and mechanism of photocatalysis phenomenon. Physical and chemical stages of photocatalytic oxidation reaction on metal oxides are considered. It is shown that the quantum efficiency of photocatalytic reaction on metal oxides, the top level of whose valence band is formed by 2p - orbital of oxygen depends upon the bond energy of surface lattice oxygen. It may be assumed that the related to semiconductor metal photocatalytic oxidation reaction does not require an active surface center.

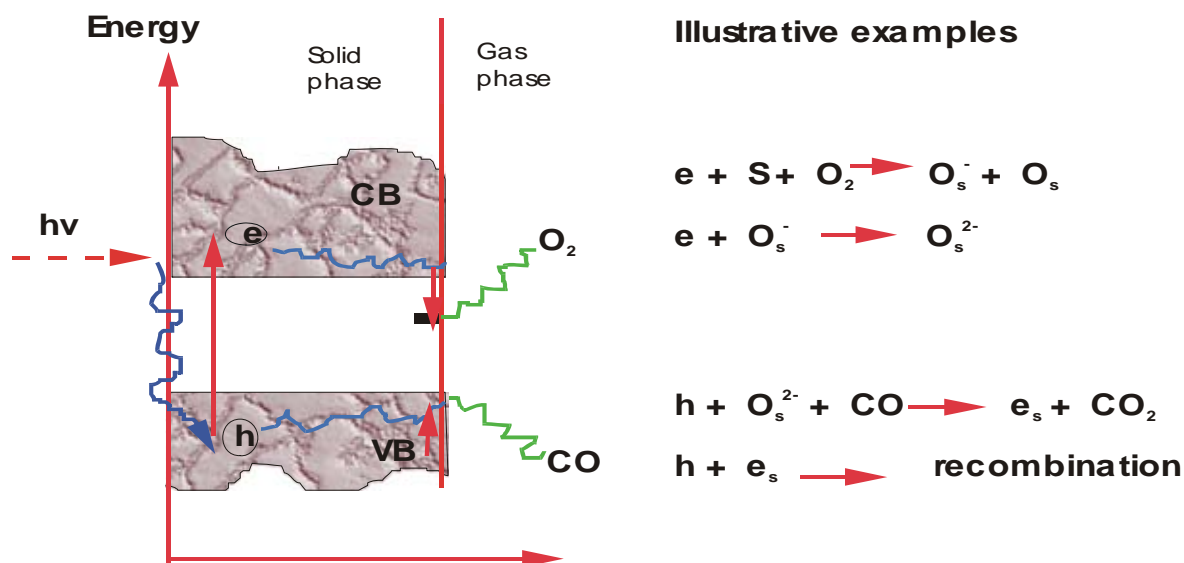
The studies of photocatalytic oxidation reactions had vastly been supported by G.K. Boreskov. He had suggested that an investigation of photocatalysis mechanism would throw light upon the catalytic action nature and mechanism of catalytic oxidation reactions.

Photocatalytic reactions are characterized by formation of “free” mobile electrons in the conductivity band and simultaneously “free” mobile holes in the valence band, after the absorption of radiation quanta with energy exceeding the width of the solid band gap [1]. Our data evidence that in the fundamental absorption region of semiconductor metal oxides (ZnO, SnO₂, TiO₂, Sc₂O₃, In₂O₃, V₂O₅, and MoO₃) the quantum yields of photocatalytic oxidation vary in a wide range from 30 % to 0.01 % under the same conditions of metal oxide pretreatment and quantum yield measurement [2]. Such considerable distinction can not only be explained by different physical characteristic of used metal oxides. These characteristics are energy structure and state density of conductivity and valence bands, size of photocatalyst micro crystals, mobility of lighted charge carriers, recombination rate, near surface electric fields and so on.

It was confirmed experimentally that photocatalytic activity is inherent in metal oxides, the top level of whose valence band is formed by 2p - orbital of oxygen (ZnO, SnO₂, TiO₂, Sc₂O₃, In₂O₃, V₂O₅, and MoO₃). As distinct from transition metal oxides (Fe₂O₃, Co₃O₄, and NiO), which have the top valence band formed 3d - orbital of metal and do not show a photocatalytic activity.

PP-I-3

It is suggested that during photocatalytic reaction of oxidation, the oxidized gas-phase molecule (CO, H₂, NO, SO₂, hydrocarbons) interacts with surface lattice oxygen at the moment of its discharge by a free mobile hole (Fig. 1) [3].



Such mechanism assumes that the quantum efficiency of photocatalytic reaction depends upon the bond energy of surface lattice oxygen; i. e. the quantum yield can also be determined by chemical characteristics of photocatalysts – metal oxides. This view substantiated that in agreement with the proposed mechanism, the related to semiconductor metal photocatalytic oxidation reaction does not require an active surface center.

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**MECHANISM OF THE COPPER SALTS CATALYZED OXIDATION OF WHITE
PHOSPHORUS BY ORGANIC PEROXIDES IN ALCOHOLS**

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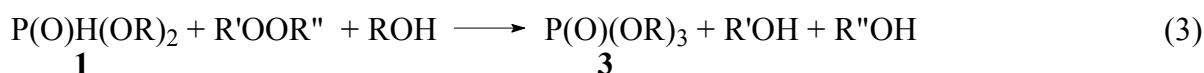
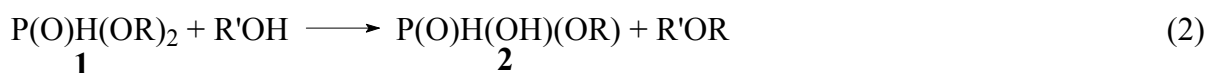
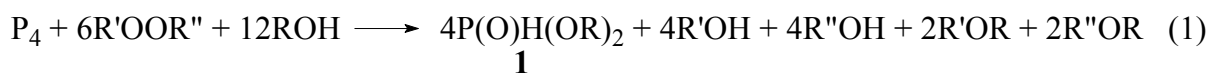
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Organic peroxides, R'OOR'', are considered simple and universal sources of radical species. The decomposition of peroxides is strongly accelerated by transition metal ions. A variety of highly efficient and environmentally appealing oxidative catalytic processes have been developed using and organic peroxides as ecobenign and efficient oxidants [1]. Scarce attention has been however focused on the oxidation of white phosphorus (P₄) by organic peroxides. This presentation sheds some light in this area giving an account of our studies on the stoichiometric and catalytic oxidation of P₄ by organic peroxides (dibenzoyl peroxide and 3-chloroperoxybenzoic acid) in aliphatic alcohols (MeOH, *n*-BuOH) at 40-60 °C under anaerobic conditions.

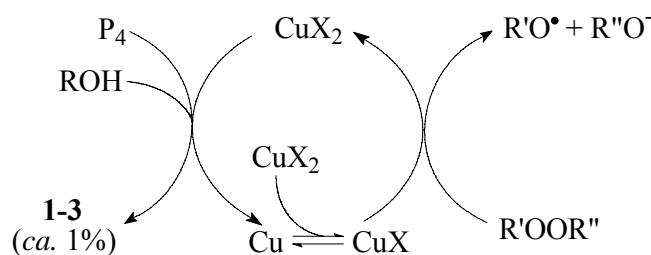
Without adding any metal promoter, the reaction results in the formation of a mixture of di- and monoalkyl hydrogen phosphonates (**1** and **2**) and trialkyl phosphates (**3**). Generally, the P(III) species are the major products of the reaction whereas the P(V) derivatives are usually produced in limited amount. The molecule of peroxide does not directly interact with P₄, but rather initiates the reaction generating radical species via homolysis of the O-O bonds. Once formed, the R'O• (or R''O•) radicals may easily react with ROH to generate RO• radicals, a powerful oxidants towards inorganic and organic substrates, which can successfully promote the radical oxidation of white phosphorus. The simple stoichiometries accounting for the formation of each reaction product are given below in equations 1 – 3.



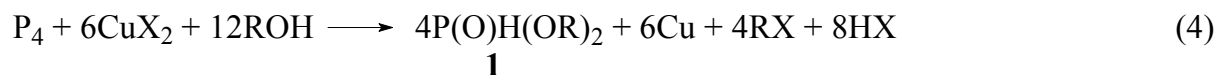
In the presence of catalytic amounts of copper(II) salts (CuX₂; X = Cl, acac, C₃H₇COO), the oxidative alkoxydation of P₄ promoted by organic peroxides is significantly enhanced with increasing of the reaction rate up to eight times. Noticeably, under optimized

PP-I-4

reaction conditions, 100% conversion of white phosphorus to organophosphorus products is achieved with high selectivity in P(III) esters (*ca.* 95%). The catalytic oxidation of P₄ by organic peroxides in alcohols is proposed to proceed with the same stepwise radical mechanism, the only difference being in the preliminary step of peroxide homolysis which is now replaced by the metal assisted reduction of the peroxide to yield the radical R'O• and the anion R''O⁻ (Scheme 1).



It should be emphasized that the active catalytic species which accelerate the decomposition of peroxides are not the initial Cu(II) but the Cu(I) ions, which are formed *in situ* via the fast reduction of Cu(II) to Cu(0) by white phosphorus followed by comproportionation of Cu(0) and Cu(II). The reduction of Cu(II) by P₄ in alcohol agrees with a heterolytic reaction pathway [2]:



However, taking into account the stoichiometry of the reaction (4) and the substoichiometric amount of CuX₂ used (5-10 mol % with respect to P₄), one can envisage that the contribution of this alternative reaction to the synthesis of organophosphorus compounds should be very low (*ca.* 1%). Our experimental results therefore show that the copper salts catalyzed oxidation of white phosphorus by organic peroxides in alcohols is almost completely accomplished *via* the radical pathway (eqs. 1-3) where the production of RO• radicals is boosted by the Cu(I) ions as highlighted in Scheme 1.

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ZEOLITE CATALYSTS FOR LIGHT OLEFINS PRODUCTION FROM METHANOL

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The conversion of methanol to light C₂=-C₄= olefins was investigated at temperatures from 350 to 450°C, $v_{\text{MeOH}} = 1 \text{ h}^{-1}$ over zeolite-based catalyst. Basic products of reaction were gaseous hydrocarbons. Catalytic properties for the conversion of methanol to light olefins depend from number of strong acid sites to a greater extent. High yields of light olefins C₂-C₄ were obtained on SAPO-34 based catalyst at 350-375 °C - 74-83 % (29-35 % C₂=, 38-47 % C₃=, 7-3 % C₄=). Yield of C₅+ hydrocarbons is inessential, basically less 1 %. After catalyst regeneration into reactor by air flow at 550°C its activity totally recovered. ZSM-5 type zeolite based catalyst showed yield of C₂=-C₄= olefins about 52-61 %, ethylene near 12 %, propylene 23-32 % and butylenes 16 %. C₅+ hydrocarbons of gasoline fraction were obtained mainly as by-products along with light olefins. ZSM-5 based catalysts differ more stable work from SAPO-34 based catalysts.

There is requirement on light olefin hydrocarbons (ethylene, propylene, butylene) owing to growth of necessity in polymer materials and petrochemical raw at present time. Pyrolysis of hydrocarbon raw is the traditional basic industrial method of olefins production. Hard demands had made to quality of ethylene and propylene as raw for polymer production. Pyrolysis-obtained ethylene and propylene needed to deep refinement.

Substitution of petrochemical raw to alternative hydrocarbon resources, for example, to natural and associated petroleum gas, is very actual, especially as a result of growth oil price on world markets. Methanol to C₂-C₄ olefins conversion is one of the stages of qualified treatment of natural and associated petroleum gas to valuable hydrocarbon products by scheme: natural gas → syngas → methanol → DME → C₂-C₄ olefins. Olefins production processes syngas based through methanol and DME were industrially realized by “Mobil” (methanol to olefins, MTO), “Union Carbide”, “UOP and Norsk Hydro” and “Lurgi” (Lurgi’s Gas to Propylene) in the world. Olefins obtained from methanol and/or DME are free from sulfur compounds.

Aim of present work is investigation of methanol conversion on SAPO-34 (Zeolyst Int.) and ZVM, analogue of ZSM-5 (Nizhniy Novgorod’s Sorbents, Russia) zeolite-based catalysts. Zeolites were characterized by XRD, IRS, TPD NH₃.

PP-I-5

Catalytic properties of synthetic laboratory samples of metal-containing zeolite catalysts were studied by labor pilot flow setup at pressure 0,1 MPa, temperature from 350 to 450 °C, flow rate of $\text{MeOH} = 1 \text{ h}^{-1}$, GHVS = 1000-3000 l/l cat*hour.

It was found, that activity and selectivity of catalyst depends from zeolite type, metal nature in catalyst composition and experiment conditions. Gaseous products of reaction contained of $\text{C}_1\text{-C}_8$ hydrocarbons, as paraffins, as olefins, normal and iso-structure both. Liquid hydrocarbons are almost non-produced. .

High yields of light olefins $\text{C}_2\text{-C}_4$ were obtained on SAPO-34 based catalyst at 350-375 °C - 74-83 % (29-35 % $\text{C}_2=$, 38-47 % $\text{C}_3=$, 7-3 % $\text{C}_4=$). Yield of C_{5+} hydrocarbons is inessential, basically less 1%. Sufficiently high selectivity of light olefins obtaining on SAPO-34 was conditioned by its crystallite frame, pore sizes equally same sizes of respondent molecules in it, and confined of obtaining of molecules with more molecular weight.

SAPO-34 based catalyst showed high selectivity during first 3-4 hours of work, then deactivated. After catalyst regeneration into reactor by air flow at 550 °C its activity totally recovered.

Obtained results are approximated to data of firms “UOP and Norsk Hydro”.

ZSM-5 type zeolite based catalyst showed yield of $\text{C}_2\text{-C}_4=$ olefins is about 52-61 %, ethylene near 12 %, propylene 23-32 % and butylenes 16 %. C_{5+} hydrocarbons of gasoline fraction, were obtained mainly as by-products along with light olefins. Formation of C_{5+} hydrocarbons on ZSM based catalysts may be conditioned by crystallite structure of zeolite and experiment conditions. Growth of methane formation was observed for ZSM-5 based catalysts with temperature increasing. These catalysts differ more stable work from SAPO-34 based catalysts.

ISOTOPIC METHODS AT THE STUDY OF ELECTROCHEMICAL AND CATALYTIC PROCESSES IN PROTONIC HETEROJUNCTIONS

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Protonic heterojunctions $\text{PdH}_x|\text{KOH.H}_2\text{O}$, $x < 0.1$, have been created by electrochemical activation of heterostructure $\text{Pd}|\text{KOH.H}_2\text{O}|\text{Pd}$. The direct interfacial exchange namely by protons has been demonstrated by using isotopes (H&D) as the label. A comparison of the experimental and theoretical values of the isotopic effects in equilibrium has showed that quantum effects contribute to the potential of protonic heterojunction. The catalytic action of the heterojunction's boundary is discussed from viewpoint of using protonic heterojunction in electrochemical devices.

Protonic heterojunctions as a particular case of ionic ones are characterized by the reversible exchange of cations of hydrogen (protons) through the boundary between two physically and/or chemically discriminate condensed phases. The possibility of a direct observation of such exchange originate from the existence of isotopically different atomic species. Such experiments allow to clarify some details of kinetic behavior or energetic state of atoms of given chemical element. It is very important at the study of catalytic and electrochemical processes. Phase interfaces are sometimes out-of-the-way places in the course of the process under study, even for modern strong different kind of a spectroscopy.

Historically, three approaches have been developed in the application of isotope methods to the investigations: isotope label, isotopic effect and isotopic exchange. To study the equilibrium and kinetic processes in the heterostructure $\text{PdH}_x|\text{KOH.H}_2\text{O}|\text{M}$, where $\text{M}=\text{Pd}$, Ag , Ni , C , synthesized firstly by us, all of this variants of isotopic method have been used.

Three interesting results have been obtained.

i) Remarkable rate of isotopic exchange at 370 K in the system, initially described as “ $\text{KOH.H}_2\text{O}(\text{solid})|\text{Pd}(\text{H,D})_x|\text{KOD.D}_2\text{O}(\text{solid})$ ”, has confirmed the reversible transfer of hydrogen ion (H^+/D^+) through the boundary “hydroxide-palladium” in both (!) directions. Note: Both hydroxide phases have had no contact with each other, being separated by Pd foil.

ii) Arising from the electrochemical activation OCV (open circuit voltage) on heterostructures “ $\text{PdH}_x|\text{KOH.H}_2\text{O}(\text{solid})|\text{M}$ ” and “ $\text{PdD}_x|\text{KOD.D}_2\text{O}(\text{solid})|\text{M}$ ” has varied depending on isotopic composition of hydrogen (1200 mV and 1320 mV, correspondingly, at $\text{M}=\text{C}$, 368 K). This result was considered as the evidence for potential-determining role of protons in equilibrium state of heterostructures under study.

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iii) The magnitude of above mentioned difference of OCV of isotopically different heterostructures (~ 120 mV) could be explained as the manifestation of the quantum effect of energy levels of protons both in hydroxide and Pd.

To deeper understanding of proton exchange process, the comparison study of isotopic exchange in three system at 370 K: a = "PdH_x-D₂" b = "KOH.H₂O-D₂", and c = "KOH.H₂O|Pd,D₂", has been performed. The experimental conditions are shortly: initial gas pressure was 5,3 kPa; surfaces of phase contacts were ~ 1 cm²; Pd foil was 100 micron thick; hydroxide layers were 1,5 mm; the ratio "gas-solid" was approximately 1:1 in all cases. In the system "c" hydroxide was covered by Pd so to avoid any contact gas-hydroxide.

Isotopic exchange in "a" system was enough fast, as expected, and determined by two processes: surface chemical reaction on foil and changing in total pressure because isotopic exchange affect hydrogen solubility. In any case the complete equilibrium has been achieved in 20 minutes.

Running of isotopic exchange in "b" was determined by surface chemical reaction. The 90%-equilibrium has been achieved in 6 hours. At chosen conditions the magnitude of rate was $\sim 10^{-7}$ mole atomH/cm²sec. By changing of gas pressure and/or size of solid it could be possible to determine the rate of proton diffusion in the bulk of hydroxide as $5 \cdot 10^{-8}$ cm²/sec.

Running of isotopic exchange in "c" was quite another than in "a" and "b". Approximately during one hour the rate was relatively slow. Most probably it is determined by hydrogen solubility in initially "empty" Pd foil. However, after ~ 90 minutes the rate of isotopic exchange sharply increased to 10^{-5} mole atom H/cm² sec, i.d. by two order of the magnitude higher, than for "b". Since systems "b" and "c" had have the same ionic phase (KOH.H₂O), one could conjuncture that increase of the rate of isotopic exchange was due to higher chemical activity of monoatomic form of hydrogen in Pd in comparison with molecular H₂ as the partner of hydroxide in case "b". Therefore one can speak about high catalytic activity of hydrogen in Pd. It is also very important to underline that in system "c" (likey in "b" too) there is no so named triple-phase-boundary, only interphase of metallic & ionic compounds, both hydrogen-containing. Basing on this optimistic conclusion one could come to a decision on the necessity to test the protonic heterojunction under our study PdH_x |KOH.H₂O as a component of model fuel cell or a rechargeable battery.

The presented results will be partially published in *Solid State Ionic* (2007) as Proceeding of International Conference on Solid State Proton Conductors (SSPC-13, September 2006. St-Andrews, Scotland, UK).

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**KINETIC STUDY OF ETHYLENE POLYMERIZATION OVER HOMOGENEOUS
AND SUPPORTED CATALYSTS BASED ON 2,6-BIS(IMINO)PYRIDYL COMPLEX
OF IRON AND COBALT**

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Method of polymerization inhibition by radioactive carbon monoxide (^{14}CO) has been used to determine the number of active centers (C_p) and propagation rate constant (k_p) for ethylene polymerization with homogeneous and supported on the different supports (SiO_2 , Al_2O_3 , MgCl_2) catalysts based on the bis(imino)pyridine complexes of iron and cobalt. Methylalumoxane (MAO) or $\text{Al}(\text{i-Bu})_3$, were used as co-catalyst. In the case of homogeneous system with both activators the rate profile of polymerization was unstable: high activity of the initial period sharply decreases. Rapid catalyst deactivation with polymerization time is shown to be connected with the decrease of the active sites number and average propagation rate constant (for instance, for catalysts based on Fe-complex in 1.5-2 and 3 times for C_p and k_p values, respectively). In contrast to homogeneous systems based on bis(imino)pyridine complexes of iron and cobalt, the supported catalysts are highly active and stable in ethylene polymerization at 70-80 $^{\circ}\text{C}$. Data on the effect of hydrogen over the calculated C_p and k_p values were obtained. Molecular-mass distribution (MMD) of polyethylenes produced was determined by gel-permeated chromatography method. Polyethylene with broad MMD was divided by using Temperature Rising Elution Fractionation (TREF) on separate fractions with narrow MMD and the distribution of C_p and k_p values on polymer fractions were determined. The obtained C_p and k_p values and data on the polymer molecular mass and MMD lead to conclusion that the nature of the support has almost no effect on the active centers structure and distribution of their reactivity. This work was supported by the Russian Foundation for Basic Research, project No. 03-03-33034.

**ONE-DIMENSIONAL AND THREE-DIMENSIONAL CONDUCTIVITY AT
AMORPHOUS CARBON MATERIALS**

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In this paper we report on properties of nitrogen containing carbon materials exhibiting one-dimensional conductivity, prepared from a mixture of o-nitroaniline and 1,2,3-benzotriazol. For samples with small number of current carriers and one-dimensional conductivity EPR spectra were observed. As the number of current carriers increased, with one-dimensional conductivity still retained, the EPR spectra widened. Validation of the assumption that EPR spectra of amorphous carbon materials are due to undercondensed carbon systems (e.g. coke-type) is given.

In previous works [1, 2] it was shown that samples of amorphous carbon materials (ACM-1, ACM-2, ACM-3) synthesized on the base of phenol and 1,2,3-benzotriazol mixture can have both one-dimensional and three-dimensional conductivity. Conductivity type depends on temperature and time carbonization. It was established that ACM-1 sample has three-dimensional conductivity and has no EPR spectra. For ACM-2 and ACM-3 samples symmetric EPR spectra $g = g_e$ and one-dimensional conductivity of a carbon materials are observed. It was revealed that after pumping out EPR spectra of these two samples do not show correlation with Curie law appropriate to isolated or weak-interactive paramagnetic centres: at decreasing of measurements temperature the integrated intensity not only does not grow but decreases appreciably.

Synthesis of ACM-4 – ACM-6 samples was carried out with the same technique [1, 3] but with using of other precursors. The nitroaniline and 1,2,3-benzotriazol mixture was used as the precursor for ACM-4 sample. ACM-5 sample was received as a result of thermal treatment of ACM-4. ACM-6 sample was prepared on the basis of 8-oxyquinoline and 1,2,3-benzotriazol mixture.

It was established that spectrum width of ACM-4 is 2.5 G at both 77 and 300 K. ACM-6 has no EPR spectra. EPR spectra of ACM-6 sample shows correlation with Curie law and has spectrum width 23 G at 293 K and 4 G at 77 K.

Low concentration of carriers of a current in an amorphous carbon material leads to suppression of metal conductivity and to localization electron conductivity in the limited area of space. In this case hopping conductivity between these areas of localization. changes to hopping conductivity with variable length of a jump and described by generalized Mott low[4]:

$$\sigma(T) = \sigma_0 \cdot \exp(-B/T)^{1/(d+1)}$$

Conditions of synthesis and calculated value of electronic conductivity at 300 K

	ACM-1	ACM-2	ACM-3	ACM-4	ACM-5	ACM-6
T, °C	900	700	900	700	900	700
Time, min	23	15	15	20	10	80
$\sigma(300K)$	0.0550232	1.0618365	4.9530324	0.0002388	0.7891491	0.337564
d	3	1	1	1	1	1

d – dimension of movement of current carriers, $B = [16a^3/k_B N(E_F)]$, a – inverse value of length where the amplitude of nuclear wave function falls down (usually $1/a \sim 8 \div 10 \text{ \AA}$), $N(E_F)$ – density of conditions on surface Fermi, σ_0 – constant.

In all temperature interval electronic conductivity described by Mott low for one-dimensional systems (d=1) in spite of temperature dependence conductivity of ACM-4 – ACM-6 samples are notably different. It is necessary to note that the one-dimensional conductivity was already observed in carbon structures with carbon chains [5 - 7], and temperature dependence of conductivity had similar character.

As indicated in the table the conductivity of the samples depends on duration and temperature of heat treatment. The sample has three-dimensional conductivity if duration of heat treatment at 900 °C more than 15 minutes (ACM-1). If duration of heat treatment at 900 °C less than 15 minutes, one-dimensional conductivity of sample grows. For example, heat treatment of ACM-4 at 900 °C within 10 minutes leads to increasing the sample conductivity by three orders and broadening of the EPR spectra (ACM-5). EPR spectra of ACM-2 and ACM-3 samples do not show correlation with Curie law. It may be connected with the presence of undercondensed carbon systems (e.g. coke-type) giving EPR spectra. It may be assumed that in order to undercondensed carbon systems disappear more higher temperature or more duration of treatment is needed for phenol and 1,2,3-benzotriazol mixture than for nitroaniline and 1,2,3-benzotriazol mixture.

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THE PROCESSES OF POLYCHROMATIC IMAGING ON THE BASE OF COLLOIDAL SILVER PARTICLES IN THE AgHal PHOTSENSITIVE LAYERS

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Condensation, dispergation and combined methods to obtain the colloidal silver particles with the purposeful regulated optical properties were realized. This allowed to form the polychromatic (multicolored) image in the black-and-white AgHal-layer without the use of organic dyes and colored pigments.

The results of the investigations carried out with the participation of V.D.Stashonok and V.V.Sviridov and used to create the new, earlier unknown photographic processes, called the polychromatic ones, are discussed.

Polychromatic image (PI) is formed on the black-and-white AgHal photographic layer. Unlike the common color image it doesn't contain the dyes and colored pigments. Unlike the black-and-white image, which consists of filamentary silver particles, absorbing the visible light in all spectral region, PI consists of colloidal silver particles. These particles scatter and absorb the light selectively in dependence on their size and shape on the different parts of the image. As the result the object of photography is represented in the symbolic colors.

PI can be obtained by condensation (1), dispergation (2) and combined (3) methods. The methods (1) are based on the catalytic reactions, in which the latent image centers (LIC) formed in the photographic layer under the light exposition enlarge their size at the expense of the reduction of Ag^+ ions, coming from the AgHal microcrystal lattice to the swelled gelatine layer during it's treatment in the solution, which contains the AgHal solvent (KCNS) and reducer (methol, phenidone, hydroquinone). The difference of formed colloidal silver particles in their size (from 25-40 to 300-350 nm) is achieved as a result of the difference in the rate of silver ions reduction on the photolayer parts with the various LIC number, determined by the exposure magnitude.

The methods (2) are based on the destruction of filamentary silver structure of the black-and-white image in the unusual solution, containing the strong oxidizer ($\text{K}_3[\text{Fe}(\text{CN})_6]$) and reducer (NaBH_4) simultaneously. In the alkaline medium their interaction is slowed down kinetically. The silver catalyzes this reaction with the formation of intermediate compounds, which then are destroyed in water. The nanosized silver particles (1-10 nm in diameter) are

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formed on their place. The PI color is determined with the packing density of such particles on the layer parts with the different optical density (D).

In the other variant the stages of oxidation and reduction follow one after another. The oxidizer is I_2 in the KI solution. The reducers are methol, phenidone and hydroquinone in various combinations. The oxidation product AgI is reduced under the action of the light during its contact with the reducing solution. Probably, the silver particles formed as a result of photolysis, catalyze the Ag^+ reduction from the AgI lattice with the colloidal silver particles formation. Their size is not equal on the parts of image, varied by the D value.

The method (3) is based on the oxidizing-reducing reactions taking place in the conditions, when the filamentary silver of the common black-and-white image can be transformed not only into colloidal silver particles, but into colored ferrous-ferric complexes as well. The rate of these reactions and the nature of their products are also determined by the silver concentration on the image part with different D initial.

MECHANISMS OF MOLECULAR HYDROGEN ISOTOPE EXCHANGE ON THE SUPPORTED METAL CATALYSTS

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The activities of industrial nickel, ruthenium and palladium supported catalysts in the molecular hydrogen isotope exchange reaction were measured and the activation energies and pressure orders within 77-700 K range were determined. The dependencies of catalytic activities of temperature and pressure were used to fit the parameters of model invoking the transition state theory and two mechanisms of hydrogen dissociation on metals. A good agreement between calculated and experimental data with realistic values of such parameters like hydrogen-metal bond energy, mean vibrational temperature *etc.* was obtained.

For various industrial reactions including molecular hydrogen its activation is the necessary stage. The homomolecular hydrogen isotope exchange (for example $H_2 + D_2 \leftrightarrow 2HD$) also belongs to this class of reactions. The VIII group transition metals are the most active catalysts of this and similar processes. The supported metal catalysts are of the great interest from the point of view of their applications. However, they are quite complicated systems and their efficiencies are determined not only by the properties of metal or support alone but also by their interaction, by size and shape of deposited particles and dynamics of their surface. Owing to its simplicity the molecular hydrogen exchange reaction mentioned above may be considered as a convenient tool for clarifying mechanisms of hydrogen activation on the metal particles because it is very sensitive to changes of reaction centers and forms of hydrogen adsorbed by metal surface.

The objects of our investigations were the samples of the following industrial catalysts: 0,5% Ru/Al₂O₃, 4% Ru/sibunit, 5% Pd/Al₂O₃, 0,5% Pd/sibunit, 15% Ni/Al₂O₃, 50% Ni/SiO₂. The purposes of this study were observing the influence of metal size particles and nature of metal and support on the catalytic activity as well as analyzing the data to make a guess about the common mechanism of hydrogen activation and isotope exchange. The dependencies of catalytic activity (K_s) on temperature (77-700 K) and pressure (15-400 Pa) and the activation energy (E_a) and pressure order (n) values at different temperatures have been obtained. These results are shown in the table below.

Properties of the Studied Catalysts

Catalyst	Ea_1 , kJ/mol (77÷140 K)	T of mechanism change, K	Ea_2 , kJ/mol (140÷690 K)	$K_s \cdot 10^{-13}$, molecule/(cm ² ·s)		T , K	Pressure order n	Metal particle size, nm
				77 K	300 K			
Ru/Al ₂ O ₃	0,14	273	3,1	53,7	107,0	77	0,9	6,1
						273	0,6	
						403	0,75	
Ru/ sibunit	0,5	343	4,4	32,2	50,3	77	0,87	6,9
						343	0,21	
						693	0,95	
Pd/Al ₂ O ₃	4,6	-	-	0,21	25,11	-	-	24
Pd/ sibunit	4,6	-	-	0,15	26,3	-	-	3,5
Ni/Al ₂ O ₃	2,5	143	8,8	0,39	94,6	77	0,9	3400
						143	0,35	
						293	0,9	
Ni/SiO ₂	5,5	-	-	0,033	-	-	-	1500

The necessary condition of the isotope exchange is the formation of hydrogen atoms on metal surfaces. They can be either the products of dihydrogen dissociation in a precursor state or fragments formed immediately when a gas-phase molecule falls down to the surface. Predomination of the first or the second mechanism depends on temperature, pressure and concentration of reaction sites since the active centers on a surface responsible for the two mechanisms may be not the same. However, in both cases the hydrogen atoms appeared after dissociation are “hot” and possess kinetic energy enough for their motion along the surface before strong adsorption. Quite a long motion of atoms and their collisions to each other give them an opportunity to recombine and form different isotopomers (for example HD if the gas mixture contained initially the H₂ and D₂ molecules only).

The equations for calculating the catalytic activities of metal particles were obtained within the transition state theory framework invoking the two mechanisms of dissociation described above. Capability of the model is proven by a good correlation between calculated and experimental values of activities as well as by realistic values of such fitting parameters like hydrogen-metal bond energies, mean vibrational temperature of adsorbed species, activation energies of elementary steps *etc.*

**OXIDATIVE DEHYDROGENATION OF ETHANE OVER MODIFIED
MULTICOMPONENT OXIDE CATALYSTS BASED ON VANADIUM AND
MOLYBDENUM**

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The oxidative dehydrogenation of ethane and genesis of multicomponent oxide catalysts (V-Mo-Te-Nb-Me-O, where Me - Ca, Bi, Zr, and others) have been studied using NMR, XRD and differential dissolution methods. The maximal yield of ethene 75% is achieved on the catalyst with the composition $V_{0.3}Mo_1Te_{0.23}Nb_{0.12}Bi_{0.05}O_x$. The genesis of the catalysts includes formation of the mixed oxo-, polyoxo- and heteropolyanions in solution, its condensation into amorphous solid during drying and decomposition of the latter giving two crystalline phases – orthorhombic (M1) and hexagonal (M2) under calcination.

Nowadays the most effective catalysts for oxidative transformation of light alkanes, viz. ethane and propane are VMoTeNb-oxide compositions [1,2]. These catalysts contain two main crystalline phases so-called M1 (orthorhombic) and M2 (hexagonal).

In the present work oxidative dehydrogenation of ethane and genesis of modified $V_{0.3}Mo_1Te_{0.23}Nb_{0.12}Me_x$ -oxide catalysts have been studied. We varied the nature of the additive (Me = K, P, Ga, Ca, Zr, Sb, Bi, Ag, Ce) and its content ($x = 0.001 - 0.1$).

The catalysts were synthesised by the rapid evaporation of an aqueous slurry and following calcination according to patent procedure [3]. The raw materials were ammonium paramolybdate (APM), ammonium metavanadate (AMV), telluric acid (TA), niobium oxalate (ON) as well as corresponding nitrates (in the case of K, Ce, Ag, Ga, Ca) or oxides (in the case of Bi, Sb, Zr) or H_3PO_4 (in the case of P) (MeX). The chemical composition and structure of the different complexes formed in solution was studied by ^{51}V , ^{125}Te , ^{95}Mo and ^{17}O NMR spectroscopy. The chemical and phase composition of the compounds formed under thermal treatment was determined by the differential dissolution method (DD) [4] and XRD accordingly.

As in the case with propane, catalytic properties of VMoTeNbO catalyst in ethane oxidative dehydrogenation are depended on M1/M2 ratio. The introduction of different additives into VMoTeNbO catalyst significantly affects catalytic properties. So, the additives with strongly different basic and acidic properties such as Ag, K and P decrease both activity and selectivity to ethene. Introduction of Ga, Sb and Ce is accompanied by reduction of activity but selectivities remain practically unchanging. Modification with Zr, Ca and Bi leads

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to increase of selectivity to ethene due to suppression of it afteroxidation, moreover in the case of Bi activity rises also. Thus, the maximal yield of ethene 75% (compared to 67% on the unmodified sample) is achieved on the catalyst with the composition $V_{0.3}Mo_1Te_{0.23}Nb_{0.12}Bi_{0.05}O_x$.

The genesis of the catalysts follows the common mechanism and includes several stages: (i) formation of individual and mixed oxo-, polyoxo- and heteropoly anions such as TeO_6^{6-} , $V_9TeO_{28}^{5-}$, $TeMo_3V_5O_{27}^{5-}$ and $TeMo_6O_{24}^{6-}$ during mixing of aqueous solutions of APM, AMV, TA and MeX, the composition and structure of these complexes being independent of additives nature; (ii) formation of an aqueous slurry when niobium oxalate was added, at that hydrolysis of niobium oxalate is observed but the composition of anions in mother liquor remains practically unchanged, only oxalate complex of VO_2^+ is additionally obtained; (iii) condensation of anions into amorphous material with heteropoly anion of the Anderson type [5] as the main building blocks as well as compounds containing individual elements at the drying stage; (iv) decomposition of the first phase with simultaneous interaction with individual compounds resulted in formation of two crystalline phases – orthorhombic (M1) and hexagonal (M2) under thermal treatment.

The nature of additive has no effect on phase composition of the samples - mixture of M1 and M2 phases, but changes M1/M2 ratio in final catalysts and affects the relative content and the composition of the phase formed during preparation procedure. As an illustration, Table 1 gives data for some catalysts improving catalytic property.

Table 1. Chemical composition of different phase in $V_{0.3}Mo_1Te_{0.23}Nb_{0.12}Me_x$ -oxide catalysts.

Me _x	Amorphous material		M2		M1	
	composition	A*, %	composition	A*, %	composition	A*, %
	$V_{0.27}Mo_1Te_{0.15}Nb_{0.03}$	82	$V_{0.3}Mo_1Te_{0.31}$	12	$V_{0.28}Mo_1Te_{0.08}Nb_{0.12}$	80
Ca _{0.1}	$V_{0.32}Mo_1Te_{0.1}Nb_{0.04}Ca_{0.08}$	70	$V_{0.51}Mo_1Te_{0.52}Nb_{0.06}Ca_{0.02}$	32	$V_{0.27}Mo_1Te_{0.08}Nb_{0.08}$	51
Zr _{0.1}	$V_{0.23}Mo_1Te_{0.13}Nb_{0.02}$	83	$V_{0.34}Mo_1Te_{0.64}$	15	$V_{0.24}Mo_1Te_{0.08}Nb_{0.12}Zr_{0.12}$	78
Bi _{0.05}	$V_{0.34}Mo_1Te_{0.13}Nb_{0.02}$	64	$V_{0.33}Mo_1Te_{0.46}Bi_{0.1}$	8	$V_{0.3}Mo_1Te_{0.18}Nb_{0.11}Bi_{0.03}$	79

* - relative content of phase.

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EFFECT OF THE HYDROGEN PEROXIDE OXIDATION OF CARBON SUPPORT OF ZINC ACETATE CATALYST FOR ACETYLENE HYDROACETOXYLATION

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The main problem of an efficient $\text{Zn}(\text{CH}_3\text{COO})_2 / \text{AC}$ (AC-activated carbon) catalyst preparation is the achievement of uniform distribution of finely dispersed rather active during catalysis salt component (SC) immobilized on support surface. We have found the decision of this task in liquid phase oxidation of activated carbon with nitric acid or hydrogen peroxide, in the mode of salt application [1, 2] and catalyst drying.

The objective of the present investigation is to study the characteristic changes of support sample AC AGN- 2 the initial (S1) one and oxidized with hydrogen peroxide (H_2O_2) (S2) as well as of the catalysts (C1) and (C2) on support (S1) and (S2), correspondingly under conventional drying at $T= 150^\circ\text{C}$ and (C3) on support (S2) under slow drying ($0,3^\circ\text{C}\cdot\text{min}^{-1}$).

For this purpose the adsorption method has been used (adsorption of benzene vapours, water, acetic acid and zinc acetate adsorption from aqueous solution). Particular distribution of zinc acetate on AC surface of C1, C2, C3 has been studied by small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM) and by X-ray microanalysis (XMA).

The catalysts were tested during the vinylacetate synthesis reaction in flow isothermal reactor by cycle method at 175, 205 and 230 °C [3].

When oxidized with H_2O_2 AC changes its texture sufficiently. Thus specific surface of S2 sample as compared with S1 increases by $50 \text{ m}^2\cdot\text{g}^{-1}$ as much as $920 \text{ m}^2\cdot\text{g}^{-1}$, the micro- and mesopores share in S2 clearly getting greater (fig. 1). The increase of available adsorption sites number as for described above texture changes and transformation of surface oxygen functional groups on AC (S2) result in increase of both adsorption capacity and differential heat adsorption both for polar (H_2O , CH_3COOH) and non-polar (C_6H_6) substances, despite their different adsorption mechanism. It was found that the maximum amount of adsorbed species at $P/P_s=0,8$ as for benzene increased by 14 % and as for water by 36 %. Simultaneously a significant increase (approximately 3 times) the adsorption capacity of zinc acetate as for S2 as compared with S1 was observed.

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The nanostructure of CS (clusters of salt) in C1, C2, C3 catalysts includes both salt clusters with wide size distribution and located in micropores highly dispersed SC states as is seen from fig. 2. It is characteristic of C1 to form large clusters of SC of considerable volume while their number in C2 is significantly lower. As for C3, close to molecular dispersion of

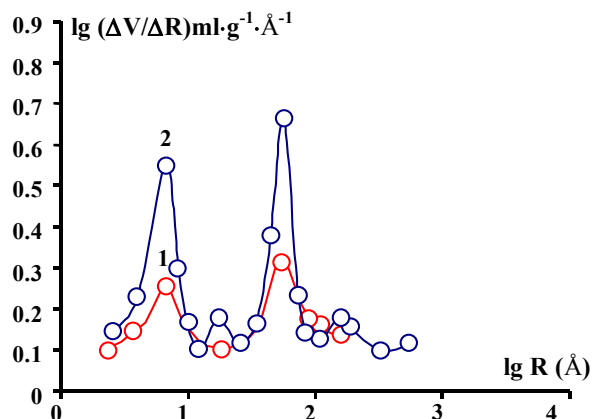


Fig.1 Differential curves of pore size distribution of AC modified with H_2O_2 (S2) and initial (S1) as to the benzene vapour adsorption isotherms.

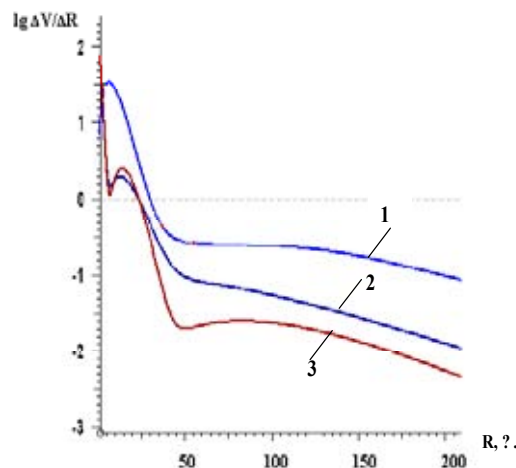


Fig.2 Differential curves of micropores size distribution and cluster of salt of catalysts C1-(1), C2-(2) and C3-(3).

SC is observed, the volume of salt clusters being further lowered. Besides, based on SEM and XMA data a considerable scattering of zinc acetate content onto several surface sites is characteristic for C1 which is indicative of immobilization of different zinc containing varieties forming disordered nonstoichiometric states of SC. The approximate equality of zinc concentration onto C3 surface demonstrates the more uniform microdistribution of SC.

As follows from these facts the activity of C2 and especially of C3 in vinyl acetate (VA) synthesis is 5-6 times that of C1. Thus at 175, 205 and 230°C the efficiency of C3 sample as for VA is as much as 42,5; 198 and 342 $\text{g} \cdot \text{l}^{-1} \cdot \text{h}^{-1}$, characteristics of C3 being more stable than those of C1 after three cycles of temperature alteration.

To conclude with, the use of modified by hydrogen peroxide oxidation AC support under conditions of slow drying may yield a stable and active catalyst for hydroacetoxylation of acetylene.

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**CO ISOTOPIC EXCHANGE OVER Rh/Al₂O₃ : NONDISSOCIATIVE EXCHANGE
ON METALLIC Rh SITES**

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The isotopic exchange reaction $^{12}\text{C}^{18}\text{C}+^{13}\text{C}^{16}\text{O}=\text{}^{13}\text{C}^{18}\text{O}+^{12}\text{C}^{16}\text{O}$ has been studied over alumina-supported rhodium catalysts 0.1%Rh/ γ -Al₂O₃, 1%Rh/ γ -Al₂O₃, 5%Rh/ γ -Al₂O₃, 10%Rh/ γ -Al₂O₃ and γ -Al₂O₃ at temperatures 173-583 K.

Since preparations, enrichment of heavy isotopes of carbon ¹³C became accessible, researchers were involved with studying reaction of an isotope exchange in molecules CO: $^{12}\text{C}^{18}\text{C}+^{13}\text{C}^{16}\text{O}=\text{}^{13}\text{C}^{18}\text{O}+^{12}\text{C}^{16}\text{O}$.

It is connected first of all with that the given reaction allows to obtain additional data on interaction of adsorbed CO with a surface of catalysts and on the mechanism of such important catalytic reactions as CO water steam conversion, CO hydrogenation, reaction of CO oxidation.

The isotopic exchange reaction $^{12}\text{C}^{18}\text{C}+^{13}\text{C}^{16}\text{O}=\text{}^{13}\text{C}^{18}\text{O}+^{12}\text{C}^{16}\text{O}$ has been studied over alumina-supported rhodium catalysts: 0.1%Rh/ γ -Al₂O₃, 1%Rh/ γ -Al₂O₃, 5%Rh/ γ -Al₂O₃, 10%Rh/ γ -Al₂O₃ and γ -Al₂O₃ at temperatures 173-583 K. Catalysts (0.1%Rh/ γ -Al₂O₃, 1%Rh/ γ -Al₂O₃, 5%Rh/ γ -Al₂O₃, 10%Rh/ γ -Al₂O) were prepared by impregnation by a moisture capacity of γ -Al₂O₃ with water solution of rhodium nitrate of mark ch. with the subsequent keeping of damp granules within a day, drying at 110 °C and heat treatment at 500 °C during 2 hours. Catalysts before testing of isotope equilibration were restored in hydrogen at 200 °C and subjected to standard vacuum processing: exhaustion at temperature 400 °C up to residual pressure 10⁻⁶ Torr. The sample was exposed to such processing before measurement at each temperature, in order to prevent distortion of results owing to influence of CO on surface properties. Thus, each measurement was spent on exposed surfaces.

Following features of isotopic mixing on the given catalysts are established:

1. On the low-percentage catalyst and on the pure carrier 2 areas of course of an exchange: low- temperature and high-temperature are observed.
2. On 5%Rh/ γ -Al₂O₃ low- temperature area is expressed much more poorly, than on 1%Rh/ γ -Al₂O₃.
3. On 10%Rh/ γ -Al₂O₃ low-temperature area is absent.

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The exchange in high-temperature area on metal rhodium and on all catalysts proceeds by the same mechanism, despite of distinctions in adsorption of CO and course of parallel processes (both CO dissociation and disproportionation) on 10%Rh/ γ -Al₂O. The calculated value of energy of activation $E_a=35\pm 0,4\text{kJ}$. It is possible to draw a conclusion, that the exchange proceeds between two adsorbed molecules CO, due to bimolecular interactions between molecules linear bonds CO with formation of corners or on bonds M-CO, or on bonds C=O that demands overcoming a significant potential barrier (energy of activation), and the elementary certificate of interaction between them also is a limiting stage, i.e. mechanism Lengmjura-Hinshelvuda takes place.

**PROPAN-2-OL CONVERSION TO DIISOPROPYL ETHER OVER SUBSTITUTED
PHOSPHOMOLYBDATE HETEROPOLYCOMPOUNDS**

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Due to the necessity of environment protection, gasoline composition has to be changed. Adding oxygenated compounds, mostly C₂-C₄ alcohols, methyl tert-butyl, diisopropyl and tert-amyl methyl ethers to motor fuels, is a part of the program of gasoline reformulation. Ethers increase the octane number, reduce the emissions of gases to greenhouse effect (CO_x and NO_x). Their introduction in the composition of gas also permits, to decrease the quantity of the products as the aromatic hydrocarbons and the alkenes, in particular C₄-C₅.

Industrial sulfocationites and ion exchange resins used as catalysts in ether synthesis show many advantages. However, they have poor thermal and mechanical stability [1, 2]. A potential route that received attention is the substitution of these catalysts by Keggin type heteropolycompounds.

In this work, the propan-2-ol conversion to diisopropyl ether (DIPE) was studied over ammonium substituted heteropolycompounds with (NH₄)_xX_yPMo₁₂O₄₀ formula where Xⁿ⁺=Sb³⁺, Bi³⁺, Sn²⁺ at 100°C. The obtained results have shown that alcohol reactivity depends on the pre-treatment temperature and composition of solid.

For the whole catalysts and at all pre-treatment temperature (150-250 °C) the dehydration of propan-2-ol produced DIPE and propene.

High both activities and selectivity to DIPE were obtained in presence of (NH₄)_{2,55}Bi_{0,15}PMo₁₂O₄₀ and (NH₄)_{0,63}Sb_{0,79}PMo₁₂O₄₀ salts.

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ROLE OF CARBON DIOXIDE IN THE ETHYLBENZENE DEHYDROGENATION COUPLED WITH REVERSE WATER-GAS SHIFT

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Dehydrogenation of ethylbenzene (EB) to styrene (ST) in the presence of CO₂, in which EB dehydrogenation is coupled with the reverse water-gas shift (RWGS), was investigated extensively. Iron and vanadium supported on activated carbon or alumina are potential catalysts, but are different in the reaction mechanism. The reaction coupling proved to be superior to the single dehydrogenation in many respects, which can be attributed to that CO₂ can eliminate hydrogen produced during EB dehydrogenation, resume the oxidative state (lattice oxygen) of reduced metal species and alleviate the catalyst deactivation.

Styrene (ST) is commercially produced by the dehydrogenation of ethylbenzene (EB) on the promoted iron oxide catalysts at 600–700 °C, just below the temperature where thermal cracking becomes significant. Due to its highly endothermic and volume-increasing character, a large amount of superheated steam is used to supply heat, lower the partial pressure of the reactant, and avoid the formation of carbonaceous deposits [1, 2]. However, much of the latent heat of steam is lost in the gas-liquid separator.

The dehydrogenation of EB to ST in the presence of CO₂ instead of steam, in which EB dehydrogenation is coupled with the reverse water-gas shift (RWGS), is believed to be an energy-saving and environmentally friendly process [3, 4]. EB conversion can be enhanced at a lower temperature (550 °C) and the energy consumption can be reduced significantly. In this work, we have carried out an extensive investigation on the EB dehydrogenation in the presence of CO₂ through both the theoretical analysis and the experimental characterization.

With the thermodynamic analysis, the superiority of reaction coupling was displayed and possible reaction pathways were suggested [5, 6–7]. As shown in Fig. 1, the equilibrium conversion of EB is improved greatly by coupling with RWGS. Moreover, the dependence of the equilibrium conversions of EB and CO₂ for the coupled EB dehydrogenation in the presence of CO₂ through different pathways can be evaluated (Fig. 2); EB conversion of the coupled dehydrogenation via the two-step pathway is a little higher than that via the one-step pathway at 350–600 °C.

The extensive catalyst screening proved that iron and vanadium supported on activated carbon or γ -Al₂O₃ with certain promoters are potential catalysts for this coupling process [6, 8]. However, they are different in the reaction mechanism, although ST yield is always associated with CO₂ conversion over various catalysts [5]. The two-step pathway plays an important role in the coupling process over Fe supported on AC or Al₂O₃, while the one-step pathway dominates the reaction over V supported catalysts (Fig. 2).

Coke deposition and deep reduction of active catalyst components are the major causes of catalyst deactivation [6, 9]. Coke deposition is directly related to the EB consumption or ST production and can not be effectively suppressed by CO₂ (there exists a roughly linear relation, as shown in Fig. 3), while deep reduction of the surface vanadium species is associated with the vanadium loading and reaction atmosphere. CO₂ can preserve the active species at high valence, and therefore alleviate the catalyst deactivation in the coupling reactions.

The superiority of the reaction coupling in the presence of CO₂ over the single dehydrogenation can be attributed to that CO₂ as a weak oxidant can eliminate hydrogen produced during EB dehydrogenation, resume the oxidative state (lattice oxygen) of reduced metal species and alleviate the catalyst deactivation.

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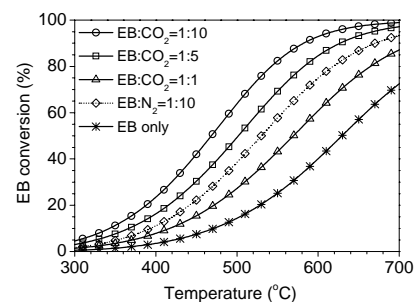


Fig. 1. Reaction coupling of EB dehydrogenation with RWGS: the effects of the feed composition (in mole ratio) and temperature on the equilibrium conversion of EB at 0.1 MPa.

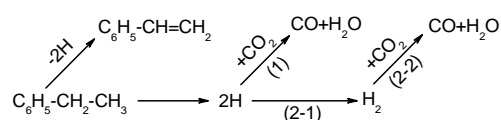


Fig. 2. Role of CO₂ in the coupled EB dehydrogenation in the presence of CO₂

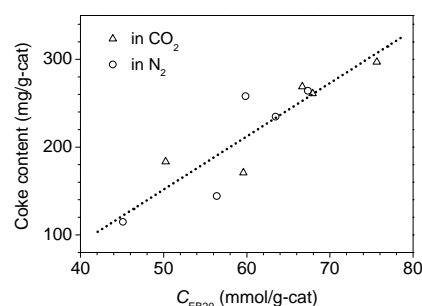


Fig. 3. Relation of coke deposition with EB consumption for EB dehydrogenation in 20 h under different atmospheres over V/Al₂O₃ with various vanadium loadings.

**DIRECT OXIDATION OF BENZENE TO PHENOL BY NITROUS OXIDE:
THE RADICAL NATURE OF ACTIVE OXYGEN INVOLVED IN THE REACTION**

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Catalytic oxidation of benzene to phenol by nitrous oxide over Fe-MFI zeolites was studied in relation to the active oxygen species taking part in the oxidation. A linear dependence of the reaction rate on the concentration of independently identified active sites generating O^- radicals (α -sites) has been obtained within a broad range of values. The dependence is interpreted as a convincing evidence of the O^- involvement in the catalytic (not only stoichiometric) oxidation of benzene to phenol.

MFI zeolites of aluminosilicate, borosilicate and titanosilicate composition were shown to be inert in the benzene to phenol oxidation by nitrous oxide, but exhibit high activity and selectivity in this important reaction after the introduction of Fe [1, 2]. The active sites of zeolite catalysts are extralattice complexes of bivalent iron Fe_{α}^{2+} (α -sites) stabilized in the zeolite matrix [3]. Upon N_2O decomposition, these sites generate the so-called alpha-oxygen represented by monatomic oxygen radical O_{α}^- , which is involved in highly selective oxidation of benzene to phenol.

The catalytic role of α -sites was studied previously in many works. However, a quantitative correlation between zeolite activity and α -sites concentration (C_{α}) under comparable conditions did not attract necessary attention. The present work considers the catalytic properties of Fe-containing zeolite catalysts of various composition with α -sites concentration varying within two orders of magnitude. The obtained linear dependence of the reaction rate on C_{α} (Fig. 1) reliably indicates that the reaction proceeds precisely on the α -sites.

This conclusion is of particular importance in connection with a long discussion in the literature on a possible role of O^- radicals in selective oxidation catalysis over V and Mo oxides. Reliable evidence of the catalytic role of O^- obtained with zeolites may renew a general interest in the once suggested but not recognized radical oxygen idea in the oxidation over widely used metal oxide catalysts.

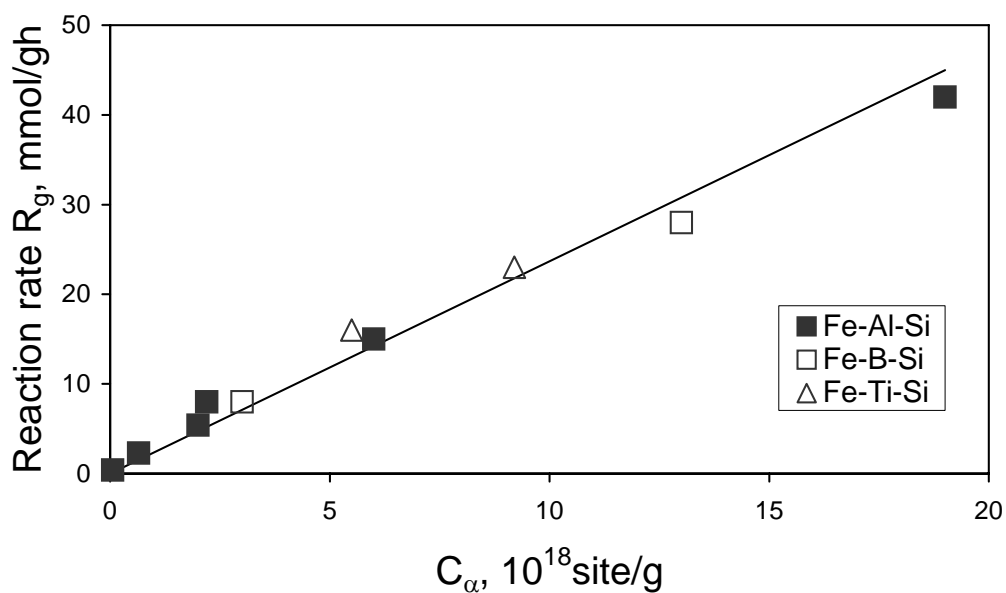


Fig. 1. Rate of benzene oxidation vs. α -sites concentration.

Acknowledgments:

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**DFT STUDY OF REDUCTION REACTIONS ON A PALLADIUM CLUSTER
SUPPORTED ON A CARBON NANOTUBE**

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Amongst metal catalysts, palladium is one of the most used. Its peculiar interaction with hydrogen made it a fundamental catalyst for hydrocarbon hydrogenation, selective reduction of functional groups, synthesis of vinyl acetate from ethylene, oxygen and acetic acid as well as for synthesis of methanol. At the same time, carbonaceous materials, namely activated carbon, graphite and more recently nanotube and fullerene derivatives, are often used as supports for catalysts, as they are stable under different conditions and allow an economical and ecological recovery of the catalytic metal by simply burning off the carbon.

We report the reduction mechanisms of two molecules of environmental and industrial interest, carbon monoxide and 2-butene, occurring on a palladium cluster supported on a portion of a single-walled armchair(6,6) carbon nanotube, investigated by means of DFT calculations. The cluster is a Pd₉-D_{3h} structure, which has been shown to be the geometry adopted on different carbonaceous supports [1]. The entire systems have been subjected to full geometry optimization at any stage of the reactions by using an ONIOM QM/MM combination, and stationary points were characterized by the analysis of the harmonic frequencies. All the different positions for the adsorption and co-adsorption of the reagents (CO, H₂, C₄H₈) on the Pd₉ have been considered. A comparison of the reaction mechanism paths and energetics occurring on supported and unsupported Pd₉ cluster has been also done. Further, the isomerization reaction of trans-2-butene has been studied by using the time

dependent-DFT approach and the influence of the Pd₉/support on the electron excitation energies of the alkene has been detailed.

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**ORIGINAL MONTE CARLO METHOD FOR HETEROGENEOUS CATALYTIC
REACTIONS SIMULATION IN TIME MODE OF REAL EXPERIMENTS**

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¹⁶O/¹⁸O isotopic exchange over CeO₂-ZrO₂ and CeO₂-ZrO₂-La₂O₃ at T = 923 K and P = 760 Torr was analyzed by original Monte Carlo method simulating these processes in the time mode of real transient kinetic experiments. The values of the rate constants of elementary stages of isotopic exchange were found at which the excellent agreement between calculated and experimental isotopic transient curves was obtained. All these kinetic data are required for the further steps of modeling isotopic exchange over Pt/CeO₂-ZrO₂ and Pt/CeO₂-ZrO₂-La₂O₃, and then partial oxidation of hydrocarbons.

Fluorite-like ceria-zirconia based catalysts are known to have high surface/bulk oxygen mobility and storage capacity, which is supposed to play a key role in the number of catalytic reactions and therefore deserves to be investigated carefully for elucidation of detailed kinetics and mechanistic pathways.

In our numerical experiments several assumptions were made as follows. a) the topological equivalent of the model fluorite-like structure in our simulations consisted of oxygen atoms and/or oxygen vacancies only, and its surface, subsurface and innermost layers were hexagonally packed; b) each Monte Carlo step considered a tiny time interval **dt** for all elementary stages of the overall process: inlet (outlet) stream, adsorption, desorption, diffusion, etc. It was supposed that during this interval **dt** concentrations of oxygen isotope molecules are constant in all the reactor volume; c) the kinetics of oxygen adsorption, desorption, bulk and surface diffusion follows a mass action law: for example, the rate of O₂ adsorption onto the surface may be represented by $W_{\text{ads}} = k_{\text{ads}}C_{\text{O}_2}\Theta_Z^2$, where k_{ads} is a function of temperature only; C_{O_2} is a gas oxygen concentration of any isotope composition; Θ_Z is the surface vacancy fraction. If we have square layers L*L in area (where L measured by oxygen diameters) and small time step **dt** ca. 0.02 - 0.05 s (vide supra), then quantity N_{ads} of elementary acts of O₂ adsorption may be written as

$$N_{\text{ads}} = [L^2dt k_{\text{ads}}C_{\text{O}_2}\Theta_Z^2] + n_{\text{ads}}$$

where brackets mean the integer part of the inner expression, and n_{ads} is the fractional part of the same expression. In our simulation advance $N_{\text{ads}} - n_{\text{ads}}$, $N_{\text{des}} - n_{\text{des}}$, $N_{\text{dif}} - n_{\text{dif}}$ etc. quantities were calculated before each successive Monte Carlo step. Then all type of Monte Carlo trials were realized randomly and numbers n_{ads} , n_{des} etc. were added to corresponding quantities N_{ads} , N_{des} etc. for the next Monte Carlo step.

The good agreement between the experimental and Monte Carlo generated time variation of fractions of differently labeled oxygen molecules (in the outlet flow)

$$f_{34}(t) = \frac{{}^{16}\text{O}^{18}\text{O}}{{}^{16}\text{O}_2 + {}^{16}\text{O}^{18}\text{O} + {}^{18}\text{O}_2} \quad \text{and} \quad \alpha_g(t) = \frac{{}^{16}\text{O}^{18}\text{O} + 2{}^{18}\text{O}_2}{2({}^{16}\text{O}_2 + {}^{16}\text{O}^{18}\text{O} + {}^{18}\text{O}_2)}$$

was obtained with following values of the rate constants of isotope exchange elementary steps

TABLE 1. Rate constants of elementary steps of isotopic exchange.

Stages	Expression of the reaction rates	Rate constants (s ⁻¹)
Adsorption: ${}^x\text{O}_2 + 2Z \rightarrow 2[{}^x\text{OZ}]$ or ${}^{16}\text{O}^{18}\text{O} + 2Z \rightarrow Z^{16}\text{O} + Z^{18}\text{O}$	$W_{\text{ads}} = k_{\text{ads}}C_{\text{O}_2}\Theta_Z^2$ or $W_{\text{ads}} = k_{\text{ads}}C_{\text{OO}}\Theta_Z^2$	$k_{\text{ads}} = 7.800$
Desorption: $2[{}^x\text{OZ}] \rightarrow {}^x\text{O}_2 + 2Z$ or ${}^{16}\text{OZ} + {}^{18}\text{OZ} \rightarrow {}^{16}\text{O}^{18}\text{O} + 2Z$	$W_{\text{des}} = k_{\text{des}}\Theta_{x\text{O}}$	$k_{\text{des}} = 0.032$
Surface diffusion: $Z_1{}^x\text{O} + Z_2 \rightarrow Z_1 + Z_2{}^x\text{O}$	$W_{\text{sdif}} = k_{\text{sdif}}\Theta_{x\text{O}}\Theta_Z$	$k_{\text{sdif}} = 0.030$
Lattice diffusion: $Z_i{}^x\text{O} + Z_j \rightarrow Z_i + Z_j{}^x\text{O}$	$W_{\text{vdif}} = k_{\text{vdif}}\Theta_{i\text{O}}\Theta_{j\text{V}}$	$k_{\text{vdif}} = 0.034$

Here x is 16 or 18; Z - oxygen vacancy; i,j - numers of layers; $\Theta_{x\text{O}}$ - fraction of surface sites occupied by ${}^x\text{O}$ atoms; Θ_Z - fraction of surface oxygen vacancies; $\Theta_{i\text{O}}$ - fraction of oxygen atoms in i-th layer; $\Theta_{j\text{V}}$ - fraction of oxygen vacancies in neighbouring j-th layer.

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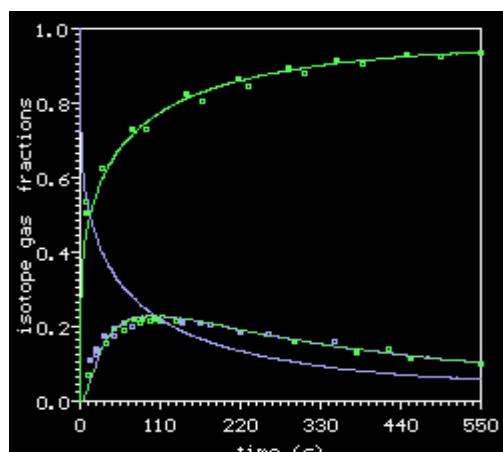


Figure 1. Closed squares, experimental $f_{34}(t)$ and $\alpha_g(t)$ for ${}^{18}\text{O}_2$ and ${}^{18}\text{O}^{16}\text{O}$ over $\text{CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3$; open squares are the same over $\text{CeO}_2\text{-ZrO}_2$. Ascending curve, calculated $\alpha_g(t)$ for ${}^{18}\text{O}_2$; descending curve, the same for ${}^{16}\text{O}_2$; hump-backed curve, calculated $f_{34}(t)$ for ${}^{18}\text{O}^{16}\text{O}$.

STUDY ON THE MECHANISM OF THE LIQUID-PHASE OXIDATION OF H₂S IN THE PRESENCE OF CoPc. A COMPARISON OF REACTIVITY OF HS⁻ AND HS_n⁻ IONS UPON INTERACTION WITH CATALYST CoPc(SO₃Na)₄ UNDER ANAEROBIC CONDITIONS

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Catalytic oxidation of H₂S plays a key role in industrial processes for gas purification from H₂S. Cobalt phthalocyanine (CoPc) and its derivatives proposed in the 1960s, proved to be the most effective catalysts for the liquid-phase H₂S oxidation with oxygen with sulfur formation [1, 2]. In a low-alkaline medium phthalocyanine catalysts reveal highest activity in the reaction of H₂S oxidation. The mechanism of the liquid-phase catalytic oxidation of H₂S with oxygen in a low-alkaline medium in the presence of phthalocyanine catalysts involves the stage of reduction of Co(II)Pc to Co(I)Pc [1]. This stage is rate-determining step in catalytic cycle.

The interaction of HS⁻ ions with Co(II)Pc(SO₃Na)₄ in the aqueous-alkaline solutions at the anaerobic conditions was studied by spectrophotometric stopped-flow method.

It was found that the reaction rate of Co(II)Pc(SO₃Na)₄ to Co(I)Pc(SO₃Na)₄ reduction has been of the first order with respect to HS⁻ ions (Fig. 1). The reaction rate depends on the value of pH (Fig. 2).

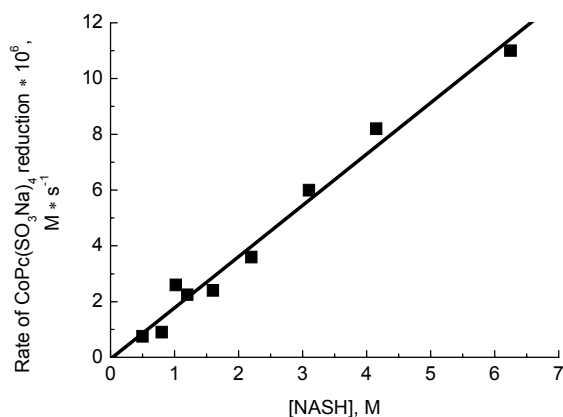


Fig. 1 The rate of CoPc(SO₃Na)₄ of reduction by HS⁻ ions *versus* concentration HS⁻ions

$t = 25^{\circ}\text{C}$, $[\text{K}_n\text{H}_{(3-n)}\text{PO}_4] = 6,26 \cdot 10^{-2} \text{ M}$,
 $[\text{CoPc}(\text{SO}_3\text{Na})_4] = 2,15 \cdot 10^{-5} \text{ M}$. $\text{pH} = 11,3$.

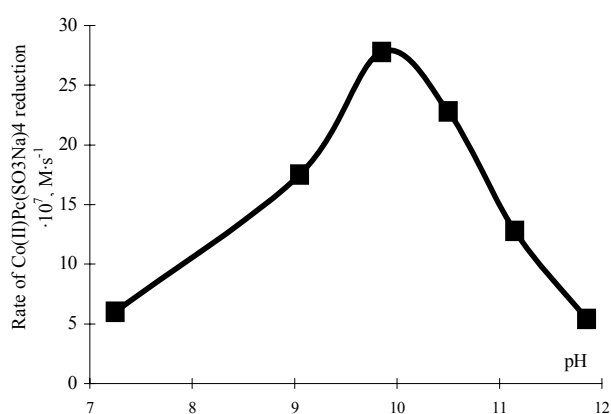


Fig. 2 The rate of CoPc(SO₃Na)₄ reduction by HS⁻ ions *versus* pH.

$t = 25^{\circ}\text{C}$, $[\text{K}_n\text{H}_{(3-n)}\text{PO}_4] = 6,26 \cdot 10^{-2} \text{ M}$,
 $[\text{CoPc}(\text{SO}_3\text{Na})_4] = 2,15 \cdot 10^{-5} \text{ M}$,
 $[\text{NaHS}] = 1,33 \cdot 10^{-3} \text{ M}$.

It was ascertained that the rate of $\text{Co(II)Pc(SO}_3\text{Na)}_4$ reduction by HS^- ions was at least two orders of magnitude lower than the rate of HS^- ions oxidation by oxygen in the presence of $\text{CoPc(SO}_3\text{Na)}_4$ under other parameters (pH, t, $[\text{CoPc(SO}_3\text{Na)}_4]$, $[\text{HS}^-]$) being equal. Taking into account that the $\text{Co(II)Pc(SO}_3\text{Na)}_4$ reduction to $\text{Co(I)Pc(SO}_3\text{Na)}_4$ was the limiting step in the oxidation of HS^- ions by oxygen, one can conclude that the above reduction occurred mainly upon the interaction of $\text{Co(II)Pc(SO}_3\text{Na)}_4$ and polysulfide ions. The polysulfide ions were fixed as intermediate products of reaction of the oxidation of HS^- ions by oxygen in the presence of CoPc [1].

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NANOSIZED METAL OXIDES AS STEREOSELECTIVE CATALYSTS OF THE HANTZSCH AND BIGINELLI REACTIONS

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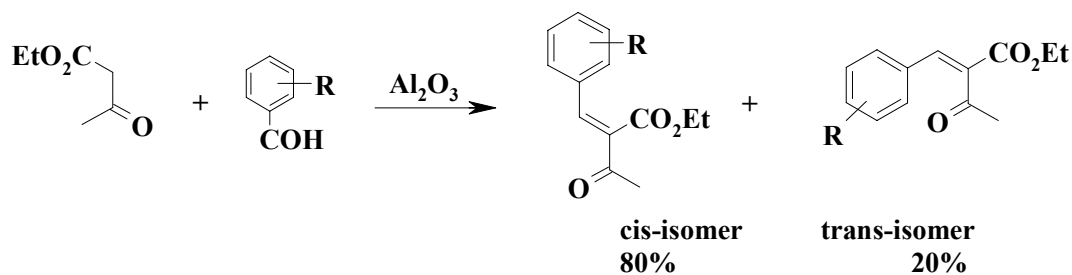
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A new approach based on the nanosized metal oxides as catalysts has been used to obtain dihydropyrimidines and dihydropyridines. Metal oxide nanopowders were produced by gas condensation method (CuO and Al₂O₃) and by hydrothermal treatment of Al nanopowder (AlOOH and Al₂O₃). It has been shown that modification of a surface of nanosized metal oxides with chiral molecules effects on stereoselectivity of multicomponent reactions.

For the first time nanosized metal oxides (Cu or Al) modified with chiral compounds have been used as stereoselective catalysts of the multicomponent Biginelli and Hantzsch reactions. It was revealed that in the presence of Al nanooxide the first stage of Hantzsch reaction (the coupling of acetoacetic ether with aromatic aldehyde) results mainly in one of two possible isomers (Scheme 1, Figure 1).



Scheme 1

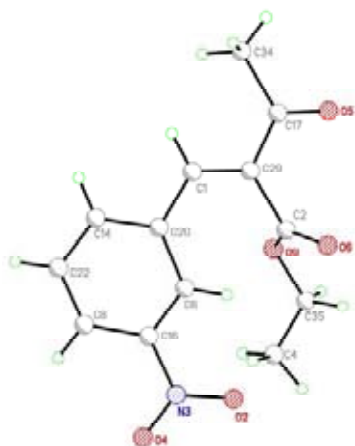
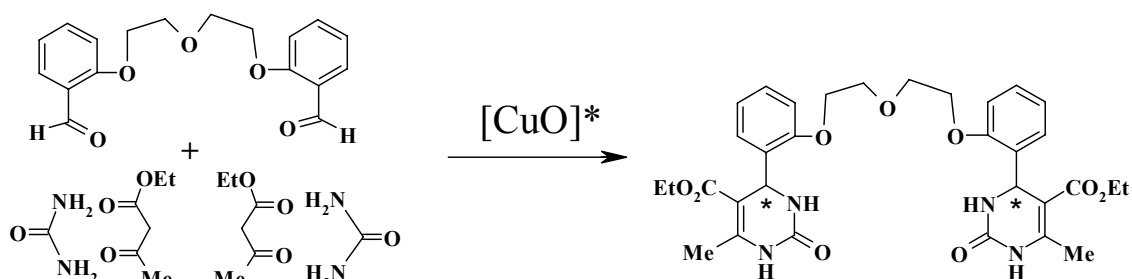
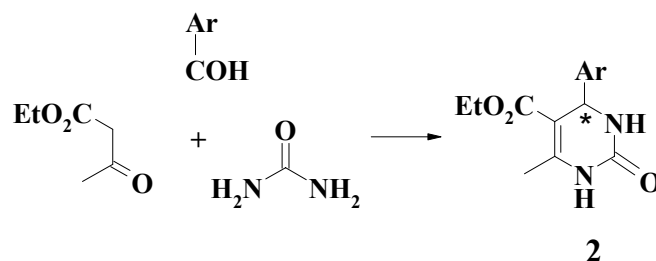


Figure 1. The structure of cis-isomer of Hantzsch reaction intermediate

The procedure to adsorption of chiral modifiers on a surface of metal nanooxides has been developed. It has been shown that copper nanooxides modified with L-tartaric acid effects on stereoselectivity of the synthesis of dihydropyrimidine podands **1** (the Biginelli reaction) (Scheme 2) and Biginelli compounds **2** (Scheme 3).



Scheme 2



Scheme 3

In the presence of HCl the ratio of diastereomers **1** was 50:50. If the reaction takes place on the surface of copper nanooxide modified with L-tartaric acid the ratio provided to be 70:30. Also, it has been shown that modified aluminium nanooxide effects on stereoselectivity of the Biginelli reaction. The results obtained can be used for the further development of catalysts for asymmetrical multicomponent synthesis.

Work is executed with financial support of the President of the Russian Federation (the Program of support of leading scientific schools, grant 9178.2006.3); Presidium of the Russian Academy of Science (the project «Heterogeneous catalysts with the use of nanosized metals and their oxides»), and also Korea Atomic Energy Research Institute (contract 01/06 «Development of new chiral catalytic systems on the basis of nanocrystalline metals and metal oxides»).

**THE STUDYING OF THE NATURE OF ALCOHOLATE COMPLEXES OF
ALUMINIUM IN ALCOCHOLIC SOLUTIONS**

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The formation of alcoholate complexes of aluminium in spirit solutions with a tetrahedral and octahedral environment of aluminium, and also complexes with pentacoordinated aluminium was shown by methods of NMR and small angle X-ray scattering.

Superpure alumina is the most efficient supporter for the catalysts for reforming, hydrotreating, Fisher – Tropsh processes and some other. This alumina is obtained by hydrolysis of aluminium alcoholates. The mechanism of hydrolysis is described in literature very poorly. The first step of studying of the mechanism of hydrolysis of alcoholate aluminium should be studying of the nature of alcoholate complexes of aluminium in spirits (in alcocholic solution). The given research is devoted to this problem.

The condition of trimethoxy-, triethoxy-, and triisopropoxyaluminium in corresponding spirits has been investigated by methods of NMR (on nucleus ^{13}C and ^{27}Al) and small angle X-ray scattering (SAXRS). The samples of solutions of aluminium alcoholate have been obtained by interaction of metal aluminium with excess amount of corresponding alcohol (spirits). It was established, that the solution of aluminium trimethylate in methanol contains a mononuclear complex $[\text{Al}(\text{OMe})_3(\text{HOME})]$ where the atom of aluminium is in a tetrahedral coordination, and also the complexes with tetra- and pentacoordinated aluminium. The complexes are formed by solvation of the molecule of aluminium trimethylate with methanol. Two types of octahedral complexes are found in the solution of aluminium triethylate in ethanol. It was shown, that there are four types of complexes: in the solution of aluminium triisopropylate in isopropanole: mononuclear with an octahedral coordination of aluminium, binuclear with octahedral coordination, polynuclear complexes with tetra- and pentacoordinated aluminium. It was made the assumption of a structure of complexes Al formed in solutions (fig. 1) on the basis of the NMR data and changes of type of spectra depending on temperature.

It was obtained the size distribution of nanoparticles of complexes of aluminium for the solution of aluminium triisopropylate in isopropanole by SAXRS. The calculated sizes of models of complexes of aluminium triisopropylate which are shown in fig. 1 agree well with a

particle size distribution obtained by method SAXRS. The molecular ratio of the complexes was calculated from these data. These data agree with the data of similar distribution obtained according to NMR (fig. 2).

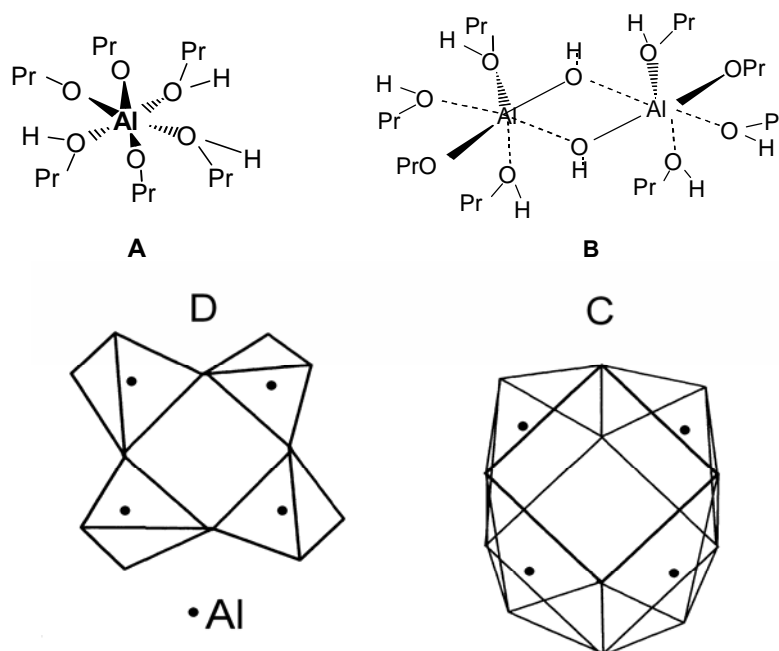


Fig. 1. A structure of complexes of aluminium triisopropylate in isopropanole. A - octacoordinated; B - dimer of an octahedron; C - pentacoordinated; D - tetraordinated.

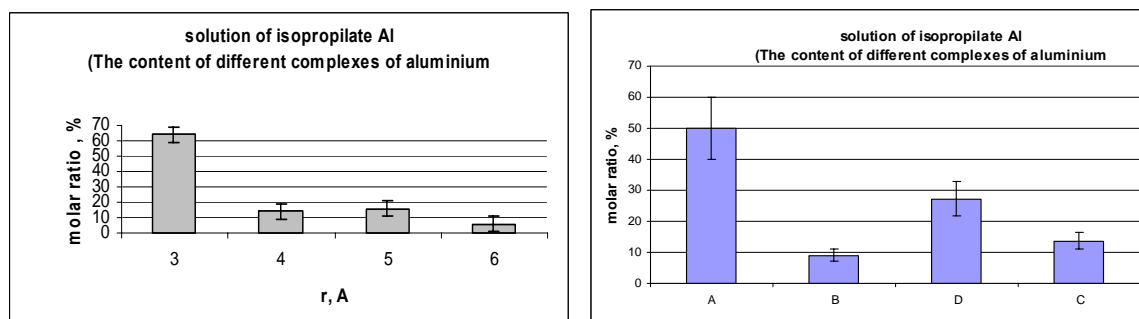


Fig. 2. The content of complexes of aluminium triisopropylate in isopropanole (A - on data SAXRS; B - according to NMR).

Thus, it was shown, that there is a set of complexes with a tetrahedral, octahedral coordination of aluminium in alcoholic solutions of aluminium alcoholates ($R = \text{OMe}, \text{OEt}, \text{OPr}^i$), and also complexes with pentacoordinated aluminium. Authors hope, that the information received in this research, will be useful in the studying of processes of hydrolysis of alcoholate aluminium with the purpose of obtaining of especially pure aluminas for catalytic processes.

SYNTHESIS OF ETHYLENE-BUTADIENE COPOLYMER WITH
TITANIUM/MAGNESIUM CATALYSTS

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Ultrahigh molecular polyethylene aligned fibers has the unique solidity and deformative properties and provides the basis of different antiballistic and constructional composite materials. Its load factor (σ_p) is 3-4 GPa and modulus of elasticity (E) is 100-150 GPa, respectively. Ultrahigh molecular polyethylene copolymer modified materials is of practical significance.

Kinetics of copolymerization of ethylene (C2) with 1,3-butadiene (C4), structural and physical-chemical properties of products are studied.

Synthesis and kinetic study of C2 and C4 copolymerization carried out in suspension conditions with $TiCl_4/MgCl_2-Al(Et)_3$ as catalyst. Synthesis temperature, equilibrium pressure of comonomers and catalytic concentration varied on interval 30-60°C, C4/C2 0,032/0,25-0,25/5 atm/atm, 0,5-1,5 g/l, respectively.

The relationship between absorption velocity of C2, molecular mass of products and concentration are studied.

The possibility of synthesis of linear ultrahigh molecular ethylene-butadiene copolymer $M_w=10^6$ with content 17.8 C=C/ 1000C double bonds in chain is determined.

Using IR and ¹³C NMR spectroscopy it was determined that entering of C4 into polymer chain occurs extremely in the case of 1,4-addition of diene. Distribution of comonomers links agree with block structure of chain. Micro heterogeneity factor $B < 1$ and varying from 0.17 to 0.31 [1].

The conclusion about block structure of chain was indirect confirmed using DSC data. The most important thermodynamic characteristics changes (T_m , ΔH_m) are observed in the case of connection of 2-3 links of C4 with macromolecular chain.

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THE MECHANISM OF SINGLE ELECTRON TRANSFER CATALYSIS BY CHLOROCUPRATES

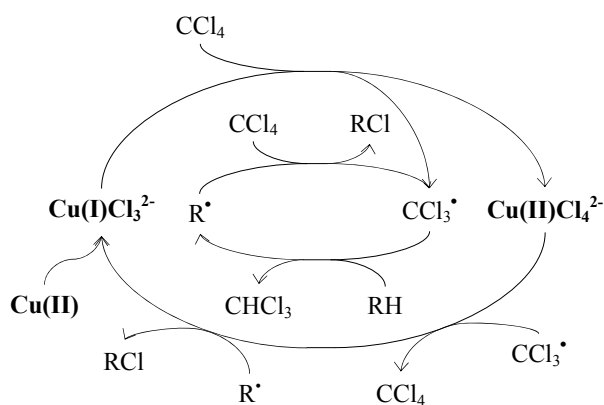
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The mechanism of single electron transfer catalysis by chlorocuprates was proved for C-Cl bond metathesis as an example. The structures of active catalysts, inactive species as well as the ways of evolution of catalytic systems based on copper complexes were established. The effect of the nuclearity of copper complexes on their activity and the mechanism of copper ions reduction in reaction media were proposed.

The very high selectivity of free radical transformations of chlorohydrocarbons is often observed. It was shown by the example of C-Cl bond metathesis, that it can not be reached using traditional initiators. The mechanism of C-Cl bond metathesis was proved. The structures of active catalysts, inactive species as well as the ways of evolution of catalytic systems based on copper complexes were established. Mononuclear tetrachlorocuprates are the most active in single electron transfer reactions producing radicals and can spontaneously form in reaction media. Binuclear chlorocuprates are nearly inactive. The reaction of chlorocuprites (I) with halohydrocarbons proceeds by single electron transfer mechanism. Chain transfer reactions of radicals and copper (II) chloride complexes compete with chain termination, reduce active centers, and provide the excellent selectivity.



The connection of the nuclearity of copper complexes with their activity and the mechanism of copper ions reduction in reaction media are under consideration. The intermediates of chlorocuprates reduction can be synthesized by photolysis and stabilized in matrixes of frozen solvents. The photolysis of $(R_3BzN^+)_2CuCl_4^{2-}$ in chlorobenzene, 2-chlorobutane and chloroform at 295 and 77 K results in formation of chlorocuprites(I) and Cl atoms. Their secondary thermal reactions generate alkyl radicals formed with ammonium cation and solvent molecules. Complexes of copper ions with organic radicals were detected. Under photolysis of $(R_3BzN^+)_2Cu_2Cl_6^{2-}$ free valenced particles are not formed, seemingly due to double electron mechanism of the reduction like in catalytic reaction.

The work was supported by RFBR (grant 06-03-32331).

REACTION OF PHENYLACETYLENE CARBOXYLATION TO ANHYDRIDE OF PHENYLMALEIC ACID ON OSCILLATING REGIME

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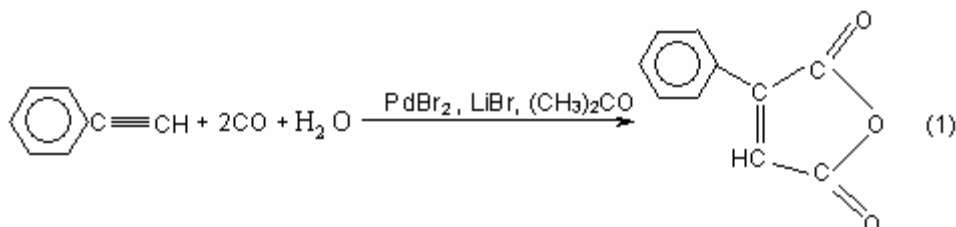
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In the field of the catalytic reactions with metal complexes new oscillatory process - reaction of phenylacetylene oxidative carbonylation to anhydride of phenylmaleic acid in the system $\text{LiBr-PdBr}_2\text{-CO-O}_2\text{-(CH}_3\text{)}_2\text{CO}$ is found. Independence of an oscillatory mode of a gases mixture composition is shown at the percentage of CO no more than 50 %. The preliminary mechanism of process was proposed.

At study of catalytic reactions kinetics not trivial dynamic behavior of reaction in homogeneous and heterogeneous systems (the critical phenomena) is even more often observed - occurrence of oscillations of intermediates concentrations, oscillations of reaction rates, polystationary, the hysteresis, chaotic behavior [1, 2]. In this article we should like to report about a new oscillatory system which is found out in our laboratory in typical process catalyzed by metal complexes - reaction of phenylacetylene oxidative carbonylation to anhydride of phenylmaleic acid proceeding in palladium complexes solutions.

Experiments on phenylacetylene oxidative carbonylation (PhA) (1) were carried out in the closed system.



In researched system oscillations of values of platinum electrode potential (E_{Pt}) (fig. 1), pH, and also the characteristic step form of a curve of gas mixture absorption (CO , O_2) have been found.

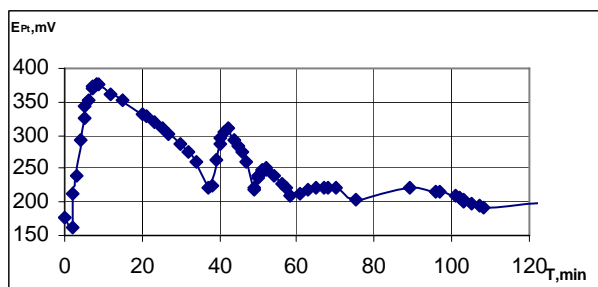


Fig. 1. The oxidative carbonylation of PhA in system $\text{LiBr-PdBr}_2\text{-H}_2\text{O-acetone}$.
 $[\text{LiBr}]_0=0,2\text{M}$; $[\text{PdBr}_2]_0=0,01\text{M}$; $[\text{PhA}]_0=0,1\text{M}$; $[\text{H}_2\text{O}]_0 = 0,75\text{M}$;
 $V_{(\text{CH}_3)_2\text{CO}}=10\text{mL}$; $[\text{CO}]_0: [\text{O}_2]_0 = 1:1$

The influence of gas mixture composition on an oscillatory mode has been investigated. In experiments were used mixtures of composition $\text{CO}:\text{O}_2 = 3:2; 1:1; 1:1,1; 1:1,2$ and $1:1,3$. Oscillations have been fixed in experiments with the percentage of CO not more than 50 %. The oscillations in researched conditions quickly decay.

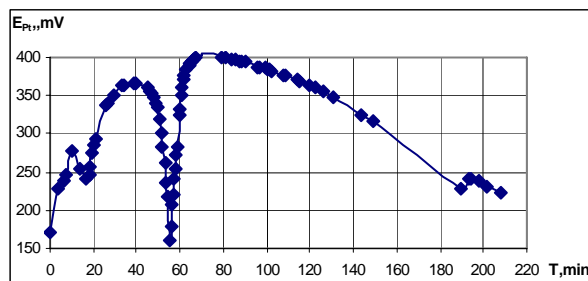


Fig. 2. The oxidative carbonylation of PhA in system $\text{LiBr-PdBr}_2\text{-H}_2\text{O-acetone}$.
 $[\text{LiBr}]_0=0,2\text{M}; [\text{PdBr}_2]_0=0,01\text{M}; [\text{PhA}]_0=0,1\text{M}; [\text{H}_2\text{O}]_0 = 0,65\text{M};$
 $V_{(\text{CH}_3)_2\text{CO}}=10\text{mL}; [\text{CO}]_0: [\text{O}_2]_0 = 1:1,3$

The preliminary mechanism of this process was proposed. As the study of an oscillatory mode of investigated reaction shows, the active form of palladium is monovalent form.

This work is executed at financial support of the Russian Foundation for Basic Research (the project № 05-03-33151).

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**EFFECT OF THE PRESSURE ON THE MECHANISMS OF THE CO₂/H₂
REACTION ON A CO-PRECIPIATED CuO/ZnO/Al₂O₃ CATALYST**

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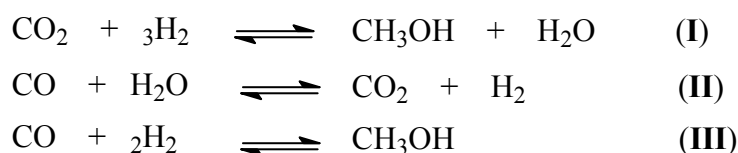
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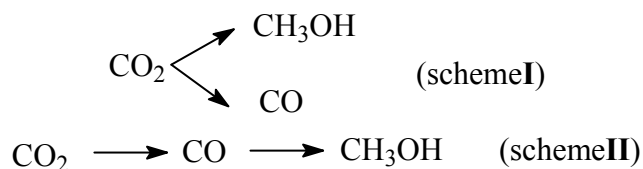
The influence of the working pressure on the mechanisms of the CO₂/H₂ reaction on a co-precipitated CuO/ZnO/Al₂O₃ catalyst has been studied. Methanol and carbon monoxide are competitively formed. The former is produced directly from CO₂ whatever the pressure whereas carbon monoxide stems either from decomposition of methanol at low pressure or from CO₂ directly at high pressure.

1- Introduction:

The synthesis of methanol from CO/CO₂/H₂ mixtures using CuO/ZnO/Al₂O₃ catalysts is currently attracting much interest due to its economical importance (1). On the other hand, the role of each oxide in the mechanism of formation of methanol (reactions I and II) is still a matter of debate (1,2) since occurs the reaction of conversion (reaction III) also:



According to Klier (3) carbon monoxide is the principal source of methanol production (reaction I) whereas for Chinchén (4), methanol is directly formed from carbon dioxide. Rosovskii (5) as well as Trambouze (6) concluded that the products are formed by parallel reactions (scheme I) rather than by successive reactions (scheme II):



However, the results obtained by Denise (7) and Baussart (8) show contradictorily that a second type of successive reactions occurs in the CO₂/H₂ in which methanol is the primary product (scheme III):

$$\text{CO}_2 \longrightarrow \text{CH}_3\text{OH} \longrightarrow \text{CO} \quad \text{(scheme III)}$$

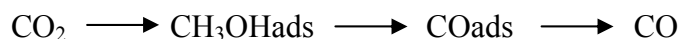
2-Results

The present work deals with the influence of the pressure on the kinetics of the CO₂/H₂ reaction on a co-precipitated CuO/ZnO/Al₂O₃ catalyst at 230 °C and total pressure from 1 bar to 75 bars. The method of investigation is the variation of the relative selectivity $\gamma = [\text{CH}_3\text{OH}] / [\text{CO}]$ as a function of the contact time 1/d. When the CO₂/H₂ mixture was fed over the catalyst, methanol was produced together with carbon monoxide and water. The obtained results show a great influence of the pressure on the reaction mechanisms. Two domains of pressure are pointed out:

- i) Up to 28 bar, γ increases sharply as 1/d tends towards zero whereas 1/ γ tends towards zero. This implies a reaction mechanism of the type represented in scheme III.
- ii) From 35 bar, γ tends towards a finite value as 1/d tends towards zero whereas 1/ γ tends towards a finite value also. Thus it appears that carbon dioxide is the immediate precursor of methanol in the CO₂/H₂ reaction whatever the working pressure. The product is probably formed, as generally accepted (1, 6), through a set of adsorbed species as following:



On the other hand, carbon monoxide formation path depends on the reaction pressure. At low pressure it seems to stem from the decomposition of methanol re-adsorbed as a methoxy species on a different site:



3-Conclusion

Our results show the great influence of the operating pressure on the kinetics of the CO₂/H₂ reaction on CuO/ZnO/Al₂O₃ catalysts. Methanol is produced directly from CO₂ whatever the pressure whereas carbon monoxide stems either from decomposition of methanol at low pressure or from CO₂ directly at high pressure. The method of preparation has no influence on the reaction mechanisms, nor does the copper content of the studied solids.

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**INTERPRETATION OF THE ETHYLENE OXIDATION KINETICS OVER SILVER,
BASED ON A SEPARATE STUDY OF THE KINETICS OF THE REACTION STEPS**

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The separate study of the kinetics of the reaction steps, corresponding to stepwise redox mechanism of ethylene oxidation over silver, has been carried out. Basing on the results, the interpretation of the catalytic reaction kinetics has been suggested taking into account the influence of the adsorption of oxygen on the surface properties of silver catalyst.

According to G. K. Boreskov, the effect of the reaction mixture on solid catalyst in many cases is associated with side processes, and also may coincide with the steps of catalytic process [1]. In present and earlier works of our group on the catalytic reaction of ethylene oxidation over silver the latter kind of the influence of reaction mixture on the surface properties of the catalyst, namely associated with the adsorption of oxygen, is discussed.

Basing on the works of G. K. Boreskov [1] and M. I. Temkin and his colleagues [2], the kinetics interpretation of the catalytic reaction of ethylene oxidation over silver has been suggested with use of the notions “standard state of silver catalyst” and “standard characteristic of silver catalytic activity” [3-5]. Metallic silver catalyst, containing the only intermediate, namely adsorbed oxygen, i.e. a pure adsorbed oxygen layer of variable concentration, may be considered as the standard state of silver catalyst. Separate study of the step kinetics on the surface of catalyst in this state allows elucidating the essential features of the reaction mechanism and the possible peculiarities of the kinetic regularities of the steps, which are accounted for by the effect of the oxygen adsorption on the properties of the silver surface.

The catalytic oxidation of ethylene over silver occurs by a stepwise redox mechanism and involves two main stages: dissociative adsorption of oxygen and interaction of ethylene with atomically adsorbed oxygen layer on silver, which causes the parallel course of partial and complete oxidation of ethylene.

The separate study of the reaction steps on the surfaces of silver powder and films has showed that dissociative adsorption of oxygen causes the essential change of the surface properties of silver catalyst. As a result, the kinetic equations of the reaction steps differ from the usual form, determined by the law of surface action. By this reason the adsorption of oxygen follows the kinetic equation of Zeldovich and Roginskii, and the dependencies of the

rates of partial and complete oxidation of ethylene on surface coverage by oxygen manifest themselves as wave-shape curves with maximum.

The standard characteristic of the catalytic activity is expressed by a system of the kinetic equations of the reaction steps, obtained as result of their separate study on the surface of catalyst under standard state. For the over-all consideration of the kinetic regularities of the catalytic reaction it may be presented in graph form as the functional dependencies of specific rates of partial and complete ethylene oxidation (the rates related to a unit ethylene pressure) on the ratio of reactant pressures, determined by applying the step steady-state conditions.

The found standard characteristic of catalytic activity has been compared with the results of the experimental investigation of the catalytic reaction on pure Ag(110) and Ag(111) single crystal surfaces, performed in the work [6]. These results best of all known literature data fit the model of the standard state of silver catalyst. The comparison has showed the principle similarity between the standard dependencies, obtained in present work, and the results of the investigation over single crystal surfaces.

The suggested method of investigation the catalytic reaction is based on the separate study of the reaction steps kinetics; therefore, despite the steps are not elementary, it allows elucidating the real features of the molecular mechanism of the catalytic process.

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**STUDY OF ONE-POT REDUCTIVE DEBENZYLATION-ACYLATION OF
SUBSTITUTED HEXABENZILHEXAAZAIZOWURTZITANES OVER
PALLADIUM-BASED CATALYSTS**

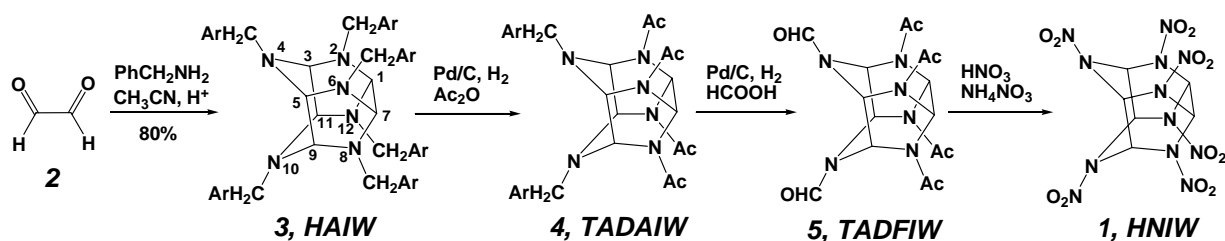
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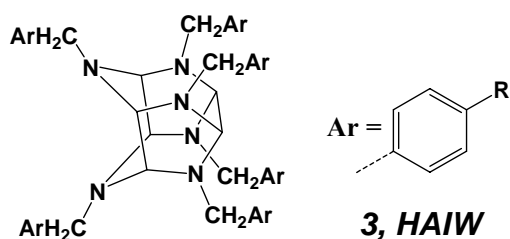
Hexanitrohexaazaisowurtzitane (HNIW) has been suggested earlier as a new generation of perspective highly energetic material. However its application is restricted because of high cost of a product synthesis. Different precursors could be used for hexaarylhexaazaisowurtzitane (HAIW) preparation which differ strongly in reaction capability. In present work we have studied of one-pot process reductive dearylation-acylation of substituted HAIW over palladium-based catalysts. The general kinetic peculiarities and Pd/C catalyst resistance to deactivation during the process are investigated.

Polycyclic nitramines is known to be high-dense and energy-rich explosives. One of them is hexanitrohexaazaisowurtzitane (HNIW) also referred to as CL-20 that has been developed as a new generation of perspective explosives. The propellants or explosives composed of HNIW are expected to increase the performance in specific impulse, burn rate, and detonation velocity [1]. A great number of studies and calculations have been published on the physical properties of HNIW and for potential military applications [2], but the published information on the synthesis of CL-20 is rather limited.



Synthesis of polycyclic nitramines usually includes three stages: formation of a polycyclic cage of hexaarylhexaazaisowurtzitane (HAIW) by condensation of benzylamines with glyoxal, cage transformation to obtain HNIW precursor (in two stages) and its nitrolysis [3]. Second two-step stage of synthesis CL-20 proceeds as one-pot reductive debenzylation-acylation over palladium-based catalyst. The latter is the most important stage in the CL-20 synthesis. At the same time Pd/C catalyst was found to be deactivated during 3→4→5 that does not permit to use it in recycles.

In our previous research we have studied influence of reaction conditions on a proceeding of reductive debenzoylation-acylation of HAIW (R=H), yield of a key intermediate (TADFIW) and stability of palladium-based catalyst [4]. In the further works the correlations between "structure-activity" and "structure-stability" are investigated for various types of Pd/C catalysts [5]. However despite of the certain improvements the stability of the best palladium catalyst was not increased significantly.



In the present work we have studied the one-pot reductive dearylation-acylation of substituted hexaarylhexaazaisowurtzitanes over palladium-based catalysts. Several benzylamines have been successfully condensed with glyoxal to produce substituted HAIW e.g. hexa(4-methoxybenzyl)hexaazaisowurtzitane (R=OCH₃) [6]. The general kinetic peculiarities of reaction are investigated. Also stability of the Pd/C catalyst in the dearylation process was studied. The opportunity of nitramines precursors synthesis without use of formic acid is checked up (dearylation of six aryl groups in one step). Data obtained can serve as a basis for the further development of a highly effective method of HNIW synthesis.

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TUNING SURFACE MORPHOLOGY OF INORGANIC SUPPORTS FOR ADSORPTIVE IMMOBILIZATION OF ENZYMATIC ACTIVE SUBSTANCES

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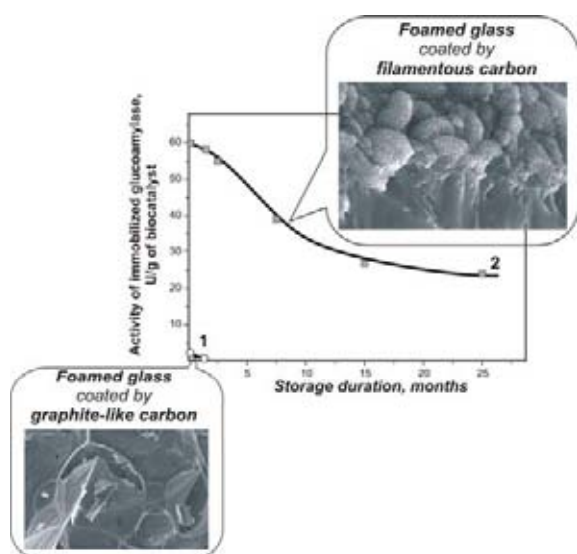
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Comparative study of inorganic supports with different morphology of carbon surface layer was carried out for adsorptive immobilization of both enzymes (glucoamylase), yeast membrane (with invertase activity) and non-growing bacteria *Arthrobacter nicotianae* (with glucose isomerase activity) to develop heterogeneous biocatalysts for the biotech processes for sweeteners production (starch treacle, syrups). As a result of tuning morphology toward immobilizing enzymatic active substances, the catalytic filamentous carbon (CFC) was found to ensure the highest stability and activity of the biocatalysts prepared due to mesoporous structure, roughness and optimal hydrophilic-hydrophobic balance of the CFC-layer.

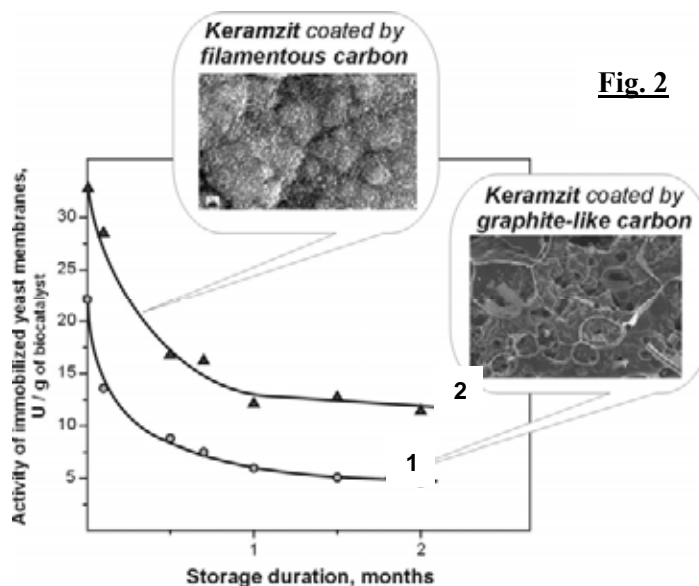
The highly stable biocatalysts based on immobilized enzymatic active substances are at the heart of the modern biotech processes performed in continuous heterogeneous mode that is undoubtedly attractive and feasible for implantation in large-scale industry. The comprehensive research of the different inorganic support distinguished by macrostructure (honeycomb monoliths, foams, granules) and morphology of carbon layer (filamentous, graphite-like, pyrolytic carbons) were carried out to study of peculiarities of adsorptive immobilizations of enzymatic active substances. The purposeful tuning the surface morphology was carried out to provide the enhancement of stability and activity of the biocatalysts prepared for the production of starch treacle, invert sugar and glucose-fructose syrups.

The biocatalytic properties (activity and stability) of immobilized enzymatic active substances were found to depend strongly on the morphology of carbon layer on the surface.



In particular, catalytic filamentous carbon layer was synthesized during hydrogen-propane-butane pyrolysis on the deposited Ni-catalyst. For foamed glass, CFC-layer was found to provide the highest long-term and operational stability of immobilized glucoamylase in comparison with graphite-like layer (fig. 1). The biocatalyst retained 50% of initial activity after 1 year-storage at ambient temperature (fig. 1, curve 2). The half-life time of the biocatalyst was more than several hundred hours of continuous dextrin hydrolysis at $50\pm 5^\circ\text{C}$ [1].

For foam-like ceramics and sintered clay (keramzit), the synthesis of filamentous carbon on the surface resulted in preparation of the effective adsorbents for immobilization of invertase-active membranes and non-growing cells of baker yeast. The biocatalyst retained ~50% of the initial activity for >2 months storage at ambient temperature (fig. 2, curve 2). In spite of that, immobilization of yeast membranes on graphite-like carbon layer provided the less activity, and the biocatalyst has lost 80% initial invertase activity for ~2 months storage (fig. 2, curve 1) probably due to hydrophobicity of the layer [2].



For adsorptive immobilization of non-growing bacteria *Arthrobacter nicotianae* that catalyzed the glucose isomerization, the CFC-layer was synthesized on bellied vermiculite and foam-like ceramics during hydrogen-propane-butane pyrolysis on the deposited Co-catalyst. It was found that non-growing bacteria *A. nicotianae* possessed a pure ability to adsorb on solid surfaces, and the adsorption value on CFC-coated ceramics was not exceed 0,5 mg of dry cells per 1g of support at static conditions. Adsorptive immobilization of *A. nicotianae* was carried out during its growth in the presence of nutrients and inorganic supports when colonization of solid surface by bacteria occurred. The initial glucose isomerase activity of the biocatalyst prepared on CFC-coated ceramics were equal to 230 $\mu\text{mol}/\text{min}/1 \text{ kg}$ and retained constant after 12 hours of operation at 70°C.

From the experimental data, the inorganic supports under study are arranged in the following order to increase enzymatic activity and stability of heterogeneous biocatalyst prepared: supports coated by graphite-like carbon layer \approx non-carbonized supports \ll macrostructured CFC-coated supports \leq pyrocarbon-coated supports. As a result of tuning morphology toward immobilizing enzymatic active substances, the catalytic filamentous carbon was found to ensure the highest stability and activity of the biocatalysts prepared due to its mesoporous structure and optimal hydrophilic-hydrophobic balance of the CFC-layer.

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HIGHLY POROUS BLOCK CELLULAR CATALYST**Kozlov A.I., Grunskiy V.N., Bespalov A.V., Beskov V.S.***Mendeleev University of Chemical Technology of Russia, Moscow, Russia**E-mail: beskov@muctr.edu.ru*

New technology of producing block highly porous permeable cellular structures for catalysts and sorbents has been developed. Elements of such structure have porosity up to 90..95%, specific surface area of active layer – 180..250 m²/g, apparent density – 0,25-0,70 g/sm³, compression resistance up to 1,0 MPa. Practical tests of new catalysts in gas-phase reduction of nitrogen oxide with ammonia, liquid-phase hydrogenation of nitro compounds to aromatic amines have confirmed their efficiency.

Highly porous cellular catalysts are represented by large elements with hard archy-labyrinth structure where free space exceeds 90 % of their volume.

A method of creating highly porous permeable cellular structure (catalysts, sorbents, distributing bed) has been developed in Mendeleev University. It is proposed to utilize highly porous cellular material as a catalyst carrier. In this method ceramic material on the basis of aluminium oxide duplicates open-cellular urethane foam matrix. After that, filling is activated, for example, with transition metals of VIII group of Mendeleev's table (palladium, nickel, etc.).

New method allows to produce block highly porous permeable cellular catalysts (sorbents, distributing bed) of any geometrical configuration (cylinders, prisms, etc.) and sizes. Elements have archy-labyrinth structure with porosity up to 90..95 % consist of cells with diameter 0,5-3,00 mm and have developed geometric surface. After carrying base layer and active component microporosity amounts to 15-20 %, micropores size – 0,1-1,2 mkm, specific surface area of active layer – 180..250 m²/g. Apparent density of the element is 0.25-0.70 g/sm³, compression strength is up to 1.0 MPa. Hydraylic resistance of block cellular catalysts is several times smaller than of granular fixed bed.

To the present time block highly porous permeable cellular catalysts are tested at pilot and industrial equipment. Reduction of nitrogen oxide with ammonia at plant unit show that at average conversion of NO is 92,2 % (max conversion reached 97 %), gas flow rate on block highly porous permeable cellular catalysts is 20 times higher than for granulated catalyst ABK-10 (Alumino-Vanadium catalyst) used now, 10 times highly than for oxide catalyst (V-Ti-O) and it allows to reduce significantly dimensions of catalytic reactors and simplify their construction.

Advantages of new catalysts are demonstrated especially in liquid-phase processes carried out under pressure and with high linear velocities of contacting reagents.

Highly porous cellular catalysts were used in developing new process of liquid-phase hydrogenation of nitro compounds in producing aromatic amines. Now this process is carried out on supported catalysts representing supports (activated carbon, zeolites, aluminium oxide) with catalysts-active metals of VIII group of Mendeleev's table. Such catalysts are destroyed after contacting mixers during reaction, pollute reaction products and it results in complication of technological process with all that it implies. Method of liquid-phase hydrogenation of nitro compounds on catalysts with new structure, and properties allowed to avoid disadvantages typical for powder-like, granulated catalysts.

Pilot production of modular cellular catalysts is mastered. Pilot unit was designed for the processes of nitro compounds hydrogenation on which different regimes of liquid-phase hydrogenation were modeled and different types of block cellular catalysts were tested. It was shown that hydrogenation processes on block cellular catalysts are carried out in soft conditions: pressure up to 1 MPa and temperature below 150 °C.

Work is executed with support of grant of the Ministry of education and sciences of RF.

**STRUCTURE OF PHOTOCATALYTIC NANOCOMPOSITES BASED ON
MOLYBDENUM OXIDE, TITANIA AND POLY-*p*-XYLYLENE**

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Nano-composites based on poly-*p*-xylylene and oxides of molybdenum and titania were synthesized. Their surface morphology and nature of paramagnetic centers were studied.

Nano-structured composites of polymers doped with different metal oxides and organic dyes are advanced photocatalytic systems. Furthermore these composites hold much promise for creation of novel electrodes and sensors. In this report we present our data on the synthesis of poly-*p*-xylylene (PPX) composites containing nano-particles of molybdenum and titania oxides and the study of their surface morphology by AFM and paramagnetic centers by UV-VIS and ESR spectroscopy.

The synthesis of composites was carried out by co-condensation technique of MoO₃, Ti and *p*-xylylene in vacuum onto quartz plates and lavsan films cooled by liquid nitrogen. When heating to room temperature and storing on-air the monomer polymerization and Ti oxidation take place.

Thin films prove to consist of PPX globules of 100-200 nm of spherical shape, which are covered with metal oxide nano-particles of 5-20 nm. The higher evaporation temperature, the less are dimensions of the particles. There is weak signal with g -tensor ca. g_e in ESR spectra of titanium oxide/PPX nano-composites. This signal is related to either F-centers or carbon-centers. Doping of phthalocyanine results in the stabilization of Ti³⁺. It turned out, that ESR spectra of molybdenum oxide/PPX and molybdenum oxide/titania/PPX nano-composites include intense narrow signal with $g \sim g_e$ and axially symmetric signal of Mo⁵⁺ with $g_{\parallel} = 1.860$, $g_{\perp} = 1.929$. Absorption in 600-800 nm characteristic for hetero-valenced molybdenum oxides is observed in electronic spectra. Addition of titania raises content of impurity ions Mo⁵⁺. The photochemical properties of nano-composites were tested under a visible-light irradiation.

The work was supported by INTAS (grant 05-1000005-7667) and RFBR (grant 06-03-32287).

MECHANISM OF N-BUTANE CONVERSION ON Cs-SALT OF PHOSPHOTUNGSTIC ACID: A STUDY BY IN SITU ¹³C MAS NMR AND EX SITU GC-MS

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Using *in situ* ¹³C MAS NMR and *ex situ* GS-MS analysis, the conversion of n-butane-1-¹³C on solid Cs-salt of phosphotungstic acid Cs_{2.5}H_{0.5}PWO₄₀ was demonstrated to proceed via two parallel reactions: (1) the migration of ¹³C-label in the n-butane molecule from methyl into methylene group and (2) skeletal isomerization into isobutane. It has been established that the migration of ¹³C-labels proceeds via monomolecular mechanism, whereas bimolecular pathway is prevalent for the n-butane isomerization into isobutane, even in the presence of CO.

Skeletal isomerization of n-butane to isobutane has attracted much attention since isobutane is an important feedstock for the synthesis of methyl tert-butyl ether, a high-octane gasoline additive, and for the alkylation of butanes as well. The use of more ecologically friendly solid acid catalyst for this reaction should be preferred. In addition, the acid-catalyzed isomerization of n-butane represents an important object for mechanistic studies. Indeed, as opposed to n-pentane and higher alkanes, a monomolecular carbenium ion mechanism for the isomerization of n-butane to isobutane would require formation of a very unstable primary carbenium ion as compared with a secondary ion in the case of higher carbenium ions.

It has been established earlier that skeletal isomerization of n-butane on solid acid catalysts, sulfated zirconia and zeolite H-ZSM-5, proceeds via bimolecular mechanism [1-3], which allows to avoid the formation of primary carbenium ions as the intermediate. For the catalysts based on solid phosphotungstic acid and its cesium salts the predominance of intermolecular pathway for n- to iso-butane conversion is also generally accepted [4]. However, basing on the observation of the selective formation of isobutane from n-butane, the monomolecular mechanism has been supposed for initial stage of n-butane conversion on Cs-salt of phosphotungstic acid [5]. So, the mechanism of n-butane conversion on solid catalysts based on phosphotungstic acid requires further comprehensive studies.

In present paper, using *in situ* ¹³C MAS NMR and *ex situ* GS-MS analysis, the conversion of n-butane-¹³C has been studied on solid Cs-salt of phosphotungstic acid (Cs_{2.5}H_{0.5}PWO₄₀) at 80-150 °C both in the absence and in the presence of carbon monoxide.

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According to the ^{13}C MAS NMR data (Figure 1) two parallel reactions occurs: (1) the migration of ^{13}C -label in the n-butane molecule from methyl into methylene group and (2) more slow process of n- into isobutane isomerization.

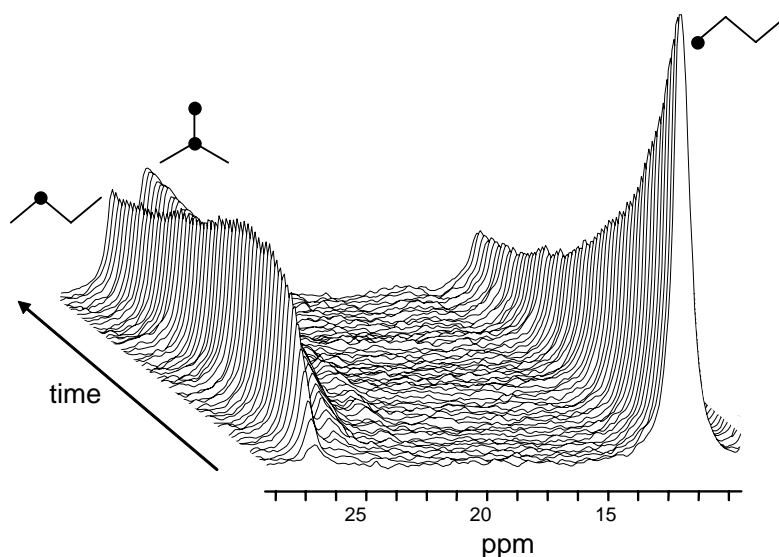


Figure. 1

The analysis of the mass-spectra of butanes formed from n-butane- ^{13}C on $\text{Cs}_{2.5}\text{H}_{0.5}\text{PWO}_4$ in the absence and in the presence of CO allows to conclude that the migration of ^{13}C - labels proceeds via monomolecular mechanism, whereas bimolecular pathway is prevalent for the n-butane isomerization into isobutane, even in the presence of CO.

The in situ ^{13}C MAS NMR study of the kinetics of n-butane conversion on $\text{Cs}_{2.5}\text{H}_{0.5}\text{PWO}_4$ revealed that both the migration of ^{13}C -label and isomerization into isobutane proceeds with the similar activation energy *ca* 85 kJ mol^{-1} , presuming the hydride-shift reaction between alkanes and carbenium ions to be the common rate determining step of these reactions.

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STEAM AND AUTOHERMAL REFORMING OF METHANE OVER NICKEL CATALYST: EXPERIMENT, MODELING, AND NUMERICAL SIMULATION

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The kinetics of steam and autothermal reforming of methane over nickel coated monolith catalyst were investigated experimentally and numerically. A multi-step heterogeneous reaction mechanism for partial oxidation and steam reforming of methane including the reverse water-gas shift reaction and methanation was developed to analyze the kinetic data. DETCHEM computational tool that use two-dimensional boundary-layer approximation including detailed models for heterogeneous reactions as well as transport phenomena was used for the numerical investigation. The gas composition and surface coverage with adsorbed species were calculated as function of the position in the monolith. The numerical simulation of conversions and selectivities are shown and compared with experimental values. The model and surface reaction mechanism developed are able to properly describe both steam and autothermal reforming of methane on Ni catalysts at the wide range of temperature and steam/methane ratio.

Steam reforming of methane has been the most widely used industrial process for the synthesis gas production. For many years, partial oxidation (POX) and CO₂ reforming of natural gas to synthesis gas have attracted much interest because of their potential to reduce the cost of synthesis gas and for application in chemical energy storage and transmission technology [1]. Recently, also the internal reforming in the anode of a solid oxide fuel cells (SOFC) operated with hydrocarbons has been extensively discussed [2]. Modeling of autothermal reforming of natural gas to synthesis gas, where both steam and oxygen are present in the feed gas demands the combination of reaction schemes of reforming as well as partial and total oxidation [3].

The kinetics of steam and autothermal reforming of methane over nickel coated monolith catalyst were investigated experimentally and numerically. A multi-step heterogeneous reaction mechanism for partial oxidation and steam reforming of methane including the reverse water-gas shift and methanation reactions was developed. The surface reaction mechanism consisting of 42 reactions among 7 stable gas-phase and further 14 adsorbed species was coupled with an elementary step gas phase reaction mechanism and two-dimensional flow models to describe the catalytic reactor applied. The numerical simulations of the reforming process at various conditions were performed using the CFD code DETCHEM^{CHANNEL} [4].

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Conversion and selectivity are discussed. The model developed well-predicts both partial oxidation and steam reforming of methane on Ni catalysts at the wide range of temperature and steam/methane ratio.

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**HYDROGEN PEROXIDE OXIDATION OF SATURATED HYDROCARBONS
CATALYZED BY IRON(III) CHLORIDE AND 2,2'-BIPYRIDINE**

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The H₂O₂–FeCl₃–bipy system in acetonitrile efficiently oxidizes alkanes predominantly to alkyl hydroperoxides. Turnover numbers attain 500 after 1 h at 60 °C. It has been assumed that bipy facilitates proton abstraction from a H₂O₂ molecule coordinated to the iron ion (these reactions are stages in the catalytic cycle generating hydroxyl radicals from the hydrogen peroxide). Hydroxyl radicals then attack alkane molecules finally yielding the alkyl hydroperoxide.

In the course of our studies of iron-catalyzed hydrocarbon oxygenations with peroxides [1] we explored the possibility of enhancing the reaction efficiency by addition of certain amines. Here we report that 2,2'-bipyridine added to iron(III) chloride used as a catalyst accelerates oxidation of alkanes with hydrogen peroxide in acetonitrile. Main features of the reaction will be discussed.

Acknowledgments. This work was supported by the Russian Basic Research Foundation (06-03-32344-a), the State of São Paulo Research Foundation (FAPESP, 2002/08495-4, 06/03984-8), the Brazilian National Council on Scientific and Technological Development (CNPq, 300984/2004-9, 300601/01-8). G. B. Sh. expresses his gratitude to FAPESP, CNPq, Faculdade de Química, Pontifícia Universidade Católica de Campinas (PUC) for making it possible for him to stay at PUC as invited Professor and to perform a part of the present work.

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STUDY OF THE MECHANISM OF CATALYTIC HYDROGENATION OF ISOMERIC NITROPHENOLS

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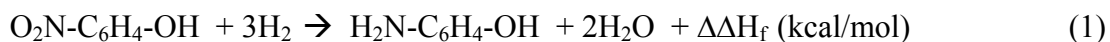
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The mechanism of reaction of nitrophenol isomers catalytic hydrogenation was studied by kinetic, electron-microscope and quantum-chemical methods. The reaction rate decreases in order $p > m > o$ which breaks the rules of substitution effects in aromatic ring. Quantum-chemical calculations of reaction heat indicate that these results can be connected with molecule adsorption on the edge of Pd tetrahedron. Electron-microscope study shows the crystal Pd-pieces of 500Å therefore we propose that adsorption type on the shelves of surface provides unusual rate order.

Hydrogenation of nitrocompounds is used for manufacture of aromatic amines widely using as half-products of dyes, medicines etc. The important and interesting process is hydrogenation of nitrophenol o-, m -, p-isomers.

Hydrogenation process of isomeric nitrophenols was carried out in a liquid phase under hydrogen pressure 1-10 MPa and temperatures 303-343 K on 4% Pd/γ-Al₂O₃ catalysts. The reaction rate was measured on hydrogen consumption. The analysis of reaction products was carried out by Gas chromatography during the reaction. The yields of reaction products are 95-96 %.

In soft conditions hydrogenation of nitrogroup runs by some stages through formation of nitrosogroup, hydroxylamine and at last to formation of aminogroup with eliminating of two molecules of water:



The measured hydrogenation rate of nitrophenols varies in an order: $p > m > o$. The error of kinetic measurements is $\pm 2-3$ %. The values of apparent activation energy are calculated from hydrogenation rates on the Arrhenius equation (Table 1).

The reaction of hydrogenation of nitrogroup of aromatic hydrocarbons is exothermic. The heats of reaction (1) are calculated by quantum-chemical semi-empirical method PM3. The account was carried out for free molecules and molecules “adsorbed” on mono-atomic and tetra-atomic tetrahedral clusters of Pd (Table 1). The molecules of nitrophenols and aminophenols were placed above a top, a side or an edge of tetrahedron (Fig. 1). It is found

that the heat effect of reaction correlates with values of apparent activation energy ($p > m > o$) only in a case of adsorption of nitroaromatic molecule on an edge of cluster.

It is well known in organic chemistry of aromatic compounds that the replacement of the more electronegative substitute NO_2 by NH_2 should easy be carried out in a meta-position of phenols as proves to be true in accounts of the corresponding molecules in absence of the catalyst, at adsorption on a top and on a side of tetrahedron. Adsorption on an edge of tetrahedron breaks alternation of heat effect of reaction.

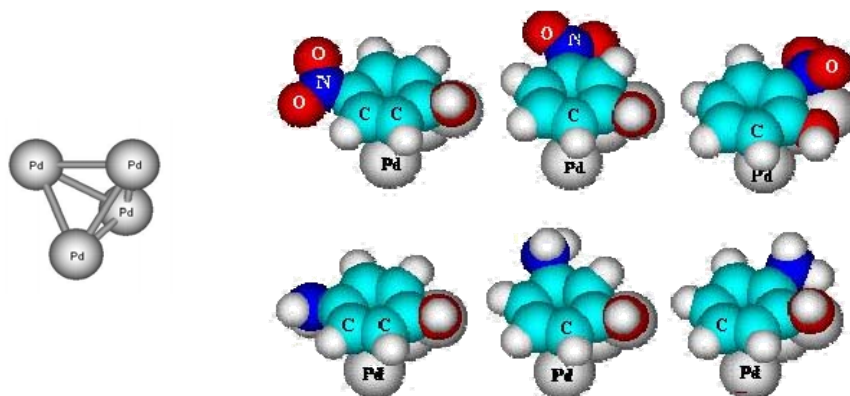


Figure 1 Cluster Pd₄ with adsorbed molecules of p-, m -, o-nitro- and aminophenols

The electron-microscopic study of the catalyst has shown that on a surface there are crystal pieces of Pd of size 500 Å and larger pieces of PdO. In the case it is possible to propose that the quantum-chemical model of “adsorption” on tetrahedron edge in a reality can correspond to adsorption on «shelf» of catalyst surface.

Table 1 PM3 calculation of total heat effect $\Delta\Delta H_f$, kcal/mol

	ΔH_f (kcal/mol)						$\Delta\Delta H_f$ (kcal/mol)		
	Nitrophenol			Aminophenol			Total heat effect		
	p-	m-	o-	p-	m-	o-	p-	m-	o-
Experimental hydrogenation rate, mmol/min.g							280	250	210
Apparent activation energy, kcal/mol							6,0	6,6	7,1
free molecule	-31.91	-29.77	-28.74	-23.45	-24.21	-22.06	-58.23	-61.13	-60.01
Pd	-53.97	-50.05	-57.89	-38.64	-40.35	-36.33	-51.33	-56.98	-45.12
Pd ₄ -top	56.68	45.46	34.56	78.09	81.75	68.65	-45.28	-30.4	-32.6
Pd ₄ (side)	-9.63	21.85	-8.90	21.47	32.91	21.64	-35.6	-55.6	-36.2
Pd ₄ (edge)	-54.01	-60.23	-86.35	-42.67	-34.61	-45.04	-55.35	-41.07	-25.38
$\Delta H_f(2*\text{H}_2\text{O}) = - 106.92$ kcal/mol									
$\Delta H_f(3*\text{H}_2) = - 40.23$ kcal/mol									

**COMPARISON CATALYTIC ACTIVITY OF SUPPORTED AND HOMOGENEOUS
CATALYSTS IN REACTION OF OXIDATION α -PINENE AND
2,3,6-TRIMETHYLPHENOLE**

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It was investigated catalytic activity of homogeneous complexes Cu (II), Co (II) and Mn (III), and also the heterogeneous species containing in the structure some transition metals (Cu, Mo, Co) in reaction of oxidation an alpha - pinene and 2,3,6-trimethylphenole.

For the investigated catalysts values of specific rate of oxidation of substrates in a reactionary mixture are determined.

The oxidation of α -pinene by O_2 and H_2O_2 continue to draw attention of researchers as when non-polluting oxidisers are used for oxidation [1, 2]. In our work catalytic activity was investigated of supported on polymeric carriers chelates Co, Cu, and also of a polymeric-salt composition of polyvinyl alcohol with ammonium heptamolybdate, in comparison with homogeneous complexes Cu (II), Co (II) and Mn (III) including those capable of reversible attach of O_2 [3]. Catalytic experiments were conducted in organic or aqueous solutions in a static system containing a glass reactor with two divisions positioned inside a thermostat. Two divisions in the reactor allow preventing mixing of individual components of reaction solution up to finishing all preparatory operations. All initial kinetics with a reaction order $\neq 0$ was treated as pseudo-first-order reactions. The initial rates of O_2 conversion were calculated by the method presented in previous article [4]. Kinetic studies have shown, that catalytic properties of homogeneous 2-methylpyridinic complexes Co (II) provide the highest initial rate of oxidation of a α -pinene from all investigated homogeneous complexes. They can be arranged depending on the activity in the following order: $(2-MeC_5H_4N)_2CuCl_2 < Co(acac)_2 < CoSalen < (2-MeC_5H_4N)_2CoCl_2$. Uniform criterion of efficiency of action of homogeneous and supported catalysts on a polymeric basis in the investigated conditions of oxidation of α -pinene was value of specific rate of oxidation divided by the initial rate of reaction to concentration (M) of ions of metal in a solution. It is shown that complex catalysts on a polymeric basis (anionite AN-251) can be used repeatedly. The assumption is confirmed about the catalytic activity of compositions on the basis of PVA - ammonium heptamolybdate

and an opportunity of catalytic management of process with the help of UV - irradiations. It is established, that photochemical reaction of partial convertible reduction of molybdenum (VI) in complexes with polyvinyl alcohol proceeds in an oscillatory mode in direct as well as on reverse direction. It, apparently, plays a positive role for catalytic activity of these compositions. Also proceeding from this, the most rational mode of the UV-irradiation of the reactionary solution for providing maximal catalytic activity is represented in a periodic mode. Compositions are used as water solutions. Catalytic reaction of oxidation the alpha - pinene proceeds in that case most intensively near to border of the unit of phases of the water and organic solution containing substrate. After reaction the catalyst mass be easily separated from compound and used cyclically practically without loss of catalytic activity.

In reaction of oxidation of trimethylphenole were used homogeneous complexes of Co (II) both giving a signal in EPR-spectrum, justifying about convertible bonding of oxygen, and not giving a signal in the EPR-spectrum. Nevertheless in test reaction of oxidation trimethylphenole appeared active on data GC both complexes. It is possible, that the mechanism of oxidation, despite of similarity of a structure of the given compounds, appeared various. Rate consumption of dioxygen was measured also volumetrically.

Table

Comparison of catalytic activity of homogeneous catalysts in reaction of oxidation of 2,3,6-trimethylphenole

Catalyst	Mol.ratio:2,3,6-TMPH:solvent:Met	$-V_0$, mol/l•min	$-V_{sp}$, mol/l•min•[Met]
$C_{16}H_{14}N_2O_2Co$	1:46,7:0,03	0,00075	12,8
$C_{12}H_{12}F_6N_2O_2Co$	1:46,7:0,03	0,00036	6,18
$C_{12}H_{12}F_6N_2O_2Co$	1:66,7:0,01	0,00010	4,96

This work is supported by RFBR (grant 02-03-32777)

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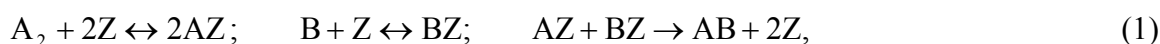
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CRITICAL PHENOMENA FOR LANGMUIR-HINSHELWOOD MECHANISM

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The adsorbate - adsorbate lateral interaction influence on the steady-state multiplicity domain and possible self-sustained oscillations of reaction rate for Langmuir-Hinshelwood mechanism has been studied. We considered a lattice gas model on square, hexagonal and honeycomb lattices as a model of adsorbed overlayer. The number of the internal steady states was shown to come up to eleven. The self-sustained oscillations of reaction rate arising as the result of Andronov-Hopf's bifurcation have been found for some sets of lateral interactions.

One of the most important model mechanism of the heterogeneous catalysis is the well known three steps Langmuir-Hinshelwood (LH) mechanism



where AZ and BZ are the adsorbed species on the catalyst Z, and A₂, B and AB the gas phase substances. The conventional mean-field (MF) kinetic equations can be written as

$$\begin{cases} dx/dt = 2k_1 P_{A_2} (1-x-y)^2 - 2k_{-1} x^2 - k_3 xy \\ dy/dt = k_2 P_B (1-x-y) - k_{-2} y - k_3 xy, \end{cases} \quad (2)$$

where x and y are the adsorbate concentrations, P_{A₂} and P_B the reactant pressures, k₁, k₂, k₋₁, k₋₂ and k₃ the rate constants for adsorption, desorption and reaction, respectively; t is time. There exist the steady-state multiplicity domain in the plane (lg P_{A₂}, lg P_B). This domain contains two internal steady states [1]. The equations (2) ignore the non-ideality of surface rate processes. We consider the MF equations incorporating the adsorbate-adsorbate lateral interactions via the coverage dependence of the rate constants. In the frameworks of the lattice gas model and transition state theory there are exact expressions for these constants [2]. We have done the analysis of the lateral interaction effect on the steady-state multiplicity domain and possibility of self-sustained oscillation appearance for LH mechanism on the square lattice in the previous works. The kinetic behavior was shown to become essentially more complex than for ideal adsorbed overlayer [3]. The goal of the present work is the comparison of the results obtained for the different lattice types such as the square, hexagonal and honeycomb lattices. We consider the same lattice gas model [3] on the square, hexagonal and

honeycomb lattices as a model of adsorbed overlayer. We assume the both adsorption steps are irreversible. The kinetic equations describing the mechanism (1) in terms of the notations $u = 2k_1 P_{A_2} / k_3$, $v = k_2 P_B / k_3$, $\bar{\mu}_A = \mu_A / RT$, $\bar{\mu}_B = \mu_B / RT$, $\tau = k_3 t$ are as follows:

$$\begin{cases} dx/d\tau = p_{00}(u - \exp(\bar{\mu}_A + \bar{\mu}_B)) \\ dy/d\tau = v(1 - x - y) - p_{00} \exp(\bar{\mu}_A + \bar{\mu}_B), \end{cases} \quad (3)$$

where R is the universal gas constant, T absolute temperature in K, μ_A, μ_B are chemical potentials, p_{00} is the probability to find an empty couple of the nearest lattice sites.

Within the framework of our model exact analytical expressions for p_{00}, x, y are absent and hence we should use an approximate technique. We use the transfer matrix method [3, 4]. The number of the internal steady states was shown to come up to eleven. The self-sustained oscillations of reaction rate arising as the result of Andronov-Hopf's bifurcation have been found for some sets of lateral interactions. Their appearance for all the lattice types was shown to be connected with the high density ordered phase. For all the lattice types it was shown that if the phase diagram of adsorbed overlayer is topologically equivalent to that of ideal one then the corresponding multiplicity diagrams are topologically equivalent. The multiplicity diagrams for the honeycomb lattice are more simple than those for the square lattice at the same model parameters. Reason of the multiplicity diagram simplification is connected with the two factors: a) contraction of the ordered phase domains; b) the decrease of the mean adsorbate - adsorbate lateral interaction energy in magnitude due to the changing of the coordination number from 4 till 3. Similarly, the multiplicity diagram complication for the hexagonal lattice as compared to the square lattice is due to: a) complication of the phase diagrams of adsorbed overlayer; b) the increase of the mean adsorbate - adsorbate lateral interaction energy in magnitude due to the increase of the coordination number from 4 till 6. On the whole the results for hexagonal and honeycomb lattices correspond to the results for square lattice.

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ISOTHERMS FOR STEPPED SURFACES: MODELING

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The simple lattice gas model of stepped surfaces is considered. In the framework of this model there are the strong and weak adsorption centers and adsorbate – adsorbate lateral interaction too. The transfer matrix method and Monte Carlo method have been applied to study this model. It was shown, the dependencies of the local coverage may be nonmonotonous functions of chemical potential.

Heterogeneity is a common phenomenon for the most of real surfaces. The simple model of stepped surfaces is considered. Our model is a lattice gas model on a square lattice. It is shown in Fig. 1. The width of terraces is noted as L ($L \geq 2$). The adsorption sites belonging to the each first (adsorption centers which are located near steps) and last row are assumed to be the strong adsorption centers and the weak adsorption centers, respectively. The nearest –

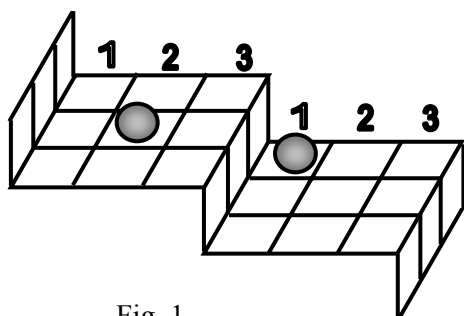


Fig. 1.

neighbors adsorbate – adsorbate lateral interactions are taken into account as well. These are independent of the adsorbed particles location. The thermodynamic Hamiltonian for developed model can be written as

$$H = \varepsilon \sum_{\langle nm \rangle} n_i n_j - \mu \sum_i n_i - \Delta_1 \sum_k n_k - \Delta_2 \sum_l n_l, \quad (1)$$

where ε is the lateral interactions energy, μ the chemical potential, Δ_1/Δ_2 the energy difference between the strong/weak adsorption centers and terrace centers ($\Delta_1 > 0$, $\Delta_2 < 0$). Here, $\langle nn \rangle$ means summation over all pairs of the nearest lattice sites. In the second term one takes the summation over all lattice sites. In the third term one takes the summation over the sites belonging to the first rows and in the fourth term one takes the summation over the sites belonging to the last rows. The transfer matrix method (TMM) has been applied to study this model. TMM is the well known method in the field of statistical physics [1-7]. TMM allows to obtain isotherms and dependencies of the local coverage on the chemical potential (gas pressure). The obtained results are in agreement with the ones of the Monte-Carlo calculations. These dependencies of the local coverage may be nonmonotonous functions of chemical potential (Fig. 2.). The mutual effect of the surface

heterogeneity and adsorbate – adsorbate repulsion on the local coverage is a reason for this interesting feature. Solid line indicates these dependencies at $\Delta_1 = \Delta_2 = 0$. The other lines

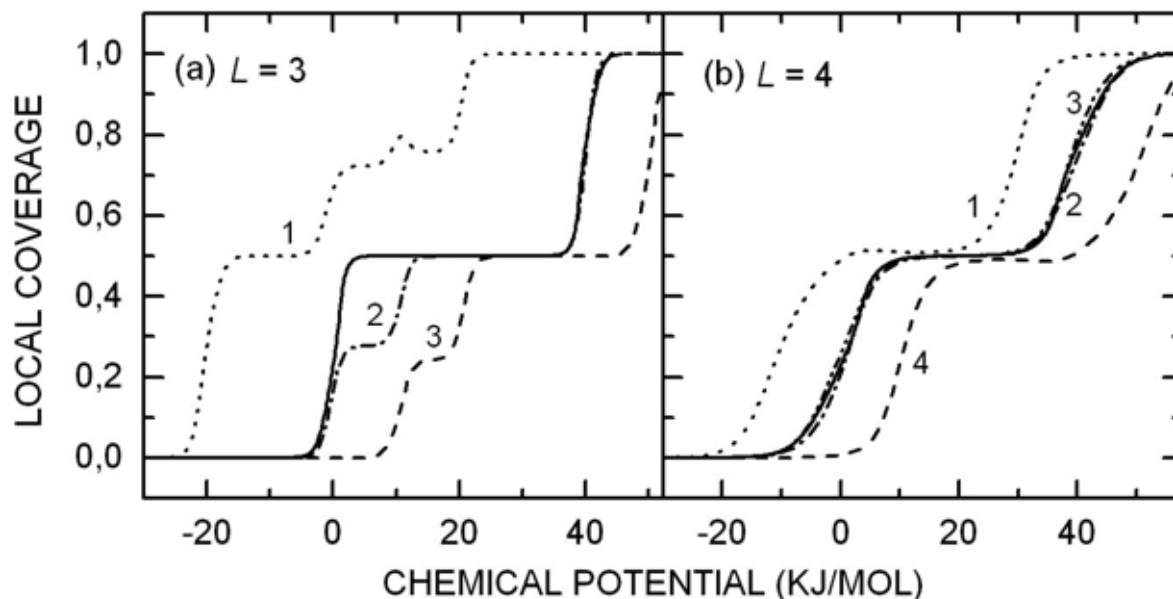


Fig. 2.

marked by numbers exhibit the dependencies of corresponding rows coverage at $\Delta_2/\varepsilon = -1$: (a) $RT/\varepsilon = 0.083$, $\Delta_1/\varepsilon = 2$; (b) $RT/\varepsilon = 0.25$, $\Delta_1/\varepsilon = 1$. Obviously, nonmonotonous behavior of the local coverage may strong affect kinetic of surface processes.

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**RESOLUTION OF CHIRAL SULFOXIDES BY LIQUID CHROMATOGRAPHY
WITH A HOMOCHIRAL METAL-ORGANIC POLYMER AS A CHIRAL
STATIONARY PHASE**

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In the past two decades, chiral sulfoxides have been finding increasing use reflecting the growing interest both in convenient auxiliaries in asymmetric synthesis and products with biological properties containing a chiral sulfinyl group. Most methodologies for synthesis of chiral sulfoxides are based on asymmetric catalytic oxidation of thioethers. However, none of the existing catalytic systems gives 100 % stereoselectivity, and removal of the minor stereoisomer is evidently a task of importance. Enantioselective chromatography is a promising method for separation of chiral sulfoxides. Successful analytical-scale resolutions of chiral sulfoxides on different chiral stationary phases have been reported; however, preparative chromatographic enantioseparations are not known so far. In this paper, we present the use of a new homochiral metal-organic polymer $[Zn_2BDC(L-Lac)DMF](DMF)_x$ ($x=0\div 1$) as a chiral stationary phase for enantioselective chromatography. The polymer prepared as described in [1] possesses a stable 3D structure with 0.5 nm pores interconnected in three directions.

First, we examined the enantioselective sorption of several substituted alkyl aryl sulfoxides by the homochiral porous material **1**. The crystalline material $1 \cdot (DMF)_x$ was stirred in solution containing a racemic mixture of sulfoxides for 3 h, collected and washed with methanol several times to extract the adsorbed guest molecules. **1** showed a remarkable sorption capability towards alkyl aryl sulfoxides. The highest sorption values were obtained for smaller alkyl aryl sulfoxides: 0.68 molecules per formula unit ($[Zn_2BDC(L-Lac)DMF]$) for PhSOMe and 0.59 for *p*-MePhSOMe. For more sterically demanding sulfoxides, the sorption was much lower: 0.27 for *p*-BrPhSOMe, 0.13 for *p*-NO₂PhSOMe and ≈ 0 for PhSOCH₂Ph. The enantiomeric excess (*ee*) values for the adsorbed guest molecules were up to 60% (PhSOMe, CH₂Cl₂ with 0.1% additives of DMF), *S*-enantiomer being in excess for all sulfoxides.

We have also shown the chiral metal-organic framework $[Zn_2BDC(L-Lac)DMF](DMF)_x$ ($x=0\div 1$) to be capable of acting as a chiral stationary phase for liquid chromatography. The

column prepared ($l = 110$ mm, $d = 8$ mm) has been used for semi-preparative enantioseparation of PhSOMe and *p*-MePhSOMe (Figure 1). For these sulfoxides, the stereoselectivity factors measured in static conditions were 4.5 and 2.5, respectively, that gives promising opportunities of dynamic preparative enantioseparation of small alkyl aryl sulfoxides, provided that the separation rate is low enough to approach the sorption equilibrium conditions.

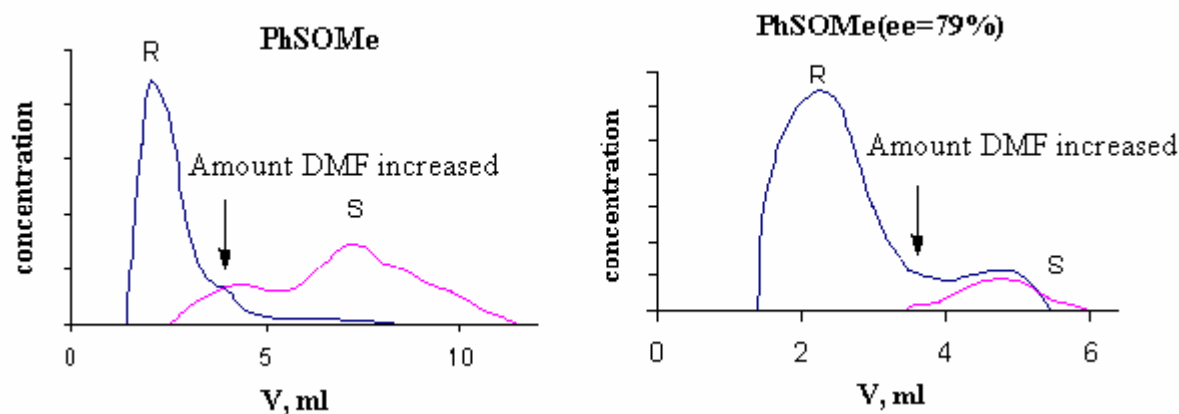


Figure 1. Separation of PhSOMe by chiral liquid chromatography with $[\text{Zn}_2\text{BDC}(\text{L-Lac})\text{DMF}]$ as the stationary phase. Eluent: CH_2Cl_2 with increasing amount of added DMF (stepwise, 0.1 vol.-% in the beginning and then 1.0 vol.-%).

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INVESTIGATION OF AMINO-CONTAINING SILICA MATERIALS

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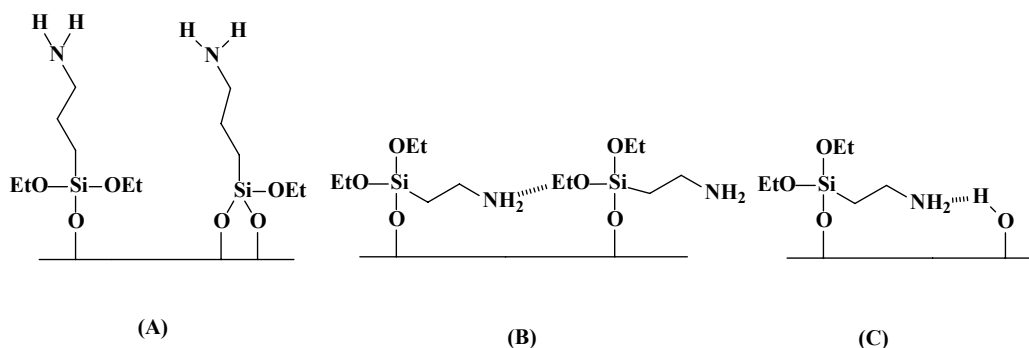
Amino-containing silica have attracted significant attention as supports for the preparation of various type catalysts due to their unique physicochemical and textural properties. $\text{NH}_2\text{-SiO}_2$ (**I**), $\text{NH}_2\text{-Si}(\text{R}^1\text{R}^2)\text{-SiO}_2$ (**II**) and $\text{NH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{-Si}(\text{OCH}_2\text{CH}_3)_2\text{-SiO}_2$ (**III**) (where $\text{R}^1 = \text{OCH}_2\text{CH}_3$ and $\text{R}^2 = \text{Cl}$) were prepared according to [1,2]. IR spectroscopy [3] and pH titration method [2] were used for characterization of base properties of these materials.

The process of chemically anchoring of NH_2 -groups was investigated by IR spectroscopy. According to IR data the band position of NH_2 -groups ($\nu_{\text{N-H}}$) in region of $3200\text{--}3550\text{ cm}^{-1}$ depends on the ligand' nature of NH_2 -groups and increases as follows: (**III**) \rightarrow (**II**) \rightarrow (**I**).

Base properties of samples (**I**)- (**III**) have been studied by IR spectroscopy (CDCl_3 adsorption as probe molecule). This method first was used for the investigation of amino-containing silica. Based on data of CDCl_3 adsorption PA value was calculated. It has been shown that PA value depends on the nature of surface NH_2 -groups. The strength of NH_2 -groups changes as follows:

$$829\text{ kJ/mol (I)} \approx 829\text{ kJ/mol (II)} < 938\text{ kJ/mol (III)}.$$

The influence of amount of chemically anchoring NH_2 -groups on the base properties of (**III**) sample was studied. It has been shown that several types of NH_2 -groups are formed on the surface of sample (**III**):



isolated (**A**) and hydrogen-bonding (**B**) NH_2 -groups. It is proposed that the weak base sites are formed due to the intermolecular interaction of NH_2 -groups (**B**) or interaction of NH_2 -groups with Si-OH groups of support (**C**). It was demonstrated that strength of base sites

increases with increase of the amount of NH₂-groups. The strength (PA value) of **(A)** sites attains to the level of 861 kJ/mol like that of initial amine used for modification of silica.

pH titration method (strong acid (HCl) as probe molecule) allowed to determine the amount and strength (K_H⁺ protonate constant) of base sites on the surface of amino-containing silica. Two type base sites were determined on the surface of samples **(I)** –**(III)** by this method. It was demonstrated that the amount and strength of the base sites increases with the increase the amount of NH₂-groups. K_H⁺ value depends on both the amount of NH₂-groups and the interaction' nature of neighbor groups with NH₂-groups of **(I)** – **(III)** and changes as follows:

$$4.0 \cdot 10^6 \text{ (I)} < 7.9 \cdot 10^7 \text{ (II)} < 2.7 \cdot 10^9 \text{ (III)}.$$

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**APPLICATION OF POSITRON ANNIHILATION SPECTROSCOPY (PAS) FOR
RESEARCH OF THE SURFACE OF POROUS SYSTEMS**

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Huge interest in heterogeneous catalysis investigations of physics and chemistry of surface processes is represented [1]. For this purpose various physical methods including the PAS method based on researches of positron and positronium annihilation [2] are used. The kinetic scheme of transformations both annihilation disintegrations of positron and positronium states in volume of a crystal, a crystal skeleton, on a surface and in volume of porous silicon is considered. The formulas, connecting intensity time a component of annihilation disintegration by constants of disintegrations and transformations of positron and positronium states in volume are received. Estimations of a constant of interaction of positronium with pore surface with formation of a surface positronium state have given value $10^7 - 10^8 c^{-1}$, and average value of radius of pores \approx of 2 nm.

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REINFORCED NICKEL CATALYSTS FOR METHANE STEAM REFORMING

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During the past decade, there has been increased interest in new branch of power engineering - fuel cells. In fuel cells electrochemical oxidation of hydrogen produced by the steam reforming of methane or other hydrocarbon fuel is occurred. For more effective operation of fuel cells, the endothermic methane steam reforming is combined with the exothermic oxidation of exhaust anode gas containing unreacted hydrogen. For this purpose, a combination of catalytic heat-exchanger reactors with catalytic and heat exchanging surfaces are used. On preparing a catalytic heat-exchanging surfaces the problem of formation of a heat-conducting catalytic layer on the metal surface is arises.

The aim of this work was to study the peculiarities of formation of nickel composite reinforced catalysts for methane steam reforming and to investigate catalytic properties of the prepared catalysts in the steam reforming reaction.

The nickel reinforced catalysts were prepared by supporting a mixture of grind industrial catalyst samples NIAP-18 or GIAP-3 (fraction < 0,25 mm), nickel powder and chromium oxide in organic glue on the reinforcing steel net, followed by calcinations at 760 °C in vacuum oven for 2 h. The catalyst contained 12.5 wt.% industrial catalyst, 84.0-87.5 wt.% Ni and 0.0-3.5 wt.% of Cr₂O₃. The textural properties and the phase composition of prepared catalysts were investigated by mercury porosimetry, electron microscopy, X-ray spectrum microanalysis and XRD. XPS was applied for investigation of sample element states. The catalysts were tested in the methane steam reforming by a flow-circulating method (at atmospheric pressure, 750 °C, H₂O/CH₄ = 2).

The XRD patterns show that Ni, α -Cr₂O₃ and α -Al₂O₃ phases are presented in the composite catalysts with adding of Cr₂O₃; the NIAP-18-based composite catalyst also contains CaO·6Al₂O₃ phase and Cr₂O₃ on NiO - based solid solution phases with lattice parameter from 4.161 to 4.138 Å depending on the treatment conditions. According to SEM data, the composite catalysts possess a corpuscle structure formed by a nickel metal matrix, in

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large pores (15–100 μm) of which corpuscles of supported industrial catalyst, fine particles from nickel powder and particles of chromium oxide are distributed.

During the initial reaction period, methane conversion on the nickel reinforced catalysts with the adding of Cr_2O_3 was not high (10–15 %) but it increased with time. The maximal catalyst activity held constant during the 40-hour test. Low activity of the composite catalysts during the first reaction period is caused by formation of an inactive oxide layer containing NiO and Cr_2O_3 . This layer is not completely reduced at 750 $^\circ\text{C}$ in H_2 because of the interaction between the nickel oxide and difficult-to-reducing chromium oxide. As follows from XRD and XPS data NiO and Cr_2O_3 interact at high calcination temperature during the catalyst preparation stage (760 $^\circ\text{C}$, vacuum oven). Activity of composite catalysts increased, probably, due to NiO reduction under reaction conditions. NiO is reduced by H atoms formed during the reaction.

A comparison of activity of the composite and industrial catalysts per weight unit shows that activity of the nickel composite catalysts exceeds the conversion value, which corresponds to the industrial catalyst content in it. This may be attributed to a contribution of the nickel metal matrix, on the surface layers of which nickel crystallites are formed from the solid solution of chromium oxide in nickel oxide during the reaction. Chromium oxide displays a stabilizing effect which suppresses sintering of Ni crystallites and increases nickel dispersion.

Table Catalytic activity of nickel catalysts in methane steam reforming reaction

Catalyst	Geometric shape	CH ₄ conversion, %	
		1 ^{**})	2 ^{**})
GIAP-3	Fraction (m=0.80g)	75	65
	½ of grain(m=2.01g; V=0.7 cm ³)	51	49
7.5% GIAP-3; 50.3% Ni; 1.2% Cr ₂ O ₃ /net	Plate (m=2.00g; V=0.7 cm ³)	20	50
12.5% GIAP-3; 85.5% Ni; 2.0%Cr ₂ O ₃ ^{*)}	Fraction (m=0.80g)	22	30
12.5% GIAP-3; 87.5% Ni	Fraction (m=0.80g)	18	17
NIAP-18	Fraction (m=0.80g)	74	69
	½ of grain(m=1.46g; V=0.7 cm ³)	69	66
7.5%NIAP-18; 50.4% Ni; 2.1% Cr ₂ O ₃ /net	Plate (m=2.23g; V=0.7 cm ³)	16	49
12.5% NIAP-18; 84.0% Ni; 3.5% Cr ₂ O ₃ ^{*)}	Fraction (m=0.80g)	10	36
12.5% NIAP-18; 87.5% Ni	Fraction (m=0.80g)	35	36

^{*)} – catalytic layer separated from reinforcing net; ^{**)} 1-initial value, 2-after 30 h for fraction; after 50 h for plates and grains;

The conversion value for GIAP-3 – based catalysts without Cr_2O_3 are less then for catalysts contained Cr_2O_3 . The conversion value for NIAP-18 – based catalysts without Cr_2O_3 are close to the catalysts contained Cr_2O_3 .

MECHANISM OF CATALYTIC CO OXIDATION ON Pd(110) : FROM LOW TO ATMOSPHERIC REACTION PRESSURE

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CO reaction with oxygen on Pd(110) has been studied by XPS, LEED and mass-spectrometry at reagent pressures varied from 10^{-7} to 10^5 Pa. At “low” pressures (10^{-7} – 10 Pa) the reaction takes place on reconstructed Pd(1x2) surface between O_{ads} and CO_{ads} . The hysteresis observed in the reaction rate dependence on temperature is due to structural transformations of the surface under the action of adsorbates. At atmospheric reagent pressures CO oxidation reaction is accompanied by the formation of surface and bulk PdO. The hysteresis observed in the reaction rate dependence on temperature at atmospheric reagent pressures is caused by the formation and reduction of bulk PdO particles.

Pt, Pd and Rh metals are widely used as active components in catalysts for automobile exhaust neutralizers and in a number of important industrial processes, such as ammonia oxidation, methane combustion, etc. [1]. Pd is used in these catalysts due to its high activity in oxidation of hydrocarbons, CO and H_2 , as well as NO reduction. To understand the mechanisms of catalytic reactions, it is necessary to study these reactions over metal monocrystals in a wide reagent pressure range from very low ($\leq 10^{-6}$ torr) to atmospheric (~ 760 torr). The goal of this study was to investigate the mechanism of CO oxidation on Pd at reagent pressures varied from 10^{-7} to 10^5 Pa. The investigation of this reaction over Pd(110) at “low” (10^{-7} – 10 Pa) and atmospheric pressures at 350-700 K using mass-spectrometry, XPS, LEED, mathematical simulation showed that the mechanism of CO oxidation by oxygen changes due to surface reconstruction, oxygen penetration into subsurface metal layers and formation of surface and bulk palladium oxides when the pressure increases from “low” to atmospheric .

Both for “low” and atmospheric pressures the dependence of the reaction rate observed when the sample was heated in the flow of CO and O_2 (heating cycle) were substantially different from those observed during cooling (cooling cycle), resulting in a hysteresis. At “low” pressures and low temperatures ≤ 350 -450 K the heating cycle reaction rates were significantly lower than those of the cooling one. It was found that such dependence of the reaction rate on temperature is due to the reconstruction of Pd(110) surface caused by adsorption and desorption of O_2 and CO, and reaction $CO_{ads} + O_{ads}$ [2]. Thus, the reaction acceleration during heating is accompanied by the surface reconstruction Pd(1x2)-p(4x2)-CO

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$\rightarrow \text{Pd}(1 \times 2) \rightarrow \text{Pd}(1 \times 1) \rightarrow \text{Pd}(1 \times 2)\text{-c}(2 \times 4)\text{-O}$, which is caused by CO_{ads} desorption, $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}}$ reaction and gradual surface filling with O_{ads} . During the cooling cycle the surface reconstruction takes place in the reverse order. However, the temperatures of these transformations are lower than during the heating cycle. This is caused by different adsorptivity of $\text{Pd}(1 \times 2)\text{-p}(4 \times 2)\text{-CO}$ and $\text{Pd}(1 \times 2)\text{-c}(2 \times 4)\text{-O}$ structures with respect to CO and O_2 . Only CO is adsorbed on the former structure, whereas both reagents can be adsorbed on the latter one and, consequently, $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}}$ reaction is possible. Thus, the hysteresis in the structural transformation on Pd(110) surface results in a hysteresis in the dependence of $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}}$ reaction rate on temperature [2].

At atmospheric pressures in O_2 excess in the reaction mixture the dependences of the reaction rate on temperature were substantially shifted to higher temperatures. In these dependences the heating cycle reaction rates were significantly higher than the cooling ones. Furthermore, reaction rate oscillations were observed during cooling at low temperatures both as a function of temperature and time. It was found that such dependence of $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}}$ reaction rate on temperature at atmospheric pressures is due to the formation and decomposition of adsorption and oxide phases on Pd(110) surface. During the heating cycle the reaction rate increase is accompanied by reconstruction of Pd(110) surface, penetration of O atoms into subsurface metal layers, and formation of surface and bulk PdO. Therefore, CO oxidation reaction includes the stages of CO reaction with O_{ads} on Pd(110) surface and with O atoms of the surface and bulk palladium oxides. At $T \leq 700$ K during the cooling cycle Pd(110) surface is covered with PdO particles. Therefore, CO reacts with O atoms of the surface layer of PdO particles. Hence, the rate during the cooling cycle is lower than that of the heating one. During CO reaction with PdO particles, oxygen vacancies formed on the surface are filled with O atoms diffusing from PdO bulk as well as due to reaction with O_2 gas. When temperature is decreased below 550 K, a continuous metal film is formed on the surface of PdO particles due to changes in the rates of the oxide surface layer reduction and oxidation. The formation and oxidation of palladium film on PdO particles lead to autooscillations of the rate of CO reaction with oxygen.

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**STUDY OF METALLOCENE CATALYTIC SYSTEM Cp₄Zr-MAO
IN THE ABSENCE OF MONOMER**

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Spectroscopic investigation of metallocene catalytic system Cp₄Zr-MAO in the absence of monomer was carried out. Obtained results can be used for detail description of polymerization mechanism.

Tetrakis(cyclopentadienyl) zirconium (C₅H₅)₄Zr is one of the simplest cyclopentadienyl zirconium derivatives. According to X-ray analysis, there are three η⁵-bonded C₅H₅-groups and one η¹-bonded C₅H₅-group in (C₅H₅)₄Zr molecule [1, 2]. In this respect, it is interesting to study catalytic properties of such compound in the polymerization process. In combination with MAO and/or other cocatalysts, (C₅H₅)₄Zr may be used as a soluble catalyst of homo- and copolymerization of ethylene, and as a base for new supported catalysts creation. Our preliminary experiments showed that the productivity of soluble catalytic system (C₅H₅)₄Zr – MAO (I) during the process of ethylene polymerization (T = 60 °C, P = 5 bar, [(C₅H₅)₄Zr] = 0.002 mmol/l, Al/Zr = 25000, 60 min) has achieved 742 kg PE/g Zr per hour. Later, it was shown [3, 4] that the productivity could be increased to 2180 kg PE/g Zr. Thus, the purpose of our work is to study the mechanism of component interaction in the described catalytic system (C₅H₅)₄Zr – MAO in the absence of monomer.

The following results were obtained during analysis of UV-Vis spectra evolution.

It was observed the fast accumulation of a product (I) (with absorbance max λ = 326 nm) in the first moment of the catalyst components mixing. The bathochromic shift may be explained by formation of polarized metal – carbon bond containing an intermediate [5]. Later, it was observed the product (I) consumption and a product (II) (absorbance max λ = 372 nm) accumulation. By our suggestion, the second bathochromic shift is associated with the further polarization of metal – carbon bond in nascent active species and the formation of contact ionic pair. The analysis of the kinetic regularities unambiguously established that the processes (I) and (II) were consecutive. After a lapse of time the product (II) concentration decreased. Obviously, it is explained by the active species collapse. Above process is accompanied by a product (III) formation. The concentration of zirconocene and the Al/Zr molar ratio do not influence on the products (I) and (II) formation. However, the increase of

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the Al/Zr molar ratio has an essential influence on the rate of the product (III) accumulation. When the Al/Zr molar ratio achieved 1000 there was no noticeable quantity of the product (III) formation observed.

The obtained kinetic data can be used for the detail description of polymerization mechanism under the action of the given catalytic system.

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HYDROGENATION of CARBON OXIDES OVER Ni-, Fe- AND Cu – ULTRAFINE CATALYSTS

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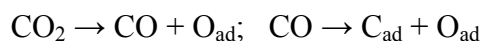
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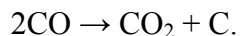
The activity of the catalysts on the base of Ni –, Fe - and Cu- ultrafine powders have been investigated for carbon oxides simultaneous hydrogenation.

Carbon oxides simultaneous hydrogenation at atmospheric pressure over the catalysts containing nano-particles of nickel, iron and copper, and also interaction of carbon oxides with a surface of ultrafine powders of metals is studied.

Carbon oxides simultaneous hydrogenation proceeds through stages of dissociative adsorptions both of mono- and bi-oxides of carbon



It is complicated by reaction of CO disproportionation:



The quantitative ratio between these reactions is defined both by concentration of hydrogen on a surface of the catalyst, and temperature of process.

It is established, that the basic products of joint carbon oxides hydrogenation are methane and ethylene, and in the lack of hydrogen - methane, ethane and ethylene, propane and propylene. Selectivity to alkenes reached 35 % over the studied nano-catalysts. Upon the adsorption of hydrogen on the metals, capable to dissolve them, there are two forms on a surface, one of which is bonded only with one atom of metal (H_I), and another - strong-adsorbed (H_{II}) - with several. Formation of hydrocarbons proceeds through a stage of formation of active carbon, however selectivity of the process to alkenes, possibly, is defined by ratio $\text{H}_I: \text{H}_{II}$ on a surface of the catalyst. Increase of concentration of hydrogen in the form of H_{II} increases output of alkenes.

Apparently, on a surface of bimetallic samples there are some types of the active centers responsible for formation CH_2 -radicals - iron or copper, hydrogen sorption on which proceeds mainly in the molecular form. Atomic hydrogen formed as a result of dissociative chemisorption on the nickel centers bonds active carbon particles with formation of methane, and oxygen - with formation of water. CH_2 -radicals formed on copper centers can be

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transferred on nickel through the gas phase (Jumpover-effect) where further hydrogenation up to methane occurred.

Atomic hydrogen can move to a catalyst surface through the borders of contact between particles from the nickel centers to copper or iron where it enters the reactions with oxygen. That means that carbon oxides hydrogenation up to alkenes occurs by means of hydrogen spillover.

The greatest activity in formation of methane and ethylene show catalysts copper content in which does not exceed the content of nickel. The equivalent quantity of copper and its excess led to lack of atomic-chemisorbed hydrogen owing to what sharp decrease in activity of the catalyst is observed.

On all investigated bimetallic catalysts it was observed synergetic effect (growth of specific catalytic activity in comparison with monometallic).

**STUDY OF AN INFLUENCE OF PREPARATION CONDITIONS OF ALUMINA
SUPPORTED URANIUM OXIDE CATALYSTS ON THEIR CATALYTIC AND
PHYSICO-CHEMICAL PROPERTIES**

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Three series of the 5%U-Al₂O₃ catalyst were prepared by impregnation, solid phase synthesis and mechanical blending methods. The catalysts were studied by S_{BET}, XRD, TPR, SEM, TEM and XPS. It has been shown that properties of the catalysts prepared by various techniques depend on a synthesis method and are caused by different degree of interaction of active component and support. A mixture of UO_x and AlO_x is presumably responsible for catalytic activity at low temperature. This phase is not identified precisely so far. The catalyst calcined at temperature around 1000 °C has finely (0.1 nm) dispersed active component consisting of nanosized uranium oxide.

Uranium oxides possess unique properties, they are new generation of catalytic materials and there is great potential to various catalytic processes. The continues series of oxygen containing compounds, which are characterized by different O/U ratio and include uranium in valence state from 4 to 6, are most interesting for catalysis. High activity of uranium oxide catalysts has been discussed in the literature. Supporting of uranium oxides allows reducing the total amount of uranium in a catalyst and increasing thermal stability of a catalyst and its lifetime [1, 2].

Uranium oxides are known to form complex oxides, such as uranates and polyuranates, with alkali, alkali-earth, rare-earth and transition elements. There are restricted data on formation of mixed uranium oxides with alumina, which is usually used as a catalyst support. Even in the X-ray database JCPDS the system U-Al-O is not described.

The objective of this paper is preparation and study of catalytic activity of nanosized uranium oxides supported on alumina depending on preparation conditions and high temperature treatment.

Three series of the 5%U-Al₂O₃ catalyst were prepared by impregnation of γ -Al₂O₃ with aqueous solution of uranyl nitrate (UO₂(NO₃)₂·6H₂O), solid phase synthesis and mechanical blending. Synthesized catalysts were calcined at 500, 600, 800, 900, 1000 °C and studied by

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S_{BET} , XRD, TPR, SEM, TEM and XPS. Catalytic activity of the samples in the reaction of methane oxidation ($1\% \text{CH}_4$ in air, 1000 h^{-1}) was studied.

It has been shown that the catalyst prepared by impregnation method exhibits higher interaction of uranium oxides and alumina in comparison with the solid phase synthesized catalyst. The catalyst prepared by mechanical blending exhibits no interaction between an active component and a support, the properties of this catalyst are determined by the properties of individual components of mechanical mixture.

One of the peculiarities of the impregnated catalyst in comparison with other catalysts is an increase of catalytic activity with an increase of calcinations temperature. The hydrogen consumption peaks in TPR shift to lower temperature region, and the activity of the catalyst in the reaction of methane oxidation increases (Fig. 1). The thermal activation of the catalyst can be explained by formation of nanosized uranium oxide particles.

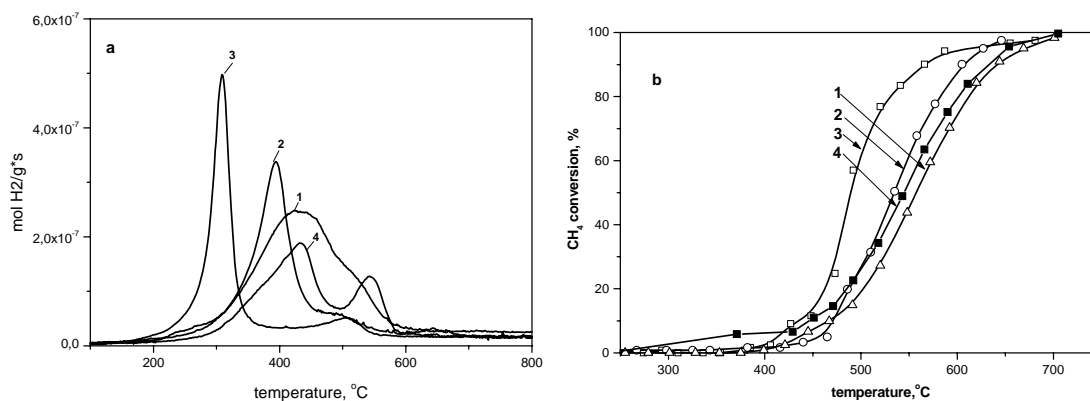


Fig. 1. TPR curves (a) and temperature dependence of methane conversion (b) on the impregnated $5\% \text{U-Al}_2\text{O}_3$ catalyst calcined at: 1 – 600°C for 4 hrs; 2 – 900°C for 4 hrs; 3 – 1000°C for 4 hrs; 4 – 1000°C for 18 hrs.

It has been shown that XRD pattern of the impregnated catalyst calcined at 1000°C and higher contains peaks attributed to U_3O_8 phase. X-ray amorphous nanosized uranium oxide particles are presented in the catalyst calcined at the temperature lower than 1000°C . High resolution TEM showed that the size of uranium containing particles in the samples calcined at 1000°C was about 0.1 nm . Further calcination of the sample at 1000°C for 18 hours leads to sintering and formation of roughly dispersed ($> 50 \text{ nm}$) particles. In general, the supported uranium oxide catalyst activity is defined by ratio of presented in the catalyst phases, including a phase consisting a mixture of UO_x and AlO_x , nanosized and roughly dispersed uranium oxides.

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TWO VARIOUS MECHANISMS OF LOW TEMPERATURE ALKANE CONVERSION BY PROMOTED ALUMINUM CHLORIDE

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Linear and branched alkanes were activated by promoted aluminum chloride at low temperatures (170-230 K). The nontrivial way of paraffin transformation resulting in formation of normal alkane containing one carbon atom less with the products of isomerization and dehydrocyclization was found. Unknown early labile intermediate particles were detected by low temperature spectroscopy and quantum-mechanical accounts. Two various mechanisms of the catalytic action of aluminum halide complexes with transition metal salts and alkyl halides were revealed.

The establishment of detailed mechanism of the alkane transformation by Lewis acids is hindered by the difficulty of registration of the active intermediates and unstable molecular complexes which are present at low concentrations, as a rule, under chemical reaction conditions. The problem becomes even more complicated in the transition to the most advanced catalytic systems including, in addition to aluminium halides, promoters such as transition metal halides. For these purposes the methods of low temperature condensation and matrix isolation have been applied. Conditions of limited molecular mobility at low temperatures allow to divide the process into separate stages and to select the most advantageous direction of reaction.

Catalysts on a basis of aluminum chloride with different promoters were prepared by the methods of the low temperature co-condensation and matrix isolation. Dynamics of the catalyst formation and their properties were monitoring *in situ* by spectral (IR, UV/vis) methods. Species of the various compositions were obtained; unknown earlier spectral characteristics and the regions of their thermal stability were revealed at 80-290 K. The structures of the observable labile particles were proposed on the basis of the vibrational spectra and quantum-mechanical accounts with use of density functional theory.

The possibility of accomplishing paraffin isomerization, cracking and dehydrocyclization by promoted aluminum chloride catalysts at low temperatures 170-230 K (including those in the solid phase) was first proved. It was established that the use of different promoters, such as transition metal halides or alkylhalides not only essentially increases the total conversion of

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normal and branched alkanes but rather changes significantly reaction selectivity. The route and mechanism of hydrocarbon transformations depends on promoter.

Secondary and tertiary butylcations have been registered for the first time at joint condensation of aluminum chloride and chloroalkanes (2-chloro-butane and 2-chloro-2-methylpropane), their IR spectra and thermal stability have been studied [1]. Aluminum chloride anions ($\text{Al}_3\text{Cl}_{10}^-$, Al_2Cl_7^- or AlCl_4^-) participating in stabilization of the carbenium ions were revealed. In contrast to tert-butylchloride, which formed carbocation in the course of co-condensation at 80 K, the creation of the secondary one occurred only at elevated temperatures. The initial stage of the interaction of aluminum halide with 2-chlorobutane was formation of unknown earlier molecular complexes, which transformed to ionic species at annealing. The carbocation stabilization by aluminum chloride should provide an opportunity of alkane activation on a classical mechanism of acid catalysis. Really the product composition, formed in co-condensates, was close to a set of reaction products in solutions [2]. Light C4-C5 hydrocarbons were mainly formed.

The nontrivial way of alkane transformation resulting to creation a normal alkane with smaller per unit of carbon chain was detected by the action of co-condensates of transition metal salt and aluminum halide. For example the basic products of the low temperature n-octane conversion were monomethylheptanes (45-50%), n-heptane (20-35%) and cyclohexane (10-15%). In the aluminum chloride-cobalt chloride system at least 4 different complexes in which the coordination number of cobalt varied from 3 up to 6 were detected [3]. The complexes of structure 1:1 and 2:1 were only precursors of the real catalyst; the active particles were forming only at interaction of the various kinds of complexes at annealing. The activity of such particles was caused by not characteristic coordination numbers of metal atoms. It was found that the presence of coordination unsaturated transitional metal was responsible for activation and unusual routes of alkane conversion even under acid catalyst.

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FORMOSE REACTION AS A CATALYTIC PROCESS WITH CHAIN MECHANISM

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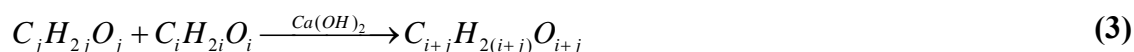
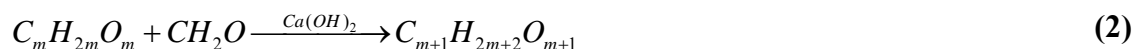
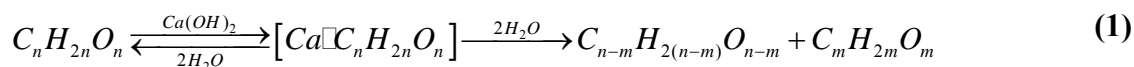
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The formose reaction can be regarded as a unique example of a catalytic process with chain mechanism with confluent branching that does not involve free radicals. The kinetics and products of the individual stages of the process were investigated. The overall detailed scheme of the reaction was proposed. A computer program for modeling of the kinetics of the formose reaction was created and results on the rate constants of different stages were acquired.

For the long time oligomerization of formaldehyde yielding carbohydrates, catalyzed by inorganic and organic bases in aqueous medium, known as the formose or Butlerov reaction was supposed to be autocatalytic. Over the XX century a variety of expected autocatalytic cycles were proposed (e.g. see the review [1]), but none of them could be supposed to represent the actual route of the carbohydrate formation from formaldehyde. Finally, it was found that the nature of the autocatalysis of the formose reaction is connected with the retroaldol cleavage of the higher monosaccharides [2-4].

As a result of the breaking up of one molecule of a higher carbohydrate two molecules of lower carbohydrates are formed. The latter condense with each other or formaldehyde in the course of the aldol condensation reactions and yield other higher carbohydrates. The overall scheme of the formose reaction is presented below:



where $n = 4-6$, $m = 2-3$; $i, j = 2-5$. ($i+j < 8$)

Actually, the above scheme can be regarded as a chain mechanism with the confluent branching (active species – lower carbohydrates C_2 - C_3 and formaldehyde) rather than a classic autocatalytic reaction $A + A \longrightarrow P + A$. If the formose reaction is initiated by higher monosaccharide $C_n H_{2n} O_n$ ($n = 4-6$), the stage (1) is the initialization stage – the formation of two lower carbohydrates $C_{n-m} H_{2n-2m} O_{n-m}$ and $C_m H_{2m} O_m$ ($m = 2-3$). If the reaction starts from a lower carbohydrate, no initialization stage is needed and the reaction starts from the chain

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growth stages **(2)** and **(3)** – condensation of lower carbohydrates with each other and formaldehyde. The confluent branching of the reaction takes place on stage **(1)** – two new active species capable of continuation of the chain elongation are formed from one of the reaction products.

Thus, the formose reaction is a unique example of the process with its mechanism which is analogous to the chain mechanism with confluent branching but does not involve free radicals.

We have thoroughly investigated the kinetics and products of the formose reaction in the presence of various initiators. The kinetics and products of stage **(3)** for the condensation of lower carbohydrates – glycolaldehyde, glyceraldehyde and dihydroxyacetone, with each other was investigated as well. It turned out that the most of the carbohydrates present in the final composition of the formose products can be formed in the course of condensation of lower carbohydrates with each other. The rates of the condensation of lower carbohydrates are relatively high; e.g., the typical time of the 90 % conversion of 5 mM glycolaldehyde with itself is about 1 min. If the reaction time is prolonged, higher monosaccharides formed from glycolaldehyde are breaking up into lower carbohydrates and glycolaldehyde is formed again.

Finally the detailed model of the formose reaction based on the condensation of the lower carbohydrates and formaldehyde was created. The computer program assigned for the modeling of the kinetics of the formose reaction was developed. This program was adapted for the solution of the reverse kinetic problem – to compute the kinetic rate constants of some individual stages of the process basing on the experimental data. Thus few apparent rate constants for several condensation reactions were determined. Besides, it was shown that a ring-chain rearrangement of higher carbohydrates which stabilize them to prevent their further transformations may play an important role in the formose mechanism. Thus these rearrangements have to be taken into account and their exclusion from the overall kinetic model of the formose reaction leads to the incorrect results.

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KINETIC STUDY OF MICROWAVE-ACTIVATED OXIDATIVE DEHYDROGENATION OF ETHANE OVER OXIDE CATALYSTS

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Microwave (MW) activated oxidative dehydrogenation of ethane is studied using kinetic approach. It consists in the comparison of apparent kinetic parameters (activation energies), and dependencies (shape of kinetic equations, “selectivity or yield vs. conversion” curves) obtained in thermal and MW modes. In the case of VMoNb oxide a distinct difference between ethane yields was observed at given conversion of limiting reactant (oxygen). Since for the same catalyst no significant difference in Arrhenius plots in two modes is noticed, one may suggest that the unusual structures existing in the conditions of MW irradiation contribute to the reaction on the stage of consecutive transformation of intermediate products.

Microwave (MW) irradiation is among the most promising and attractive methods for catalyst activation due to following distinctive features: (1) the MW treatment provides a tool for non-equilibrium changes in catalyst structure, which cannot be achieved by conventional thermal and chemical treatments, neither in *ex situ* (during catalyst preparation), nor in *in situ* (in the course of catalytic reaction) modes; (2) frequency and intensity variation of the applied field enables a tunable and targeted modification of the solid system.

Most of authors explain positive effect of MW treatment by the formation of so-called “hot spots” - areas having higher temperatures compared to their surroundings due to their greater interaction with microwaves and slow heat dissipation. However, it is still debated whether or not the effect of MW treatment can be explained by overheating of certain zones in the catalyst or it produces some non-thermal effect on the reacting species and/or solid system. In this work we suggest a kinetic approach for studying catalytic processes under the MW treatment. It consists in the comparison of apparent kinetic parameters (activation energies), and dependencies (shape of kinetic equations, “selectivity or yield vs. conversion” curves) obtained in two modes (thermal vs. MW). This approach has been applied to the study of oxidative dehydrogenation (ODH) of ethane over a series of complex oxide catalysts.

A series of vanadium-containing mixed oxide catalysts (VSb, VMo, VMoNb) was prepared by conventional evaporation-precipitation method and tested for ethane ODH at conventional thermal heating (by electric furnace) and under MW irradiation. In the second case, the reactor with a catalyst was placed into the cavity of low-power (≤ 50 W) MW

system operated at frequencies ranging from 3.4 to 3.8 GHz. Measuring circuit allows to measure both incident and reflected MW power. The catalyst temperature was varied by tuning the incident MW power and monitored using a MW-transparent optical fiber sensor.

Two series of experiments in each mode were carried out: gas flow rate variation at constant temperature (450 °C) and temperature variation at constant flow rate. Reaction mixture was analyzed by conventional on-line GC.

Preliminary test showed that the catalysts under study can be heated in air easily in a MW mode to typical ethane ODH temperatures (400-500°C). The most promising results were obtained while heating the VMoNb-oxide catalyst. Heating in air in MW mode results in some changes in XRD patterns of this sample. Also, its color is changed from green to orange. This is an evidence for a deep oxidation of constituent cations (in particular, vanadium transformation to V^{5+} state), what cannot be reached by regular thermal oxidation in air. Even after treatment in the reaction mixture ($C_2H_6 : O_2 : N_2 = 2 : 1 : 3$) in a MW mode this sample retained spots of orange color on the external surface of the grains.

The analysis of reaction kinetics demonstrated that in both modes of operation the overall rate can be satisfactorily described by a simple first-order equation. However, as shown on Fig. 1, whereas for VSb oxide no difference in "ethane yield vs. conversion" curves obtained in two modes is observed, in the case of VMoNb oxide a distinct difference between ethane yields is observed at given conversion of limiting reactant (oxygen). Since for the same VMoNb-catalyst no significant difference in Arrhenius plots in two modes is noted (see Fig. 2), one may suggest that the unusual structures existing in the conditions of MW irradiation contribute to the reaction on the stage of consecutive transformation of intermediate products. By contrast, in the case of VMo-oxide two Arrhenius plots differ significantly.

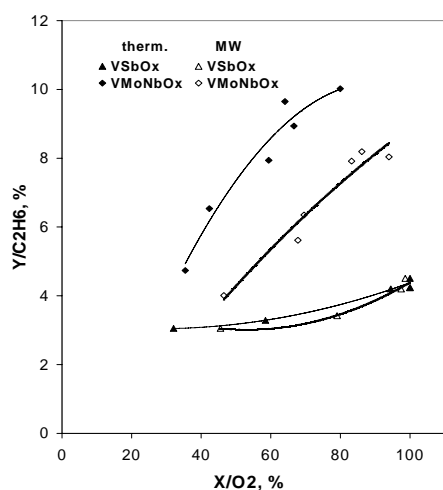


Fig. 1.

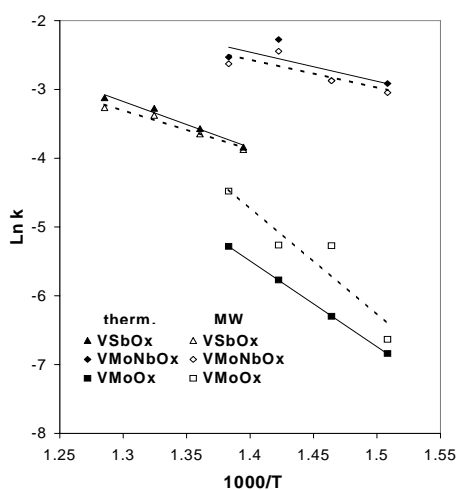


Fig. 2

LIQUID-PHASE OXIDATION OF TRIMETHYLHYDROQUINONE CATALYZED BY COPPER (II) CHLORIDE IN THE PRESENCE OF CELLULOSE INORGANIC COMPOSITES

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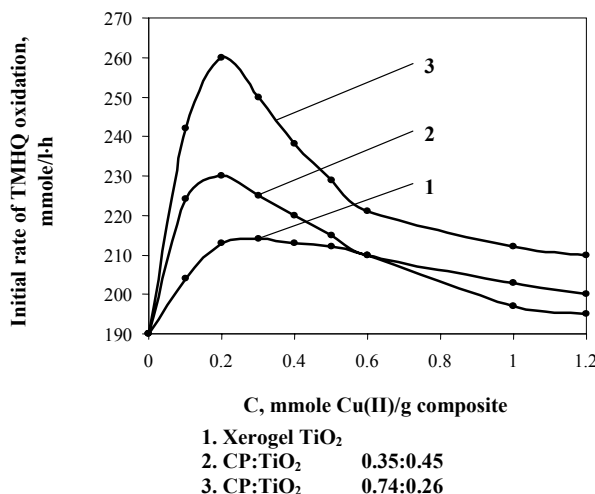
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Cellulose inorganic composite materials with a variable ratio between the cellulose powder and titanium dioxide were synthesized. When the systems were used as the catalyst carrier, a relationship between the reactivity of copper sorbed on them and the matrix structure was established. It was shown that the active agent in the composite during the model process of the liquid-phase oxidation of trimethylhydroquinone was the inorganic component. It was found that the initial rate of H_2O_2 decomposition increased with the proportion of CP in the composite and its maximum decomposition rate was 7 times faster than the decomposition rate on the titanium dioxide xerogel.

An earlier study [1] dealt with the model process of the liquid-phase oxidation of trimethylhydroquinone (TMHQ) by air oxygen in the TiO_2 gel synthesized by the hydrolysis of a methanol solution of tetrabutoxytitanium (TBT).

The EPR spectroscopic examination showed that several types of copper compounds were formed in the phase of inorganic gels depending on the $Cu(II)/TiO_2$ ratio. $Cu(OH)_2$ and bridging polynuclear structures had the largest reactivity. The catalytic reactivity of such systems is much higher than their reactivity in the homogeneous variant. However, from the technological viewpoint, it is preferable to use inorganic oxides in the form of xerogels, although their reactivity is lower than the reactivity of hydrogels. With this in mind, new composite materials were prepared by adding a cellulose powder (CP) before the TBT hydrolysis. The IR spectroscopic examination revealed the formation of composites with a supramolecular system of hydrogen bonds of hydroxyl groups.

Fig. 1. Initial rate of TMHQ oxidation vs. copper(II)-composite ratio in the reaction sphere (the concentration of $Cu(II)$ in the reaction is 6 mmole/l)



The reactivity of these materials in a model process was determined. The kinetic data are given in Fig. 1.

The reactivity of copper (II) increased with growing proportion of CP in the material. The obtained results suggested that interparticle interactions between the reagents played a considerable role. Indeed, the analysis of IR spectra of TMHQ sorbed on the composite showed that hydroxy groups of titanium dioxide and water bound to these groups interacted with hydroxy groups and the aromatic system of TMHQ via hydrogen bonds. The organic component of the composite did not show itself during sorption and its role was obviously limited to the role of a sparser. The active agent in the composite was the inorganic component.

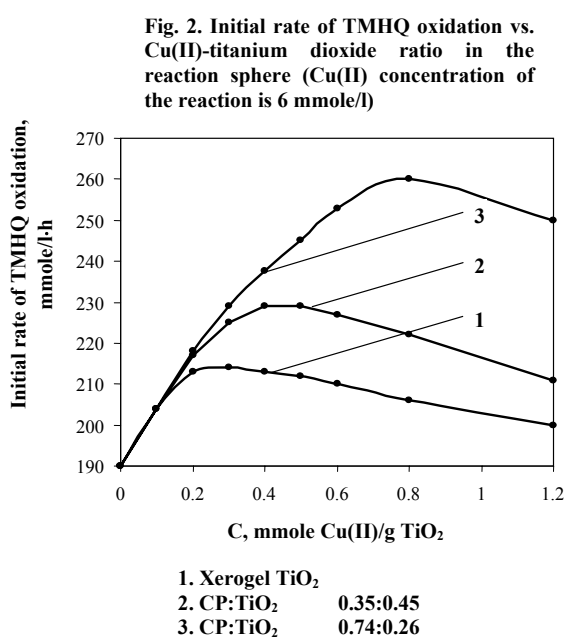


Figure 2 presents kinetic data in terms of TiO₂. The copper reactivity maximum shifted to larger Cu(II)/TiO₂ ratios on the composite as the CP concentration increased. That is, the most catalytically active polynuclear compounds of Cu(II) were formed in the phase of the material at a smaller concentration of TiO₂. This fact can be due to the growth of the specific surface of titanium dioxide in the composite as the CP/TBT ratio increased at the hydrolysis stage.

The catalytic reactivity was also determined on the composites. The initial rate of the H₂O₂ decomposition increased with the proportion of CP in the composite and its maximum decomposition rate was 7 times larger than the decomposition rate on the titanium dioxide xerogel.

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DENDRIMER BASED CATALYSTS IN WACKER-OXIDATION: UNEXPECTED SELECTIVITY TO TERMINAL DOUBLE BONDS

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The esthetically appealing structures of dendrimers have attracted the interest from many different disciplines of science. We demonstrated the unusual change of substrate and process selectivity of catalytic system Pd(II)/Cu(II)/dendrimer based on polypropyleneimine and different diaminoalkanes with terminal nitrile groups for different linear and aromatic olefins. This catalytical system can be easily recycled.

The selectivity to the reaction product plays a key role in minimizing of wastes. A smart way to improve selectivity is design of ligands able to bind and orientate substrate due to supramolecule interaction such as cyclodextrins, calixarenes and dendrimers (a polymers having a regular branched structure). Dendrimers are characterized by a well-defined highly branched architecture that is obtained via step-wise addition of a number of layers of branched segments to a multifunctional core. They are able to bind guest molecules and might be considered as nanosized macromolecular carriers. Dendrimers were shown to improve selectivity for certain reactions depending on the number of branches in the dendrimer molecule.

In the present paper we demonstrated the unusual change of substrate and process selectivity of catalytic system Pd(II)/Cu(II)/ dendrimer based on polypropyleneimine and different diaminoalkanes with terminal nitrile groups (PPI (CN)₄ –G0.5; PPI (CN)₈- G1.5; PPI (CN)₁₆-G2.5).

Various linear and aromatic 1-alkenes, styrene, cyclohexene, allylbenzene were taken as substrates. The reaction products were the corresponding ketones, along with the formation of which the isomerization of the double bond was also observed (more than 90 % of alkene-1 after 5 min). If dendrimer is absent or the reaction is performed in a homogeneous system, the selectivity with respect to methyl ketone is low (50%). If the reaction is carried out in a two-phase system in the presence of dendrimer, the process selectivity changes. The results of our experiments on the oxidation of C₇–C₁₆ alkenes show that, when the ligand is the dendrimer molecule, the fraction of forming methyl ketones substantially increases for the substrates C₇–C₁₀. Also with an increase in the generation from G0.5 to G2.5, the fraction of methyl ketones with respect to isomeric ketones increased by a factor of more than two. It was shown, that reaction rate is affected by the positions of double bond in substrate: in the case of dendrimers the marked rate was observed only in the case of alkene-1.

**RECONSTRUCTION OF THE Pd(poly) SURFACE IN VACUUM AND OXYGEN
ATMOSPHERE**

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The microstructure of the surface of polycrystalline Pd foil was studied by scanning electron microscopy at 600-1400 K under vacuum and in the O₂ atmosphere. The foil temperature was found to determine the size of the grains, whereas the environment was observed to control the microstructure of their surface. Both under vacuum and in the O₂ atmosphere the grains gradually grew from 0.5-1.0 to 10-50 μm with the temperature increase. A grain boundary separating the initial 0.5-1.0 μm grains was observed on their surface under vacuum. In O₂ atmosphere the surface of the grains was gradually covered with facets having crystal faceting.

The catalyst chemical composition and structure are known to determine its activity. Meanwhile, the environment interacting with the catalyst alters its composition and structure. To understand the mechanism how the environment affects the structure of catalysts, we studied microstructural reconstruction of the surface of 40 μm polycrystalline palladium foil under vacuum and in the O₂ atmosphere at 600-1400 K by scanning electron microscopy. When temperature was increased, both under vacuum and in the O₂ atmosphere a grain boundary was found to appear and grow on the foil surface, which indicates the growth of the grains from 0.5-1.0 to 10-50 μm. The surface structure of these grains was found to depend significantly on the environment. Under vacuum a grain boundary separating 0.5-1.0 μm grains was observed when temperature was increased above 700 K. The outlines of this boundary remained on the surface of 10-50 μm grains formed after heating to 1100-1300 K. In O₂ atmosphere PdO particles with dimensions ≤ 50 nm were formed on the surface at T ≥ 700 K. At T ≥ 1100 K these particles were observed to decompose forming a grain boundary separating 10-20 μm grains on the surface. Structural elements with different shapes (facets) were observed on the surface of these grains. After heating to 1400 K the grains grew to 10-50 μm. Their surface was covered with facets having crystal faceting and definite orientation. Thus, it was found that the sample temperature determines the size of grains on polycrystalline Pd foil, whereas the environment controls the microstructure of their surface.

**«AUTOCATALYTICAL» EFFECT OF INCREASE OF GROWTH RATE OF
Ge_xSi_{1-x} LAYERS IN MIXED HYDRIDE AND DICHLORINE-SILANE PROCESSES
IN LASER AND PULSE MODES**

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Si-Ge solid solutions are widely used in manufacturing of heterojunction-based bipolar transistors and in modern technologies of opto-, nano- and microelectronics [1-4]. Epitaxial growth in stationary mode or in laser and impulse mode of hydride mixed and dichlorine-silane processes with the using of GeH₄+SiH₄ and GeH₄+SiH₂Cl₂ gas mixtures are usually used for the deposition of Ge_xSi_{1-x} layers. It was determined [1, 2] that the presence of germane in the gas mixture sharply increases the growth rate of Ge_xSi_{1-x} layers as compared with the growth rate of Ge layer and Si layer separately, i.e. the catalytic effect is observed [1, 2]. In the case of hydride process the growth rate increases approximately in 10 times due to the catalytic effect, while in the dichlorine-silane mode V_p increases approximately in two orders of magnitude.

The introduced reaction schemes of growth processes of Ge_xSi_{1-x} layers naturally explain the catalytic effect of increase acceleration of growth rate of germanium layers deposited in germane-silane and germane-dichlorine-silane processes in laser and impulse modes and the decrease of the J parameter of the growth model that were revealed during the experiments [1, 2]. The calculation of constant J using formula (1) with given P_j at T=625 °C has shown that parameter J isn't constant if P_{GeH_4} varies. It shows that the growth rate in experiments with GeH₄ and SiH₂Cl₂ isn't limited by adsorption phase only but it can be limited by other processes such as gaseous kinetics, surface nucleation, desorption of oxygen and chlorine.

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INTERMEDIATE PRODUCTS IN PARTIAL OXIDATION OF AROMATIC HYDROCARBONS

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The purpose of this work is development and research of highly selective heterogeneous catalytic systems, which contain vanadium and molybdenum oxides, for processes of partial oxidation of aromatic hydrocarbons. The nature of oxidizer and a role of intermediates were defined. The role of hydroquinone as the basic intermediate substrate, forming maleic anhydride, was determined in partial catalytic oxidation of toluene.

Selection of the catalytic systems, revealing high selectivity for processes of heterogeneous oxidation of hydrocarbons is one of the most important problems of petrochemistry. Liquid-phase oxidation of toluene is carried out in the industry in presence of bromine compounds, however process is complicated by necessity of allocation of homogeneous catalyst and recycling of by-products. Way out from this situation is development of technologically more perfect heterogeneous catalytic systems based on metal oxides, but process is low selective. To understand and eliminate lacks of these systems it is necessary to study chemistry of process more deeply. Particularly, an essential gap is absence of data on the nature of an oxidizer, i.e. forms of molecular oxygen, and also about a role of intermediate products.

According to literary data, primarily toluene was oxidized up to benzaldehyde and then - up to benzoic acids. Further on reaction of decarboxylation benzene formed, which through hydroquinone turns into maleic anhydride and carbon oxides.

The purpose of the present work was to establish the contribution of hydroquinone as the basic intermediate substratum forming maleic anhydride in partial catalytic oxidation of toluene.

Reaction of oxidation of toluene, as well as a mixture of benzene with hydroquinone (2-10 % of weights. hydroquinone) is carried out in the flowing reactor at temperature 300-500 °C on vanadium and molybdenum oxides. The volume concentration of feed in a steam-air mix was maintained about 2 % vol., rate of feed 0,5-1 p⁻¹.

Except for the base products of oxidation of toluene for all models in small or negligible quantities (less than 1 % of weights.) quinone, hydroquinone, anthraquinone are found. Formation of benzene is not fixed.

After the carried out researches, the following conclusions had been formulated: introduction of hydroquinone does not influence the products composition and do not reduce the formation of base product, i.e. plan of oxidation of aromatic hydrocarbons though hydroquinone foiled. Scheme for oxidation of aromatic hydrocarbons of singlet oxygen was proposed.

**Ru(III)-BASED HOMOGENEOUS CATALYTIC SYSTEM FOR
ENANTIOSELECTIVE HYDROGENATION OF C=O BOND**

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Ruthenium catalysts (P*P)RuCl₂ (P*P is chiral bisphosphine ligand) for homogeneous asymmetric hydrogenation reactions are traditionally prepared from RuCl₃, most accessible ruthenium starting reagent, by means of its transforming into intermediate complexes such as [(COD)RuCl₂]_n or (COD)Ru(2-methylallyl)₂ with subsequent replacement of COD (cycloocta-1,5-diene) ligand by chiral bisphosphine. We report now about using of new catalytic system: RuCl₃-BINAP-HCl [BINAP is (*R*)- or (*S*)-2,2'-bis(diphenylphosphine)-1,1'-binaphthyl] for asymmetric hydrogenation of C=O bond. This system proved to be highly competitive by its activity and enantioselectivity with similar Ru(II)-based catalytic systems, but for all that no intermediate π -olefine or allyl ruthenium complexes are required to prepare before. Using the new Ru(III)-based system for asymmetric catalytic hydrogenation of a number of ketoesters R-C(O)-CH₂CH₂COOMe (R = Me, Et, Pr, *iso*-Pr, Ph) has been performed to give chiral γ -hydroxyesters. In the course of hydrogenation ([ketoester]: [HCl]:[Ru]:[BINAP] = 200:5:1:1, MeOH, $p(\text{H}_2)$ = 15-60 atm, 65 °C, 6 h) hydroxyesters are cyclized into γ -alkylbutyrolactones characterized by high optical purity (up to 99 % ee). The results obtained open up possibilities to realize scaled-up process of enantioselective hydrogenation of γ -ketoesters taking into consideration that chiral γ -alkylsubstituted butyrolactones are valuable building blocks for pharmaceutical goals.

**MOLECULAR MECHANISM OF LOW TEMPERATURE DECOMPOSITION OF
HYDROGEN SULFIDE INTO HYDROGEN AND ELEMENTAL SULFUR**

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A new pathway of low temperature catalytic decomposition of hydrogen sulfide into hydrogen and sulfur is found. The reaction occurs at ambient temperature over sulfide catalysts in the following elementary steps: molecular adsorption of two molecules of hydrogen sulfide on two adjacent atoms of Co^{III} with d^6 electronic configuration \Rightarrow a dissociative chemisorption of hydrogen sulfide \Rightarrow the formation of S–S bond in the surface intermediate $2\text{Co}^{\text{III}}-\mu(\text{S}_2)_a$ following the release of the first hydrogen molecule into the gas phase \Rightarrow the release of the second hydrogen molecule into the gas phase \Rightarrow the formation of the cyclooctasulfur in the surface reaction ($4 \text{S}_2 \rightarrow \text{S}_8$). The first three steps can occur spontaneously without an activation energy. The thermodynamic driving force of the overall reaction appears to be the S–S bond formation inside the surface key intermediate together with the release of the dihydrogen molecule into the gas phase. The catalytic cycle is terminated with recombination (oligomerization) of molecular sulfur S_2 into cyclooctasulfur S_8 and removal of the second hydrogen molecule into the gas phase.

Experiments on the catalytic decomposition of hydrogen sulfide into hydrogen and elemental sulfur were carried out both in flow regime at room temperature. The sulfide catalyst was additionally sulfided in situ in a flow of H_2S at $400\text{ }^\circ\text{C}$, cooled down to $200\text{ }^\circ\text{C}$ and flushed out with argon or helium. Hydrogen was detected both by a thermal conductivity and thermochemical detectors. H_2S was passed through a catalyst bed at room temperature with concentration in helium (argon) ranged from 0.018 to 6 vol. %. After saturation of the catalyst surface with adsorbed H_2S , the catalyst was isolated and the closed system was heated to $40\text{--}70\text{ }^\circ\text{C}$ to avoid sublimation of elemental sulfur from the catalyst surface. In the gas phase only hydrogen was detected. The cycles H_2S adsorption \Rightarrow heating were repeated for several times until the catalyst surface was blocked with elemental sulfur. To remove sulfur, the catalyst was heated to $100\text{--}200\text{ }^\circ\text{C}$.

Acknowledgements

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**HYDROGENATION CATALYST ON THE BASE OF NANOCOMPOSITE Ni@C_{am}.
SYNTHESIS AND PROPERTIES OF CARBON-ENCAPSULATED METAL
NANOPARTICLES (Me@C_{am}, Me-Ni, Fe, Co, Al, Bi, Ag, Mg, Pd, Cu)**

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Metal-carbon nanocomposites on the base of different metals (Ni, Fe, Co, Al, Bi, Ag, Mg, Pd, Cu) were synthesized using gas condensation technique. Structure, morphology, physical and chemical properties of these composites were investigated. Ni@C_{am} nanocomposites were found to reveal extremely high catalytic activity in the reaction of magnesium hydrogenation during mechanical milling at room temperature.

The synthesis and investigation of metal carbon-encapsulated nanoparticles has attracted much attention due to potential technological applications, particularly, in magnetic storage media, in biotechnology, medicine and as catalyst materials for chemical processes. A very important feature of such nanocomposites is that the carbon-encapsulated nanoparticles are effectively protected from degradation since the carbon shell prevents interaction with environment.

At present the investigations of carbon-encapsulated metal nanoparticles have mainly focused on the preparation technique and characterization of nanocomposites, while little is known about their physical and chemical properties (for instance, catalytic activity and others).

In the given talk we report a new method of synthesis of the relatively stable carbon-encapsulated metal nanoparticles and the results of investigation of their physical and chemical properties.

Using the gas-condensation technique we succeed to prepare the nanocomposites Me@C_{am} in which different metals (Me = Ni, Fe, Co, Al, Bi, Ag, Mg, Pd, Cu and others) are encapsulated (@) in the carbon matrix C_{am}.

X-ray diffraction analysis, transmission electron microscopy, Raman spectroscopy and magnetic measurements were used to investigate the structure and physical properties of the obtained metal-carbon nanocomposites. It was shown that the structural state of carbon and quality of coating depends on synthesis regimes and type of the coated metal. The thickness of carbon coating amounts to few nanometers and depends on the type of metal, whereas the carbon structure was found to be amorphous (“glassy”) for all metals. The average particle

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size of metals encapsulated in carbon matrix varies from few nanometers up to tens nanometers for different metals and regimes of preparation, while for a given composite the particle size distribution is rather narrow.

To clarify the catalytic ability of nanocomposite Ni@C_{am} we used the reaction of magnesium hydrogenation in the process of mechanical milling of Mg in hydrogen atmosphere at room temperature. The hydrogenation of Mg alloys at mechanical activation in H₂ atmosphere is known to require the introduction of a catalyst. Mechanical activation of Mg with an addition of the well-known catalyst V₂O₅ allows us to synthesize 50% of MgH₂ hydride after 7 h of milling (in comparison with 60 h required to do the same without catalysts). The abnormally high catalytic activity was observed when the carbon-encapsulated nickel was applied as a catalyst in hydrogenation reaction at ball-milling of Mg in hydrogen atmosphere. The rate of Mg hydrogenation in the appearance of Ni@C catalyst exceeds at least one order magnitude than the utmost catalyst on the base of V₂O₅.

In the report we will discuss the possible mechanisms of catalytic activity of Ni@C_m for formation of MgH₂ during the mechanical activation in H₂ atmosphere and suggest the perspectives of the practical applications for Me@C_{am} nanocomposites for other purposes.

Acknowledgments.

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**COMPARATIVE STUDY OF THE EFFICIENCY OF Pt-, Pd- AND Ni-CATALYSTS
ON PILLARED TAGAN MONTMORILLONITE IN HYDROISOMERIZATION
OF n-HEXANE**

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Comparative results on the efficiency of Pt-, Pd- and Ni-catalysts on the base of aluminum pillared Tagan montmorillonite (MM) in reaction of n-hexane hydroisomerization are considered.

Experimental part

Method of preparing of pillared montmorillonite was described earlier [1]. Hydroisomerization of hexane was carried out in flow reactor at 250-400 °C, atmospheric pressure of hydrogen, molar proportion $H_2:C_6H_{14}=3,5$ and volume rate of n-hexane $0,82 \text{ hour}^{-1}$. Series of Pt, Pd, Ni-catalysts was tested. It was prepared by method of impregnation. Content of Pt and Pd was 0,35 mass.%. Content of Ni was 5 mass.%. An aluminum/clay ratio was 2,5;5,0 $\text{mmol}\cdot\text{g}^{-1}$. Reaction products and hexane were analyzed by gas chromatography with a capillary column and FID detector. The pillared samples have been studied by transmission electron microscopy (EM-125K). X-Ray diffraction pattern was recorded by a DRON-4*0.7 diffractometer using CoK_{α} radiation. The textural characteristics of samples were determined using the BET method.

Results and discussion

The textural characteristics of synthesized pillared AlMM are presented in Table 1.

Table 1 – Textural characteristics of pillared AlMM

Catalyst	$d_{001}, \text{Å}$	$\Delta d \text{ Å}$	$S_{m^2/g}$	$V_{ads}, \text{sm}^3/g$
MM	14,1	-	245,1	0,468
AlMM(2,5mmole Al^{3+}/g MM)	19,0	4,9	284,2	0,256
AlMM(5,0mmole Al^{3+}/g MM)	18,2	4,1	255,0	0,480
AlMM(7,5mmole Al^{3+}/g MM)	18,1	4,0	258,8	0,362

The intercalation is well occurred with a d_{001} -spacing increasing from 14,1 to 19,0-18,1Å. At the same time, the specific surface area increased from 245,1 to 284,2-258,8 $\text{m}^2\cdot\text{g}^{-1}$.

With introduction of Pt, Pd, Ni metals into pillared samples leads to disappearance of micropores and extention of mesopore zone. Changes of textural characteristics influences on

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activity of synthetic catalysts. Results of n-hexane isomerization are given in table 2 at ratio 2,5; 5,0 and 7,5mmole Al³⁺/g MM.

Table 2 – Hydroisomerization n-hexane on Pt-, Pd- and Ni-catalysts at 350-400⁰C.

Catalyst	T ⁰ C	α, %	S _{C6+}	Composition of reaction products, %							
				n-C ₅	i-B	2MB	2,2DM B	2MP	3MP	2,4D MP	3,3DM P
Pt/AlMM (2,5mmole/g)	350	58,1	100	-	-	-	0,5	38,6	18,3	-	0,7
	400	53,5	100	-	-	-	-	29,4	24,1	-	-
Pt/AlMM (5mmole/g)	350	39,0	99,5	-	-	0,1	1,5	20,7	13,9	1,3	1,5
	400	46,9	98,1	0,9	-	-	1,9	21,1	14,4	3,0	5,6
Pt/AlMM (7,5mmole/g)	350	49,8	98,8	0,5	-	0,1	2,4	26,7	17,1	1,2	1,8
	400	50,1	97,2	0,9	0,2	0,3	1,9	21,8	14,7	3,3	7,0
Pd/AlMM (2,5mmole/g)	350	29,3	100	-	-	-	0,3	7,3	21,7	-	-
	400	37,2	100	-	-	-	1,0	20,8	14,3	0,4	0,7
Pd/AlMM (5mmole/g)	350	28,9	100	-	-	-	0,1	18,6	10,0	0,1	0,1
	400	51,8	100	-	-	-	9,0	26,6	16,0	0,1	0,1
Pd/AlMM (7,5mmole/g)	350	25,3	100	-	-	-	0,4	16,8	8,0	0,1	-
	400	19,4	100	-	-	-	0,5	11,3	7,6	-	-
Ni/AlMM (2,5mmole/g)	350	8,7	87,4	-	-	1,1	-	4,3	3,0	0,3	-
	400	10,6	92,5	-	-	0,8	-	5,3	3,7	0,4	0,4
Ni/AlMM (5mmole/g)	350	4,5	100	-	-	-	0,5	2,0	1,6	0,4	-
	400	23,4	100	-	-	-	-	1,0	0,8	0,4	21,2
Ni/AlMM (7,5mmole/g)	350	4,9	98,0	-	-	0,1	-	2,6	2,0	0,2	-
	400	5,3	96,2	-	-	0,2	-	3,4	1,4	0,3	-

n-C₅-pentane; i-B-izobutane; MB-methylbutane; DMB-dimethylbutane; MP-methylpentane; DMP-dimethylpentane

Practically full absence of hydrocracking products is characteristic peculiarity of isomerization on the pillared MM. The Pt-catalyst showed the highest conversion (58,1 %), the Pd/AlMM gave 51,8 % conversion and Ni - 23,4 %. The reaction took place with 100 % selectivity to C₆₊-hydrocarbons. According to the electron microscopy data in the case of preliminarily reduced samples Pt- and Pd metal particles covered surface of carrier uniformly. Sizes of Pt particles were 30-50 Å and Pd - 50-110Å. Ni-catalysts contained an agglomeration of small particles with different degree of reduction (NiO, Ni₂O₂). Reduction didn't take place.

Absence of micropores and homogeneous distribution of metal particles can be the possible reason of high selectivity of metals on the AlMM surface.

NH₃ TPD results were shown that Al(2,5) MM had optimal acidity 277,5 mkmmole NH₃/g MM. Share of weak acid centers was 58,7 %. Introduction of metals increased the content of weak acid centers to 8,7-13 %. It was shown that the conversion of n-hexane with the content of middle (200-300 °C) acid centers (mkmmole NH₃/g MM): Pt(76,6)>Pd(76,4) >Ni(64,8) correlated.

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**MECHANISTIC STUDY ON THE OXIDATION OF FUNCTIONALIZED PHENOLS
AND NAPHTHOLS IN Ti-MMM-2/H₂O₂ AND FePcS-SiO₂/^tBuOOH SYSTEMS**

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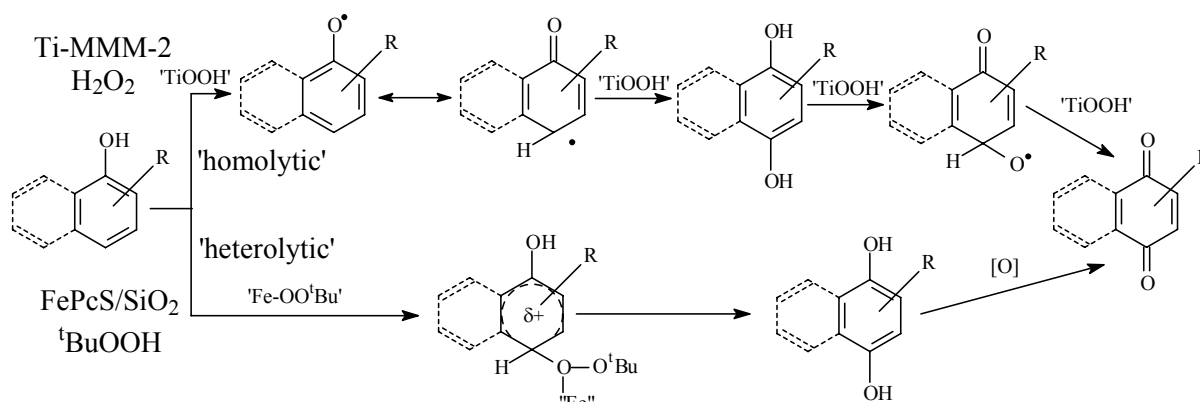
The mechanisms of the selective oxidation of alkyl-substituted phenols and naphthols with H₂O₂ and ^tBuOOH in the presence of heterogeneous catalysts, mesoporous titanium-silicate Ti-MMM-2 and silica-supported iron tetrasulfophthalocyanine FePcS/SiO₂, respectively, have been suggested based on the analysis of the main processes' regularities, by-product structures, and the results of the ESR study using spin traps.

Quinones bearing different functional groups are important products and intermediates in fine chemistry. For example, 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) is a precursor in the synthesis vitamin E and 2-methyl-1,4-naphthoquinone ('menadione', vitamin K₃, MNQ) is a synthetic analog of vitamin K widely used as a blood-coagulating agent. The development of environmentally benign methods for the production of functionalized quinones *via* oxidation of the corresponding phenols with clean oxidants over true heterogeneous catalysts is a challenging goal.

Recently we have found that oxidation of 2,3,6-trimethylphenol (TMP) and 2-methyl-1-naphthol (MNL) with H₂O₂ over hydrothermally stable mesoporous titanium-silicate catalyst Ti-MMM-2 [1-3] and with *tert*-butylhydroperoxide (^tBuOOH) over iron tetrasulfophthalocyanine (FePcS) anchored on silica [3-5] afford TMBQ and MNQ with a moderate to high yield. The different effects of the substrate concentration and catalyst amount on the selectivity to quinones observed in the two catalytic systems indicated different oxidation mechanisms. The product study by ¹H NMR and mass-spectrometry revealed that the main by-products formed in the Ti-MMM-2/H₂O₂ system are C-C-coupling dimers, which is consistent with a homolytic oxidation mechanism. Indeed, intermediate aryloxy and oxyaryloxy radicals were identified by ESR using the spin trap DBNBS (3,5-dibromo-4-nitrosobenzene-sulfonic acid). On the contrary, no C-C-coupling by-products and radical intermediates were found in the FePcS/SiO₂/^tBuOOH catalytic system. The main by-products of MNL oxidation in this system were 2-methyl-2,3-epoxy-1,4-naphthoquinone and 1,2-dihydro-2-*tert*-butylperoxy-2-methyl-1-oxonaphthalene. All these facts collectively allowed

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us to suggest that oxidation of alkylphenols (naphthols) in the Ti-MMM-2/H₂O₂ and FePcS/SiO₂/^tBuOOH systems proceeds via the homolytic and heterolytic mechanisms, respectively (Scheme 1).



Scheme 1.

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THE CHARACTERISTICS OF INDIVIDUAL HYDROGEN FORMS CONNECTED BY THE SURFACE OF THE SKELETAL NICKEL CATALYST IN SOLUTIONS

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Thermodynamic characteristics of individual forms of hydrogen adsorbed on the surface of the skeletal nickel catalyst of various nature and structure solvents are calculated according to the data of adsorption–calorimetric experiment. The quantitative redistribution between the individual forms of the adsorbed hydrogen is shown to be a principal cause of solvents nature and structure influence on the laws of adsorption.

The numerous researches of real catalysts properties on the basis of metals and their oxides, skeletal nickel catalysts included, have shown their surface to be energetically heterogeneous. The principal cause of power surface heterogeneity is the existence of various forms of the reacting substances adsorbed on the active centers of the catalyst. Thermodynamic characteristics of the adsorption stages of hydrogen on catalytic active surfaces are known to define the energy of intermediate interactions, speed and selectivity in liquid phase hydrogenation reactions.

The analysis of literature data and the adsorption–calorimetric measurements evidence that there are three individual forms of hydrogen on the surface of the skeletal nickel catalyst at a room temperature – one molecular α_1 –form and two atomic γ – and β_2 –forms, the bond energies with the surface being 20÷40, 60÷100 and 125÷250 kJ/mol, respectively. Nowadays thermodynamic characteristics of adsorbed hydrogen individual forms have been obtained for the processes, proceeding in a gas phase on ideal monocrystals surfaces. Moreover, the findings are often unreasonably transferred to liquid phase catalytic systems. The laws of hydrogen adsorption in liquid phase processes significantly depend on the nature and structure of a solvent. However, the reasons of solvent influence on the laws of hydrogen adsorption on the surface of metals and catalysts in solutions remain obscure.

Data about the quantity of the adsorbed hydrogen, sizes of adsorption at various pressures of hydrogen, heats of adsorption depending on a coverage in various solvents at 303 K, obtained by an adsorption–calorimetric method, as well as literature data, allowed us to calculate thermodynamic characteristics of the individual forms of the hydrogen. They were adsorbed from solutions on the surface of skeletal nickel catalyst. These thermodynamic

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characteristics are as follows: limiting adsorption $a_{m_{i,j}}$, adsorptive factors $b_{i,j}$, standard heats $\Delta_a H_{i,j}^o(H_2)$ and changes of the Gibbs energy $\Delta_a G_{i,j}^o(H_2)$ and entropy $\Delta_a S_{i,j}^o(H_2)$ of the adsorptions. Calculations were made for the catalytic systems, consisting of the skeletal nickel catalyst and solvents, such as aliphatic spirits, dimethylformamide, ethylacetate, their aqueous solutions and also aqueous solutions of sodium hydroxide. Thermodynamic model of a surface with discrete heterogeneity was used for ideal surface calculations within two alternative schemes, considering the various formation mechanisms of atomic forms. Some results of the calculations are listed in the table.

Table. Thermodynamic characteristics of hydrogen individual forms adsorbed from solutions on surface of skeletal nickel catalyst.

Solvent		Water	Ethanol	2-propanol	Aqueous solution of ethanol with $x_2=0,28$
$a_{m_{i,j}}$, cm ³ H ₂ /g Ni	α_1 -form	2,1±0,1	1,9±0,1	3,0±0,2	7,2±0,4
	γ -form	8,1±0,4	9,8±0,4	12,0±0,6	10,2±0,5
	β_2 -form	9,7±0,5	7,8±0,4	4,0±0,2	3,1±0,2
$b_{i,j}$	α_1 -form	327,3±16,4	125,0±6,3	120,0±6,0	48,0±2,4
	γ -form	(4,1±0,2)·10 ³	(5,9±0,3)·10 ⁴	(2,6±1,0)·10 ⁴	(1,1±0,1)·10 ³
	β_2 -form	(9,5±0,5)·10 ⁵	(3,1±0,2)·10 ⁶	(4,4±2,0)·10 ⁶	(2,4±0,1)·10 ⁶
$-\Delta_a H_{i,j}^o(H_2)$, kJ/mol	α_1 -form	26,0±1,3	32,9±1,6	30,9±1,5	32,2±1,6
	γ -form	62,0±3,1	59,8±3,0	50,0±2,5	63,3±3,2
	β_2 -form	138,3±6,9	138,5±6,9	144,0±7,2	142,5±7,1

The results of calculations showed that thermodynamic characteristics of individual forms of the hydrogen depend on the nature and structure of solvents. Their influence occurs through the changes of the limiting adsorption, adsorptive factors, standard heats of the adsorptions and also the change of entropy and normal affinity of hydrogen as a result of structure arrangement of a metal surface and its specific solvation by solvent. Quantitative redistribution between individual forms of the adsorbed hydrogen, caused by the displacement of the superficial balances under action of a solvent is a principal cause of influence of the nature and structure of solvents on the laws of hydrogen adsorption on the skeletal nickel catalyst.

CARBON INDUCED FCC-COBALT SURFACE RECONSTRUCTION**Ciobîcă I.M., van Santen R.A.¹, van de Loosdrecht J.², van Berge P.J.²***Sasol Technology Netherlands B. V., Eindhoven University of Technology**P. O. Box 513, 5600 MB Eindhoven, The Netherlands*¹*Schuit Institute of Catalysis, Eindhoven University of Technology,**P. O. Box 513, 5600 MB Eindhoven, The Netherlands*²*Sasol Technology (Pty) Ltd, 1 Klasie Havenga Street, 1947 Sasolburg, South Africa**E-mail address: Ionel.Ciobica@Sasol.com*

The interaction of carbon with cobalt surfaces is extremely important due to the technological relevance of the system, particularly in the field of heterogeneous Fischer Tropsch synthesis (FTS) catalysis (integral part of the Gas-To-Liquids process), and the fundamental interest in explaining the nature of the carbon induced surface reconstructions. Several types of carbon may be present on the surface, for example, active carbon is formed at lower temperatures and polymeric or graphitic carbon is formed at higher temperatures. This paper focuses on the role of carbon and other potential Fischer-Tropsch synthesis species which are present on the cobalt surface and can induce surface reconstruction of specific cobalt surfaces.

DFT calculations were performed with the VASP code (Vienna *ab initio* Simulation Package). The model for the unreconstructed cobalt surfaces consists in 4, 5 and 7 layers for FCC-Co(111), FCC-Co(100) and respectively FCC-Co(110) and 5 layers of vacuum. For the reconstructed cobalt surfaces we used 5 layers from which 3 internal layers of FCC-Co(111) structure, plus 2 reconstructed layers. Full optimisation of the systems was carried out and no symmetry constraints were applied. The comparison of the (111), (100) and (110) slabs is not made based on the adsorption energies but rather on the total energy of the system.

Due to the fact that small cobalt crystallites in Fischer Tropsch synthesis catalysts are in the FCC phase [1], the focus of this paper will be on this FCC phase, rather than on the HCP phase. O, CO, C, CH and CH₂ were selected to preliminary investigate as possible candidates to effect (111) to (100) and (111) to (110) cobalt surface reconstructions, as they are typical FTS intermediates.

The difference in absolute energy of the Co(111) and Co(100) bare surfaces is 2.2 eV, which corresponds to a 2×2 unit cell (4 metal atoms on each layer, so 4 metal atoms at the surface as well). Adsorbing C atoms on the cobalt surfaces results in a decrease of the difference to 0.1 eV at 25% coverage and most important, the order of stability of the two

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surfaces changes at 50% coverage, with a difference of 3.0 eV. It can thus be concluded that C can induce a surface reconstruction. Carbon favours the more open surface, which is opposite to O and CO. If one C atom is positioned subsurface the difference is less, 1.2 eV, but the order is still changed.

For a coverage of 50 % carbon on the Co(100) there are two different surface configurations possible. One would be when carbon atoms form rows on the surface (in this case each C atom shares two metal neighbours with the next C atom) or when they forms zig-zags (each C atom shares one metal neighbour with the next C atom). Only the second one would be suitable for the clock reconstruction similar to the Ni(100) [2]. The adsorption energy of carbon in the two original situations as well as the clock reconstruction structure are: -732.46, -760.96 and respectively -774.47 kJ/mol with respect to the bare Co(100) surface and C in the gas phase. This shows that carbon induced clock reconstruction of the Co(100) is possible from an energetic point of view.

The barrier for carbon induced clock reconstruction of FCC-Co(100) was found to be extremely small (about 1 kJ/mol) for a reconstruction starting with carbon atoms in the diagonal arrangement. So the process of reconstruction is not kinetic hindered.

Other species, B, CH, N and O are not able to induce the clock reconstruction of FCC-Co(100) surface. Adsorbed carbon prefers adsorption on five coordinated sites, on surfaces as well on clusters. Binding is strongly covalent with carbon atom connected to four metal atoms in the plane and one below. The strong interaction with the latter is confirmed in our calculations. To optimise its local coordination is the main driver for the clock reconstruction and also explains the extreme stability of carbon adsorption on the (100) surface of FCC-cobalt.

From the series of adsorbates: O, CO, CH₂, CH and C, we predict that only the latter is able to induce a surface reconstruction from FCC-Co(111) to FCC-Co(100), such a surface reconstruction has been experimentally reported for Ni(111) to Ni(100). Looking at the clock reconstructions, again C is the only species which can induce this reconstruction on the FCC-Co(100) surface, again similar to experimental and theoretical conclusions on Ni(100). The unique behaviour of carbon appears to be related to its stability when adsorbed in four fold hollow site with five metal atoms neighbours.

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**THE PACKAGE STEP+ FOR NUMERICAL STUDY OF AUTONOMOUS SYSTEMS
ARISING WHEN MODELING CATALYTIC PROCESSES**

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In this paper we present the package STEP+ realizing a complex of methods for numerical analysis of autonomous systems of differential equations. Study of behavior of solutions of the given class of systems in dependence of parameters is one of the important parts of the general problem of constructing mathematical models adequate to experimental data. This package includes algorithms for numerical study of abstract autonomous systems consisting of N equations of the form

$$dy/dt = f(y,p), \quad (1)$$

where $p \in R^m$ is a vector of parameters. Among these algorithms there are integration of systems of the form (1) with given initial conditions (Cauchy problem), constructing stationary solutions in dependence of a parameter α , $\alpha \in p$, i.e., solutions of the system of nonlinear equations

$$f(y, \alpha) = 0, \quad (2)$$

and study of asymptotic stability of the obtained stationary solutions.

The package STEP+ is intended for numerical study of autonomous systems and systems of nonlinear transcendent equations. The present version of the package for Windows is a version of the package STEP (Fadeev et al, 1998). The kernel of STEP+ is universal and allows the user to research numerically arbitrary systems consisting of N ordinary differential equations of the form (1). The package STEP+ uses original computational algorithms elaborated at the Sobolev Institute of Mathematics SB RAS for study of dynamical systems: a variant of the parameter continuation method, the Godunov-Bulgakov method (so called κ -criterion) for study of stability of solutions. These algorithms make it possible to research systems of arbitrary orders and take into account nonlinear effects (hysteresis, strong parametric sensitivity, self-oscillations and etc.) observed, as a rule, in mathematical models describing catalytic processes. In this package we realized also standard methods of numerical integration for stiff problems; in particular, multistep Gear's method of fractional accuracy order (Gear, 1971) and etc. Detailed descriptions of the methods can be found in the textbook (Fadeev et al, 1998). The package STEP+ allows us:

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- 1) using the parameter continuation method, to establish numerically dependence of stationary solutions $y(\alpha)$ of the system (2) on parameter α and indicate domains of multiple solutions;
- 2) to study stability of the stationary solutions and mark points, on the diagram of the stationary solutions, where an unstable stationary solution passes into a stable limit cycle (Hopf bifurcation);
- 3) integrating autonomous systems, to obtain self-oscillations or start looking for stationary solutions which can be chosen as initial solutions for the continuation method;
- 4) to point out domains of α , where all stationary solutions are unstable, i.e., self-excitation of self-oscillations for any initial data.

The structure of the package STEP+ is intended for organization of numerical experiments to study mathematical models presented by autonomous systems and systems of nonlinear equations. This package consists of four divisions: “Model development”, “Cauchy problem”, “Stationary solutions”, and “Nonlinear systems”. The package STEP+ provides for automatic input right-hand sides of autonomous systems of differential equations by means of a converter-program. To run any calculated program and input calculated parameters by means of user interface we produced a program for generation of DLL library. Owing to special input form of right-hand sides of systems of differential equations, this generator finds analytically the Jacobi matrix $df_i / dy_j, i = 1, \dots, N, j = 1, \dots, N$, and the matrix consisting of partial derivatives with respect to parameters $df_i / dp_j, i = 1, \dots, N, j = 1, \dots, m$. Admissible order of dynamical systems is equal to 1000. The package contains a series of models among which are mathematical models of catalytic processes, developed at the Boreskov Institute of Catalysis SB RAS (Gainova et al, 2006), and models from the literature. The package STEP+ is realized in the visual programming environment Visual Basic.NET and intended for Windows 2000/XP.

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**QUANTUM-CHEMICAL STUDY OF Zn AND Ni ATOMS INTERACTION WITH
PHENYLPROPARGYL AND CINNAMIC ALCOHOLS MOLECULES**

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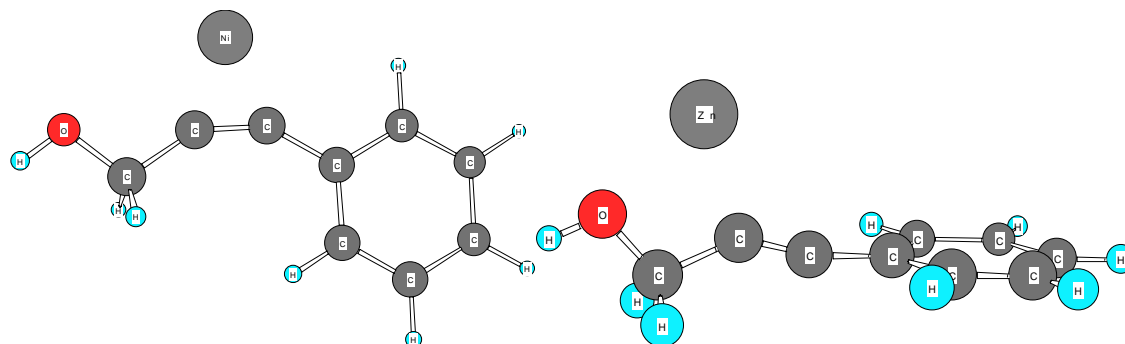
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The analysis of interactions of Zn and Ni atoms in their complexes with phenylpropargyl and cinnamic alcohols is performed on the base of quantum-chemical calculations by B3LYP/6-31G(d,p) method.

The electrocatalytic hydrogenation of the triple carbon-carbon bond in phenylpropargyl alcohol (PhePA) proceeds to the end by using of skeletal Ni for a cathode activation, and stops on the stage of cinnamic alcohol (CA) in the case of using Zn skeletal catalyst [1]. The different catalyzing effect of the metals is caused by the electronic structure of their external shell: Ni ...3s²3d⁸4s² and Zn ...3s²3d¹⁰4s². The calculations for model complexes M + PhePA and M + CA (M= Ni, Zn) carried out by means of B3LYP/6-31G(d,p) method with the aim of the more detailed analysis of the interaction of Ni and Zn atoms with phenylpropargyl and cinnamic alcohols.

According to the obtained results, Ni atom interacts with acetylenic bond of PhePA forming a rather stable π -complex that is attended by the *cis*-bending of PhePA molecule:



In the case of Zn the weak stable σ -complex is formed, in which Zn atom connects stronger with one of the carbon atoms of acetylenic bond, as well as with oxygen atom of OH-group. A small *trans*-bending of PhePA molecule is taking place in the complex. This is in a good agreement with experimental data [1] indicated that *trans*-isomer of cinnamic alcohol is a dominant product of electrocatalytic hydrogenation of PhePA on the Zn catalyst.

As a result of coordinating interaction the partial positive charges arise on Ni and Zn: 0,285 and 0,120 respectively. This indicates the electron density transition from the metal

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atoms to PhePA molecule. In so doing the partial negative charges on carbon atoms of triple bond increase with their evenly distribution in complex Ni + PhePA and with their greater polarization in complex Zn + PhePA by comparison with individual PhePA molecule. The C≡C bond length increases by 0,100 Å in complex Ni + PhePA and by 0,030 Å in complex Zn + PhePA that is enough for the successful adding of hydrogen.

In complex Zn + CA the interaction of Zn atom with carbons of the ethylenic bond falls off, but it enhances with oxygen of OH-group. The small negative charge (-0,055) appears on Zn atom. The C=C bond elongates negligible (by 0,006 Å), and its hydrogenation does not happen. To put this another way, the hydrogenation of C=C bond on Zn catalyst is impassible because of the discrepancy of orbital symmetry of the interacting molecular orbitals of CA molecule and Zn atomic orbitals.

In complex Ni + CA the interaction of Ni atom with ethylenic π -bond weakens too, but supplements with the connecting of oxygen atom. This can be illustrated by the values of bond orders: in complex Ni + PhePA they are equal to 1,011 and 0,999 for Ni...C¹ and Ni...C² bonds. In complex Ni + CA they are 0,821 and 0,733, and 0,336 for Ni...O bond. The C=C bond length grows by 0,132 Å (by a comparison with CA molecule), and hydrogen adds without hindrance to the bond.

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THE HETEROGENEOUS CATALYSIS LAW

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There is defined a relation having a universal character and imposing a restriction upon kinetics of a catalytic reaction. A quantitative criterion for a definition of catalytic reaction mechanism is determined.

Gas molecule chemisorption on the surface of solids is carried out through a precursor state – an intermediate state conditioned on that that gas molecules captured with the surface lost energy of forward and rotary movements not immediately, but during a period of $\sim 10^{-11}$ s. Being in a precursor state molecules react with adsorbed molecules of other nature. In the case of catalytic reaction passing on the boundary of a solid and a gas mixture ($\sum_i M_i$) molecules M_i caught by a surface in a precursor state and pass in one of three possible competitive states according to a condition:

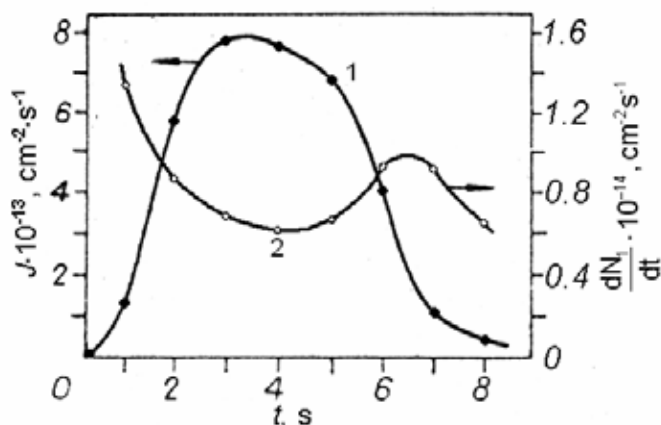
$$q = q_1 + q_2 + q_3 \quad (1)$$

where q, q_1, q_2, q_3 - flows of M_i passed accordingly: q – from atmosphere into a precursor state; q_1 – from a precursor state into atmosphere; q_2 – in a state of chemisorption; q_3 – in a state of a constituent of product molecule (or a particle of transient formation) of reaction. Equality (1) is carried out at an arbitrary point of time because of that that the life span of molecules in a precursor state is lesser of a typical period of relaxation on an adsorption layer for many of orders. Therefore condition (1) imposes a restriction upon kinetics of heterogeneous process just as conservation laws of impose restrictions upon possible nuclear reactions. Equality (1) is universal inasmuch as it is correct at the interaction of arbitrary atmospheres with the surface of arbitrary solids (including, when $q_3 = 0$). Condition (1) can be considered as a decree of nature as applied to heterogeneous processes.

The energy of activation for chemical transformations with the participation of molecules in a precursor state is considerably less than a potential barrier for competitive processes of product molecule formation in the layer of chemisorbed particles. If the phase of a heterogeneous chemical reaction being described with condition (1) limits formation of product or a product molecule are formed directly in this stage then for the reaction rate we obtain expression $J = q_3 = q - q_1 - q_2$. As an example we present results obtained at the

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interaction of CO molecule beam with oxygen adsorbed on the verge of Pd (111) (Fig.) [1]. The procedure of slope opposition of kinetic curves for a CO₂ formation rate (curve 1) and a CO chemisorption rate (curve 2) [provided that condition (1) is observed] is conditioned on the competition of transitions of physically adsorbed molecules of CO in two states: chemisorption and some molecules of CO₂.



A time change of CO₂ formation rate (1) and a rate of concentration changes in chemisorbed molecules of CO₂ on the verge of Pd (111) covered with adsorbed oxygen under the influence of CO molecular beam at $T = 374K$. Firm lines – experimental results [1], dots – calculated.

It is ascertained that for definition a catalytic reaction mechanism it is necessary to use a quantitative criterion. The reaction passes according to Langmuir-Hinschelwood mechanism at the condition compliance: $\tau J_0 \theta_0^{-1} < 1$, where J_0 and θ_0 - a rate of reaction and concentration of chemisorbed molecules under steady conditions; τ - relaxation time at the change of surface cover degree after step starting or ending of the gaseous matter flow reacting to the surface of a catalyst. It is defined: in all heterogeneous reactions researched through time-dependent methods: $H + H \rightarrow H_2$, $O + O \rightarrow O_2$, $CO + O \rightarrow CO_2$, $2H_2 + O_2 \rightarrow 2H_2O$ and $2CO + O_2 \rightarrow 2CO_2$ gas particles in a precursor state take part in molecule formation. On the basis of this established regularity one can expect that the overwhelming majority of other heterogeneous reactions also submit to condition $J = q - q_1 - q_2$.

Models of heterogeneous reactions must describe correctly the adsorption of gas molecules reacting on the surface. The neglect of the intermediate precursor states in which molecules are most chemically active, leads to a wrong interpretation of experimental data.

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DEVELOPMENT OF KINETIC MODELS OF CELLULOSE-BASED BIOMASS PYROLYSIS

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The kinetic models of cellulose-based biomass pyrolysis were investigated at the inert atmosphere using TGA and DTG analysis in isothermal or dynamic (non-isothermal) mode. The non-isothermal decomposition was studied at different heating rates and for the different particle size fractions. It was shown that the kinetic nucleation model of auto-accelerated decomposition reaction has a best fit to weight-loss of sample. The kinetic parameters of reactions (values of pre-exponential constant and activation energy) were determined using the method of Coats-Redfern and numerical model. Correlation between weight-loss and composition of gaseous products of pyrolysis was also defined.

In view of the increase of energy demand, the high costs of fossil fuels and disposal, as well as the environmental concern about levels of CO₂ in the atmosphere, the use of biomass to provide partial substitution of fossil fuels for steam and power generation is of growing importance. The flash and slow pyrolysis of biomass is the main method for bio-fuel production. A lot of parameters influences on yield and quality of biomass pyrolysis products: gas, liquid and solid. The temperature, thermotreatment time, type of cellulose-based biomass, impurities content, size of biomass particles are most important factors influencing on the composition and distribution of products.

Knowledge of the chemical composition, the thermal behaviour and the reactivity of agricultural and wood waste during pyrolysis is very important for the effective desing and operation of the thermochemical conversion units, given that solid devolatilization is always a fundamental step. Thermoanalytical techniques, in particular thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) allow this information to be obtained in a simple and straightforward manner.

The aims of this work were to investigate the thermal behaviour of agricultural and forestry waste during the pyrolysis process, to develop a kinetic model for these lignocellulosic materials (sorghum, rice husk, pine sawdust), to study the influence of impurities and catalyst content, size of feedstock particles and operating conditions on the process characteristics and the kinetic parameters. In this work thermogravimetric analysis carried out both in dynamic mode at the constant heating rate between 3 and 72 °C/min and in isothermal mode at the various temperatures kept constant between 240 and 310 °C. In both

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cases method of Coats-Redfern and numerical model were used for determination of kinetic parameters of decomposition of sample components. The main components of the biomass samples are cellulose, hemicellulose and lignin, in addition to extractives, water and mineral matter.

A variety of kinetic models were tested, including first-order, nucleation (Avrami-Erofeev and Prout-Tompkins models), diffusion and phase boundary reactions. It was shown that the kinetic nucleation model of auto-accelerated decomposition reaction has a best fit to weight-loss of sample. The dynamic and isothermal pyrolysis carried out in the presence of sodium, potassium and nickel salts displayed a dramatic increasing of decomposition rate of each component of lignocellulosic materials. The obtained results show a decreasing of activation energy as compared to decomposition of pure components of biomass (cellulose, hemicellulose and lignin).

In order to investigate the influence of the particle size on the peculiarities of pyrolysis process a several fractions with different size were analyzed ($d < 50 \mu\text{m}$, $50 - 100 \mu\text{m}$, $125 - 160 \mu\text{m}$ and $200 - 315 \mu\text{m}$). The heating rate employed in these experiments was $3^\circ \text{C}/\text{min}$. The results shown that decomposition of smaller fraction occurring at lower temperature, this effect can be observed as a shift in the peak maximum temperatures on DTG curves.

For experiments in isothermal and non-isothermal modes the numerical model including three parallel reactions of cellulose, hemicellulose and lignin decomposition is simulated and the best values of pre-exponential constants and activation energies were found.

The present work constitutes the first attempt to achieve successful fits to a consistent number of TGA curves with nuclei-growth model and by using a single set of kinetic parameters of real operating biomass materials.

The work was financially supported by Program “Leading Scientific Schools” (grant NSh-6526.2006.3) and Integration projects N 2 and 24 SB RAS.

**NOVEL STATISTICAL LATTICE MODEL FOR THE PHYSICOCHEMICAL
PROCESSES PROCEEDING OVER THE SUPPORTED NANOPARTICLE**

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The aim of the study is to reveal the mutual influence the shape and the surface morphology of the supported nanoparticles on the reaction kinetics. The analysis has been provided by means of the novel statistical lattice model, imitating the physicochemical processes over the supported particles. The influence of monomolecular and dissociative adsorption on the equilibrium shape and surface morphology has been studied. The model reaction $2A+B_2 \leftrightarrow 2AB$ has been studied taking into account the roughening of the particle surface and the spillover phenomena of the adsorbed A_{ads} over the support.

The influence of monomolecular and dissociative adsorption on the equilibrium shape and surface morphology has been studied. To simulate the active metal particle the finite Kossel crystal located on the inert support has been chosen. To simulate the diffusion of the metal atoms over the metal and support surfaces the standard the Metropolis algorithm [1] has been used.

It has been shown that at increasing of interaction energies «adsorbate-metal» the reshaping of the initial equilibrium (hemispheric) particle into cone-shaped one occurs induced by adsorption. In the case of bimolecular dissociative adsorption the surface regions of the metal particle become the pronounced «chessboard» structure (alternate vacancies and point defects). The adsorption isotherms simulated with taking into account the interaction between atoms of metal and adsorbate differ noticeably from the ideal Langmuir isotherm.

The model reaction $A+B_2$ has been studied (monomolecular adsorption of A , dissociative adsorption of B_2 and reaction between A_{ads} and B_{ads}) taking into account the roughening of the particle surface and the spillover phenomena of the adsorbed A_{ads} species over the support.

The kinetic dependencies of A_{ads} and B_{ads} coverages normalized on the number of the active sites of the catalyst particle *versus* molar ratio $Y_A = P_A/(P_A+P_{B_2})$ (P_i are the partial pressures of the reagents in the gas phase) obtained at different variants of the model reaction performance (with or without A_{ads} species and/or metal atoms diffusion, various ratios of interaction energies, etc.) has been compared with ones of the well-known Ziff-Gulari-Barshad model [2]. In our case ZGB-model corresponds to the performance of the reaction only on the initial flat uniform surface of the catalyst particle without any diffusion of

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adsorbates and metal atoms. Introducing into the model the A_{ads} molecules diffusion over the metal and support surface leads to the considerable decrease of the unit B_{ads} coverage region observed in ZGB-model and to a minor shift (from 0.51 to 0.48) of the reaction rate maximum to the smaller values of Y_A (in contrast to the behavior of ZGB-model with A_{ads} diffusion) [3, 4]. This effect is connected with additional source of A_{ads} molecules due to the spillover from the support to the active particle. In that way, the spillover effect leads to the effective increasing of the A reagent partial pressure. Two reaction channels exist in this case. The first channel is the diffusion one. The reaction occurs via the adsorption of A -molecules on the support followed by diffusion to the particle and proceeds on the boundaries of the B_{ads} atoms island with the dense core. The diffusion channel takes place at all values of Y_A starting from very low Y_A . The second channel is an adsorption one that leads to the rarefaction of the dense core of adsorbed B_{ads} island.

When the reaction proceeds on the non-regular roughened surfaces all the regions with sharp stepwise changing of adsorbates coverage disappear (in this case the number of active sites convenient for B_2 adsorption is restricted). Introduction of the diffusion channel leads, as earlier, to the shift of the reaction window to the smaller values of Y_A . In this case we can observe, again as earlier, the preferred occurrence of the reaction at the boundaries of the dense core of adsorbed B_{ads} island at low values of Y_A . Introduction into the model the diffusion of surface metal atoms results in the further change of the kinetic dependencies which is connected with the dynamic change of the surface morphology determining the geometric impediments for B_2 adsorption.

Thus it has been shown (in the frames of the proposed model) that the shape of the active particle can change under the influence of the adsorbed layer, even in the absence of the “adsorbate-metal” interactions and that the kinetics on the nanometer-size particle can be remarkably different from those corresponding to the infinite surface.

Also it has been shown that the shape of the active particle change in the presence of the “adsorbate-metal” interaction too.

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**KINETICS OF ACID-BASE CATALYZED HYDROLYSIS OF
PENTACHLOROPHENOL AND BROMOXYNIL IN AQUEOUS MEDIA**

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The rate of acid catalyzed hydrolysis of the pentachlorophenol (PCP) can be described by the general equation $-d[\text{PCP}]/dt = k_{\text{exp}}[\text{PCP}]$. The experimental pseudo-first order rate constant generally increases with increase of H^+ concentration, but this dependence has a complex character. A kinetic model, which takes into account the pK_a of PCP and a combination of catalyzed and un-catalyzed reaction was suggested. This model is consistent with experimental results in the whole range of pH studied.

The rate of base-catalyzed hydrolysis of the nitrile herbicide bromoxynil (3,5-dibromo-4-hydroxy-benzonitrile) is described by the equation $-d[\text{bromoxynil}]/dt = k[\text{bromoxynil}][\text{OH}^-]$. Extrapolation of laboratory results to environmental conditions (pH 6-8, moderate temperature) predicts that the hydrolytic stability of these pesticides can be much higher than previously reported.

Pentachlorophenol (PCP) and Bromoxynil (Bromox) are highly to extremely highly toxic to aquatic organisms, and highly soluble in water. It is commonly believed, that when released into water they will be partly absorbed to sediment and particulate matter with consequent biodegradation on the bottom of the pond. In subsurface water (10-20 cm deep) they can be destroyed by photolysis. However, fate of truly dissolved PCP and Bromox between subsurface water and pond sediments remains unknown. Numerous water monitoring data show, that low concentrations of PCP and/or Bromox are commonly found in natural aqueous environments. Taking into account high toxicity of PCP and Bromox to aquatic life, hydrolytic stability of these substances is of much interest. Unfortunately, it was impossible to study the stability of PCP and Bromox to hydrolysis at conditions close to environmental (neutral solutions, reasonable temperature). Aqueous solutions of PCP and Bromox have shown no sign of destruction after 90 days in the darkness at room temperature. Even after 9 hrs of boiling, neutral (pH 6-8) solutions of PCP and Bromox did not show any significant traces of decomposition. We have found, however, that decomposition of PCP can be accelerated in acidic media, while decomposition of Bromox is catalyzed by bases. The reaction of Bromox disappearance was studied at concentration of NaOH 10^{-4} - 10^{-1} M, while acid-catalyzed kinetics for disappearance of PCP was studied at H^+ concentration 0.5M - 10^{-5}M . Data obtained at high temperature and relatively high OH^- or H^+ concentration

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were extrapolated then to the region of interest, pH 6-8 and temperature 25 °C. Results of such estimations show, that both Bromox and PCP should be very stable at moderate temperatures and pH in pure dissolved state in main water body. This can explain discrepancies between reported half-lives of Bromox and PCP in subsurface water measured merely by days, and in sediment by months, and constant presence of PCP and Bromox in natural water samples long after they were used in surrounding areas.

**CALCULATIONS OF CO ADSORPTION ENERGY ON TRANSITION METAL
CARBIDES AND OXIDES BY IBM AND UBI-QEP METHODS**

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Results of estimation of CO adsorption energy on the surfaces of some transition metal oxides and carbides by empirical methods of interacting bonds (IBM) and UBI-QEP are presented. The results are compared with experimental values of adsorption energy and results of *ab initio* calculations; it is shown that IBM allows to obtain better qualitative and quantitative agreement between estimated and experimental values rather than UBI-QEP, and so it is a promising method for vast calculations of properties of reaction intermediates on real catalytic surfaces.

The development of the approach to realization vast calculations of characteristics of intermediate species and elementary reactions in catalysis and, accordingly, to a prediction of catalytic action approved earlier [1] with the use of variational empirical methods – interacting bonds method (IBM) [2] and UBI-QEP [3] – is presented. IBM advantage over wide-known UBI-QEP has been shown on the examples of CO and CH₃ adsorption energy calculations for ideal and defected surfaces of some transition metals [1]. IBM not only has shown better agreement between estimated adsorption energies and experimental and *ab initio* values than UBI-QEP, but also appeared to be able to describe correctly changes of adsorption energies on some defects (step, kink), that is impossible in principle for UBI-QEP. Moreover, IBM basic equation determining atomisation energy H_{ar} of a species

$$H_{ar} = \sum \gamma_i (2 - \gamma_i) E_i - \sum \sum_{i>j} \gamma_i \gamma_j \Delta_{ij} \quad (\gamma_i \text{ is varied independently})$$

as against apparently similar UBI-QEP equation

$$H_{ar} = \sum \gamma_i (2 - \gamma_i) E_i \quad (\text{for the selected bonds } \sum \gamma_i = 1)$$

has a quantum mechanical validation [2].

Just as the presentation [1] have targeted a model transition from ideal metal catalysts to realistic ones so the next logical step is an application of IBM and UBI-QEP for calculations of adsorption energies on chemically nonuniform catalytic surfaces; here CO adsorption on the surfaces of VIII group metal oxides and carbides is considered. The obtained results show that UBI-QEP (as against a situation with defective surfaces) is able in principle to take into

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account an influence of oxygen or carbon near-surface lattice atoms on CO adsorption performance; however, as well as in [1], better qualitative and quantitative agreement of adsorption energy estimated values with experimental data (and *ab initio* results also) is achieved by IBM. At the same time, IBM inherent defects (inaccessibility of chemical accuracy in general, inability a priori to predict preferable coordination molecular adsorbate) are kept; a probable way of their overcoming is a revision of simplifications made at the derivation of the IBM basic equation.

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ADSORPTION OF RHODIUM (I) DICARBONYL ON ZEOLITE: AN EMBEDDED CLUSTER DENSITY FUNCTIONAL STUDY

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The structure and bonding of rhodium dicarbonyl cation located in faujasite cavities was studied computationally by DFT method in combination with scheme of cluster models embedded in an elastic polarizable environment that allows one to account for electrostatic field and mechanical constraint of substrate. According to our calculation bonding of $\text{Rh}(\text{CO})_2^+$ at two oxygen atoms of support near an aluminum center, belonging one twelve-ring of the supercage wall is energetically most preferred.

Mononuclear rhodium complexes supported on surface of covalent oxides, e.g. zeolites, are active catalysts of such reactions as, for example, methanol carbonylation, alkene hydroformylation and polymerization. To understand origin of the chemical reactivity of these complexes, it is of necessity to investigate structure of catalytically active center at atomistic level. Here we report the characterization of rhodium dicarbonyl anchored at internal surface of faujasite.

Experimental studies using EXAFS and IR spectroscopies has identified the surface rhodium species on NaY as site isolated rhodium dicarbonyls [1]. Basing on the measured parameters three models of the local structure of surface rhodium complex have been suggested. They differ by the number of support oxygen atoms (2 or 3) to which rhodium dicarbonyl complex $\text{Rh}(\text{CO})_2^+$ is bonded; the Rh-O bond distances vary in a range 2.10-2.15 Å. However, on the basis of experimental data only it was impossible to distinguish these models. To assist in discrimination of the models theoretical calculations [1] have been performed that indicated that $\text{Rh}(\text{CO})_2^+$ is bonded to two oxygen centers nearby Al center. This earlier study was carried out using isolated cluster models to represent zeolite substrate. To avoid artificial distortion of model clusters special restrictions on movement of cluster centers were imposed. Present computational study was aimed to re-investigate these systems with more accurate theoretical approach – the elastic polarizable environment cluster embedding approach, EPE [2], which allows to relax all degrees of freedom of embedded cluster and take into account electrostatic field as well as polarization of the cluster environment by the active center. Moreover, several sites for coordination of $\text{Rh}(\text{CO})_2^+$ that differ by the crystallographic position of the oxygen atoms to be involved in the bonding have

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been considered. With this advanced approach preferable adsorption sites of rhodium ion Rh^+ and rhodium dicarbonyl complex $\text{Rh}(\text{CO})_2^+$ at internal surface of faujasite have been established as well as interaction energy and frequencies of CO vibration have been calculated.

Rhodium ion Rh^+ and its dicarbonyl complex $\text{Rh}(\text{CO})_2^+$ owing to their big sizes are adsorbed in the largest faujasite supercage accessed through twelve-membered rings. Therefore, in EPE modeling the fragments of zeolite walls facing supercage were included in QM clusters. The QM clusters containing 5 and 8 centers in tetrahedral (T) positions, 5T and 8T QM clusters, have been used; one silicon atom in each cluster has been replaced by aluminum. DFT calculations were carried out with the computer code Paragauss [3] using the gradient-corrected exchange-correlation functional of Becke and Perdew.

According to our calculation Rh^+ ion is located at three oxygen atoms of support near the aluminum center; the obtained Rh–O bond lengths are 2.25–2.44 Å. $\text{Rh}(\text{CO})_2^+$ is located at two support oxygen atoms forming two shorter Rh–O bonds at 2.13–2.14 Å. The calculated binding energies of rhodium dicarbonyl at different sites vary within 40 kJ/Mol; adsorption on two oxygen atoms of support belonging one twelve–ring of the supercage wall is the most preferred. The calculated vibrational frequencies of CO bond for zeolite-supported rhodium complex agree well with those found in experiment. CO vibrational frequencies are decreased by 73–84 cm^{-1} after adsorption of rhodium dicarbonyl at zeolite compared to unsupported rhodium dicarbonyl complex that indicates on the notable charge transfer from support onto rhodium complex.

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NEW POSSIBILITIES OF THE XPS METHOD APPLIED TO Ru/MgO SYSTEMS

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It is widely accepted that nanosize properties are due to high surface/bulk atom ratios. The surface to bulk atoms ratio changes significantly with nanoparticle size. Since the electronic structure of surface atoms greatly differs from the bulk ones, the overall properties of nanoparticles are also different. A straightforward way to detect these particular changes is XPS spectroscopy due to its ability to gain deep into the electronic structure of atoms: from core to valence atomic energy levels. The shortcoming of this approach is due to the overall XPS spectrum is an average of many individual ones. In most cases it is almost impractical to obtain samples of uniform size nanoparticles. This difficulty should be considered as the main obstacle in a way to get well-calibrated XPS technique, which is in principle able to distinguish the particle sizes and morphology.

Ab initio quantum chemical methods allow one to solve this problem. Calculated DOS (density of states) spectrum is usually in good confinement with real XPS spectrum, and it also can be correctly expanded in terms of localized density of states (LDOS) related to some sort of atoms, for example, surface atoms. The reconstruction of total density of states from arbitrary chosen LDOSes to simulate various surface/bulk ratios effects becomes possible.

Here we report some preliminary results of the XPS investigation applied to Ru/MgO system. The Ru/MgO samples were prepared via the incipient wetness impregnation of MgO with acetone solution of the ruthenium complexes at the room temperature. The reduction was carried out by the H₂ stream together with sample heating up to 450°C. According to XRD and TEM data, the most part of Ru was 3-30 nm nanoparticles. Two narrow bands additional to wide metallic-character Ru-band were found in XPS difference spectra at 4.1 and 7.1 eV. The origin of these bands was established with the aid of ab initio calculation of RuO₂ and bulk Ru DOS. The bands were assigned to the RuO₂ species. Thus, the existence of small Ru oxide particles stabilized in the Ru/MgO systems was proved.

**MODIFICATION OF ELECTRONIC STRUCTURE OF METAL NANOPARTICLES
BY INTERACTION WITH OXIDE SUPPORTS**

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Fine metal particles supported on various oxides are an important class of catalytic systems. The structure and properties of these catalysts depend on many factors such as the state of the support, the procedures used for introduction of the metal component and the conditions of the oxidation-reduction treatments. Oxide surface can strongly affect the degree of dispersion, electronic structure, adsorption and catalytic properties of supported metal nanoparticles. The aim of the work consists in the determination and analysis of the most important factors affecting the electronic structure of Pt nanoparticles supported on various oxides.

Pt₆ particles, supported on partially dehydroxylated gamma-alumina, FAU and MFI type zeolites have been studied by the cluster model DFT approach. All calculations were performed with B3LYP functional along with ECP-31G** basis set. To describe oxides surfaces, a cluster approach were used. The cluster modeling dehydroxylated alumina surface was derived from the gamma-Al₂O₃ structure using X-ray diffraction data and was constructed from MgAl₂O₄ ideal spinel unit. The clusters used to simulate MFI and FAU zeolites were obtained directly from their respective largest cavities. MFI zeolite was simulated with 20T cluster (19 silicon and one aluminum atoms arranged in two parallel rings). FAU zeolite was represented by a 6T cluster (3 silicon and 3 aluminum atoms arranged in 6-member ring). Two main features affecting the electronic structure of Pt₆ particles were found: basicity of framework oxygen anions and the presence of the surface hydroxyl groups. The transfer of the hydrogen atoms of hydroxyl groups onto metal particle (reversed spillover) is observed, accompanied by partial oxidation of metal species. The energetic characteristics of this process are evaluated and electron structure and charge distribution of supported Pt₆ particles discussed. Two factors mentioned above result in the concurrent electronic density transfer. The hydrogen transfer causes the positive charging of metal particle, while the interaction with basic sites results in the electron-enriched metal cluster. The calculated changes in d-states of Pt particle are in qualitative agreement with earlier described XAFS experimental data on the supported platinum nanoparticles.

METHOD FOR PREPARATION OF DICYCLOPENTADIENE EPOXIDES BY HYDROGEN PEROXIDE OXIDATION

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Method for preparation of dicyclopentadiene epoxides by hydrogen peroxide oxidation in presence of phase transfer catalyst was developed. Dicyclopentadiene epoxides can be applied in polyesters, laprols productions and for fine chemistry. Epoxidation was prepared in 20 to 70 °C temperature interval, without any sort of organic solvents. There was noted that best yields of dicyclopentadiene epoxides is obtained at reaction temperature below 65 °C, higher temperatures lead to significant part of byproducts in reaction mixture.

Dicyclopentadiene is formed from cyclopentadiene upon its dimerisation. Cyclopentadiene is one of the byproducts of pyrolysis process. Dicyclopentadiene epoxides can be applied in polyesters, laprols productions and for fine chemistry. The use of oxygen, peroxides and peracids for direct oxidation of alkenes to epoxides is the main method for industrial applications. Epoxidation with oxygen is only used for ethylene oxide production. This method is not efficient for other alkenes due to large amount of byproducts. A lot of epoxides are produced by the metal catalysed liquid phase oxidation of alkenes using organic hydroperoxides produced by hydrocarbon autoxidation. Homogeneous Mo(VI) and heterogeneous Ti(IV) are used as efficient catalysts for epoxidation with hydroperoxide. Epoxidation of substituted alkenes can be widely used in fine chemicals industry successfully achieved by peracids method. But peracids epoxidation is not a pure method because acid wastes are produced. The safety is associated with handling peracids is also a matter for concern. The employment of hydrogen peroxide is an attractive option both on environmental and economic grounds. It is cheap, readily available and gives water as the only byproduct. Many catalytic systems based on different metals such as tungsten, manganese, rhenium and titanium have been reported for the epoxidation using hydrogen peroxide. One of the most effective catalytic systems using hydrogen peroxide is peroxotungstate catalytic system. An active complex as rule is formed in situ from sodium tungstate phosphoric acid (or theirs analogs) in hydrogen peroxide medium and phase transfer agent (in most cases it is lipophilic ammonium or phosphonium salts). For dicyclopentadiene epoxidation we used sodium tungstate dihydrate and phosphoric acid as cocatalysts, tertiary ammonium salt as phase transfer agent and 35 % aqueous hydrogen peroxide as oxidant. Despite the fact, that in the

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most of described methods chlorinated or aromatic solvents are used for epoxidation we carried out epoxidation without organic solvents. As result of reaction dicyclopentadien epoxide insoluble in water is formed precipitate which may be out and separated by simply filtration. Dependence of epoxide yield from reaction temperature was investigated. The temperature interval was from 20 to 70 °C. In result we find, that epoxidation effective even at room temperature, increasing of temperature leads to higher reaction speed but lower selectivity. Substrate conversion was more than 90 % in investigated temperature interval, obviously for reaction at room temperature needs more time than at 70 °C. In table 1 shown results of dicyclopentadiene epoxidation.

Table 1. Results of dicyclopentadiene epoxidation.

T, °C	reaction time, hours	H ₂ O ₂ selectivity, %	DCPD conversion, % mass	yield of epoxides, %
20	26	62,9	91,2	88,1
40	10	60,5	93,9	85,3
60	4,5	56,0	95,4	78,4
65	4	43,8	95,2	60,5
70	3	38,5	96,0	54,3

As shown in table dicyclopentadiene epoxidation is more effective when the temperatures below than 65 °C, at that temperature occurs significant decreasing of yields. However hydrogen peroxide dicyclopentadiene epoxidation in presence of phase transfer agent was successful.

WAYS OF CARBON SUPPORT STRUCTURE AND PROPERTIES FORMING

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The ways of forming the structure and properties of active carbons (AC), which are intended to use as carbon supports in catalysis, were investigated. It was established that the most perspective raw material for producing such AC is polymeric resins from the class of thermosetting plastics and packed vegetative raw material (shell and bone of a fruit).

At the present moment the fields of application of adsorption technologies based on AC are headily broadening. It is stipulated with three reasons: first, active carbons allow solving the sharpest problems of biosphere and harmful emissions; second, they provide a high purity of agents, materials and products; third, they are conducive to introduce manufacturing intensive technologies, including catalysis.

For solving of these problems it is necessary to get active carbons having the developed sorbing pore volume (micro and meso pores), high strengthening properties and minimal content of ash elements.

Such properties of new perspective active carbons may be achieved by means of:

- usage of low-ash raw material and its modification with chemical compounds,
- special modes of granules forming and their thermal treatment (drying, carbonization and activation);
- deep ash removal of active granules (cleaning).

At producing active carbons as carbon supports for catalysts the best results are achieved with the use of polymeric raw material, bone and shell of fruit trees drupes and anthracites.

The perspective polymeric raw materials for carbon support production are phenol-formaldehyde resin (carbons of FTD type), polyvinylidene chloride (carbons of PAY type) and furfural copolymers (carbons of FAS type).

Table 1 shows the qualitative indexes of polymeric active carbons.

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Table 1

Polymeric active carbons

Indexes	Polyvinylidene chloride	Textolite	Furfural
	PAY	FTD	FAS
1. Bulk density, g/dm ³	670	420	500
2. Strength, %	94,0	93,1	99,5
3. Ash value, %	0,5	0,8	0.01
4. Pore volume, cm ³ /g			
V _{mi}	0,45	0,600	0,41
V _{me}	0,010	0,100	0,39
V _{ma}	0,010	0,160	0
V _Σ	0,470	0,860	0,80

Another type of perspective carbon support may be produced from packed vegetative raw material (shell and bone of a fruit). Table 2 shows qualitative indexes of active carbons of that type.

Table 2

Active carbons made of bone raw material

Indexes	Fruit bones		Coconut carbonizat	
	MEKS	AKY	VSK	VSK-A
1. Bulk density, g/dm ³	400	400-500	530	380
2. Strength, %	91	93	92	85
3. Ash value, %	1,0	5,0	5,0	6,8
4. Pore volume, cm ³ /g				
V _{mi}	0,510	0,390	0,325	0,580
V _{me}	0,110	0,120	0,120	0,200
V _{ma}	0,200	0,225	0,110	0,160
V _Σ	0,820	0,735	0,555	0,940

At the present moment in connection with the quick development of catalytic processes in organic chemistry and petrochemistry the aim of creating of large-capacity native high-strengthening carbon support manufacturing became especially actual.

STYRENE PRODUCTION BY CATALYTIC DEHYDROGENATION OF ETHYLBENZENE WITH SULFUR

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The influence of temperature, reaction mixture composition and contact time on the styrene formation by interaction of ethylbenzene with sulfur vapor at the presence acid-base catalysts has been studied. The optimal conditions of catalytic dehydrogenation of ethylbenzene by sulfur vapor with preferable formation of styrene have been determined.

Catalytic dehydrogenation of ethylbenzene is the basic industrial process of styrene production – one of the basic monomers for plastic manufacture. In the similar way α -methylstyrene and divinylbenzene are obtained from cumene and diethylbenzene, respectively, which are applied widely as copolymers.

Performance of the dehydrogenation process with elemental sulfur as the dehydrogenating agent has the same advantages, as oxidative dehydrogenation in the presence of oxygen, and allows approximately 40 percents reducing of the heat absorption of reaction and displacing the thermodynamic equilibrium of reaction towards products. Molecular sulfur is a milder dehydrating agent compared to molecular oxygen; it seems realistic to provide a quantitative aromatic olefins yield through the reaction of alkylaromatic hydrocarbons with sulfur. The cyclic S_8 molecule is low reactive, its activation needs destruction of the cycle. Sulfur molecules containing less than eight sulfur atoms are more reactive. Thermal decomposition of S_8 molecules to produce low-molecular S_2 – S_8 species is achieved at temperatures above 300 °C [1]. The S_8 ring also can be opened in the presence of catalysts of the acid-base type or the ones containing transition metal ions, much more reactive surface-linked polysulfide chains being formed [2].

Study of the new process of dehydrogenation of ethylbenzene by sulfur vapor at the presence acid-base catalysts has been fulfilled under following conditions: atmospheric pressure, the temperature range between 400 and 650 °C, the contact times in the range 0.1 to 1,5 s, the ethylbenzene concentration in the reaction mixture 2-50 % vol., ratio $S_1/C_2H_5C_6H_5$ – 0.25-0.9. The influence of temperature, reaction mixture composition and contact time on the selectivity for styrene has been studied. It has been found that the reaction of catalytic dehydrogenation of ethylbenzene by sulfur vapor proceeds fast enough at temperatures not

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lower than 450 °C with practically full conversion of sulfur in H₂S. However because of existence of side reactions (polymerization and interaction of styrene with sulfur) yield of styrene falls at the temperatures lower than 500 °C and at the contact times greater than 1.5 s. It has been established that at the ratio $S_1/C_4H_{10} > 0.7$ the formation of sulfurorganic compounds takes place. The optimal conditions of catalytic dehydrogenation of ethylbenzene by sulfur vapor with preferable formation of styrene have been determined. The results obtained at 550 °C and ethylbenzene concentration ≤ 40 % vol. demonstrate attainability of high selectivity for styrene (95-99 %) at a high conversion of ethylbenzene (65-70 %).

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**DFT SIMULATION OF PROCESS OF KEY INTERMEDIATE FORMATION UPON
CATALYTIC OLEFIN HYDROALUMINATION**

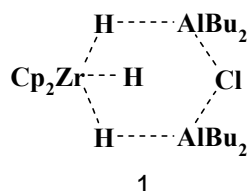
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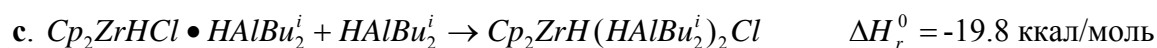
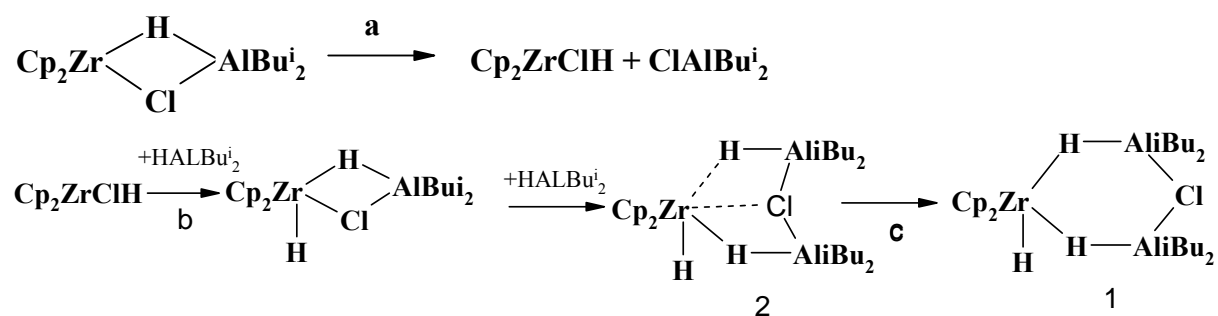
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Within the mechanism investigation of olefin hydroalumination by HAlBu_2^i in the presence of Cp_2ZrCl_2 catalyst it was determined the structure of the key intermediate Zr,Al-complexes **1** by means of dynamic NMR spectroscopy [1]. It has been shown that complex **1** is inactive in olefin hydroalumination.



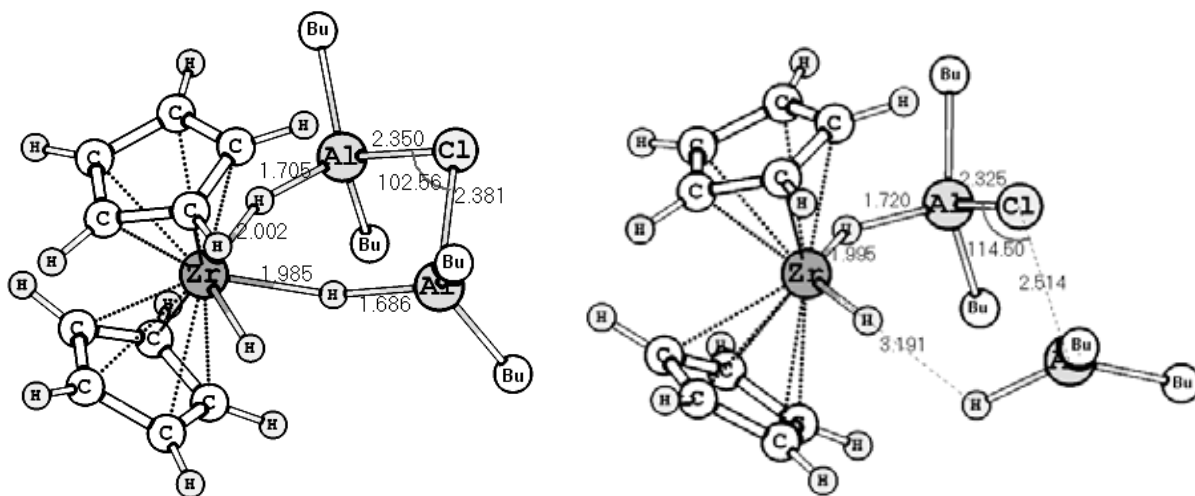
We performed quantum chemistry calculation of formation of complex **1** by the DFT method - PBE/3z, program “Priroda 4.07”, Dimitri Laikov, Moscow State University, in the gas-phase at $T=203.15$ K (Scheme 1). It was found that formation of **1** occurs *via* the steps **a-b-c**. Summarized enthalpy of process is $\Delta H_r^0 = -49.1$ kcal/mol.

Scheme 1



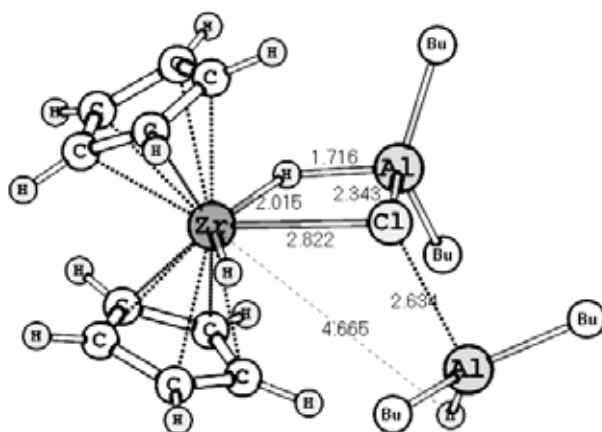
DFT energy profile has the local minimum and transition state, which is shown in Fig. 1 and Fig. 2.

Fig. 1. Optimized structure of complex $\text{Cp}_2\text{ZrCl}_2(\text{HAlBu}^i)_2\text{Cl}$ **2** Fig. 2. Optimized structure of local minimum **3**



The calculated potential barrier is $E_a=4.7$ kcal/mol. Optimized structure of transition state **4** $\text{Cp}_2\text{ZrCl}_2(\text{HAlBu}^i)_2\text{Cl}$ ($\nu_{\text{MH}}=-92,8$ cm^{-1}) is shown on Figure 3.

Fig. 3. Optimized structure of complex **4** $\text{Cp}_2\text{ZrCl}_2(\text{HAlBu}^i)_2\text{Cl}$ **2**



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**CHEMICAL REACTIVITY OF ZINC EXCHANGED ZSM-5 ZEOLITES:
A COMPREHENSIVE DFT STUDY**

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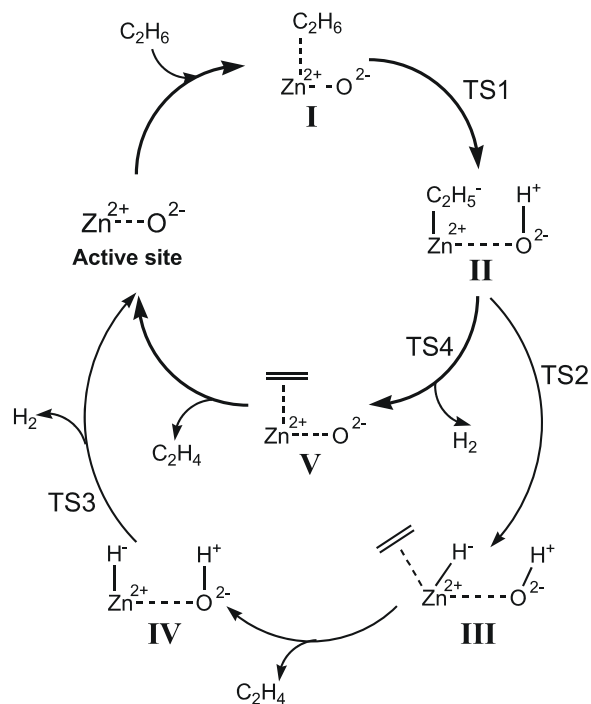
Possible reaction pathways of alkane dehydrogenation over different zinc containing intrazeolite cationic species were studied by means of a density functional theory cluster modeling. It is shown that the isolated zinc ions stabilized at the charge alternating cation site with distantly separated anionic $[\text{AlO}]_2^-$ framework units are the most probable active sites. In addition a novel mechanism of ethane dehydrogenation is proposed. The presented theoretical results allow the precise explanation of the recent unusual experimental data.

Zinc-exchanged H-ZSM-5 zeolites (Zn/ZSM-5) are known to be effective catalysts for promoting the selective conversion of light alkanes to aromatics [1]. The reaction mechanism is thought to consist of a complex scheme involving dehydrogenation, oligomerization, and ring-closure steps [2]. The modifying cations play key roles in dehydrogenation of paraffins, whereas Brønsted acid protons catalyze the oligomerization of the olefins thus produced and possibly their subsequent aromatization. Despite numerous experimental and theoretical studies have been devoted to investigation of the mechanism of catalytic dehydrogenation of light alkanes over Zn exchanged ZSM-5 zeolite, the structure of the active intrazeolite cationic species and, accordingly, the mechanism of hydrocarbon activation have not been fully elucidated.

In this work we present a comparative cluster DFT study of the reactivity of various cationic species such as Zn^{2+} , $[\text{Zn-OH}]^+$ and $[\text{ZnOZn}]^{2+}$ stabilized in the zeolite. In addition, for isolated Zn^{2+} sites we discuss the dependence of their chemical properties on the aluminum distribution in ZSM-5 zeolite. Possible reaction paths for ethane dehydrogenation over the zeolitic zinc sites are schematically shown in Scheme 1. Initial activation of light alkanes over all of the abovementioned cationic species proceeds via heterolytic C-H bond cleavage (**I**→**II**) resulting in formation of an alkyl group grafted to the Zn ion and an acidic proton attached either to the basic lattice oxygen in case of Zn^{2+} ions or to the extraframework O atom of the $[\text{Zn-OH}]^+$ and $[\text{ZnOZn}]^{2+}$ species.

The reactivity of the isolated Zn^{2+} strongly depends on the aluminum distribution in the zeolite. The most active Zn^{2+} ions are those stabilized at the distant anionic sites of the zeolite

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Scheme 1

(Zn Z_d). The catalytic cycle starts with the heterolytic C-H bond cleavage of the C_2H_6 molecule strongly adsorbed on the Zn^{2+} cation with distantly located charge-compensating $[AlO_2]^-$ framework units. Initial proton abstraction is preferred to the O-sites neighboring to the ring where the cation is located rather than to the oxygen atoms of the same zeolitic ring. The resulting intermediate **II** decomposes via one-step formation of H_2 and C_2H_4 (**II**→**V**), whereas the consecutive ethylene and hydrogen elimination (outer cycle in Scheme 1) is unfavored. The activation energy for the one-step reaction is strongly

dependent on the relative position of $[Zn-C_2H_5]^+$ and H^+ species. Therefore, the presence of acidic protons in the catalyst can promote the regeneration of the active sites. Subsequent desorption of ethylene from the thus formed molecular complex **V** regenerates the initial active site. To our knowledge such mechanism (inner cycle in Scheme 1) has never been reported before for this type of catalytic reactions.

Bivalent zinc ions stabilized at the conventional ion-exchange sites (Zn Z_s) are less likely active sites. The low-energy path for the catalytic reaction over these sites consists of the same elementary steps as for the $Zn Z_d$, which, however, face significantly higher activation energies.

The $[Zn-OH]^+$ ions show remarkably lower activity in the initial C-H activation as compared to the parental isolated Zn^{2+} cations. Moreover, it is found that the catalytic reaction over these sites leads to their decomposition via water desorption and generation of the more reactive Zn^{2+} ions. On the other hand, although binuclear $[ZnOZn]^{2+}$ sites show the highest initial activity, the heterolytic C_2H_6 dissociation results in formation of very stable species. Subsequent transformations of the thus formed intermediates are found to be strongly unfavored. We conclude that these oxygen-containing zinc species cannot be responsible for the dehydrogenation activity of Zn/ZSM-5 zeolites, while the most probable active sites are the isolated Zn^{2+} ions stabilized at the distant anionic sites of the zeolite.

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PHOTOCATALYTIC REDUCTION OF NITRATES DISSOLVED IN WATER OVER Ag/TiO₂ CATALYSTS

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Relation between preparation procedure and catalytic behavior of Ag/TiO₂ catalysts in nitrate reduction was studied. The materials with homogeneously distributed fine silver clusters showing high photocatalytic efficiency were synthesized by a triblock copolymer induced reduction of [Ag(NH₃)₂]⁺ under ambient light illumination. The effects of Ag loading, carrier composition and nature of hole scavengers were systematically investigated. Using fomic acid as such agent, a nitrate conversion of 98 % and selectivity ca. 100 % can be achieved after 30 min of irradiation.

From an environmental standpoint, one of the most acceptable methods for removal of nitrates, which cause health hazards, is to convert them into N₂. Recently developed photocatalytic nitrate reduction using TiO₂ supported Ag nanoparticles [1, 2] is promising approach due to chemical stability, nontoxicity and low cost of the catalyst. In this reaction silver enhances photocatalytic activity of titania promoting charge separation and inhibiting recombination of electron–hole pairs, while sacrificial electron donors (hole scavengers) are essential for the reduction of NO₃⁻. However, it is still desirable to find out an appropriate procedure for the catalyst preparation and optimal reaction conditions to produce a quality standard for drinking water.

In this study, the influence of preparation mode potentially effecting photocatalytic behaviour of Ag/TiO₂ materials in nitrate reduction was investigated. The procedures of the catalyst activation, regeneration and reaction conditions providing maximum efficiency of NO₃⁻ removal from water were also evaluated.

The catalysts were prepared using different modifications of TiO₂ by a conventional chemical reduction method, a pH-controlled photocatalytic process [1] and by a triblock copolymer induced reduction of [Ag(NH₃)₂]⁺ in ethanol [3] under ambient light illumination of varied duration. In the later case, PEO₂₀PPO₇₀PEO₂₀ (Pluronic P123) and EO₉₇PO₆₉EO₉₇ (Pluronic F127) surfactans were utilized. The silver content was varied between 0.5-2.5 wt %. The catalysts were characterized by means of ICP, X-ray diffraction, X-ray photoelectron spectroscopy, UV-ViS spectroscopy and transmission electron microscopy.

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Photocatalytic reaction was carried out as described in Ref. [1] with initial concentration of nitrate anions 23 mg N l^{-1} (calculated by nitrogen weight). The catalytic activity was defined as the amount of nitrate anions reduced per minute and active metal weight.

Over all catalysts under study, no nitrate reduction was observed without a hole scavenger. The use of formic acid as sacrificial electron donor greatly improved both the reaction rate and selectivity for nitrogen avoiding formation of undesirable nitrite and ammonium ions. The amount of HCOOH equal to $0.02\text{-}0.04 \text{ mol l}^{-1}$ was sufficient to reduce nitrate totally. The highest catalytic activity was observed for the catalysts derived from TiO_2 with mixed anatase-rutile composition. This fact indicates importance of hetero-junction existed in Ag/TiO_2 multiphase nanocomposite for enhancement of its photocatalytic activity.

The preparation procedure significantly effects catalyst efficiency towards nitrate reduction. The samples prepared via a triblock copolymer induced reduction of $[\text{Ag}(\text{NH}_3)_2]^+$ in ethanol under ambient light illumination are the most active. Depending on the carrier structure, composition, grain size and silver loading, the average activity was ca. $40\text{-}70 \text{ mmol NO}_3^- \text{g}^{-1} \text{Ag min}^{-1}$. Enhanced dispersion of strongly anchored silver nanoparticles to the surface of TiO_2 can be considered as a possible explanation for this finding. Composition of triblock copolymer also controls activity of the Ag/TiO_2 catalyst, which is higher in the case of Pluronic P123. By repeating the ambient light radiation, the deactivated catalysts could be regenerated again. The catalyst regeneration efficiency depends on both the titania composition and duration of illumination. All these results showed the impact of studied aspects on denitrification properties of Ag/TiO_2 nanocomposite catalyst.

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THE EFFECT OF MODIFICATION ON PHYSICO-CHEMICAL PROPERTIES OF HYDROTREATMENT CATALYSTS SUPPORTS

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The effect of modification with boron and phosphorus compounds on the properties of hydrotreatment catalysts supports has been studied. The modification with phosphorus has been shown to be more efficient compared to that with boron.

It is known, that one of the major elements of hydrotreatment catalysts technology is the synthesis of the support as which activated aluminum oxide (AAO) is used most frequently. Now there is a commonly accepted concept that each raw material to be processed requires certain pore size of the catalysts support. For this reason, the studies on the structural and textural characteristics of activated aluminum oxide (AAO) as well as procedures for the preparation and modification of supports with given properties are rather actual. The «AC and OSP Co.Ltd.» has implemented an import industrial line for producing aluminum oxide supports with given properties for various catalysts. The implemented technology enables one to produce aluminum oxide with various characteristics.

Results of studies on the optimization of support structure depending on the assignment of process and quality of raw materials were used for the development of producing technology of hydrotreatment catalysts with use of phosphorus and boron compounds as modifiers. During that the technology has been developed and the manufacturing has been implemented for producing hydrotreatment catalysts for diesel fractions to give low sulfur diesel fuel; for hydrotreatment of vacuum gasoil, the material for catalysts cracking; for hydroreforming vacuum distillates to produce oily fractions with cold resistance properties; for hydrogenation of unsaturated hydrocarbons and sulfuric compounds to benzene-toluene fractions.

It has been established that the greatest changes in size of support crystallites their textural and acidic characteristics might be reached by modifying with phosphorus, combined modifying with phosphorus and boron or incorporating wide-porous zeolites into the composition of the support (AAO). The use of such modified catalysts supports has allowed to improve the efficiency of hydrotreatment process as known industrial ones.

**FRAGMENT COMPOSITION OF DIESEL FRACTIONS OBTAINED BY
HYDROTREATMENT OVER *Co-Mo* AND *Ni-Mo* CATALYSTS**

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The effect of catalysts on the hydrocarbon composition of diesel fractions obtained by hydrotreatment process has been studied using ¹H and ¹³C NMR spectroscopy and factorial analysis.

Studies on the fragment composition of the substance, intermediate stages and products of technological process for producing diesel fractions using quantitative ¹H and ¹³C NMR technique have been carried out to reveal sensitivity of NMR method for the control of technological process. The necessity of the study is caused by growing demands to operational characteristics of diesel fuels, which are reached by involving high index oils in refining. The estimation of substrates from the point of view of potential composition and quality in the special importance. In this connection, the use of instrumental express methods of analysis of diesel fuels might be quite perspective.

The feature of the analysis of group composition of the substrates by NMR spectroscopy is its statistical character: the measured of calculated values of parameters of fragment composition present average results of characteristics of many individual compounds and various classes of organic substances.

Advantages of the approach are the universality of the investigation of objects containing aromatic, heteroaromatic, hydroaromatic, olefinic and saturated hydrocarbons, differentiation of compounds with same brutto-formula and high reliability of the information due to its obtaining way.

Possibilities to monitor the composition of diesel fuels by NMR method are exemplified by the hydrotreatment of diesel fuel over *Co-Mo* and *Ni-Mo* catalysts under diverse conditions.

It has been shown that the increase in the hydrogen to substrate ratio at constant volume supply rate of substrate parallels the decrease in content of heteroatomic (H_{arg}), highly

condensed (H_{ark}) and bicyclic (H_{arb}) component and increase in content of monoaromatic alkylbenzenes (H_{am} , H_{av}) and naftenic hydrocarbons (H_n).

It has been established that the increase in operation temperature by 30°C results in the change of process efficiency, as the decrease in values of structural parameters H_{arg} , H_{ark} , H_{av} and H_{arb} as well as the increase in ones of H_{arm} , H_n , H_v were observed. It might be assumed that in this case polyarenes decompose to molecules with smaller number of rings, and the heteroatomic and monoalkylaromatic compounds are hydrogenated. Residual aromatic compounds of the hydrotreatment products are presented by less condensed with lowered coke ability.

Sulfur presents in diesel fuel substrates in forms of condensed thiofene compounds, sulfides and disulfides and its removal has to be done by the hydrogenation. For the catalysts studied a symbatic change in the depth of removal of sulfur and the decrease of amount of aromatic hydrogens of condensed system has been observed. At the same time, depending on the catalyst composition a different ratio of these two processes is observed, which may be markedly noted by the comparison of sulfur and H_{arb} concentrations.

For a series of samples at rather close values of H_{arb} , $H_{ark}+H_{arg}$ parameters divorces in depth of desulfurization are valueble ($\sim 70\%$). Observed regularities prove the commonly accepted concept that the hydrogenation and C-S bond cleavage proceed with different active species and the hydrodesulfurization is proceeded in two ways: one suggests the formation of hydrogenation products in the first step without C-S bond cleavage, and according to another C-S bond cleavage precedes the hydrogenation of hydrocarbon maioties. The amount of products of certain transformation should be dependent on the catalyst properties and first of all, on the ratio of hydrogenating action and cracking – the abilities to C-S bond cleavage.

The change in H_n parameter is abiguous. Hydrogenation of aromatic compounds gives rise to an increase of amount of naphtene hydrocarbon (H_n), while the cracking leads to a decrease. At the same time at simultaneous increase both hydrogenationg and cracking activitives of catalysts the parameter remains unchanged.

**QUANTUM-CHEMICAL STUDIES OF H_{ads} , O_{ads} , OH_{ads}
ON Pt(100) AND Pt(111) BY DFT**

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Adsorption of atomic hydrogen, oxygen and OH-groups at coverages of 1 and 0.25 ML has been investigated by DFT within the local density approximation (LDA). Threefold hollow sites (fcc and hcp) for adsorption of H and O atoms are preferred compared to weakly-bond energy sites (on-top or bridge). Hydrogen atoms can occupy subsurface sites (fcc* and hcp*).

It's known that hydrogen oxidation by platinum metals is one of the classical model reaction of heterogeneous catalysis. The reaction is described by Langmuir-Hinshelwood step-to-step mechanism, including dissociative hydrogen and oxygen adsorption with the formation of OH_{ads} . Nowadays we can see many studies of nature of H and O atoms, adsorbed on Pt(100) and Pt(111) surfaces, due to modern theoretical and experimental surface science techniques.

The aim of this work is to calculate adsorption energies, equilibrium heights above the surface, vibration frequencies of adsorbed H- O- atoms and OH-groups on Pt(100) and Pt(111) based on density functional theory (DFT).

Adsorption of atomic hydrogen and oxygen at coverages of 1 and 0.25 ML has been studied by DFT within the local density approximation (LDA). The simulations were conducted using ADF2003-BAND and ESPRESSO-3.1 programs. We have employed a three layer slab for simulation of Pt(100) and Pt(111) surfaces.

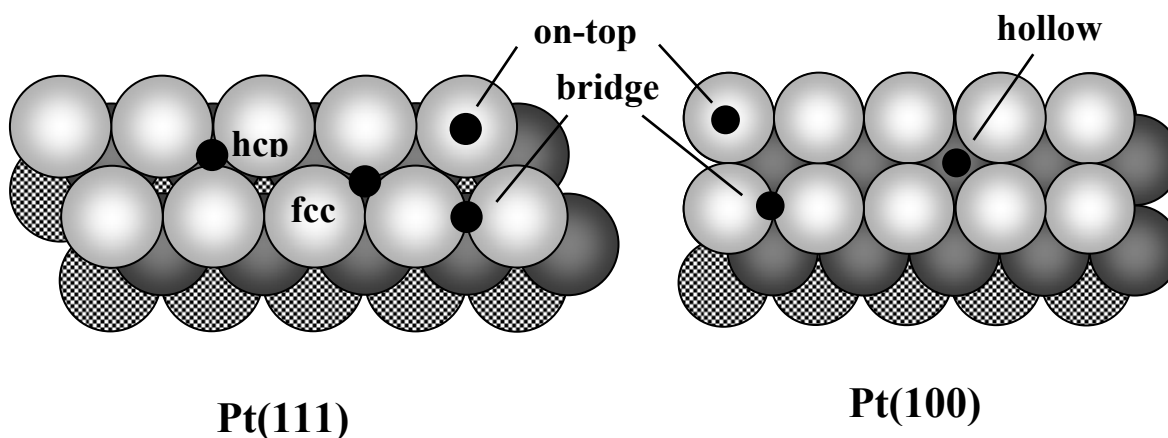


Fig. 1. Adsorption sites of H and O atoms on Pt(100) and Pt(111) surfaces.

Adsorbing hydrogen and oxygen atoms can occupy following states: two threefold hollow sites, namely the fcc and hcp, twofold bridge site and on-top. Computed frequency of symmetrical valence vibrations occurring perpendicular to the surface heavily depends on the number of metal atoms coordinating with the atom. Vibration frequency dramatically increases with decreasing of number of bonds in adsorption center.

Table 1. Computed adsorption energies (E_{ads}), zero point energy effects have been included, equilibrium heights (r_0) above the surface, vibration frequencies (ν) of adsorbed H and O atoms ($\theta = 1$ ML) for following adsorption sites on Pt(100) and Pt(111).

	Site	E_{ads} , eV/atom	r_0 , Å	ν , cm^{-1}
H/Pt(111)	on-top	-0.99	1.6	2022
	bridge	-1.36	1.15	1318
	hcp	-1.48	1.0	1290
	fcc	-1.54	1.0	1281
	fcc*	-0.99	-1.1	752
	hcp*	-0.50	-0.6	1102
H/Pt(100)	on-top	-0.88	1.6	2027
	bridge	-1.42	1.1	1359
	hollow	-1.62	0.5	710
O/Pt(111)	on-top	-1.41	1.8	772
	bridge	-1.47	1.4	642
	fcc	-1.73	1.2	564
	hcp	-1.22	1.25	611

Threefold hollow sites (fcc and hcp) for adsorption of H and O atoms are preferred compared to weakly-bond energy sites (on-top or bridge). It is shown that hydrogen atoms can occupy subsurface sites (fcc* and hcp*). So we considered OH-groups adsorbed on Pt(100) and Pt(111) on-top and bent configurations.

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**INFLUENCE OF CHEMICAL TREATMENT AND PROCESS CONDITIONS ON
CATALYTIC PROPERTIES OF NANOFIBROUS CARBON IN H₂S DIRECT
OXIDATION**

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The influence of chemical pretreatment, water vapour content and oxygen excess on catalytic characteristics of nanofibrous carbon in direct hydrogen sulfide oxidation reaction have been investigated. It was shown, that preliminary acid treatment as well as water vapour excess in reaction mixture improved selectivity and stability of nanofibrous carbon. Nanofibrous carbon can work efficiently in wide range of oxygen excesses.

Importance of the efficient catalysts design for the direct selective oxidation of hydrogen sulfide into sulfur and water is caused by wide application of the direct oxidation in new technologies for gas purification from hydrogen sulfide and the improvement of the current technologies. This is for example SuperClaus process [1] and others, providing the purification of low-concentrated waste gases from hydrogen sulfide by its selective oxidation with molecular oxygen to yield sulfur and water at the last step. At present this process is performed in the presence of supported metal oxide catalysts such as ICT-27-42 [2] and others. Unfortunately, these catalysts exhibit insufficient activity at temperatures below 200°C and tend to activity or selectivity decreasing in the presence of water vapour and oxygen excess. Nanofibrous carbonaceous materials (NFC) produced by hydrocarbons decomposition with 8-group metals catalysts are the materials of the new class and can be applied in various spheres. Recently the unique properties of NFC have been revealed. NFC can catalyze the reaction of selective molecular oxygen oxidation of hydrogen sulfide [3].

The goal of this research was to find the influence of chemical pretreatment, water vapour content and oxygen excess on catalytic characteristics of nanofibrous carbon in direct hydrogen sulfide oxidation reaction.

The NFC samples were obtained in the result of decomposition of methane over nickel-containing catalysts at the temperature 550 °C in the form of mesoporous granules of diameters about 3 mm, which consist of tightly twisted graphite-like fibers of diameters of

5-150 nm. The inner surface of granules is formed by edges of graphite basal planes, which are oriented to the surface angularly dependent of NFC origin catalyst [4].

It was revealed that in the absence of water vapour NFC with nanofibers structure of “fish-bone” showed unstable low selectivity at long testing time in this reaction, with the exception of NFC that was preliminary oxidized. When the water vapor excess was used in reaction medium the selectivity increased significantly and also not sufficient conversion increasing occurred.

By the example of NFC with nanofibers structure of “pack of cards” it was shown that decreasing of 30-fold oxygen excess to 2,5-fold excess decreases hydrogen sulfide conversion, but at the same time it more sharply increases selectivity (maximum sulfur yield at 200 °C was reached).

Thus, nanofibrous carbon samples are attractive for purification of low concentrated hydrogen sulfide containing gas in presence of large water vapour content and in wide range of oxygen excess.

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**ADSORPTION OF SMALL SILVER SPECIES ON DEFECT SILICA SURFACE.
QUANTUM CHEMICAL STUDY**

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Adsorption of small Ag_n ($n=1, 2, 4$) species on defect sites of silica surface has been studied. The hybrid approach combining density functional method and cluster models embedded in an elastic polarizable environment have been applied to characterize the bonding and structures of the metal species at the following sites: oxygen vacancies (V_O , V_O^+), nonbridging oxygen center (NBO^-) and Si dangling bond (E').

Our scientific interest has concerned small silver clusters adsorbed on surface of SiO_2 . Both adsorbate and support have practical importance because of their role in variety of technological applications and heterogeneous catalysis in particular. Supported silver clusters are active catalysts in epoxydation and hydrogenation of hydrocarbons. SiO_2 in microporous crystalline form is the ideal framework for heterogeneous catalytic reactions, while amorphous silica is widely used for chromatography, adsorption, and metal deposition in supported catalysis.

This study aims to identify preferred adsorption sites and geometries of small Ag_n ($n=1, 2, 4$) clusters on defect silica surface. Calculations were performed by hybrid quantum mechanics/molecular mechanics (QM/MM) method **covEPE** [1] implemented in quantum mechanical density functional package PARAGAUSS [2] and allowing embedding of QM clusters in MM elastic polarizable environment.

To consider isolated defects of silica surface new models based on the idealized structure of wall forming hexagonal channels of mesoporous MCM-41 silicalite were elaborated. Such surface is represented by two honeycombed structure layers of interconnected tetrahedrons SiO_4 . Two dimensional unit cell of the model slab was optimized with the MM force field of **covEPE** model. Three types of possible surface defects were considered: neutral and positively charged oxygen vacancies $\equiv\text{Si}-\text{Si}\equiv$ (V_O and V_O^+), Si dangling bond $\equiv\text{Si}^*$ (E') and nonbridging oxygen center $\equiv\text{Si}-\text{O}$ (NBO^-). V_O and V_O^+ centers are formed by removing bridging oxygen atom from the top layer. E' and NBO^- defects are obtained by subtracting OH and H^+ , respectively, from the terminal Si-OH group.

It was found that silver species are most strongly adsorbed on positively charged oxygen vacancies V_O^+ with adsorption energy $E_b= 2.20-3.06$ eV. Substrate-adsorbate bonds of

intermediate strength are formed on interaction with NBO^- and E' centers ($E_b = 1.07\text{-}1.82$ eV). The most weakly silver species interact with neutral oxygen vacancies V_O . Calculated adsorption energies of all considered Ag clusters do not exceed 0.2 eV. It was found that effect of nucleation of Ag atoms is hindered by strong interaction with defect site. In particular, nucleation is calculated to be unfavorable when metal species are bound to V_O^+ and E' centers.

According to calculations dimmers Ag_2 are adsorbed in upright orientation. Plane rhombic structure of Ag_4 clusters characteristic for that species in gas phase is preserved in interaction with V_O and NBO^- defect sites. Adsorption of Ag_4 on V_O^+ site results in distorted rhombic structure with inter-plane angle of 150° . Interaction with E' center leads to formation of tetrahedral Ag_4 species.

This work is supported by SB RAS Integration project N79.

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EXPLOSION SAFETY IN GAS TRANSFERRING SYSTEMS WITH THE USE OF LAYER OF CATALYST

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After the flame has been extinguished due to gas flow phlegmatization by the products of catalytical oxidation the lowering of bed temperature down to initial temperature before ignition is provided within the specified range of gas flow rate. Layer-by-layer cooling of fixed catalyst bed occurs using cold make-up mixture of combustible gas. Thus the method of explosion protection for gas transferring systems provides for independent, external control-free effective flame localization and extinguishing without interruption of combustible gas flow.

Flame arresters used in industry at present localize burning without extinguishing it. To stop burning the flow of combustible mixture has to be cut off. A new approach is proposed to extinguish flame without interrupting the flow based on use of catalytically active material as a flame arrester package. Investigations in this area found out the presence of a high-temperature zone of catalytical oxidation of combustible components. The influence of gas flow rate through the bed on position stability of the high-temperature zone and its locity in longitudinal direction has been studied. The data obtained were used to develop a novel method of explosion protection in operation of gas transferring systems.

Flame arrester design is radically simplified when maintain the corresponding gas flow rates which provide cooling of catalyst bed after the combustion mixture has extinguished the flame. It allows to eliminate measures maintaining temperature regime of catalyst supplying heat carrier to heat exchanger and therefore to exclude the heat exchanger from reactor design. Preliminary determinations of heat propagation velocity of catalytical oxidation zone are required for this method as well as starting velocity of catalyst fluidization.

Gas flow rate in flame arresting element under normal conditions and free cross-section is limited by $W_p < W_n < W_B$ range for non-contracted fixed catalyst bed and $W_p < W_n$ for contracted fixed catalyst bed, where W_p - heat propagation velocity of catalytical oxidation zone; W_n - gas flow rate in flame arresting element under normal conditions and free cross-section; W_B - starting velocity of catalyst fluidization.

The upper limit of gas flow rate for contracted fixed catalyst bed is not defined, that is maximal velocity is not limited.

**DENSITY FUNCTIONAL THEORY MOLECULAR CLUSTER STUDY OF COPPER
INTERACTION WITH NITRIC OXIDE DIMER IN Cu-ZSM-5 CATALYSTS**

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The various quantum chemical models of catalytic active site in Cu-ZSM-5 zeolites are analyzed. The density function theory (DFT) is used to calculate the electronic structure of molecular cluster (HO)₃Al-O-Cu-O-Cu modeling the catalytic active site in Cu-ZSM-5 zeolites and study the interaction and decomposition of NO. It is assumed that the rate-determining stage of the low-temperature selective catalytic reduction of NO is the formation of the π -radical (N₂O₂)⁻ on electron donor sites of Cu-ZSM-5 catalysts.

After discovery of direct NO decomposition and selective catalytic reduction (SCR) of NO by hydrocarbons over Cu-ZSM-5 zeolites, the interest in catalytic active sites of Cu-ZSM-5 and in activated forms of adsorbed NO grew considerably. Stabilization of isolated Cu²⁺ and Cu⁺ ions, as well as oxide CuO- and Cu₂O-like clusters, [Cu-O-Cu]²⁺ and bis-[Cu- μ -(O)₂-Cu]²⁺ dimers, and (-Cu-O-Cu-O-) chain structures in Cu-ZSM-5 has been observed by spectroscopic methods. These copper states each have been suggested to act as catalytic active sites in NO decomposition and SCR by hydrocarbons.

We have observed isolated Cu²⁺ ions in zeolite cation-exchange positions, copper oxide chain structures in the zeolite channels, and square-planar oxide clusters by electron spin resonance (ESR) and diffuse reflectance spectroscopy [1,2]. The most interesting among the above states of copper ions are chain structures Cu²⁺—O²⁻—Cu²⁺—O²⁻— because of the easiness of copper reduction and reoxidation in them as well the ability to stabilize bonded states of copper ions with mixed valence Cu²⁺...Cu⁺.

Together with high electron affinity of the molecular dimer ONNO (E_a = -1.3 ÷ -1.7 eV), this may result in the formation of surface anion π -radical (ONNO)⁻ in such systems that is similar to the organo-zirconium surface complex with (N₂O₂)⁻ observed by ESR [3].

On the other hand, the formation of a strong bond between nitrogen atoms in such radical (N-N = 1.4Å) clearly indicates that decomposition of the intermediate form — (N₂O₂)⁻ to a N₂O molecule and — (O)⁻ is the preferred decomposition pathway. Indeed, the ONNO dimer adsorbed on the metal surface Ag(111) shows a surprising low-temperature reactivity producing directly N₂O adsorbed molecules with a low activation energy of 2.0 kcal/mol:

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$(\text{ONNO})_{\text{ad}} \rightarrow \text{N}_2\text{O}_{\text{ad}} + \text{O}_{\text{ad}}$. Thus, on the basis of the above data, it is natural to suppose that the rate-determining step of the low-temperature selective catalytic reduction of NO is the formation of the π -radical $(\text{N}_2\text{O}_2)^{\cdot-}$ on electron donor sites of Cu-ZSM-5 catalysts. One of possible electron donor sites in Cu-ZSM-5 is the copper oxide chain structure.

In the present study, we used DFT to calculate the electronic structure of molecular cluster $(\text{HO})_3\text{Al-O-Cu-O-Cu}$ modeling a fragment of the copper oxide chain structure in Cu-ZSM-5 zeolites, comparison of their theoretical and experimental electronic spectra, and study the ONNO interaction and decomposition on this catalytic active site.

We analyzed various models to represent the structure of catalytic active site (CAS) in Cu-ZSM-5 zeolites. All calculations, geometry optimizations, and search of a transition state (TS) were performed with the Gaussian-98 package at the DFT level using the hybrid exchange-correlation functional B3LYP. On the basis of the B3LYP/LANL2-DZ calculations, we examined $(\text{Cu-O-Cu})\text{—ONNO}$ complex in zeolites and discussed the formation of an N—N bond on a Cu site. DFT calculations showed that in contrast to the weakly bound cis-dimer ONNO with the equilibrium distance N—N $\approx 2 \text{ \AA}$, the anion radical $(\text{ONNO})^{\cdot-}$ is characterized by a strong bond between the nitrogen atoms (N—N $\approx 1.4 \text{ \AA}$).

Analysis of the molecular orbital structure of the dimer and its anions led us to a hypothesis on the reason of preferable stabilization of the nitric oxide dimer in cis form. The calculated high electron affinity ($E_a = -1.3 \text{ eV}$) of the ONNO dimer and significant strengthening of the N—N bond in the anion radical confirms the experimental data on the formation of surface anion π -radical on electron donor sites.

The DFT calculated electronic structure and excitation energy spectra for the model system $(\text{HO})_3\text{Al-O-Cu-O-Cu}$ show that it is a satisfactory model for description of experimental UV-VIS spectra of Cu-ZSM-5, containing (-O-Cu-O-Cu-) chain structures in the zeolite channels [4]. The calculated reaction energy profile of ONNO adsorption and decomposition on the model catalytic active site shows the possibility of the low-temperature decomposition of dimer $(\text{NO})_2$ with low activation energy and the important role of chain copper oxide structures (-O-Cu-O-C-) in the channels of Cu-ZSM-5 zeolite during selective reduction of NO.

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POSTER PRESENTATIONS

SECTION II DESIGN OF HETEROGENEOUS AND HOMOGENEOUS CATALYSTS



**CATALYTIC ACTIVATION OF UNFAVOURABLE REACTIONS BY
M,ReO_x/Al₂O₃ CATALYSTS**

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Introduction.

The possibility of the non oxidative catalytic dehydrocyclohexamerization (DHCH) of methane into benzene, the low-temperature dehydroalkylation (LTDHAB) of benzene by propane and low temperature dehydrogenation (LTDH) of propane into propene with participation of non-reduced metalaluminorhenium catalysts have been studied earlier by us [1-4]. In the case of M,ReO_x/Al₂O₃ catalysts the source of bound oxygen is a supported Re oxide. The reactivity of oxygen bound with Re can be connected with M. In this case, the nature of M interaction with rhenium in M,ReO_x/Al₂O₃ is of a special importance for proceeding of above reactions.

Hence, the aim of the present work is to show influence of M on reactivity of oxygen bound with rhenium.

Experimental.

The studying objects were M,ReO_x/Al₂O₃ catalysts prepared by adsorption (a) and impregnation (i) methods. For comparison the catalysts containing only one supported component - M or Re were prepared by analogous procedure. M and rhenium content in the catalysts prepared were 0.3-0.5 wt %, respectively. The M average particle size was determined by chemisorption and electron microscopic data, and the state of supported metals was characterized by diffuse reflection IR spectroscopic method using CO as a molecular probe. Catalyst tests were carried out in fixed bed flow quartz reactor at atmospheric pressure GHSV (gas hourly space velocity) 1450 h⁻¹, temperature 650°C. The reaction products were analyzed by gas chromatograph.

Results and discussion.

The investigations carried out show that only M,ReO_x/Al₂O₃(a) samples prepared by adsorption method are able to convert efficiently methane into benzene and carry out the other reactions. Benzene formation begins at the fifth minute of the experiment and its yield

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increases reaching maximum value with the experiment duration to 15th minute, which remains constant some time, and then decreases. The data in Table demonstrate the interaction of the reactant, H₂ and CO with the catalysts.

Table

		<i>M, ReO_x/Al₂O₃(a), d_{pt}=0.8</i>						
Substance	Time on stream	3	7	10	15	30	60	120
H ₂	n ₁ mg/g _{cat} (H ₂ O)	1.00	1.06	1.07	1.07		1.07	
CO	n ₂ mg·g ⁻¹ _{cat} (CO ₂)	0.71	0.79	0.82		0.87	0.89	0.92
CH ₄	n ₁ mg·g ⁻¹ _{cat}	0.31	0.42	0.46	0.47	0.51	0.60	0.64
	n ₂ mg·g ⁻¹ _{cat}	0.25	0.27	0.29	0.29	0.29	0.29	0.30
	n _Σ mg ⁻¹ _{cat}	0.56	0.69	0.75	0.76	0.80	0.89	0.94
		<i>M, ReO_x/Al₂O₃ (i), d_{pt}=0.3</i>						
CH₄	n _Σ mg ⁻¹ _{cat}	0.88	1.07	1.12	1.14		1.14	

Data obtained show that during the methane interaction with M, ReO_x/Al₂O₃(a) as CO₂ liberation stops (since fifth minute of experiment), the benzene formation and increase of its yield with experiment duration begin to be observed.

As it was established, only 35% of the bound oxygen contained in catalysts can take part in the process. As the bound oxygen is consumed, the benzene yield per one atom of removed oxygen (O_r) increases from zero to 76.5 molecules.

The removal of bound oxygen from the active M,ReO_x/Al₂O₃ catalysts by methane unlike inactive one, can be divided into two parts: rapid and slow. Producing of the methane DHCH, benzene NDHA and propane NDH proceeding requires the participation of oxygen contained in the catalyst is formation and increase of benzene yield connected with the slow stage of M,ReO_x/Al₂O₃(a) reduction which is characterized by decrease of H₂O molecules yield with the duration of the experiment (Table). Hence, the formation of M,ReO_x/Al₂O₃ active catalysts is a result of certain interaction of high dispersity M with supported rhenium oxide.

Due to M fixed in highly dispersed state the bound oxygen containing in M,ReO_x/Al₂O₃ acquires the above-mentioned reactive non-homogeneity characteristic for a high dispersity M (for instance Pt). After completion of reactions of products formation the reduced [Pt,ReO_x'] is oxidized by interaction with H₂O molecules:



The noted lowering of the catalyst activity with the experiment duration is a result of the decrease of the bound oxygen concentration.

Therefore, the observed increase of the benzene molecules number per one liberated oxygen atom with experiment duration is a result of increase of probability for formed H₂O molecules meeting with the [M,ReO_x] sites.

Conclusion.

1. Oxygen containing in rhenium oxide acquires a reactive non-homogeneity under influence of a supported metal phase of high dispersity.

2. On activation of unfavorable reactions by M,ReO_x/Al₂O₃ (M=Pt, Ni or Co) catalysts a part of reactive non-homogeneous oxygen participates in the cyclic process of H₂O formation and splitting. Proceeding of unfavorable process is facilitated due to mutual induction and conjugation of all stages of surface reactions.

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SYNTHESIS OF MONOPHASE URANIUM OXIDES UO_2 , U_4O_9 , U_3O_8 OF SPECIFIED COMPOSITION BY ELECTROLYSIS OF OXIDE SALT MELTS AND INVESTIGATION OF THEIR PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES

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Bulk monophasic uranium oxides UO_2 , U_4O_9 and U_3O_8 of specified composition were synthesized by electrolysis of oxide salt melts. Optimal electrolysis conditions for synthesis of uranium oxides of given chemical and phase composition were selected. Prepared uranium oxides were characterized by XRD, S_{BET} , SEM, TPR, TPO and FTIR. Catalytic activity of uranium oxides in the reactions of thiophene hydrodesulfurization and butane oxidation was tested.

This work is devoted to investigation of methods of synthesis of uranium oxides (UO_2 , U_4O_9 and U_3O_8) of specified composition by electrolysis of oxide salt melts. The goal of the work is a choice of optimal electrolysis conditions for synthesis of monophasic uranium oxides, which can be used as active components of uranium oxide catalysts.

The oxygen coefficient of uranium oxides, their structure, and current efficiency were studied as influenced by the electrolyte composition, deposition potential, and temperature of electrolysis.

On the results of the experiments, optimal composition of salt melt electrolytes and electrolysis conditions were selected to provide synthesis of cathode product of specified chemical and phase composition and to obtain maximal uranium oxide yields. It was found that the optimal conditions for UO_2 phase synthesis are the electrolyte containing 48.33 K_2WO_4 – 36.24 $K_2W_2O_7$ – 15.43 UO_2WO_4 (mol. %), electrolysis temperature $T = 900^\circ C$ and deposition potential $E = -1.00V$ relative to $Pt(O_2)$ reference electrode. Synthesis of U_4O_9 was performed in the electrolyte 48.33 Na_2MoO_4 – 36.24 $Na_2Mo_2O_7$ – 15.43 UO_2MoO_4 (mol. %) at $T = 900^\circ C$ and $E = -0.80V$. U_3O_8 phase was synthesized by electrolysis of eutectic mixture $(Li, Na, K)_2SO_4$ with addition of 30 mol. % UO_2SO_4 at $T = 800^\circ C$ and $E = -1.00 V$.

Microphotographs of the cathode deposited crystals are presented in Fig. 1.

The samples of uranium oxides were studied by XRD. The atomic O/U ratio of uranium oxides UO_{2+x} and U_4O_{9-y} was calculated from cubic lattice parameter a_0 obtained by XRD using known empirical equations, and equals 2.02 and 2.44, respectively.

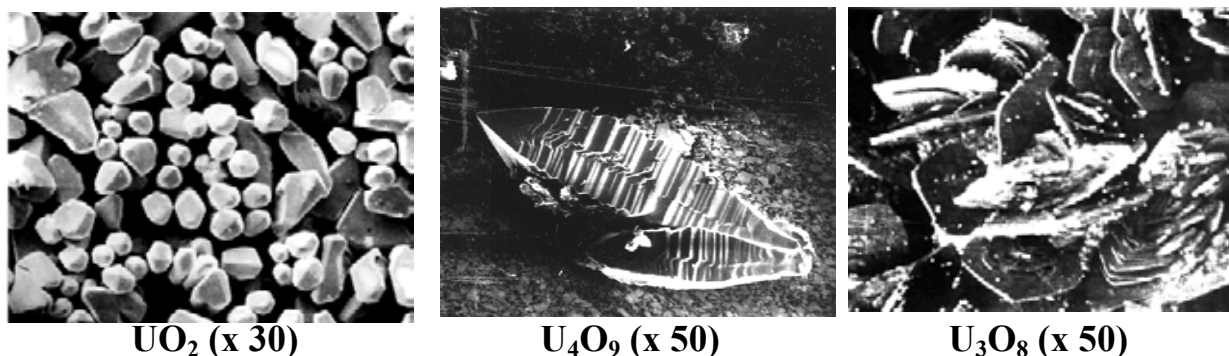


Fig. 1. Microphotographs of uranium oxide crystallites.

The bulk uranium oxide samples were studied by TPR and TPO. It was shown that after reduction by H_2 the oxygen consumption by the samples UO_2 , U_4O_9 and U_3O_8 was similar (1.5 mmole O_2/g). The reduction-oxidation behavior of uranium oxides was studied.

Uranium oxides prepared by electrolysis of salt melts were tested in the model reactions including hydrodesulfurization (HDS) of thiophene and deep oxidation of butane.

The results of testing in the HDS reaction ($P=1$ atm, $1.2 \cdot 10^{-3}$ mole/l thiophene, 400°C) have shown that UO_2 and U_4O_9 have very small catalytic activity. The activity of bulk U_3O_8 is close to that of the sample of uranium oxides supported on alumina and containing 15% U. The results of investigation show that uranium oxides can be used as modifying additives for commercial Co-Mo catalysts of hydrodesulfurization of motor fuels.

The samples of bulk uranium oxide were tested in the reaction of C_4H_{10} deep oxidation (1% C_4H_{10} in air, 1000 h^{-1}). The sample of UO_2 is inactive in the reaction, when the activity of U_4O_9 and U_3O_8 are similar. Temperature of 50% butane conversion on these samples was 480°C .

This work was performed in the frame of joint complex project between Siberian and Ural Branches of the Russian Academy of Sciences.

**CHROMIUM CATALYSTS FOR OXIDATIVE DEHYDROGENATION OF
C₃-C₄-PARAFFINS. PREPARATION, TESTS AND INVESTIGATIONS**

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Chromium catalysts prepared by method of wet precipitation, evaporation of metallic Cr and hydrothermal incorporation of chromium ion in structure of silicas, were tested in oxidative dehydrogenation of C₃-C₄-paraffins. Spectroscopic investigations showed that catalyst deactivation is connected with an increase of chromium particle size with oxidation extent lower than 6+.

Oxidative dehydrogenation in CO₂ presence is alternative process of direct dehydrogenation in which used supported chromium catalysts lose their activity very quickly and work short cycles: dehydrogenation-regeneration. Carbon dioxide shifts the equilibrium of the dehydrogenation reaction at the expense of the interaction with hydrogen and that results in a decrease of formed coke amount. We propose to use the following methods for chromium catalysts preparation: vacuum evaporation of metallic Cr on SiO₂, hydrothermal incorporation of chromium ion in structure of silicas (MCM-41) and traditional wet precipitation for Cr/SiO₂. The catalysts were tested in oxidative dehydrogenation of C₃-C₄-paraffins in the presence of CO₂ or mixture of oxidants: CO₂ and O₂. The experiments were carried out in a flow unit at 550-700 °C at atmospheric pressure. Volume space velocity (w , h⁻¹) was varied in the range 67-3000. The initial reaction mixture were of the following compositions (% vol.): (C₃H₈ or i-C₄H₁₀) (15), CO₂ (30), N₂ (55) or (C₃H₈ или изо-C₄H₁₀) (15), CO₂ (30), N₂ (50), O₂ (5,0). Chromium content was changed in the range (% wt) 0,25 –10,0. It was shown that the optimal concentration of chromium was 5,0-6,0 %. The comparison of catalysts under study was conducted at 600 °C and $w=200$ h⁻¹ for the optimal chromium concentration. At these conditions the conversion of propane over chromium catalysts prepared by wet precipitation during 16 h is decreased from 81,0 to 60,0 % (the selectivity to propene is increased from 70,0 to 82,4 % for this time). After the regeneration of this catalyst by the air, the initial propane conversion was 63,0 %. It means that the catalyst deactivation is irreversible owing to a change of active component state and chromium agglomeration. Over the catalyst prepared by a evaporation of metallic chromium on SiO₂, the initial propane conversion was higher than in previous case (86,5 %) but it is decreased to 55,0 % through 8 h and did not increased till initial level after regeneration. Only on the

catalysts prepared by hydrothermal incorporation of Cr in the structure of MCM-41, the initial propane conversion remained on the constant level after 4 cycles of regeneration. In this case separated chromium ions are fixed in silicas matrice .and their agglomeration is difficult.

The using of mixture of oxidants (CO_2 and O_2) allows to increase of the conversion of propane and isobutane, the selectivity to sum of olefins and in more extent to increase the stability of catalysts after study under some decreasing of the selectivity to propene and isobutene.

The specific surface area, total pore volume and pore were measured. Catalysts were characterized by UV-vis and FTIR spectrometry. On Figure there are shown UV-spectra of fresh chromium catalysts on SiO_2 prepared by wet precipitation (a) and metal vapor synthesis (b) for different content of chromium.

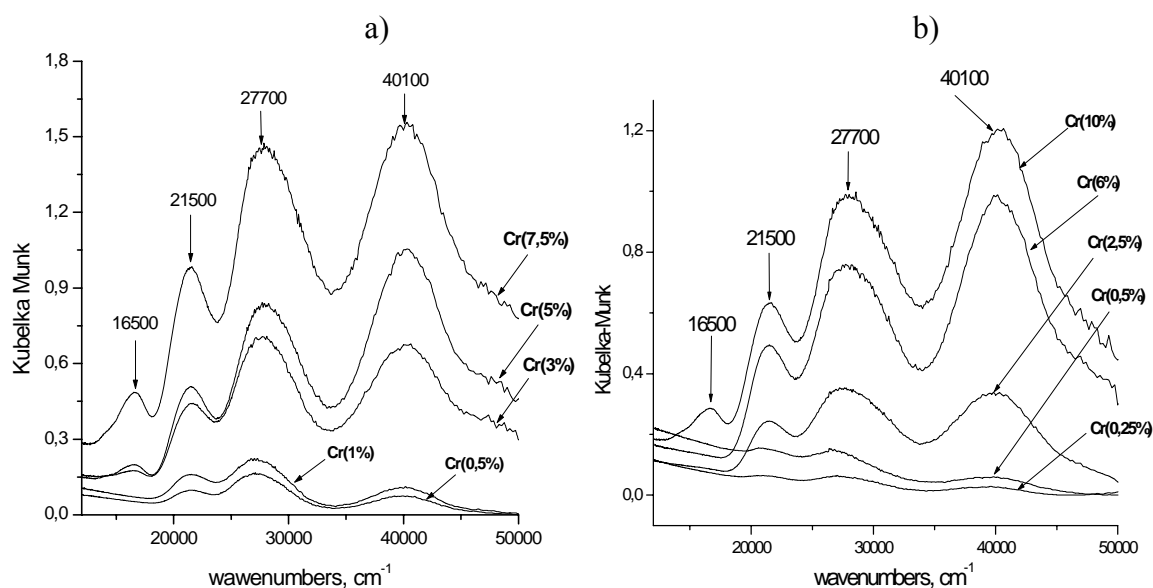


Figure. UV-Vis spectra of chromium catalysts prepared by wet precipitation (a) and metal vapor synthesis (MVS) (b) on SiO_2 in air at room temperature.

At low chromium loading (0,5; 1,0 wt.% Cr) there are one dominant band at 27700 and another wide bands at 21500 and 40100 cm^{-1} in fresh catalysts prepared by wet precipitation. These bands are corresponded to Cr^{+6} . A band at 16500 cm^{-1} , connected with formation of chromia 3^+ , appeared at 3,0 % chromium loading. In catalysts prepared by method of MVS a band with 16500 cm^{-1} appeared in fresh catalysts only at high chromium loading (10 %) but after reaction it became detectable in catalysts containing $\geq 1,0\%$ Cr. This band is absent in catalysts prepared by hydrothermal incorporation and does not appear after 24 h of work. Irreversible deactivation of chromium catalysts prepared by methods of wet precipitation and MVS was connected with decrease of specific Cr surface owing to an increase of chromium particle size with oxidation extent lower than 6+. The IR-investigations showed that for the sample with optimal chromium contents the ratio between Brønsted and Lewis acidities is maximal.

The data obtained indicate that proposed chromium catalysts are effective for oxidative dehydrogenation of C_3 - C_4 -paraffins.

**Pt-CATALYSTS FOR POLYADDITION VULCANIZATION OF SILICONE
POLYMERS, EFFECTIVENESS AND ANALYSIS**

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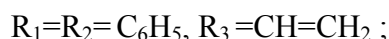
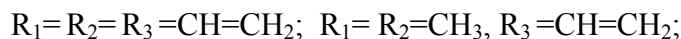
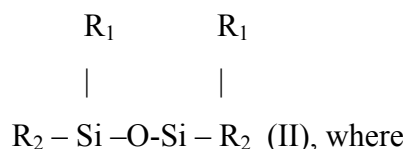
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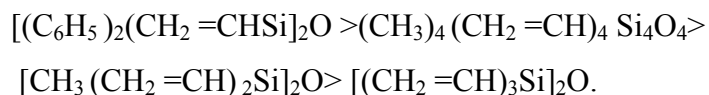
Stability and catalytic activity of complex catalysts was studied with respect to synthetic conditions and technology of preparation. It was showed that activity of Pt complex catalyst depends on ligand structure. In the presence of nitrogen atom in ligand catalyst can be used as catalyst-auto inhibitor. X-ray fluorescence spectrometry as universal analysis has been employed to calculate quantity of Pt in different catalysts of hydrosililation reaction.

Stability and catalytic activity of complex catalysts was studied with respect to synthetic conditions and technology of preparation. Real silicone compositions were created using complex catalysts based on Pt so that control of both temperature and rate of polymerization is achieved over wide range of parameters – from room temperature to 180 °C and from several hours to few seconds, respectively. Hydrosililation reaction catalysts, that are adducts of Pt with polyunsaturated silicon compounds as ligands were synthesized. The general formula of synthesized compounds is presented by $[\text{CH}_3(\text{CH}_2=\text{CH})\text{SiO}]_4$ (I) or by (II) below:



Catalytic activity and selectivity of synthesized catalysts was studied during polyaddition reaction under simulated conditions and with variable compositions of mixed elastomers. Catalytic activity of Pt complex catalysts was determined to decrease in the raw:





Besides a series of complex Pt catalysts on the basis of quaternary salts of tetra and bivalent Pt are investigated. Due to nitrogen atom presence they are able simultaneously demonstrate both catalytic and inhibiting features, i.e. serve as catalyst-auto inhibitor. This allowed to develop single-component polyaddition compositions with high viability under standard conditions and readily vulcanized at elevated temperatures.

For obtaining of silicon materials with optimal properties it is necessary to regulate the Pt content within well-defined limits. Method of X-ray fluorescence spectrometry as universal analysis has been employed to calculate quantity of Pt in different catalyst independently on its structure. In order to decrease the influence of ligands and solvents on composition and density of silicon matrix it was offered to add catalyst on the basis of 10-100 ppm Pt. As the result there were achieved limits of detecting for Pt 4 ppm and concentration sensitivity up-to-date concentration 50 ppm $\Delta C_{Pt}=2$ ppm in silicon matrix.

**THE NEW SULFONIC CATION RESIN CATALYSTS FOR PREPARING OF
ECOLOGICALLY PURE ADDITIVES TO GASOLINES**

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It is known that sulfonic cation resins based on cross-linked copolymers of styrene with divinylbenzene find a wide application as ion-exchange catalysts for different etherification, dimerization, oligomerization, alkylation and other processes [1-3]. However, the important drawback is their low strength and swelling in many reaction mediums.

In order to remove these drawbacks the new sulfonic cation resin catalysts have been synthesized that are based on styrenecontaining graft polyolefins such as polyethelene, α -polypropylene, polystyrene, ethylene-propylene rubber. Sulfonic cation resins developed have been tested in reaction of interaction of isobuthylene (which is contained in C₄ catalytic cracking and pyrolysis fraction) with bioethanol. The new sulfonic cation resins in comparison with traditional ones are more effective (97,5 % of main product yield) versus ethyl-tertbutyl ether which is ecologically pure high-octane additive (115-118 of octane number) to gasoline.

Sulfonic cation resin on the basis of graft polyolefins are characterized by 4-4,96 mg.eqv./g. of statistical exchange capacity, 210-300 % of water swell, 135-147 °C of termal stability, 12-16 kg/mm² of Brinell hardness. There have been studied the effect of graft chain length in sulfonic cation resins on their catalytic properties. It is shown that relatively effective copolymers are the graft ones with the short and frequent situated graft chains in which graft degree is 75% mass., graft polystyrene chain distribution frequency is 3-21 and the molecular weight of graft chain is changed within 3000-20000.

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THE NEW Ni, Zr, Ti-CONTAINING “LIGANDCHARGED” CATALYSTS FOR ETHYLENE (CO)POLYMERIZATION AND THEIR ACTION MECHANISMS

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During the last years the non-metallocene type catalysts for α -olefin polymerization have attracted a great attention. In this connection it have been developed the new highly effective readily available Ni, Zr, Ti-containing “ligandcharged” precursors on the basis of sterically hindered substituted phenol compounds. These precursors in combination with various aluminumorganic compounds (table 1) and modifiers (table 2) provide the polyethylene synthesis with controlled MWD parameters (2,3-89,5), molecular weight (117103-511500) and crystallinity (29-77,3 %). These precursors have been synthesized by one-stage method and their EPR analysis have been conducted. It was shown that the mixing of ethylene polymerization catalytic systems components, “ligandcharged” precursors and aluminumorganic compounds results in the formation of paramagnetic complexes of Ti^{3+} . Magnetic-resonance characteristics (MCR) and the stability of these complexes mainly depend on the presence of the sterically hindered phenols in the system and their nature. It have been discovered the bifunctional properties of “ligandcharged” precursor compounds. By the effectiveness the catalysts based on these precursors are found to be on the same level with metallocene type catalysts.

The development of such catalysts results in obtaining of the new important petrochemistry products with the unique microstructure and a wide variety of properties.

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Table 1. Examples of ethylene polymerization in the presence of the catalysts based on the three-component precursor systems (P_x) and aluminumorganic compounds (D)

Catalyst				Polymerization condition		Catalytic activity kg PE/ g metal/ h	PE properties			
P _x	D	Metal compound/D, mmol	Metal/Al mol	P _{ethylene} , atm	T, °C		T, °C	Cr. deg. %	Mw	MWD
P ₁	MAO	0,015/75	1/5000	20	25	105	133	64	321050	77
P ₂	MAO	0,016/32	1/2000	15	25	102	133	62,3	425031	78,9
P ₃	MAO	0,012/60	1/5000	15	25	100	132	67,6	310850	71,1
P ₃	MAO Et ₂ AlCl	0,01/5 0,01/0,5	1/500 1/50	15	25	204	133	64	302840	89,5
P ₇	MAO Et ₂ AlCl	0,013/3,9 0,013/1,3	1/300 1/100	20	20	221	132	64,1	355780	87,4
P ₁₂	MAO Et ₂ AlCl	0,01/4 0,01/4	1/400 1/100	20	25	250	134	68	394152	72,3
P ₁₅	MAO Et ₂ AlCl	0,012/12 0,012/2,4	1/1000 1/20	20	20	300	132	72,5	438290	78,8
P ₁₇	MAO	0,015/75	1/5000	20	20	156	134	73	395280	62,3
P ₁₇	MAO Et ₂ AlCl	0,016/6,4 0,016/0,8	400 1/50	25	22	217	132	62,3	384953	76,4
P ₁₈	MAO	0,015/45	1/3000	20	25	102	132	69,8	251204	60,34

Table 2. Examples of ethylene polymerization in the presence of the catalysts based on the two-component precursor systems (P_y) and aluminumorganic compounds (D)

Catalyst				Polymerization condition		Catalytic activity kg PE/ g metal/ h	PE properties			
P _y	D	Metal compound /D, mmol	Metal/Al mol	P _{ethylene} , atm	T, °C		T, °C	Cr. deg. %	Mw	MWD
P ₁₉	MAO	0,01/50	1/5000	20	25	112	133	29	339500	4,1
P ₂₀	MAO	0,018/36	1/2000	15	25	89	133	45,3	280000	3,73
P ₂₁	MAO	0,016/80	1/5000	15	20	120	133	58,4	329800	2,3
P ₂₁	Et ₂ AlCl	0,018/9	1/500	15	25	106	133	43,4	511500	5,61
P ₂₆	MAO	0,015/15	1/1000	15	25	87	133	73,6	186000	2,8
P ₂₉	MAO	0,012/36	1/3000	20	25	105	132	71,2	298147	16,2
P ₃₂	MAO	0,01/20	1/2000	30	70	112	131	77,3	117103	21,2
P ₃₂	MAO Et ₂ AlCl	0,012/6 0,012/1,2	1/500 1/100	30	70	234	131	72,1	208565	53,4
P ₃₆	MAO	0,018/18	1/1000	30	80	108	131	72	411038	58,8
P ₃₆	MAO Et ₂ AlCl	0,012/6 0,012/0,3	1/500 1/25	30	70	189	132	74,2	394259	62,5

**SPATIALLY RESOLVED UV-VIS MICRO-SPECTROSCOPY:
A PHYSICO-CHEMICAL STUDY ON THE PREPARATION OF METAL-ION
SUPPORTED CATALYST EXTRUDATES**

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Spatially resolved UV-Vis micro-spectroscopy is a newly developed technique to study the physicochemical processes involved in the elementary steps (impregnation and drying) of mm-sized catalyst extrudates preparation. The metal ions under study were Ni^{2+} , Cu^{2+} , Pd^{II} and Pt^{IV} . Different preparation conditions were used (PZC, ionic strength, drying temperature and nature of the complexes in solution) in order to monitor the influence of them on the metal ion distribution or speciation. By following the d-d and charge transfer transition bands of the respective metal ion complexes during impregnation and after drying it was possible to observe different distributions by modifying the PZC, the ionic strength or the nature of the ligands in the solution and different species being formed as a function of the position inside the catalyst extrudates as a function of the drying temperature.

Introduction The elemental steps of impregnation and drying in the preparation of different hydrogenation catalysts containing Ni^{2+} , Cu^{2+} , Pd^{II} and Pt^{IV} were under study. To do so, a newly developed technique was applied, UV-Vis micro-spectroscopy, which is able to monitor the physico-chemical processes involved during the preparation of mm-sized supported catalysts with both spatial and time resolution.

UV-Vis micro-spectroscopy

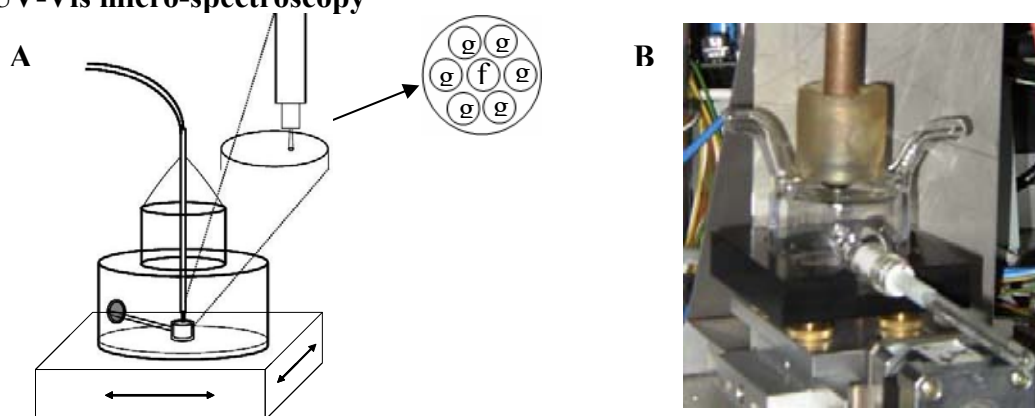


Figure 1. UV-Vis micro-spectrometer. (A) Scheme of the set-up: (a) UV-Vis probe, (b) measuring cell, (c) movable platform, (d) sample holder. UV-Vis probe formed by one collecting fiber (f) and six illuminating fibers (g). (B) Illustration of the set-up.

UV-Vis micro-spectroscopy enables monitoring the metal-ion speciation along the cross section of bisected catalyst bodies in the UV-visible-NIR region (250-1100 nm) with a spatial

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resolution of around 200 μm . Measurements can be done both in the wet and in the dry stage of the preparation process thanks to the measuring cell. The set-up (shown in Figure 1) consists of a UV-Vis probe containing 7 optical fibres ($\varnothing=100\ \mu\text{m}$), six of them connected to a light source and the other one to a detector. A step motor allows the movement of the measuring cell (x, y directions) and the probe (z direction) [1].

Results In the case of $\text{Pd}^{\text{II}}/\text{Al}_2\text{O}_3$ catalysts the impregnation step was monitored. The ligand-to-metal-charge-transfer transition at 280 nm and the Pd^{II} d-d band at 474 nm of $[\text{PdCl}_4]^{2-}$ complexes were measured. The latter band shifted to shorter wavelengths with aging time, indicating a change in the coordination sphere of the metal ion. Moreover, both bands remained with time in the outer rim of the pellet. Pd^{II} distribution could be modified by adding excess of NaCl to the impregnation solution giving a Pd^{II} egg-yolk distribution after 4 days of aging.

The influence of the drying temperature was studied on $[\text{Ni}(\text{en})_3]^{2+}/\text{Al}_2\text{O}_3$ pellets. UV-Vis spectra, collected after drying at room temperature, showed two Ni^{2+} d-d transitions bands at 549 and 890 nm, present in all the positions inside the pellet indicating a uniform distribution of $[\text{Ni}(\text{en})_3]^{2+}$ (Figure 2a). Drying at 60 °C yielded a shift of the bands to longer wavelengths from the edge to the core of the pellets (Figure 2b). The shift of the bands indicated that a gradual change in the coordination sphere of Ni^{2+} occurred from the outer part of the pellet to the core, in which ethylenediamine groups were partly substituted probably for hydroxyl ligands from the support [2].

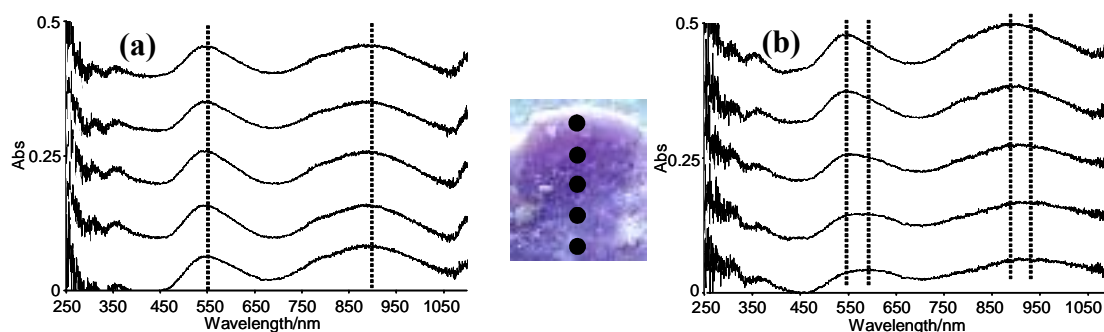


Figure 2. UV-Vis spectra collected along the cross-section of an impregnated pellet with 0.5 M $[\text{Ni}(\text{en})_3]^{2+}$, after 2 h of aging followed by drying at room temperature (a) and at 60 °C (b).

Conclusions Spatially resolved UV-Vis micro-spectroscopy enables studying the physicochemical processes involved during catalyst preparation. It allows monitoring both the wet and dry steps, giving information of the metal ion surroundings and how this can be modified. Thus, this technique helps to understand catalyst preparation processes which is of prime importance for the design of industrial catalysts.

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**POLYOL MEDIATED SYNTHESIS OF NANOSCALE COPPER/ZnO PARTICLES:
INFLUENCE OF SYNTHESIS CONDITIONS ON THE PARTICLE SIZE**

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1. Introduction: Considerable attention has been paid in the past two decades to unusual properties and potential application of copper metal nanoparticles in many fields such as electronic industry in the manufacture of various electronic devices [1], conductive films [2], photonic devices [3] and new types of catalysis. Non-agglomerated, spherical, uniform copper/metal oxide particles are desired for many catalytic reactions, for example methanol decomposition to CO and H₂ for fuel cells [4], dehydrogenation of cyclohexanol [5], and liquid phase oxidation of benzene to phenol [6]. A number of chemical and physical methods such as microemulsion [7], electrochemical deposition [8], microwave irradiation [9], reduction of copper salts solutions with various reducing agent NaBH₄, N₂H₄·H₂O [10, 11] were used for the preparation of metal and bimetallic powders but little has been done to synthesize metal-metal oxides *in situ*. Cable and Schaak et al. [12] synthesize nanocrystalline powders of many late transition-metal and post transition-metal intermetallic compounds such as CoSb₃, Cu₆Sn₅, Co₃Sn₂, PtPb and PtBi by using polyol process and since Zhu et al [11] synthesize well dispersed copper metal nanoparticles with a diameter of 15 nm by reducing CuSO₄ with hydrazine in EG under microwave irradiation. This method is characterized by a quick reaction rate but the agglomeration of particles are often substantial when the precursor concentration is above 10⁻²M [13]. Yu et al [14] produced non-agglomerated rodlike Nickel particles in micrometer size range by combining some advantages of polyol process and chemical reduction methods. Solution based synthetic strategies like polyol process offer several important advantages over traditional high-temperature methods. For example solution route can precipitate nanocrystalline powders at low temperature [15] and also solution methods often allow control over nanostructure and morphology, providing a convenient medium for growing size and shape controlled nanocrystals [16].

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In this work the synthesis of well dispersed copper/metal oxide nanoparticles in ethylene glycol without using a protective polymer was studied. A systematic study of reaction parameters has been done. In order to control size, shape and the agglomeration; reaction temperature, time of reduction using a reducing agent $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, basicity of the reaction medium, effect of water content and the nature of the metal salt were varied. In addition the oxidation products of EG were studied.

2. Experimental: The experiments were carried out using $\text{Cu}(\text{acetate})_2\cdot\text{H}_2\text{O}$, $\text{Zn}(\text{acetate})_2\cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{acetate})_2\cdot\text{H}_2\text{O}$, $\text{Mg}(\text{acetate})_2\cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, ZnCl_2 as metal precursors, ethylene glycol, NaOH , N_2H_4 . All the experimental reagents were analytically grade. The standard procedure is as follows; First specified amounts of metal precursors were dissolved in 100 ml polyol like ethylene glycol or diethylene glycol. Then the solution was transferred to a tree necked flask with a distillation attachment and placed on a magnetic stirrer. The solution was then first heated up to 80°C and NaOH was added. The molar ratio of $\text{OH}^-/\text{total metal ion}$ was increased from 0 to 1 respectively. Then the reaction was carried out at the boiling point of the polyol for 150 min. During this time metal precursors undergoes dissolution and are reduced to metal ions and metal oxides form and then the formation of nucleus and particle growth takes place. The volatile compounds of the reaction medium were collected for further analysis. The reaction flask was cooled down to room temperature naturally; the obtained black precipitate was decanted, filtered and washed with ethanol. The final product was obtained after it was dried at 80°C for 6 hours.

The structure and morphology of the as-prepared copper on oxide particles were analyzed using Rigaku D/max-2200 X-Ray diffractometer with $\text{CuK}\alpha$ radiation. From X-Ray diffractograms, phases and crystallite sizes by using scheerer equation were estimated. The morphology of the final products was determined by Scanning Electron Microscopy (SEM) Jeol JSM-6335F and the oxidation products were identified through FTIR

3. Results and Discussion: The reduction of copper acetate in ethylene glycol was an interesting color-changed process in which the color of the suspension gradually turned from Cambridge blue to deep blue, then to henna and a black product was eventually formed. In every 30 min samples were collected at different phases. Figure 1 shows the FTIR spectra of ethylene glycol used as starting material and liquid samples collected at different reaction phases. Figure-2 shows the X-Ray patterns for different Cu/ZnO catalysts. For all samples no

CuO phase were detected, suggested that CuO component in Cu/ZnO catalysts was reduced completely to metallic Cu by reducing agent. Figure 3 shows the crystallite size estimated with Scherer Equation using the FWHM values. Figure 4 shows SEM image of sample 2. It can be seen that the sample consist of uniform spherical particles. Figure 4 shows TEM images of sample 5, sample 1 and sample 2. The diameters of the particles are in the range 20-50 nm, respectively, in accord with the XRD results.

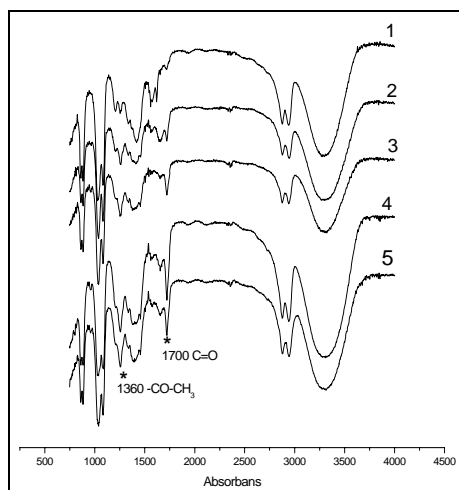


Fig. 1 800mmol/l %70 Cu %30 ZnO FTIR

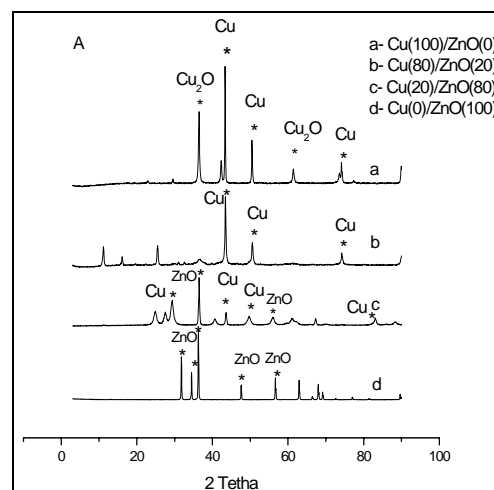
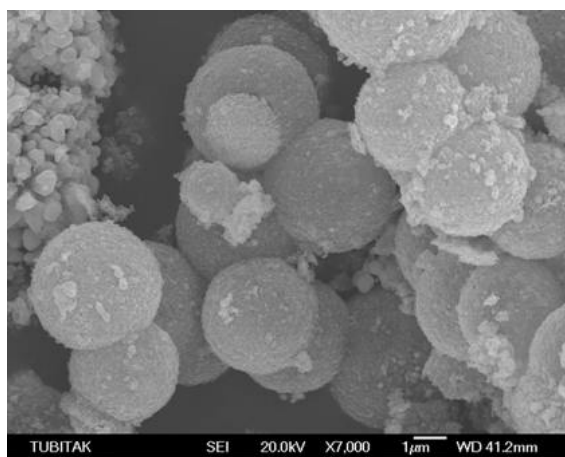


Fig. 2 X-Ray Patterns



20nm

Fig. 3 SEM image of Cu(70) / ZnO(30) water distilled Fig. 4TEM image of Cu(70) / ZnO(30)

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SHS-INTERMETALLIDES ON THE BASE OF Ni, Co, Fe AS THE CATALYSTS FOR CO₂ REFORMING OF METHANE

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The methane reforming with CO₂ seems to be a promising reaction system useful to reduce the greenhouse contribution of both gases into the atmosphere. It was investigated over SHS-intermetallide catalysts. A series of Ni-Al, Co-Al, Fe-Al catalysts were prepared by self-propagating high temperature synthesis (SHS). X-ray diffraction (XRD) and SEM, TG, DTA techniques were applied to characterize the catalysts. The catalysts exhibited high activity and good stability at stoichiometric methane and carbon dioxide feed.

Catalytic conversion of methane by carbon dioxide remains of strategic interest, essentially since it provides a CO/H₂ ratio (1:1) adapted to the gas-to-liquid processes (methanol, dimethyl ether, methylmethacrylate and other oxygenates). This reaction is very important from ecological point of view due to utilization of greenhouse gases.

A new method of self-propagating high temperature synthesis (SHS) has been used. It allows to obtain intermetallide catalysts. Besides, new technology of manufacture of our catalysts leads to decrease power consumption, expenses for raw material and the duration of the production cycle is less in comparison with the wetness impregnation. SHS-process is pure from ecological standpoint because industrial wastes are absent.

A series of Ni-Al, Co-Al, Fe-Al catalysts prepared by self-propagating high temperature synthesis were investigated using a wide variation of constituent contents. Our catalysts were tested in flow catalytic set up (in a temperature-programmable quartz tube reactor operated at atmospheric pressure) in the following conditions: temperature range 600 – 950 °C, space velocity range of gas stream 100±50ml/min and molar ratio CO₂/CH₄=1±1:1±1. The exhaust gases were analyzed using a thermal conductivity detector on-line.

It was shown that Ni₃Al and Fe₃Al had the highest activity at temperature of 800-950 °C. Conversion of methane and CO₂ achieved 90-95 %. Significant conversions was obtained on Co-based catalysts (especially on samples with Co content more than 94 % weight)

According to the X-ray diffraction it was shown that the composition of samples changed after the reaction: in the system of Ni₃Al, besides Ni₃Al, some quantities of NiAl phase and metallic Ni were detected. The inactive systems NiAl, Ni₂Al₃ are both monophased before as well as after the reaction. High activity of Ni₃Al system can be referred to an increase of the

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number of active Ni metal sites present on the catalytic surface of the multiphase samples or presence of interphase boundaries. Co- and Fe -based catalysts contained the following phases: CoAl, Co_{cub.}, Co_{hex.} and Fe₃Al, some traces of Fe и Fe₂Al₅, respectively. However, the initial conversions of CH₄ and CO₂ over the latter catalysts decreases in time in consequence of agglomeration (sintering) of Co and formation of considerable quantities of FeO.

Using scanning electron microscopy it was shown that some catalysts of carbon dioxide reforming of methane undergo nonessential morphological changes in redox conditions. For example, the surfaces of Ni₃Al and Fe₃Al loosened as a result of catalytic erosion and carbon deposition. The surface of metallic Fe transformed from globules to pyramidal particles. Therefore, catalytic activity decreased in consequence of carbonization. The coke filaments formed on the surface of Co catalysts, therefore their activity decreased too.

TG-DTA-analysis showed that the most coked catalysts lost 10-15% of their weight. Mass changes (TG and DTG curves) is accompanied by exothermal effect caused by combustion carbon deposits formed during catalytic tests. At the same time, taking into consideration the possibility of formation of different forms of coke, the most significant weight change at 600 °C (for Ni₃Al), is caused by combustion of amorphous carbon which burns out in the first place.

In fact, with regard to the dry reforming reaction, the highest methane conversion has been reached using Ni₃Al and massive Co catalyst. Catalytic activity is a function of Ni and Co quantities in the intermetallides.

CO OXIDATION IN HYDROGEN STREAMS OVER Au/CeO₂

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Nowadays, hydrogen-fueled PEM fuel cell seems to be the most promising technology for transport applications. For automotive applications, hydrogen could be manufactured on-board by hydrocarbon steam reforming and afterwards, Water Gas Shift reaction (WGS) eliminates most of the CO in the reformat gas, by the way enhancing H₂ content. However, the hydrogen-rich effluent from WGS still contains CO (about 1 mol %) which should be lowered to below 20 ppm before be fed to PEM fuel cell, to prevent the electrode poisoning by CO [1]. Selective CO Oxidation is an efficient and cost-effective method for removing low levels of CO from H₂-rich gas streams [2]. For such reaction, where CO is selectively oxidized with molecular oxygen, very active and selective catalysts are needed with moderate H₂ consumption (high selectivity). Since PROX unit is placed between WGS (180-200 °C) and PEM fuel cell (80-100 °C) units, it should operate between these temperatures in order to avoid additional heat exchange, thus increasing total device volume. Finely dispersed Au supported on a reducible oxides is a good low-temperature CO oxidation catalyst [3]. In this work, Au has been supported on high surface ceria (BET=164 m²/g) by deposition-precipitation with NaOH [4], achieving Au particles smaller than 5 nm (as evidenced by TEM microscopy).

The catalyst has been characterized by TEM microscopy to evaluate the Au dispersion. BET surface area has been evaluated by N₂ adsorption. XRD technique has been used to analyze catalyst structure. In order to evaluate the catalyst reducibility, H₂-TPR has been employed. CO-TPD and O₂-TPD coupled to MS quadrupole allowed us to elucidate different CO adsorption sites as well as different oxygen sources for CO oxidation, following the evolution of formed CO₂ in the catalyst exhaust gases. Finally, FTIR has been used to investigate the possible mechanism during selective CO oxidation in hydrogen rich streams.

Catalyst lightoff curves have been obtained in plug flow reactor in temperature ramp of 3 °C/min. Operational variables such as oxygen-to-CO ratio (λ -value) and presence of CO₂ and H₂O in the feedstream have been evaluated in catalytic test as well as FTIR.

In Figure 1 is shown the CO conversion for 1%CO, 60%H₂ for different λ -vales.

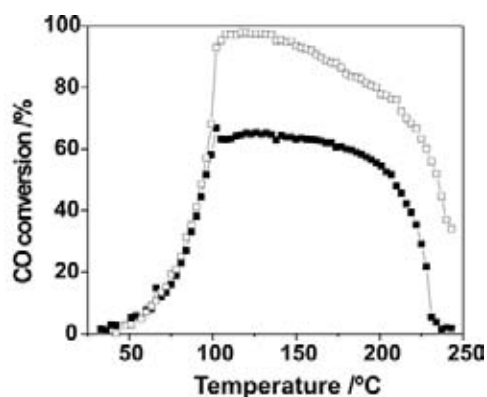


Figure 1: CO conversion for $\lambda=1$ (filled symbol) and $\lambda=2$ (open symbol).

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CATALYTIC PERFORMANCE OF COPPER CERIUM OXIDE SYSTEMS FOR THE HYDROGEN PRODUCTION REACTIONS

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Copper-cerium oxide systems have been studied as the catalysts for the reactions of methanol steam reforming and dimethyl ether steam reforming to hydrogen-rich gas mixtures. Hydrogen and carbon dioxide were the main reaction products, the CO content was insignificant. To provide CO cleanup to 10 ppm – a fuel cell tolerable level - the reaction of preferential CO oxidation has been used. Copper-cerium oxide catalysts were used for this reaction as well.

Based on the results obtained, the nature of active centers, reaction mechanisms and potentials of copper-cerium oxide catalysts for hydrogen production in two-stage reactors have been discussed.

Recently, copper-cerium oxide systems have been proved to be efficient catalysts for numerous reactions and processes including fuel reforming to hydrogen-rich gas for fuel cell applications.

This report presents the results on the development and studies of copper-cerium mixed oxide catalysts prepared by various methods for dimethyl ether steam reforming, methanol steam reforming and preferential oxidation of carbon monoxide in hydrogen-rich gas mixtures. The catalyst performance was studied in a flow setup with on-line chromatographic analysis of the reaction products. The dependencies of the catalyst performance on the temperature, inlet composition and feed rate of the gas mixture have been determined. The experiments on dimethyl ether steam reforming and methanol steam reforming were performed at GHSV = 5000 ÷ 20000 h⁻¹ and temperature 150-400 °C; experiments on CO preferential oxidation - at GHSV = 5000 ÷ 60000 h⁻¹ and temperature 50 ÷ 250 °C.

The fresh and spent copper-cerium oxide systems were characterized by means of TPR, TPO, TPD, XRD, XPS and TEM techniques. The FTIR spectroscopy *in situ* was applied for detailed characterization of the functioning catalysts.

In our experiments, copper-cerium oxide catalysts showed excellent performance for the reaction of methanol steam reforming. At low temperatures (200-250 °C), the main reaction products were hydrogen and carbon dioxide. 100 % methanol conversion was achieved at

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320 °C, but the reaction products contained, besides hydrogen and carbon dioxide, some amount of CO, which most likely was formed by reverse water-gas shift reaction.

To perform the reaction of dimethyl ether (DME) steam reforming, bifunctional catalysts have been developed based on alumina supported copper-cerium oxide (1-20 wt.%) systems. The Cu/Ce molar ratio was varied from 1 to 4. The acidic centers of alumina were shown to catalyze the reaction of DME hydration to methanol, while copper-cerium oxide catalyzed the reaction of methanol steam reforming to hydrogen-rich gas. The catalyst of composition 20 wt.%(CuO-CeO₂)/Al₂O₃ (molar ratio Cu/Ce=3) showed the highest hydrogen productivity. Based on the results obtained, reaction mechanisms of methanol steam reforming and DME stem reforming have been discussed.

Copper-cerium oxide systems were proved to be active and selective catalysts for the reaction of CO oxidation in hydrogen-rich gas mixtures. It was found that copper segregates on ceria surface in a labile state depending on the catalyst pretreatment conditions. The reaction of CO oxidation in hydrogen-rich gases on copper-cerium oxide systems is catalyzed by dispersed copper which most likely exists in a form of two- and three-dimensional surface clusters containing the Cu⁺ ions. The probable mechanism for the reaction of CO oxidation in hydrogen excess on copper-cerium oxide catalysts is suggested.

The work is supported partially by grants BRHE Y4-C-08-12, INTAS № 06-1000014-5774, “Global Energy” Foundation, FASI State Contract № 02.442.11.7239, FAE Scientific research work №1.10.06.

FORMATION OF RADICAL CATIONS OVER CATALYSTS WITH STRONG ONE-ELECTRON ACCEPTOR SITES

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In the current communication we shall review the properties of the strong one-electron acceptor sites present on sulfated zirconia and alumina catalysts and compare them with such sites on Cu-ZSM-5 catalysts. Both types of materials will be shown to have exceptionally strong one-electron acceptor sites, which may contribute to their unique catalytic properties.

Ionization of various aromatic molecules to the corresponding radical cations is known to occur on a variety of zeolites and other acidic materials [1]. Of special interest are the materials possessing exceptionally strong one-electron acceptor sites capable of ionizing compounds with very high ionization potentials, such as benzene (IP = 9.24 eV) or even alkanes. So strong sites can initiate catalytic reaction of the hydrocarbons. The resulting radical cation intermediates may play an important role in the catalytic reactions taking place over such catalysts.

Sulfated zirconia and alumina exhibit unique acidic properties and catalytic activity in isomerization, cracking, acylation and alkylation processes at low temperatures. After more than two decades of intense research there are still lots of debate on the nature of their active sites. This makes direct comparison of various active species on the surface of such catalysts prepared by different methods especially important for understanding the nature and structure of their active sites. In particular we shall compare conventionally prepared samples with varied amounts of sulfates with nanocrystalline aerogel-prepared catalysts. The latter have very high surface areas and small particle size that is expected to affect their electron acceptor properties.

Sulfated zirconia proved to have very strong acceptor sites capable of ionizing benzene and methylbenzenes to corresponding radical cations. Visible-light illumination was also effective in the generation of the radical cations. The presence of gaseous oxygen appeared to strengthen the acceptor sites shifting the red edge of the photoprocesses to 579 nm and making thermal ionization of the weakest donors possible. Chlorobenzene appeared to be the most suitable probe molecule for testing the strongest acceptor sites of sulfated zirconia

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catalysts. A good correlation between their presence and concentration, and the catalytic activity in butane isomerization has been observed [2].

We investigated in detail the formation and parameters of hexamethylbenzene (HMB) radical cations after HMB adsorption from different organic solvents on various sulfated alumina catalysts. We observed the values of the hyperfine constant in the HMB radical cations to depend on the choice of solvent, temperature and catalyst pretreatment. At any temperature, the hyperfine constant was found to increase following an increase in the solvent ionization potential. We believe that this is caused by fast electron exchange between HMB radical cations and the solvent molecules, which becomes more and more significant as the ionization potential of the solvent goes down and approaches that of HMB. Also we have found that an increase of sulfur concentration up to monolayer coverage leads to considerable increase in the concentration of HMB radical cations and decrease of their hyperfine constant reflecting the growing strength of acceptor sites.

Cu-ZSM-5 zeolites attract world-wide attention of researchers due to their high activity in selective catalytic reduction of NO by hydrocarbons. Samples with Si/Al =17 and Cu concentration ranging from 0 to 3.41 wt.% were used in the study. The starting H-ZSM-5 zeolite used for synthesis of Cu-exchanged samples was found to have one-electron acceptor sites capable of ionizing adsorbed benzene to its radical cations. After the copper introduction the acceptor sites were found to grow both in number and strength.

All Cu-ZSM-5 samples were found to ionize chlorobenzene, which is not ionized over H-ZSM-5 samples. The concentration of sites capable of ionizing chlorobenzene was approximately proportional to the copper concentration at low exchange levels up to $\text{Cu}/\text{Al}_{\text{at}} = 0.35$. Although the concentration of very strong acceptor sites continues to grow after further increase of the copper concentration, the rate of such growth becomes slower. So, Cu-ZSM-5 has very strong one-electron acceptor sites comparable to those of sulfated zirconia. Further studies are needed to evaluate their role in the catalytic activity of Cu-ZSM-5.

Financial support by the Russian Foundation for Basic Research (Grants 06-03-32712 and 06-03-33107) is acknowledged with gratitude.

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**CATALYSTS MOLECULAR DESIGN BY SURFACE SYNTHESIS OF THE
PLATINUM POLYHYDROXOCOMPLEXES AS PRECURSORS**

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The paper deals with the problems of “metal complex – support” interaction at the stage of the precursor contact with the high surface area oxide support and the development of synthesis methods to modify greatly catalytic properties of an active metal.

The hydrolyzed Pt-species as precursors were offered. The advantage of this Pt-species is a firm metal grafting due to the exchange of complex's OH-ligands and the surface hydroxogroups of alumina. Besides, an ability of hydroxocomplexes to form a bridge oxo- and hydroxogroups provides polynuclear structures and thus a formation of active sites geometry at the initial stage of synthesis. The novelty of this research is to carry out a synthesis of Pt-hydroxocomplexes directly on the support surface by thermal hydrolysis of pre-adsorbed chloride precursor.

There are various opinions of surface reactions mechanisms in interacting a support and precursor solution available in the literature. The investigation of surface metal complexes by the method dividing surface Pt-species in amount according to the nature of their interaction with the oxide support was conducted. The desorption technique suggested was used in two versions. In the first case, the removal of surface forms was a result of the competitive sorption of anions essentially differing by the sorption selectivity onto alumina. In another case, the desorption of surface anion Pt-complexes was carried out due to the charge state change of the alumina surface. The simultaneous proceeding of both ion exchanged processes in which Pt-complex keeps its nature in transferring from the solution onto the surface, and the coordinated interaction accompanying by the entering surface groups into coordination sphere was determined to be available in the process of metal deposition. The chemical composition of ion exchange and coordinately bounded complexes were investigated by ESDR and EXAFS methods. In the coordinately grafted complexes there are present the hydrolyzed species with the average composition $[\text{PtCl}_2(\text{OH})_4]/\text{Al}_2\text{O}_3$ and/or $[\text{PtCl}_2(\text{H}_2\text{O})_4]/\text{Al}_2\text{O}_3$. Their reduction occurs at higher temperatures and formed Pt-crystallites show the specific adsorbed properties. However, the part of coordinately grafted species in the samples prepared from chloride precursor is not in excess of 30 %.

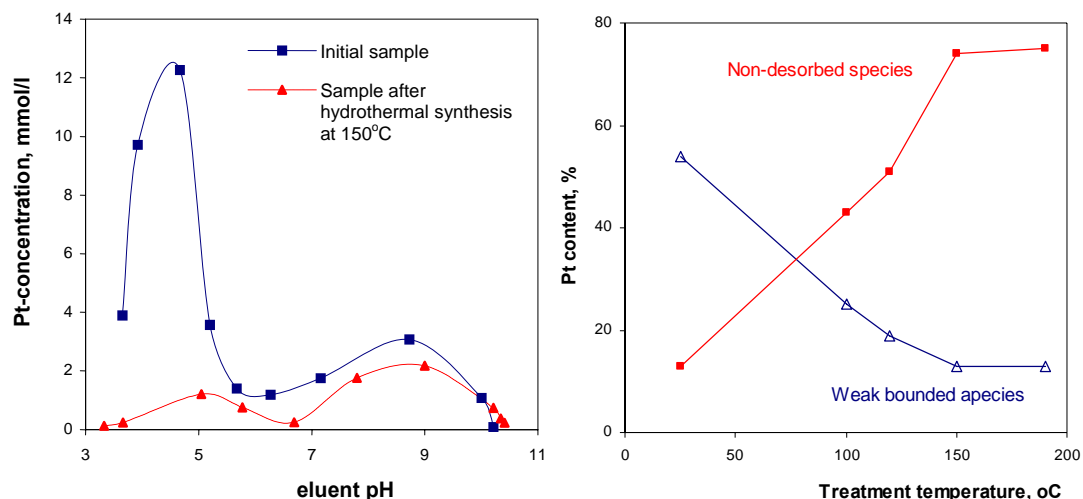


Fig.1. Desorption data as a function of the eluent pH for 2% Pt/Al₂O₃ samples.

The ion exchange part of surface Pt-species considerably decreases by using hydroxocomplexes surface synthesis method (hydrothermal synthesis). The part of coordinately bounded non-desorbed complexes increases up to 80 %. The change of the temperature and the exposure time provides a desired ratio of different species. Thus, the application of the surface hydrolysis stage in the synthesis scheme leads to obtaining the deeply hydrolyzed species onto the surface. They are able to react with oxide support by coordination mechanism.

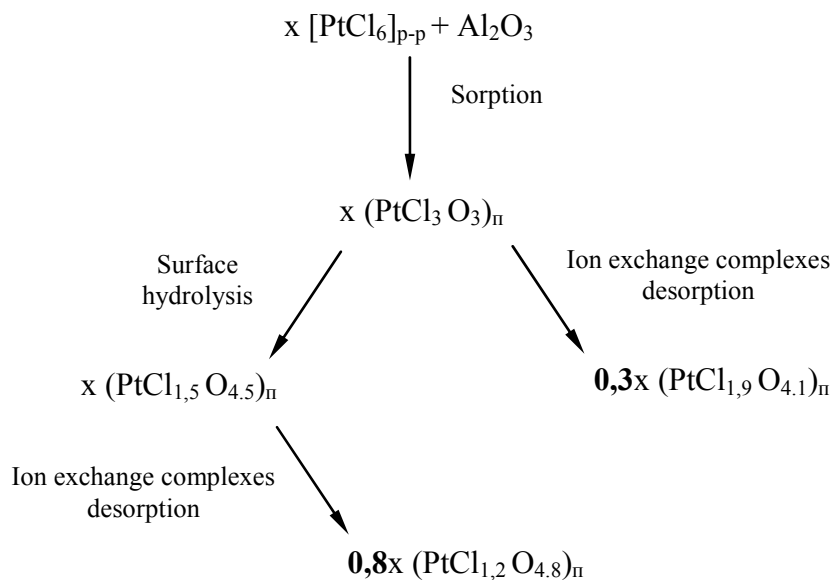


Fig. 2. Transformation scheme of chloride precursor of platinum in interaction with alumina and surface synthesis of hydroxocomplexes.

This work was supported by the Russian Foundation for Basic Research (grant 06-03-32862).

THE CATALYTIC ACTIVITY OF FUNCTIONAL POLISILOXANS IN REACTION OF LIQUID-PHASE OXIDIZING DEHYDROGENATION OF HYDROXYARENS

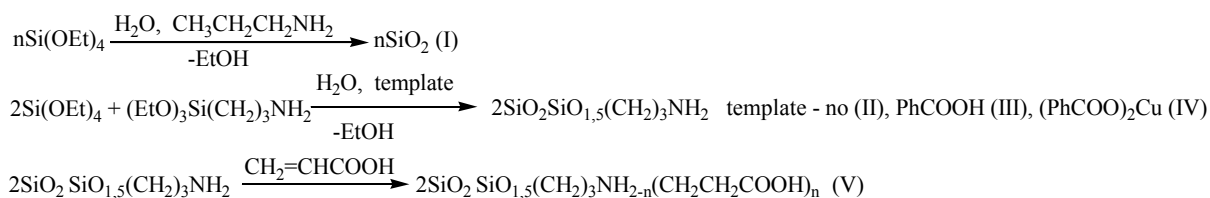
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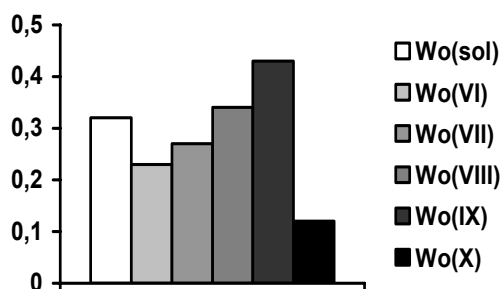
Catalytic activity of modified by functional groups polysiloxanes in modeling reaction of liquid-phase oxidizing dehydrogenation thrimethylhydroquinone was studied by method of initial rates. Essential activity of copper-containing aminopropylpolysiloxane, synthesized in the presence of template – copper benzoate, in comparable with the similar catalyst is shown on the basis of hydrogel oxide silicon.

The purpose of the present work was studying catalytic activity, hybrid organo-inorganic materials - aminopropylpolysiloxane, in modeling reaction of liquid-phase oxidizing dehydrogenation of trimethylhydroquinone, before described in [1]. Catalysts (I-IV) synthesized by a sol-gel method: by polycondensation tetraethoxysilane in the presence of propylamine, copolycondensation of tetraethoxysilane and aminopropyltriethoxysilane, including, in presence of templates - benzoic acids and copper benzoate, carboxyethylation of compound (II) it is obtain polysiloxane (V).



Substrates containing copper (VI-VIII, X) were obtained by processing appropriate polysiloxanes (I-III, V) solutions of copper acetate from compound (IV), benzoic acid deleted extraction with the help of a solution triethylamine in chloroform, the residue used, as the catalyst (IX).

According to the received data, use of compounds (I-V) as catalysts renders essential influence on process: initial speed of process W_0 grows in 8 and 14 times at the presence of compounds (I, II), and the catalyst (V) completely inhibited reaction. At oxidation thrimethylhydroquinone with participation of ions Cu^{2+} (the contents of copper in sphere of reaction 6 mmol/l), compounds (VI-X) ratio of initial speeds of reaction is built in the following number: $W_{0(\text{sol})}:W_{0(\text{VI})}:W_{0(\text{VII})}:W_{0(\text{VIII})}:W_{0(\text{IX})}:W_{0(\text{X})} \approx 10:7:8:11:14:4$.



The speed of reaction $W_{o(VI)}$ corresponds those for monocomplexes Cu^{2+} on the basis of hydrogel oxide of silicon, and $W_{o(X)}$ - to set of monocomplexes and bridge polynuclear compounds of copper (0,02 and 0,9 mol fraction) in the same phase in similar conditions of realization of process of oxidation [2].

So copper-containing aminopropylpolysiloxane, obtained at presence template - copper benzoate, has the most essential activity, thus as against any hydrogel the specified catalyst, undoubtedly, is more stable.

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**OXIDATION TRIMETHYLHYDROHYNONE IN THE PRESENT
IMMOBYLIZATHON NITROXYL RADICAL**

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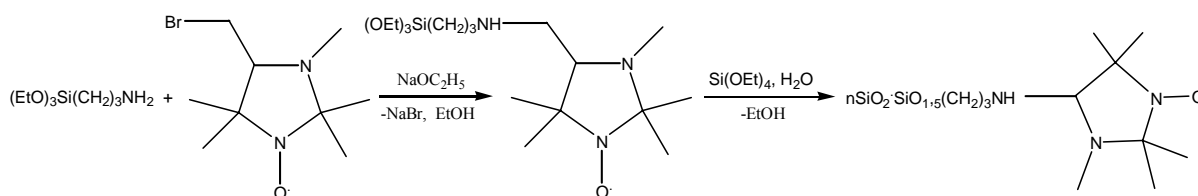
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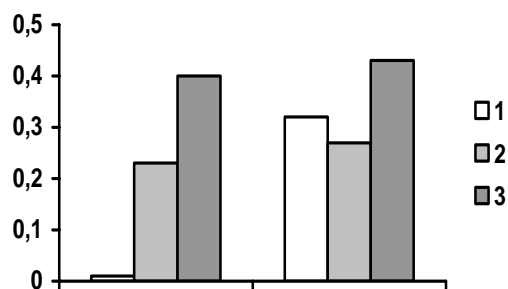
It is investigated catalytic activity modified by nitroxyl radicals aminopropylpolysiloxanes in modelling reaction oxidations of thrimethylhydroquinone.

It is known, that a 2,2,6,6-tetramethylpiperidinyloxy radical immobilizing on silica catalized oxidation of alcohols by salts copper [1]. Oxidation of phenols in similar systems is not described. The purpose of the present work was comparative research of catalitical activity modified by nitroxyl radical aminopropylpolysiloxane in modeling reaction liquid-phase oxidation of thrimethylhydroquinone oxygen of air in a water-methanol solution.

For researches it is used silica gel (1), synthesized by hydrolysis tetraethoxysilane at presence propylamine; aminopropylpolysiloxane (2) received cohydrolysis of tetraethoxysilane and aminopropyltriethoxysilane (molar retio - 2:1) and aminopropylpolysiloxane (3) modified 2,2,5,5-pentamethylimidazolyl-1-oxyl radicals (3), which synthesis carried out on the scheme (content radical 8 mol%/NH₂):



The technique of experiment is stated in [2]. Diagrams of dependence of initial speed of oxidation from structure of the catalyst (not containing copper - at the left and containing it - on the right) are submitted below.



Apparently from the submitted data, introduction of nitroxyl radical essentially is accelerated with process, the additive or copper additional accelerating action does not caused. Thus, the synthesized compound - aminopropylpolysiloxane modified 2,2,5,5-pentamethylimidazolyl-1-oxyl radicals is the effective catalyst of oxidation of thrimethylhydroquinone oxygen of air, presence of copper ions does not influence appreciable effect on activity of this catalyst.

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TECHNOLOGY CONCEPTS ON DEVELOPING OF CATALYSTS AND SORBENTS OF BLOCK AND BLOCK-GRANULAR TYPES

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Methods of producing large catalyst elements of block and block-granular type directly from active blend were developed. Preparation of blend for forming block catalyst is based on structure-kinetic modification of active catalyst mass. From modified charge blend it is possible to prepare honeycomb catalysts of thin structure directly from active catalyst mass. Producing of large-sized elements of block-granular type catalyst is based on gluing catalyst granules in the form of ready formations, modeling structure and geometry of fixed bed. The developed method allows to save accessibility of outer surface, specific surface area and stability of initial catalyst.

Development of industrial catalyst chemistry requires working out effective solutions on technology of catalysts and sorbents of new geometrical shapes, in particular, of block and block-granular types. Thus moulding of large catalyst element immediately from active blend is considered to be more promising direction in comparison with treating technology.

The choice of a method of active fusion mixture modification for creating necessary plasticizing, greasing, dispersive and stabilizing properties has fundamental importance both for moulding of elements of complicated shape and their heat treatment. Well-known methods of preparing block catalysts from active blend are based on joint grinding and mixing of primary components. As practice shows it is rather difficult to transfer original particles of rough sizes into more active colloidal-disperse state and achieve necessary homogenization of active fusion mixture. Structure inhomogeneities of molding compound transfer to semi-finished material of block catalyst and result in significant defects after further heat treating.

We offer method of structure-kinetic modification for homogenization of active fusion mixture, increasing mobility of its structure units, securing its aggregative stability, minimizing mechanical defect formation at extrusion and units heat treatment stages. Investigations allowed to base mode of preparation from active fusion mixture of molding compounds possessing set of rheological properties that are necessary for the following stable moulding of elements of complicated shape. The method has been tested for producing block catalysts and sorbents for ammonia conversion, sulphur dioxide oxidation and catching of aerosols of platinoids.

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During preparation of molding compound and specially its streaming through shaping–tool effect of “bead mill” is implemented when particles of cordierite play the role of grinding elements. Modification of active fusion mixture increases significantly mobility of its structural elements, accelerates relaxation processes, improves frictional properties of molding compounds and results in more uniform product yield from drawplate.

Working out methods of conglutinating of granules as ready formations, modeling structure and geometry of stationary fixed bed is another direction in developing technologies of large-sized catalysts.

It is necessary to solve two main problems in technology of block-grainy catalysts. Firstly, in order to save interior surface before using agglutinants it is necessary to conduct hydrophobization of hydrophilic surfaces of grains with substance that can also take part in forming stable adhesive bonds between grains. Secondly, nature of agglutinants and sequence of their input in active fusion mixture have to provide with extraction of cementing phase that possesses sufficient strength and penetration for reacting molecules.

By the example of vanadium catalyst for sulphur dioxide oxidation it is reasonable to use chromiferous surfactant as hydrophobisator and potassium aluminate and aluminium phosphate solutions as agglutinants. These substances contain compounds that are promoters of vanadium sulfuric acid catalysts and their using in limited concentrations can be reflected positively on activity. Comparative data on basic properties of block-grainy and grainular catalyst are shown:

Characteristics of grainy and modular-grainy catalysts.

Catalyst	Rate constant, $\text{sec}^{-1}\text{MPa}^{-1}$ under temperature, K		Mechanical strength, MPa	Specific surface area, m^2/g
	693	758		
Grainy	4,9	15,5	0,31	8,4
Block-grainy	6,2	16,0	0,45	7,7

It can be seen that modular-grainy catalyst can be highly competitive with industrial grainy catalyst on activity, specific surface area and strength.

Work is executed with support of grant of The Ministry of Education and sciences of RF

**ACTIVATION OF POST-TITANOCENE OLEFIN POLYMERIZATION
CATALYSTS WITH METHYLALUMINOXANE: THE INTERMEDIATES**

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Cationic intermediates formed upon activation of post-titanocene(IV) olefin polymerization catalysts (bis(salicylaldimine), or bis(phenoxy-imine), (FI)₂TiCl₂, bis(pyrrole-imine) (PI)₂TiCl₂, and mixed-ligand (salicylaldimine)(pyrrole-imine) (FI)(PI)TiCl₂) with MAO and AlMe₃/CPh₃⁺B(C₆F₅)₄⁻ with MAO or AlMe₃/CPh₃⁺B(C₆F₅)₄⁻ have been detected and characterized by ¹H, ¹³C, ¹⁹F NMR.

Metallocene and post-metallocene based single site olefin polymerization is one of the most exciting achievements in the field of catalysis in recent years. For the active catalysts to form, the starting complexes must be activated by Lewis acidic co-catalysts such as methylaluminoxane (MAO), B(C₆F₅)₃ or [CPh₃][B(C₆F₅)₄], MAO remaining the most widely used co-catalyst for metallocene and post-metallocene based catalysts.

It was found that the interaction of MAO with post-titanocene complexes (FI)₂TiCl₂ [1], (PI)₂TiCl₂, (FI)(PI)TiCl₂ [2] resulted in the formation of outer-sphere ion pairs of the type [LL'TiMe(S)]⁺[Me-MAO]⁻ (where S stands for a solvent molecule) which are the precursors of the real polymerizing species. In the first system (FI)₂TiCl₂/MAO (and (FI)₂TiCl₂/[CPh₃][B(C₆F₅)₄]/AlMe₃) capable of conducting living olefin polymerization, the true intermediates [(FI)₂TiP]⁺[Me-MAO]⁻ (and [(FI)₂TiP]⁺[B(C₆F₅)₄]⁻) were detected (P= growing polymeryl chain) [1]. It was found that the main deactivation pathways for the (FI)₂TiCl₂/MAO system are the salicylaldimine ligand transfer to aluminium, as well as reduction to titanium(III). The (PI)₂TiCl₂/MAO system deactivates mainly via ligand transfer, whereas for the mixed-ligand system (FI)(PI)TiCl₂/MAO, reduction to titanium(III) prevails [2].

Correlation between the structures and stabilities of the intermediates and their reactivities in olefin polymerisation are discussed and compared with those established for

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classical titanocene systems $\text{Cp}_2\text{TiCl}_2/\text{MAO}$, $\text{rac-C}_2\text{H}_4(1\text{-Ind})_2\text{TiCl}_2/\text{MAO}$ and $\text{C}_5\text{Me}_5\text{TiCl}_3/\text{MAO}$ [3].

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STRUCTURE FEATURES OF NANOCRYSTALLINE COBALT OXIDE REDUCTION

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In situ X-ray powder diffraction was used to characterize the structure of the Co catalyst supported on the γ -Al₂O₃ and the model samples. We researched reduction process for the supported and non-supported Co₃O₄. The two-stage reduction for the supported catalyst was observed. Co₃O₄ was reduced to CoO and then to the metallic Co with fcc structure. On the contrary the crystal phase of CoO wasn't observed during the reduction of the non-supported Co₃O₄ sample which was reduced to the metallic Co with hcp structure in one step.

The Fischer-Tropsch synthesis (FTS) is one of the processes producing synthetic liquid fuel and valued chemical compounds from syngas (i.e. mixture of CO and H₂). The supported metallic catalysts are widely used in FTS. The cobalt based catalysts are suited to produce high yields of long alkanes in FTS [1]. Catalysts are activated by reduction of Co₃O₄ in hydrogen. It is important to understand how the reduction conditions influence on the structural parameters of catalyst.

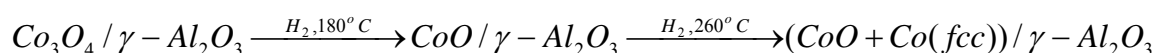
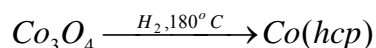
It is impossible to study structural parameters and phase composition of activated catalyst by *ex situ* methods owing to reoxidation process which can take place in the air atmosphere. So the information concerning the phase composition and the crystallite size of the metallic particles during the reduction was obtained by *in situ* X-ray diffraction (XRD). The XRD camera-reactor [2] and D-500 Siemens diffractometer with CuK α -radiation were used.

We have researched the supported and non-supported nanocrystalline Co₃O₄ samples to compare its behavior during reduction. The non-supported samples were prepared from cobalt carbonate. Supported catalysts were prepared by the incipient wetness impregnation using cobalt nitrate aqueous solution. The γ -Al₂O₃ was used as the support.

To carry the comparative analysis between the supported and non-supported samples correctly we have taken the samples with the same average size of the Co₃O₄ crystallites (~100 Å). Therefore we did not use non-supported samples prepared from a cobalt nitrate since the average sizes of obtained Co₃O₄ particles were essentially larger than in the supported sample. The initial structures of the both types of the samples are similar according to the XRD structural analysis and contains vacancies in the cation positions. *In situ* X-ray

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diffraction investigations show that there are some features which are the same for the both types of the samples but the reduction process is different on the whole. The reduction processes for the supported and non-supported samples start at the same temperature of about 180 °C (at definite conditions). The structure mechanism of the reduction process beginning is the same also. We observed decreasing the quantity of cation vacancies and filling the non-spinel octahedral position by Co ions. This indicates on the appearance of clusters with the structure of CoO inside the structure of Co₃O₄. Appearance of the CoO clusters is common feature for the both types of samples. But further reduction process is different for the supported and non supported samples.



The average crystallite size of CoO is 80 Å. We don't observe the CoO crystal phase during the reduction of the non-supported cobalt oxide. The average crystallite size of the metallic cobalt (hcp) was found to be 350 Å. In the case of the supported sample the average crystallite size of metallic cobalt (fcc) was found to be 70 Å. Metallic Co (hcp) and Co (fcc) particles have very high concentration of stacking faults. The non-supported sample is reduced to the metal Co (hcp) at the temperature T=180 °C without formation of intermediate CoO phase i.e. the non-supported sample is reduced in one step. In contrary the supported cobalt oxide is reduced in two steps. Reduction of Co₃O₄ to CoO clearly identified by XRD is the first step. The second step (CoO→Co) begins at 260 °C and it is not fully completed at the temperature of 400°C. At this temperature CoO and Co (fcc) phases are coexist. It seems cobalt ion diffusion into the structure of alumina leads to species that are difficult to reduce. The differential dissolution (DD) experiments confirmed this version. According to the DD data there are two cobalt containing phases. One of these phases dissolves together with Al ions. It may be combined oxide with Co-Al-O composition. The second phase dissolves in the other conditions and is determined as Co₃O₄.

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THE H₂ ROLE IN SELECTIVE NO_x REDUCTION BY PROPANE OVER MECHANICAL MIXTURE OF OXIDE CATALYSTS

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The synergistic phenomenon observed over the mechanical mixture of commercial NTK and Ni-Cr-oxide catalysts in NO_x selective reduction by propane is explained by the distinctions in the reaction mechanism over the individual mixture components. Hydrogen formed over Ni-Cr-oxide catalyst in propane oxidation significantly increases the rate of interaction between surface nitrate and acetate complexes. Besides, there is an additional input made by the route of NO_x reduction in H₂ presence over NTK.

The methods of catalytic cleaning are the most effective for the removal of highly toxic NO_x from exhaust and flue gases by converting them into non-toxic N₂. Such processes as selective catalytic reduction of nitrogen oxides by hydrocarbons (HC-SCR NO_x) provide required removal efficiency for a long period of time at relatively low temperatures characteristic of industrial gas emissions.

Particular attention is paid to the studies of various ways to enhance catalytic activity, such as promotion, initiation, etc. Synergism is frequently considered a useful mean to affect the catalysis. Considerable attention is given to catalytic systems with a synergistic effect, to which mechanical mixtures belong [1-3]. Mechanical binary mixtures of commercial catalysts Ni-Cr-oxide and NTK (Cu-Zn-Al-oxide) reveal synergistic effects of achieving higher activity for the combined system compared to the sum of activities of catalyst components. To elucidate the nature of synergism, it is necessary to know the mechanism of the process and the role of each component of a mechanical mixture.

Mechanism of redox reactions proceeding in NO_x SCR by propane over individual oxide catalysts, as well as over the mechanical mixture of catalysts, was studied by quantitative spectrokinetic measurements *in situ*. It is found that nitrite-nitrate and acetate surface complexes are the intermediates in this process. The transformation rate of surface complexes under reaction conditions was measured. It is shown that there are differences in mechanism of reaction over catalysts NTK (Cu-Zn-Al) and Ni-Cr.

Principal differences in the behavior of catalysts NTK and Ni-Cr-oxide toward NO adsorption can be revealed. NO adsorption on the Ni-Cr-oxide catalyst is observed up to

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250 °C. On the Cu-Zn-Al-oxide catalyst, the main surface form of NO is the high-temperature one which desorbs in the range 300-500 °C.

No oxygen adsorption was observed over the NTK catalyst. Oxygen adsorption on the surface of Ni-Cr-oxide catalyst is negligible, but oxygen participates as in NO activation (with formation of nitrite-nitrate complexes), so in propane activation (with formation of acetate structures).

Propane practically does not adsorb on the surface of NTK at room temperature. For its activation, the presence of oxidizing agent in the feed or a temperature higher than 300 °C is needed. Under these conditions, C₃H₈ interacts with the same centers on the catalyst surface over which the formation of nitrate complexes proceeds. The main product of C₃H₈ oxidation over NTK is CO₂.

The interaction of propane with the surface of Ni-Cr-oxide catalysts at the reaction temperature leads to significant reduction of the catalyst surface and, as the consequence, to rapid increase of the catalyst's own spectral absorbance, which makes spectral measurements more difficult. Due to this, the spectrokinetic studies were made using the mixture C₃H₈+O₂. In the interaction of propane and oxygen with the surface of the catalyst surface, the acetate complexes are formed. In the products of C₃H₈ oxidation over the Ni-Cr-oxide catalyst significant amounts of H₂ and CO₂ and a certain amount of CO were found at about a complete absence of the products of mild oxidation, oxidative dehydrogenation, and cracking.

Wrapping up the literature data [4-5], it can be said that the role of H₂ is thought of as that of the reducing agent which maintains the catalyst surface in reduced state, so oxygen and nitrogen oxides are able to dissociate over it, and highly active oxygen centers are formed in the result. These centers participate in effective activation of both NO, with the formation of nitrite-nitrate structures, and hydrocarbons, which give surface acetate complexes. It can be suggested that over NTK NO_x reduction with hydrogen proceeds by the mechanism which is characteristic for supported metals of platinum group. According to this mechanism, oxides which comprise the catalyst are reduced by hydrogen into metals, over which NO dissociation proceeds. It is followed by recombination of nitrogen atoms into N₂ which is released into gas phase, and by re-oxidation of the catalyst surface by oxygen atoms giving H₂O. No formation of NH₃ or N₂O was detected.

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THE *IN SITU* FTIR STUDY OF THE FORMALDEHYDE OXIDATION OVER SUPPORTED VANADIA CATALYSTS

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The kinetics of the formation and decomposition of surface intermediates in formaldehyde oxidation and formic acid decomposition over V_2O_5/TiO_2 , V_2O_5/Al_2O_3 , V_2O_5/SiO_2 catalysts was investigated *in situ* by FTIR spectroscopy. The effect of the support on structure of surface intermediates and their reactivity was displayed.

Introduction

Supported vanadia catalysts are extensively employed as catalysts for many hydrocarbon oxidation reactions. Testing a large number of oxide catalysts in formaldehyde oxidation showed that an enhanced yield of formic acid is obtained with V_2O_5 -based catalysts [1]. Formaldehyde is found to be oxidized with a high selectivity to formic acid over the vanadia-titania catalysts at the temperature range of 100 to 140 °C [2].

The objective of the present work is to investigate the mechanism of formaldehyde oxidation over supported vanadia catalysts.

Experimental

The samples 20% V_2O_5/TiO_2 , 30% V_2O_5/Al_2O_3 , 20% V_2O_5/SiO_2 were prepared by the incipient wetness impregnation. The samples were dried at 110 °C and calcined at 400 °C for 4 h in a stream of air.

The *in situ* IR experiments were performed with a BOMEM MB-102 FTIR spectrometer. A flow-through quartz high-temperature IR cell-reactor with the CaF_2 windows was employed.

Results and discussion

According to XRD and FTIR data, V_2O_5/Al_2O_3 and V_2O_5/SiO_2 catalysts are the mixtures of crystalline V_2O_5 and support ($\gamma-Al_2O_3$ or SiO_2), whereas V_2O_5/TiO_2 catalyst represents vanadium-doped anatase phase, only traces of crystalline V_2O_5 was determined in this sample.

The *in situ* FTIR spectra of surface species collecting at passing the reaction mixture of 2% CH_2O in air and 1% $HCOOH$ in air through the IR cell-reactor are presented in Fig. 1.

Only poly- and dioximethylene species were detected during formaldehyde adsorption on V_2O_5/SiO_2 catalyst at 60-80 °C. These complexes desorb completely at 100 °C. We do not observe any oxidized formaldehyde complexes at 60-200 °C in the case of V_2O_5/SiO_2 catalyst.

Bidentate ($\nu_{as}(COO) = 1590$, $\nu_s(COO) = 1390$ cm^{-1}) and asymmetrical formates ($\nu_{as}(COO) = 1640$ cm^{-1}) forming during formaldehyde adsorption on V_2O_5/Al_2O_3 catalyst.

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Bidentate formate ($\nu_{\text{as}}(\text{COO}) = 1560$, $\nu_{\text{s}}(\text{COO}) = 1370 \text{ cm}^{-1}$) is the main form of the interaction between formaldehyde and $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst. The readsorption of formic acid on $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst leads to formation of asymmetrical formates ($\nu_{\text{as}}(\text{COO}) = 1668$, $\nu_{\text{s}}(\text{COO}) = 1220 \text{ cm}^{-1}$).

The adsorption of HCOOH on investigated catalysts leads to the formation of bidentate formates ($\nu_{\text{as}}(\text{COO}) = 1587 - 1552$, $\nu_{\text{s}}(\text{COO}) = 1383 - 1360 \text{ cm}^{-1}$), asymmetrical formates ($\nu_{\text{as}}(\text{COO}) = 1668$, $\nu_{\text{s}}(\text{COO}) = 1220 \text{ cm}^{-1}$) and H-bonded formic acid ($\nu_{\text{as}}(\text{COO}) = 1730 - 1714$, $\nu_{\text{s}}(\text{COO}) = 1190 - 1170 \text{ cm}^{-1}$) (Fig 1, b).

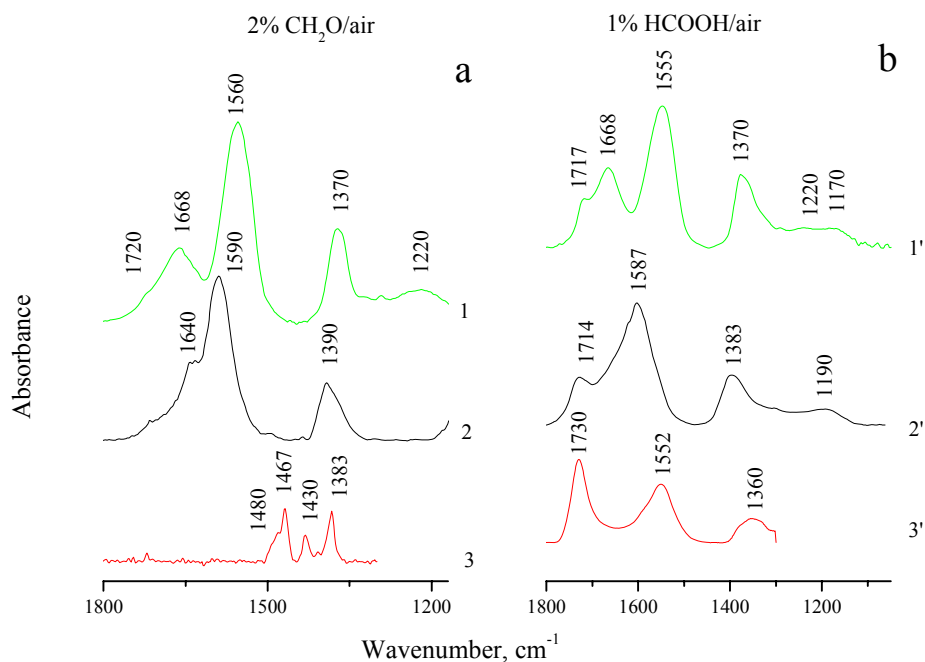


Figure 1. *In situ* FTIR spectra of surface species during formaldehyde oxidation (a) and formic acid decomposition (b) over supported vanadia catalysts: 1, 1' - $\text{V}_2\text{O}_5/\text{TiO}_2$ (120 °C), 2, 2' - $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ (120 °C), 3, 3' - $\text{V}_2\text{O}_5/\text{SiO}_2$ (80 °C)

The kinetics of the formation and the decomposition of surface formates arising during formaldehyde oxidation and formic acid decomposition over supported vanadia catalysts was studied. The effect of the support on the structure and the reactivity of surface intermediates was displayed.

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LUMINESCENT DIAGNOSTICS OF CATALYSTS PROPERTIES AND THEIR SYNTHESIS PARAMETERS

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For the first time, we present the results of the investigation of carriers samples. We investigated three structural types of zeolites: beta (BEA), ZSM-5, mordenit (MOR) and catalysts with Pt, Pd, Co, Cr based on those carriers. The correlation between intensity of luminescence and catalytic activity is established in the field of 350-800 nm. Spectra of luminescence depend on the type of a crystal lattice, a way of synthesis of the catalyst, concentration impurity ions of metals (Fe^{3+} , Cr^{3+} , etc.), thermal processing (incideration, roasting).

The research works were carried out on the lazer-luminescent installation in Angarsk State Technical Academy. The diagnostic method of catalysts and their properties based on luminescent characteristics has been developed as a result. This method allows to perform the diagnostics of catalysts and their carriers during a synthesis and operation.

It is established, that the synthesized samples of zeolites have a luminescence at excitation by laser radiation (337 nm). Spectra for zeolite (BEA) of the different time of crystallization are presented in fig. 1. For all samples the band with a maximum 400 nm is typical. The band intensity increases with increase of crystallization time. The structure of the luminescence centres is probably connected to features of a crystal lattice. In particular, the luminescence may be caused by radiation autolocated excitons. We studied the luminescence of various types of zeolites before and showed that it is connected to the luminescence of the lattice [1].

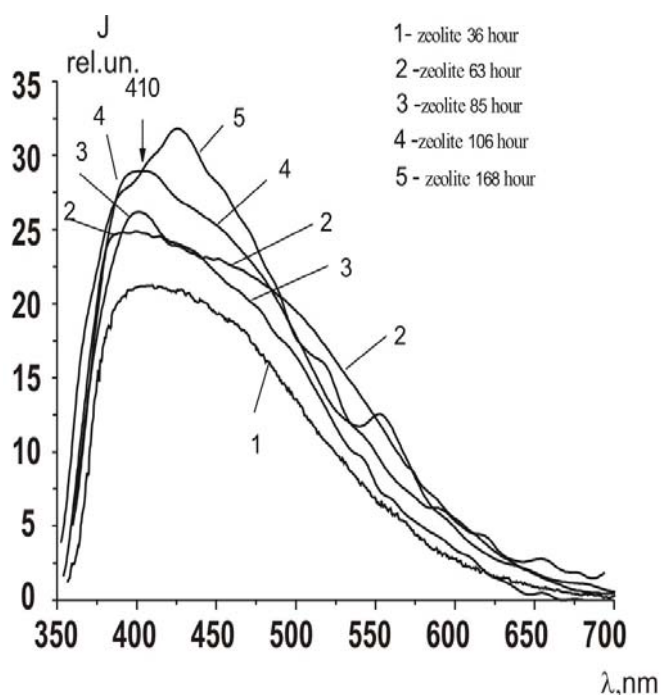


Fig. 1. Spectra of a luminescence of zeolite for different times of crystallization

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It is shown, that the Pt – containing catalysts are the luminescing in the bonds with the $\lambda = 450$ and 750 nm. The bonds intensive correlated with the activity values and the structural type of the zeolites. The luminescence intensity decreased in the carrier's row of the BEA, MOR and ZSM-5. These facts were explained in this work.

The luminescence characteristics ($\lambda = 370$ and $\lambda = 410$ nm) of Co – containing catalysts depend essentially on the concentration and methods of cobalt deposits, carriers types (γ – or θ – modification) and the thermal treatment. The change of the samples colour was observed during the thermal treatment. This can be caused by cobalt valence transformation ($\text{Co}^{2+} \rightarrow \text{Co}^{3+}$). The luminescence in the bands of with $\lambda = 370, 380$ and 410 nm was connected to the radiation of the lattice excitons (Osi^* , OAl^*), while the band with the $\lambda = 740$ nm was caused by the admixture of the Fe^{3+} ions.

It is established, that the increase of the palladium contents (0,05-0,1 %) results in reduction of the luminescence intensity (Fig. 2). The forecasting model of Pd contents on intensity of the luminescence has been obtained.

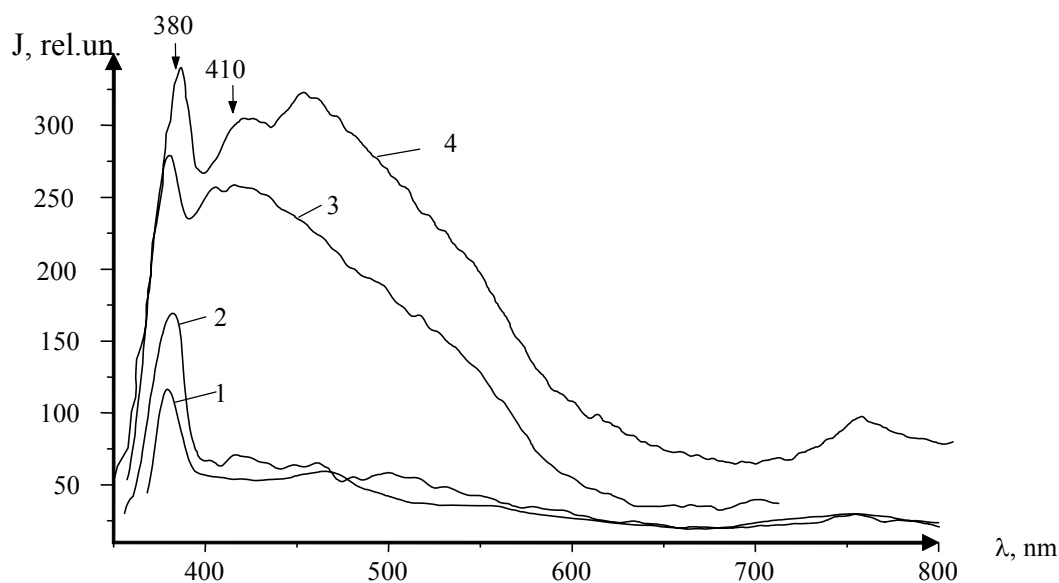


Fig.2. Spectra of a luminescence of palladium: 1 – 1,0% Pd, 2 – 0,7% Pd, 3 – 0,3% Pd, 4 – 0,1% Pd

Thus, this laser – luminescence method allows to get an important information about the interaction of the metal with crystal lattice of the catalyst carrier along with about catalytic activity. It is represented not only theoretical, but practical interest as well.

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**MODIFICATION OF PROPERTIES OF CATALYTICALLY GROWN CARBON
NANOFIBROUS MATERIALS BY HIGH TEMPERATURE TREATMENT**

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Present study is aimed at studying of the effect of high temperature heat treatment on properties of carbon nanofibrous materials which were obtained by means of methane catalytic decomposition using various catalysts. For examination of the effect of this type of treatment, carbon nanomaterial samples were treated at 1700 °C, 2200 °C and 2600 °C during 0.5 and 3 hours. Samples were studied by XRD, HRTEM, BET methods before and after high temperature heat treatment and indexes of electro-conductivity were obtained by State Standard 4668-75. It was revealed that high temperature heat treatment heavily effects structural, textural and electro-conductive properties of carbon nanofibrous materials.

Carbon nanofibers, which were obtained by catalytic decomposition of hydrocarbons or disproportionation of CO using catalysts based on metals of VIII group are new graphitic materials. These carbonaceous materials possess variable textural, structural and chemical properties depending on catalysts type, initial carbon source and synthesis conditions. Investigations were carried out in many countries and they showed that carbon nanofibrous materials have unique physical-chemical properties and allow to forecast a wide range of application of these materials in future in different spheres of machinery.

For studying the effect of high temperature treatment on the properties of nanofibrous carbon three samples were synthesized. Samples of nanofibrous carbon were obtained by catalytic decomposition of methane using 90%Ni-Al₂O₃, 70%Ni-20%Cu-Al₂O₃ and 60%Fe-15%Ni-Al₂O₃ catalysts and then were marked as №1, №2 and №3, respectively. Carbon samples №1, №2 and №3 have structure of stacked cones of graphitic shells, of “card pack” structure and multi-walled nanotubes, respectively.

HRTEM data showed that there are reconstruction processes on the surface of carbon nanofibers, which lie in closing of ends of graphitic edges. Surface reconstruction was observed to a greater extent in structures of stacked cones and «card packs» (carbon samples

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№1 and №2). The same enclosing of graphitic edges in the structure of graphitic shells was observed only on the ends of the nanotubes.

BET method's data showed that specific surface area of samples after high temperature treatment similarly depends on the initial structure of carbon nanofibers. The specific surface area of samples №1 and №2 decreased in more than 2 times under the maximum temperature and time of high temperature treatment. Such a tendency was not observed for textural properties of the carbon sample №3. It was concluded that this phenomenon is connected with surface reconstruction. XRD method and measurements of electro-conductivity proved that there was a process of graphitization and improvement of electro-conductivity in carbon samples.

Complex of physical-chemical methods showed that chosen conditions of high temperature heat-treatment do not finish the process of graphitization of carbon. These conditions lead to a restructuring of the surface of carbon nanofibers that effects the textural properties of carbon nanomaterials. Moreover, analysis of the data showed that the process of high temperature heat treatment can be used for synthesis of new types of carbon materials, for elimination of defects on the surface of the multiwalled nanotubes and for removal of residual metal of the catalyst.

FTIR STUDY OF THE REACTION MIXTURE (SO₂+H₂O+ AIR) EFFECT ON THE STATE OF Pd CATALYSTS SUPPORTED ON Al₂O₃ AND ZrO₂

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Surface properties of Pd catalysts supported on ZrO₂, Al₂O₃ before and after reaction mixture (SO₂+H₂O+air) treatment was studied by FTIR spectroscopy of adsorbed CO. Bulk and surface sulfates were found on the supported metal catalysts after sulfation, whereas only surface sulfates were formed on the supports. The variation of the numbers and strength of acidic site of supports, modification of the morphology and the state of metallic nanoparticles, and appearance some electron-deficient metal entities (Pd^{δ+}, Pd¹⁺, Pd²⁺) were observed after sulfation.

Supported Pd catalysts are used for a variety of technologically important processes, for example for purification of diesel exhaust gases. One of the key problem for the these catalysts is their stability with regard to SO_x poisoning. The details of the mechanism of interaction of SO₂-containing gaseous mixture with both oxide and supported metal catalysts are still under discussion. In the present work, the surface state of pure and modified Al₂O₃ and ZrO₂, and supported Pd catalysts before and after interaction with reaction mixture (SO₂+H₂O+air) was studied by FTIR spectroscopy of adsorbed CO and H₂O.

The supported Pd catalysts were prepared by impregnation of δ-Al₂O₃, ZrO₂/Al₂O₃, TiO₂/Al₂O₃ and ZrO₂ with water solution of Pd(NO₃)₂. Samples were treated by reaction mixture (50 ppm SO₂+10 % H₂O+air) during 18 h at 300 °C. The acidic properties of fresh and sulfated samples were studied by FTIRS technique using CO adsorption at 77 K. The morphology of metallic nanoparticles was characterized by TEM.

The formation of several surface sulfates (a.b. at ν_{S-O} 900-1100 cm⁻¹ and ν_{S=O} 1300-1400 cm⁻¹) was observed after interaction of the reaction mixture (SO₂+H₂O+air) with both supports and supported metal catalysts. It was very interesting that the formation of bulk sulfates (a.b. at 1110-1260 cm⁻¹) was detected only on the supported metal catalysts. The mechanism of bulk sulfates formation and effect of metallic nanoparticles are discussed.

It was shown that the metallic particles increase several times in size and spread over the surface after SO₂-steam-air treatment. The state of metallic nanoparticles of fresh and sulfated samples was studied by CO absorption at 77 and 293 K within pressure range of 0.1-10 torr. The decrease of the intensity of absorbance bands of bridge-bonded CO and the change of the intensity of a. b. of on-top CO on metallic Pd nanoparticles after SO₂-steam-air treatment was found. The appearance of some electron-deficient metal entities (Pd^{δ+}, Pd¹⁺, Pd²⁺) was observed after sulfation of supported Pd catalyst as well.

STEAM METHANE REFORMING CATALYSTS BASED ON POROUS NICKEL

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Generation of synthesis gas by methane steam reforming is a preferred catalytic method. To perform the endothermal methane steam reforming reaction it is necessary to provide intensive heat transfer from an external heat source to the reaction zone. For this reason, the observable catalyst should possess high thermal conductivity. The application of the metal supported catalysts is very promising.

This work was aimed at elucidating the effect of synthesis conditions on the phase composition and texture of the porous nickel supports with MgO precoating and the supported nickel catalysts and studying the catalytic properties of the prepared catalysts in the methane steam reforming reaction.

The nickel porous plates (thickness 0.5-1 mm) prepared by rolling ($S_{sp} \sim 0.1 \text{ m}^2/\text{g}$, $V_{\Sigma} \sim 0.1 \text{ cm}^3/\text{g}$, $r_{prevailing} \sim 5-30 \text{ }\mu\text{m}$) were used as catalyst support.

MgO support (5 wt.%) was deposited on nickel plates by impregnation with aqueous solution of $\text{Mg}(\text{NO}_3)_2$ and subsequent drying and calcination at $550 \text{ }^\circ\text{C}$ in a flow of N_2 (support I) or H_2 (support II); nickel (5-9 wt.%) was deposited by impregnation with aqueous solution of $\text{Ni}(\text{NO}_3)_2$ and subsequent drying and calcination at $450 \text{ }^\circ\text{C}$ in N_2 . The prepared catalysts were characterized by XRD, the nitrogen adsorption at low temperatures, mercury porosimetry and electron microscopy along with X-ray spectrum microanalysis. Catalytic activity in the methane steam reforming reaction was determined by the flow-circulating method at atmospheric pressure (750°C , $\text{H}_2\text{O}/\text{CH}_4=2$, space velocity 11.8 l/h). The samples were reduced at 750°C in hydrogen flow.

According to XRD data, the phase of nickel is presented in metal support, whereas support I also contains phases of NiO and MgO with lattice parameter 4.206 \AA , support II contains MgO phase with lattice parameter 4.218 \AA . The reduced catalyst (7.2 wt.% Ni deposited on support II) exhibits phases of nickel and solid solution NiO in MgO (lattice parameter 4.205 \AA). According to the reference data, the lattice parameter of MgO is 4.211 \AA .

As follows from SEM data, the metal support has a corpuscular porous structure formed by round conglomerates (3-15 mkm in size) grown together in contact places; support MgO forms a porous loose covering 2-3 mkm thickness, which completely covers the pore walls. According to the nitrogen adsorption at low temperatures data MgO in support II has thin

pores (the average diameter is 40-80 Å); the sample specific surface area is 7.7 m²/g. As hydrogen is changed by dry nitrogen during decomposition of Mg(NO₃)₂ (support I), a portion of thin pores in the MgO decreases and the specific surface area reduces to 0.8 m²/g.

In supports I and II, nickel is detected by EDX spectra of MgO as spectral lines of weak intensity corresponding to a nickel concentration of ~ 2 at.%. Intensity of the nickel lines differs for different parts of MgO, which indicates different degrees of interaction between MgO and NiO from the oxide film during the heating. One may suggest that the contacting particles of MgO and NiO react upon each other to yield surface solid solutions [1,2] whereas the MgO particles outlying from the NiO are not transformed and do not contain nickel. TEM data suggest that after additional reduction (750°C, H₂) dispersed nickel crystallites (25 – 70 Å) are appeared on the surface of MgO of the support I. For the MgO surface in support II, nickel is observed only on the EDX spectra, however, the sample tested in the reaction also exhibits the presence of nickel crystallites 20–70 Å in size.

The methane conversion value of the porous nickel support (fraction is 0.25–0.50 mm, m=0.80 g) is 20 %. After deposition of support MgO, formed in a flow of N₂ (support I) the conversion value increases to 52 % and the deposition of MgO formed in a hydrogen flow (support II) increases - to 65 %. The additional deposition of nickel results in the increase of conversion. Note that the prepared nickel catalysts on supports I and II are characterized by comparable conversion values, which is probably associated with neighboring average sizes of the supported nickel particles.

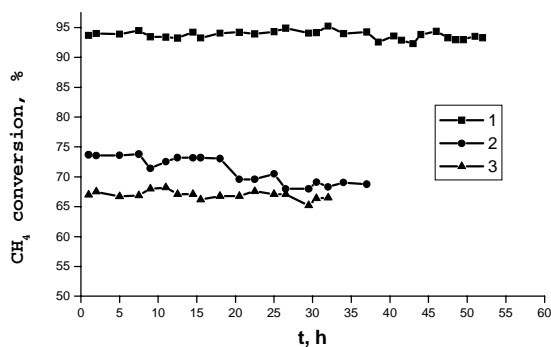


Fig. Influence of reaction time on methane conversion in steam reforming reaction: 1 – 7,2% Ni/pNi + 5,0% MgOII (plate, m=3.07g, V=0.7 cm³); 2 - NIAP-18 (fraction 0,25–0,5 mm, m=0,80g); 3 – NIAP-18 (1/2 of grain, m=1,46 g, V=0,7 cm³).

Figure shows the effect of reaction time on the catalytic activity of the supported nickel catalyst. The catalyst activity was stable during 50 hour tests. From TEM it was shown that there are not any carbon deposits in the tested catalyst sample. For the supported catalyst containing 7.2 wt.% of Ni (plate) the products composition and conversion is close to equilibrium.

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HIGH EFFICIENCY TECHNOLOGY FOR LIQUID-PHASE OXIDATION OF CARBON C₃-C₄ WITH HYDROGEN PEROXIDE OVER HETEROGENEOUS CATALYSTS TO OBTAIN IMPORTANT PRODUCTS OF ORGANIC SYNTHESIS

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High efficiency technology to obtain propene oxide and methyl-ethyl ketone based on liquid-phase oxidation of propene and n-butane, accordingly, with hydrogen peroxide in the presence of heterogeneous catalyst - titanium silicate, has been developed.

Propene oxide and methyl-ethyl ketone are important products of basic organic synthesis. Having a range of valuable qualities, they have a wide application in chemical industry and refineries. For instance, propene oxide is used for basic polyethers, propeneglycol, nonionogeneous surface active substances; methyl-ethyl ketone is used as solvent in refineries for oil deparaffinization, etc. It is worth mentioning, that there is a great unsatisfied demand for this type of production in Russia, the most part of which is being satisfied by import. In addition, there is a steady tendency to the growth of demand for propene oxide and methyl-ethyl ketone, on average 3-4% a year. Therefore, the development of high efficiency technology to obtain the products mentioned above is a timely and vital problem.

Til recently, the main method of industrial production of these substances was ecologically unfriendly oxidation with the use of large amounts of expensive and toxic agents. The analysis, carried out by us, has shown that the most effective method for high selective production of propene oxide and methyl-ethyl ketone, eliminating the existing shortcomings, is liquid-phase oxidation of propene and n-butane, accordingly, with water solutions of hydrogen peroxide in the presence of titanium silicalite. The research has shown a high efficiency of titanium silicalite in these processes. The distinguishing characteristic of these processes is that they are conducted at mild temperatures (30-60 °C), low pressures (3-7 atm) and are considered to be attractive from the point of view of ecology protection.

With the goal to work out the optimal conditions to obtain propene oxide and methyl ethyl ketone, we have studied the influence of different factors based on the regularity of the propene and n-butane oxidation processes with hydrogen peroxide. For analysis we have chosen the following factors: the ratio of propene (n-butane) / hydrogen peroxide, the nature

and the amount of the dissolvent, pH of the medium, the composition of the catalyst. To develop the unit for the isolation of the target products, phase equilibriums liquid-liquid and liquid-vapour in the system of synthesis products have been studied.

Besides, we have revealed a principal possibility to increase titanium silicalite activity due to the optimization of the preparation stage and application of special additives.

In conclusion, the research carried out let us to obtain detailed information for the engineering of larger-scale trial industrial units for the propene oxide and methyl-ethyl ketone production.

**THE USE OF CARBON-COATED SILICA-ALUMINA'S AS CATALYST SUPPORTS
IN FISCHER-TROPSCH SYNTHESIS**

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Gas-to-liquid (GTL) technology has been around since the 1920's. Cobalt based catalysts are typically used as they are ideally suited to produce high yields of long chain hydrocarbons under Fischer-Tropsch synthesis conditions. A majority of the work reported in the literature has focused on the use of additives such as zirconium, magnesium, silicon, platinum and rhenium in order to increase the dispersion and/or reducibility of the cobalt oxide crystallites to metallic cobalt and as support modifiers in order to improve the activity, selectivity and stability of the corresponding catalysts under realistic Fischer-Tropsch reaction conditions. In the quest to improve catalyst activity per unit mass of cobalt loaded we would like to report the use of carbon-coated silica-alumina supports as a means of increasing the cobalt dispersion in the surface of the catalyst support, rendering a more uniform void space between cobalt crystallites. A significant increase in dispersion and decrease in Co_3O_4 crystallite size was observed. TEM, XRD and various adsorption studies were carried out to characterise the catalysts in order to link physical properties with FTS activity of these types of catalysts.

ACTIVITY OF PALLADIUM CATALYSTS IN THE HECK REACTION DURING ITS RECOVERY BY REVERSE FLOW ADSORPTION TECHNOLOGY

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Reverse Flow Adsorption (RFA) is a novel technology for recovery and recycling of the homogenous catalyst. The Heck reaction is selected as a test reaction to measure the catalytic activity of PdCl₂(PPh₃)₂ catalyst in DMF at very low concentrations. The RFA set-up is built to continuously adsorb and desorb PdCl₂ and the Heck reaction is used in the subsequent step to test the activity. The results show that after four cycles of continuous adsorption and desorption of PdCl₂, homogeneous catalyst still performs a constant activity.

Although homogeneous catalysts offer a number of advantages compared to heterogeneous catalysts [1], they have a major problem: recovery. Leaching of the very expensive metals as well as deactivation of the homogeneous catalyst are two main drawbacks of present recovery methods. Therefore a novel concept for the recovery and recycling of homogeneous catalysts is proposed: Reverse Flow Adsorption (RFA) [2]. In the reverse flow adsorption, the feed periodically changes the flow direction while the homogeneous catalyst is separated from the reaction mixture by adsorption downstream of the reactor.

In this work we show that the homogenous catalyst is still active after several cycles of the reversible adsorption/desorption of the metal salt, PdCl₂. The Heck reaction is selected to test the activity of the catalyst. First the Heck reaction as proposed in the work of Zhao et al. [3], is reproduced and afterwards optimized for our catalytic system. 0.1 [mmol/l] of catalyst concentration is selected to clearly show influence of the active catalyst concentration on reaction conversion. Initial RFA experiments with PdCl₂ in DMF (C=1[mmol/l]) were performed in the RFA experimental set-up. After each desorption cycle of the PdCl₂, a sample is taken and its concentration adjusted to 0.1 [mmol/l] to perform the Heck reaction. Results illustrate that after four cycles of continuous adsorption and desorption of PdCl₂, a homogenous catalyst is still active without loss of performance.

Furthermore the influence of reactants, products and ligands on the adsorption of catalyst, and as well to study the reversible adsorption of active catalyst form combined with a Heck

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reaction activity test. The initial results support the Reverse Flow Adsorption concept as a promising technology for the reversible recycling and recovery of homogenous catalysts while remaining a constant catalyst activity.

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MODIFIED POLYOXIDE CATALYSTS FOR SYNTHESIS OF OXYGENCONTAINING COMPOUNDS FROM OIL GASES

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The supported polyoxide catalysts on the base of Mo and W, and also natural Kazakhstan's clay in the process of oxidative conversion of propane and propane-butane mixtures are investigated. The influence of reaction temperature, contact time and introduction of water vapor in a reactionary gas mixture are determined. The important petrochemical products - acetone (500-550 °C) and acetaldehyde (300-350 °C) are the main liquid products of reaction on natural Kazakhstan's clays and also on clays modified by Mo, Bi, Cr, Ga ions.

Supported polyoxide catalysts on the basis of Mo, Cr, Ga, Bi, and Ce as well as natural clays of Kazakhstan, were tested in the process of oxidative conversion of propane-butane mixture. The influence of reaction temperature, contact time, composition and content of active component of catalyst were determined. The experiments were carried out at atmospheric pressure in a continuous-flow unit with a fixed-bed quartz-tube reactor. The gas mixture used for oxidation contained C₃H₈-C₄H₁₀ from 14 to 80 % and oxygen from 4 to 18 % in different ratios at 300-700 °C and W=330-15000h⁻¹. Analysis of the reactants and products was carried out chromatographically with an "Agilent Technologies" instrument. The catalysts were characterized by XRD and EM analysis, and their surface area, porosity, and elemental composition were determined.

It was found that the partial oxidation of propane-butane mixture with varying the catalytic mixture composition and the contact time yielded acetone, methyl ethyl ketone, methanol, acetaldehyde, crotonic aldehyde, butanol, and acetic acid, as well as C₂-C₃ unsaturated hydrocarbons. It was shown that conversion proceeds with the formation of gaseous and liquid products. Important petrochemicals, such as acetone (500-550 °C) and acetaldehyde (300-350 °C) are main liquid products. Ethylene is the main product of gas phase. Yield of ethylene increases starting from 450 °C. Ternary catalyst is more active than two-component samples. Optimal space velocities for catalysts with different content of active phase over carriers were determined. Up to 23 % of acetone and 35 % of methyl ethyl ketone on 1%MoCrGa/Clay were produced at W=1350h⁻¹. Increase of content of acetone up

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to 31 % in catalyzate was observed at reduction of propane-butane in reaction mixture. The determination of the product composition showed that the process follows a complex mechanism including oxidation, oxidative dehydrogenation, and cracking.

Modification of carrier by zeolite ZSM-5 in the presence of aluminium oxinitrate promoted increase the content of acetone in catalyzate up to 70-80 %, but decreased the content of acetaldehyde, Fig.1. The content of acetone was higher the whole temperature interval.

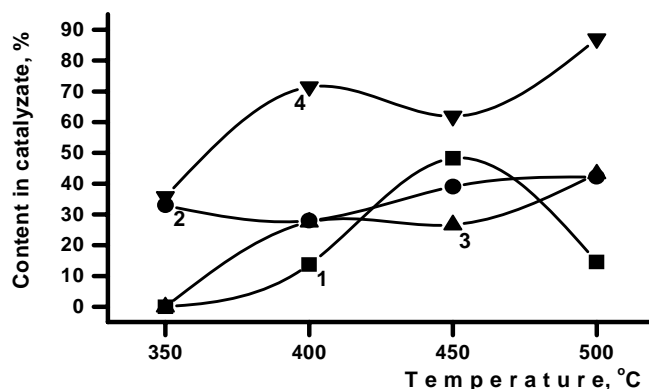


Fig.1 – Influence of the temperature on content of acetone in catalyzate at oxidation of propane-butane mixture. C_3-C_4 HC:O₂:N₂:Ar=33.33 %:7,0%:26,0%:33,67%. W=1350h⁻¹. 1 - 1%MoCrGa/TБГ; 2 - 5%MoCrGa/TБГ; 3 - 10% MoCrGa/TБГ; 4 - 5%MoCrGa/TБГ+ZSM-5 + Al_n(OH)_{3n-1}NO₃.

This screening study aimed at searching for appropriate compositions and technological parameters of the oxidative conversion of propane-butane mixture show that the chosen line of research is promising and makes it possible to obtain good results in the synthesis of hydrocarbons and oxygenated compounds.

PRODUCTION OF HYDROGENCONTAINING MIXTURES FROM METHANE

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The prospecting investigations of catalytic oxidative conversion of alkanes to H₂-containing mixtures show an opportunity for application of low percentage catalysts supported on granulated and block carriers on a base of polyoxometallates and production sufficiently high yields of H₂ from CH₄.

The hydrogen formed in composition of products of oxidative conversion of alkanes, represents independent interest as a marketable product. The rapt attention is given to synthesis of hydrogen and hydrogen-containing mixtures for producing of hydrogen fuels. Hydrogen is practically inexhaustible renewed source of energy. The hydrogen exceeds on power consumption all compounds, which can serve as fuel: 2,6 times - natural gas, 3,3 times - liquid hydrocarbons of oil, 5 times - coal, 6,6 times - methanol etc. The hydrogen is unique ecologically clean fuel and reagent, product of which oxidation is water vapor or liquid water /1,2/. Using the hydrogen addition into different types of fuel points to perspective of such direction for intensification of combustion processes. Delphi (USA) and Toliyati Technical University (Russia) have developed a method for reduction of harmful gas emissions via addition of hydrogen to gasoline. The partial oxidation of fuel without essential modifying of engines and more effective catalytic work is provided at optimum temperature /3-5/.

Catalytic action of supported catalysts on the base of the Mo and W polyoxometallates and mixed oxides of Mo, Ni, Fe, Cr for the processes of partial oxidative conversion of CH₄ to H₂-cotaining mixtures was carried out. It is known that using of the gas fuel with H₂ as addition to gasoline and diesel fuel increases combustion efficiency of fuel and decreases exhaust of CO, NO and other waste gases. It improves ecological situation in regions. Tests were realized in reaction mixture, containing methane, oxygen and inert gas (Ar) with water vapor or without it. Granulated and block ceramic carriers are used for preparation of catalysts. The concentration of active component is varied from 1 to 20 vol.%. The size of catalytic granules, contact time and relation of components are varied widely.

Increase of temperature up to 850 °C sharply raises conversion of CH₄ (to 67,1 %), yield and selectivity to H₂. It was established that the activity of investigated compositions of

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catalysts in synthesis of H₂ are increases in series: [BiSiMo₁₂] (Y=2,5 %, S=44 %) < [ZnSiMo₁₂] (Y=12,8 %, S=43,6 %) < [MgSiMo₁₂] (Y=19,4 %, S=61 %) < [NH₄NiMo₆] (Y=56,9 %, S=84,8 %).

W-containing polyoxometallates of different composition was investigated in the process of oxidative conversion of CH₄ to H₂-containing mixtures too. Yield of H₂ on the catalyst Ba_x[PW₁₁Ni] attains 80,8 % (850 °C). Aluminosilicate as carrier was more active and selective from the series of carries (silica gel, aluminosilicate, alumina, fluorinated alumina, cordierite, zeolite with clinoptilolite structure).

Block carrier from cordierite was investigated in the process of oxidative conversion of methane. As a result of investigation it was shown that supporting method of active component over block porous carrier by variation of secondary carrier, binding agent, protective layer play an important part in the process of selective production of hydrogen. The yield of H₂ on 5%(NH₄)₄NiMo₆O₂₄ over carrier attains 53,0 %. W-containing samples supported over block porous carriers are more perspective. It was carried out the investigation of the physical-chemical properties of catalysts by complex methods (IRS, XRD, ESDR, TPR) and determined the correlation between catalytic and physical-chemical properties.

The prospecting investigations of catalytic oxidative conversion of methane to hydrogen-containing mixtures show an opportunity for application of low percentage catalysts supported on granulated carriers on a base of polyoxometallates and production sufficiently high yields of hydrogen from methane.

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**INFLUENCE OF COMPOSITION AND STRUCTURE OF THE GRAFTING
[Pt(OH)_xCl_y]/ γ -Al₂O₃ SPECIES ON Pt-ALUMINA CATALYSTS PROPERTIES**

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Processes of decomposition, reduction and oxidation of the grafting on γ -Al₂O₃ chloro- and hydroxocomplexes Pt (IV) preparing by surface hydrothermal synthesis from [PtCl₆]²⁻-precursor have been investigated. The analysis of TPR spectrums, seems to indicate that the reduction of the platinum hydroxocomplexes are proceeds more difficult than of the platinum chlorocomplexes. However it was found that platinum particles dispersity is higher for the Pt-Al₂O₃ catalysts produced from platinum hydroxocomplexes. Catalytic properties of these systems were analysed in model reaction of benzol hydrogenation to determine the energetic heterogeneity of surface platinum active centres. The results are discussed by the concept of the interaction effect “precursor-support” - “metal-support”.

The primary goal of the research has been the analysis of the influence of the composition and structure of anchored on the surface of γ -Al₂O₃ individual and mixed chloro- and hydroxo- complexes Pt (IV) on the properties of alumina-platinum catalysts. Earlier the nature of the complexes [Pt(OH)_xCl_y]/ γ -Al₂O₃ was determined by the UV-VIS diffuse reflectance and EXAFS spectroscopy [1].

Systematic investigations of thermochemical processes of decomposition, reduction and oxidation of the grafting complexes of different types have been carried out by the means of the STA and TPR-TPO methods. It has allowed to characterize these systems directly during the process of heat treatment. The using of the methods of adsorption, pulse chemisorption and TPD has allowed to study the characteristics of a series of final alumina-platinum catalysts (for example, texture, dispersity and electronic state of the Pt-particles).

Influence of the hydrolysis depth and the conditions of surface reactions on the degree of interaction “precursor-support” has been determined according to the changing of position of the temperature peaks of decomposition or/and reduction of various adsorbed forms Pt (IV) (fig. 1). Accordingly, it has been found using pulse chemisorption of H₂ and CO method that the platinum particles dispersity is higher ($D_{Pt}=90-100\%$) for the Pt-Al₂O₃ catalysts produced from the platinum hydroxocomplexes.

It has been shown that the effect of the interaction of chloro- and hydroxo-complexes Pt (IV) with the support plays the basic role for energy and structure heterogeneity of the formed

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clusters of platinum (Pt^0 and Pt^{+n}). The used model reaction of benzol hydrogenation on the investigated catalysts (fig. 2) has been confirmed by the formation of appropriate selective platinum centres in these systems.

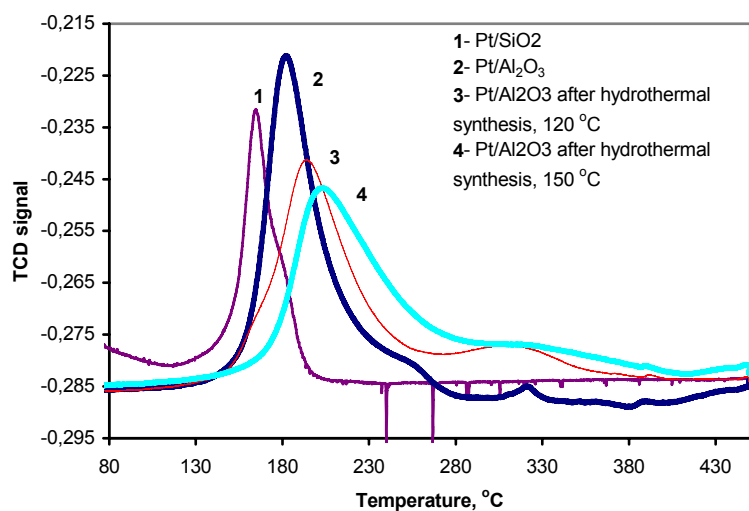


Fig. 1. TPR-curves of the platinum chloro- and hydroxo-complexes on the SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ preparing by surface hydrothermal synthesis from $[\text{PtCl}_6]^{2-}$ -precursor (2%mass. Pt).

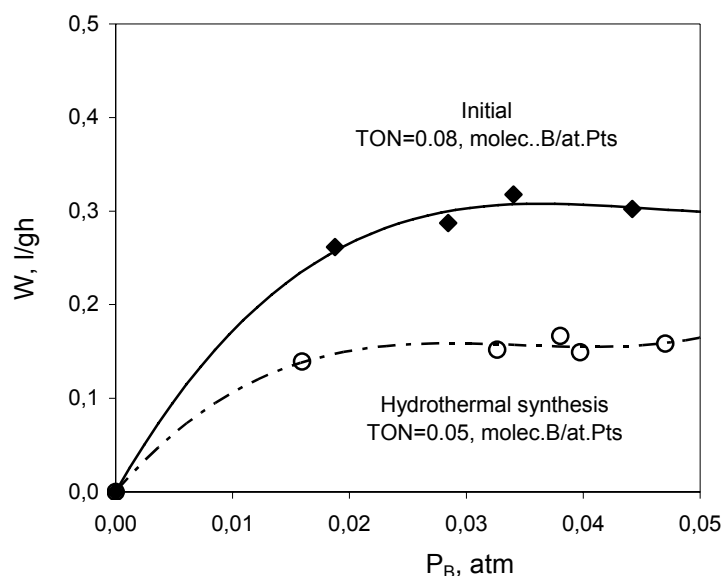


Fig.2. Dependence of the benzol hydrogenation rate on the 1,0 %mass. $\text{Pt}/\text{Al}_2\text{O}_3$ (initial and after hydrothermal synthesis) from benzol gaseous pressure.

Acknowledgments

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NEW COMPOSITE OF A POLYACETYLENE WITH SINGLE-WALLED CARBON NANOTUBES AND STUDY OF ITS ELECTROCHEMICAL PROPERTIES

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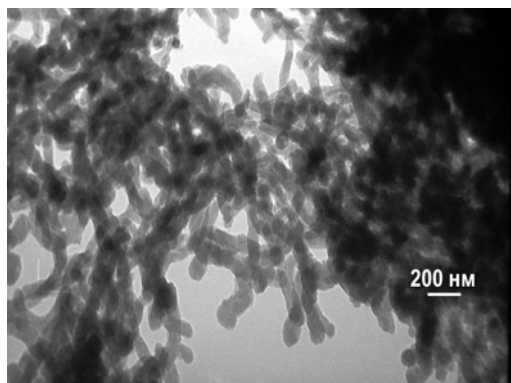
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A new composite material consisting of single-walled carbon nanotubes (SWNT) (2.4 wt %) covered by polyacetylene (PA) has been prepared. PA synthesized directly on single-walled carbon nanotubes is a defectless long-chain polymer composed of *trans* and *cis* units with a sufficient length (60 % *trans* and 40 % *cis* isomers). The currents of Li^+ intercalation for composite material near the percolation threshold are 50 times higher as compared to starting PA.

The insertion of electroconducting filler, namely, graphite, SWNT and multi-walled nanotubes (MWNT) into starting PA by mechanical blending sharply enhances conductivity and air stability of the resulting composite. A percolation threshold for PA-SWNT composites [1] is close to 3 v/v.%. A rise in conductivity to 10^{-1} – 10^0 S cm^{-1} was explained by the injection of electrons from the filler particles. The polymerization of propylene carried out directly on graphite treated by a Ziegler–Natta catalyst yields composites in which the size of graphite particles and a distance between them are appreciably decreased compared to those in the mechanical mixture [2]. Since in fact SWNTs are bundles of twisted tubes, it is expected that with the use of this method, the interface between an SWNT and polyacetylene will increase; as a result, the electrochemical characteristics of the resulting composites will improve.

In the present work we synthesized PA directly on SWNT (mass content of nanotubes equal to 80-90 %) in the presence of Ziegler - Natta catalyst, $\text{Al}(\text{i-C}_4\text{H}_9)_3$ and $\text{Ti}(\text{OBU})_4$, in toluene ($[\text{Al}]/[\text{Ti}] = 4/1$, $[\text{Ti}] = 3 \cdot 10^{-3}$ mole/l). The monomer pressure was maintained at a level of 300 mmHg in the course of polymerization.

Composite (2.4 wt % SWNT) morphology was characterized using a JEM- 100 CX transmission electron microscope. The composite was found to consist of SWNT covered by a polyacetylene shell. An average diameter of structural units of the composite was determined to be ≈ 80 nm. No free polyacetylene was observed between the tubes covered by PA. This indicates that polymerization occurs only on SWNT possibly due to the adsorption of catalytic centers on an outer surface of SWNT. Such adsorption can be accompanied by separation of bundles formed by SWNT to single nanotubes. Obviously, the composite volumes are 2-2.5 times higher than that of PA of the same mass due to loose packing of



composite particles. The presence of SWNT in a catalytic mixture does not affect high yield of polymer (96 %). However, the polymerization time is becomes two times longer. Possibly, a catalyst forms a less catalytically active complex with nanotubes and the rate of growth of polyacetylene chains is comparable with the rate of their crystallization to the solid phase. According to the data of IR, PA bound to SWNT is a defectless, highly ordered, long-chain polymer comprising extended enough both trans- and cis-rings (60 % of trans- and 40 % of cis-isomers).

The dc conductivity of the pressed samples are $5 \cdot 10^{-10}$ (polyacetylene), $8.2 \cdot 10^{-9}$ $1.8 \cdot 10^{-7} (\Omega \text{ cm})^{-1}$ (composite). A rather insignificant growth of conductivity with an increase in the content of the SWNTs in the composites compared to the mechanical mixing of components is apparently associated with the insulating effect of a thick polyacetylene shell that hampers direct contacts between nanotubes. Electrochemical behavior of the electrodes pressed from a PA-SWNT composite was studied using cyclic voltammetry (CVA) in 1 M LiPF_6 dissolved in ethylene carbonate – diethyl carbonate – dimethyl carbonate (1:1:1) mixture. At 1 mV/s scan rate, the currents of Li^+ intercalation for the composite are 50 times higher as compared to starting PA. An increase in conductivity is more distinct in electrochemical measurements when the doping of polyacetylene by lithium cations occurs and polyacetylene transforms into the conducting state.

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SOME ASPECTS OF THE SELECTION OF STRUCTURE OF IRON-OXIDE CATALYTIC SYSTEMS FOR DEHYDROGENATION OF HYDROCARBONS

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Influence of iron(III) oxides of different modification, and also compounds of alkali metals, rare-earth elements and compounds of transition metals of variable valence on catalytic activity of reaction of dehydrogenation of ethyl benzene in styrol is investigated.

Now dehydrogenation catalysts used in an industry differ by a diversity of structures and methods of synthesis which in many respects define production characteristics of catalytic systems.

Despite of an abundance of experimental data and theoretical premises till the present moment there is no common opinion about the nature of the active component of the catalyst.

The analysis of literary data has shown, that iron(III) oxides of different modification, ferrites, and also compounds of alkali metals, rare-earth elements and compounds of transition metals of variable valence are used upon synthesis of iron-oxide catalysts.

Therefore the problem of elucidating of the role of separate components and their interaction upon catalysts synthesis is actual.

Activity testing of catalytic systems in model reaction of dehydrogenation of ethyl benzene (EB) to styrene were carried out in flowing microcatalytic installation at temperature 600 °C and weight ratio H₂O:EB 3:1. The analysis of reaction products was carried out by a chromatographic method. Research of phase structure was carried out by a method of X-ray diffraction analysis and Messbauer spectroscopy.

Synthesized catalytic systems represented the oxygenous compounds keeping except for iron oxides also compounds of potassium, chrome, molybdenum, cerium, etc. [1, 2].

Experimental data on research of catalytic activity of single-component iron-oxide systems has shown, that γ -iron(III) oxide and magnetite have the greatest activity. Conversion and selectivity of compounds is 28-35 % and 79-82 %, accordingly.

The greatest increase of conversion at simultaneous increase of selectivity in contrast to one-component systems is observed at insertion of compounds of potassium in the structure of the catalyst. Probably, increase of activity of catalyst is connected with formation of ferrites of a potassium during synthesis.

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Insertion in structure of the catalyst of compounds of cerium or molybdenum results in increase of selectivity of the process (up to 88-91%) at rather small growth of activity. Probably it is connected with formation of solid solutions, for example Ce_2O_3 in iron(III) oxide.

Fe-Cr-O sample shows rather low selectivity in contrast to activity of oxide compounds, at slight increase of conversion.

Synthesized Fe-K-Ce and Fe-K-Mo compounds, and also synthesized on the base of these compounds four-component systems has conversion of 72-76 % and selectivity of 92-93 %, that is at a level of domestic and foreign dehydrogenation catalysts tested in simulated condition.

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HYDROTREATING CATALYSTS MODIFIED BY ADDITIVES OF VANADIUM AND HETEROPOLYACIDS OF KEGGIN STRUCTURES

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In the given work influence of additives of heteropolyacid (HPA) of molybdenum and tungsten of 12-th lines and additives of vanadium was studied. It is established, that joint application of vanadium and HPA allows increasing activity of the catalyst in a wide interval of temperatures. The complex of modifying additives in the best way is proved in case of use cobalt as promoter.

One of the ways to increase activity of hydrotreating catalysts is their modifying by various inorganic additives. It allows to increase hydrodesulfurization (HDS) and hydrogenation activities of catalysts, stability of an active phase, to regulate acid properties of the catalyst, etc.

In the work influence of additives of heteropolyacid (HPA) of molybdenum and tungsten of 12-th lines and additives of vanadium was studied. Various content of additives, ways of their introduction and methods of synthesis of the modified catalysts were studied. All synthesized samples contained identical contents of MoO₃ and NiO or CoO. Molybdenum was introduced from ammonium paramolybdate (NH₄)₆Mo₇O₂₄*4H₂O (PMA) or from H₄[SiMo₁₂O₄₀]*nH₂O (SiMo₁₂-HPA). Some samples contained also modifying additives W or V. Tungsten was introduced from ammonium paratungstate (NH₄)₁₀[H₂W₁₂O₄₂]*4H₂O (PTA) or from H₄[SiW₁₂O₄₀]*nH₂O (SiW₁₂-HPA).

The synthesized catalysts were tested in a bench-scale flow reactor unit in the process of hydrotreatment of diesel fraction. The tests were conducted at temperatures of 320, 340, 360, and 380⁰C; a pressure of 3.0 MPa; a feed space velocity of 2.5 h⁻¹; a hydrogen : feedstock ratio of 450 NI/l; and a catalyst volume of 10 cm³.

For initial fraction and received hydrogenates contents of sulfur and polycyclic aromatic compounds (PCAC) was determined, it have allowed to determine HDS and hydrogenation activity of catalysts.

In fig. 1 dependence of HDS degree for Al-Ni-Mo catalysts modified by tungsten with the additive of vanadium (a sample 10) and without vanadium (a sample 9) is given. Apparently from figure, HDS degree for sample 10 containing of vanadium is higher, than for a sample 9 (without the modifier) on the average on 8 rel %. The catalyst 8 allows to obtain hydrogenates with residual contents of sulfur of 0.002 wt % and hydrogenation PCAC more than on 40 rel % (fig. 2).

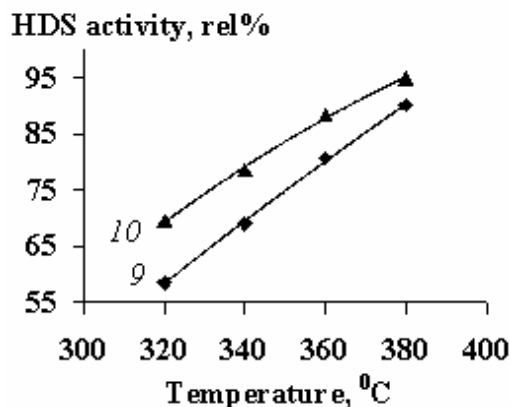


Fig. 1. Influence of the additive of vanadium on activity of Al-Ni-Mo catalysts modified with tungsten

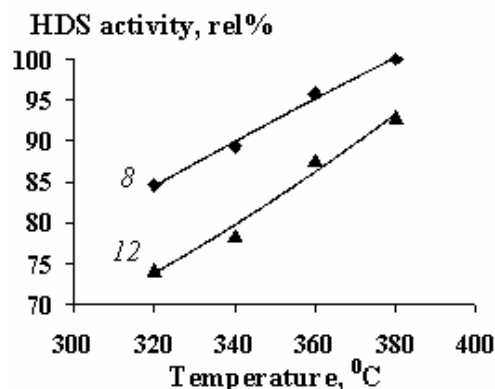


Fig. 2. Influence of the additive of vanadium on activity of Al-Co-Mo catalyst containing SiMo₁₂-HPA and SiW₁₂-HPA

The complex of modifying additives in the best way is proved in case of use cobalt as promoter. The data submitted in fig. 2 show, that the additive of vanadium to Al-Co-Mo catalyst containing SiMo₁₂-HPA and SiW₁₂-HPA, essentially raises its HDS activity.

In fig. 3 influence of the additive of tungsten on HDS degree for Al-Ni-Mo catalysts modified with vanadium is shown. The sample 13 does not contain any tungsten; the sample 10 is modified with tungsten (WO₃ is introduced from PTA).

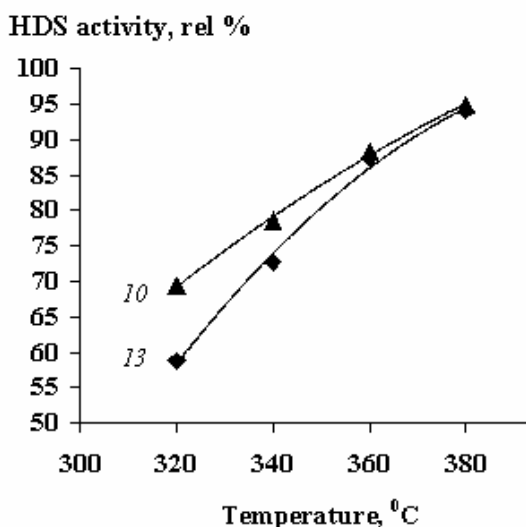


Fig. 3. Influence of the additive of tungsten on HDS activity of catalysts modified with vanadium

From fig. 3 it is visible, that introduction in catalytic composition of tungsten essentially increases HDS activity at low temperatures (at 320 °C by 10.6 rel %), but at higher temperatures influence of tungsten is insignificant.

It is established, that joint application of vanadium and HPA allows increasing of activity of the catalyst in a wide interval of temperatures.

NORBORNADIENE IN NEW SHAPE-SELECTIVE CATALYTIC SYNTHESSES

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A wide range of carbocyclic compounds, which are very difficult to synthesize via conventional routes, can be manufactured through catalytic reactions with norbornadiene (NBD). These substances can be used as high-density fuels, special materials; they can be applied in medicine, agriculture, microelectronics; besides, they are capable of accumulating sunlight energy. NBD is derived from cyclopentadiene, a large volume byproduct of petrochemical processes like steam cracking. This is one reason why commercializing NBD-based processes can help in creating wasteless technologies.

NBD usually react through multiple routes giving rise to a number of products. Hence the selectivity of NBD-based reactions is of a primary importance.

We have demonstrated the possibility to control the rate and the selectivity in cyclodimerisation, co-dimerisation and allylation of NBD. Kinetic regularities have been studied and consistent mechanisms were developed.

A series of unsaturates has been synthesized. These compounds possess a set of double bonds with different reactivities, and hence they can be applied for creating modified rubbers.

New co-dimerisation reactions between NBD and unsaturated esters and ketones, and supercritical CO₂, have been discovered and studied [1]. New polycyclic esters and lactones have been synthesized: they are applicable to a range of various purposes.

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**STUDY OF THE HYDROISOMERIZATION REACTION OF MONOTERPENES
OVER THE NOBLE METAL CATALYSTS**

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Reaction of the double-bond migration is a key-stage for producing vitamins, drug substances and fragrances such as: myrcenol, menthol, nerol, lylal, geraniol¹. Alpha-pinene is much more abundant and has been less valuable as a starting material for chemical synthesis. Amounts of β -pinene that are consuming in production is much bigger than amounts that can be produced from turpentine, so grand amounts of β -pinene can be obtained by the isomerization reaction of α -pinene. Analysis of the literature data show that the most ecological and promising way is the isomerization process over Group VIII metals and gold.

In the present work the mixture of pinenes was used: α -pinene – 94.91%, β -pinene – 2.34%. Ru/C, Au/ δ -Al₂O₃, Au/SiO₂, Au/ γ -Al₂O₃ were used as catalysts. In the previous work the influence of the solvent (hexane, octane, DMF, ethanol, benzene, propanol-2, i-buthanol) on the content of products and rate in the hydroisomerization reaction of the mixture β -pinene and α -pinene has been studied.

The influence of the particles' size of the gold catalyst on the content of products has been studied. The mechanism of the isomerization reaction has been proposed².

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CATALYTIC SYSTEMS BASED ON RUTHENACARBORANES IN CONTROLLED SYNTHESIS OF MACROMOLECULES

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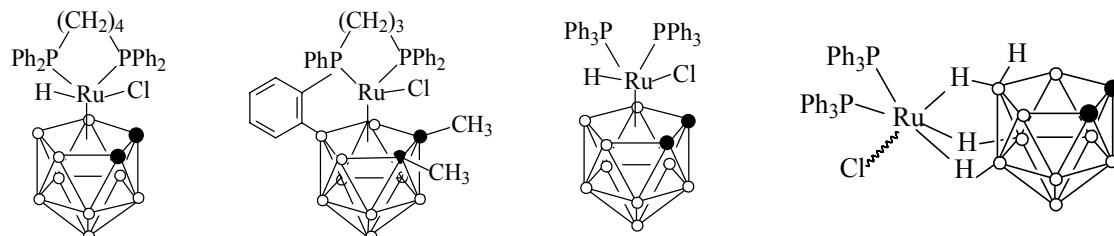
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New catalytic systems, based on carborane complexes of ruthenium for “living” radical polymerization of vinyl monomers were proposed. The influence of the structure of metallocomplexes on the kinetics of polymerization and molecular weight distribution of polymers was investigated. The original scheme of polymer chain propagation in the presence of ruthenacarborans was proposed.

Catalytic systems, based on transition metal complexes are widely employed for precision synthesis of macromolecules. Nowadays Atom Transfer Radical Polymerization (ATRP) is one of the most promising directions in the given field [1].

In the present work the new catalytic systems based on a number of ruthenacarboranes of *closo*- and *exo-nido* structure for controlling the chain propagation in the polymerization of vinyl monomers were advanced [2, 3]:



The bulk polymerization was carried out under a residual pressure of monomer at 80° or 90°C in the presence of carbon tetrachloride or methyl(chloroacetate) as initiators.

It was found that the carborane complexes of ruthenium exert substantial influence on the kinetic parameters of polymerization of methyl methacrylate (MMA) and styrene as well as the molecular-mass characteristics of macromolecules. It was shown that the polymerization of MMA in the presence of ruthenacarboranes proceeds without spontaneous acceleration till high degrees of conversion. A linear form for the kinetic relation of the logarithm of ratio of initial monomer concentration and current one against time pointed to the absence of irreversible chain termination that is characteristic of “living” polymerization processes. The molecular-mass distributions of the polymers were unimodal and relatively narrow and shifted to high molecular weights with monomer conversion. The number-average molecular

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weight linearly increased with conversion. At the same time polydispersity decreased with conversion.

The “living” character of polymerization in the presence of ruthenacarboranes was confirmed with the recommencement of the process on adding a new portion of a monomer (post-polymerization) and the possibility of block-copolymer synthesis.

ATRP of styrene with using the above systems proceeds with a lower rate than the synthesis of polymethylmethacrylate under similar conditions. Besides, unlike the polymerization of MMA, the smallest polydispersity ratios were obtained in the presence of ionic ruthenium complexes.

It was shown that the examined diamagnetic carborane complexes of ruthenium compare favorably by their catalytic activity with cyclopentadienyl derivatives of ruthenium that are able to efficiently initiate the synthesis of macromolecules only in the presence of aluminium alkoxides but with a considerably smaller rate and conversion.

It was established that the addition of amines to the catalytic system leads to a dramatical increase of the polymerization rate.

The original scheme of polymer chain propagation in the presence of the ruthenacarborans was proposed.

The work was carried out with the financial support of the Russian Foundation Basic Research (grant 05-03-32668).

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**EFFECT OF PHYSIOCHEMICAL PROPERTIES OF NANOSIZE MAGNESIUM
OXIDE IN LIQUID PHASE MEERWEIN-PONNDORF-VERLY REDUCTION
OF CYCLOHEXANONE INTO CYCLOHEXANOL**

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Metal oxides with the size of grains in the nanometer range have been of considerable interest in various fields of nanotechnology [1]. In recent years also applications of nanosize materials have been extended to catalytic systems. Among nanosize metal oxides, magnesium oxide with a large surface area and alkaline property is a promising catalyst for the liquid phase Meerwein-Ponndorf-Verly reduction of ketons to alcohols [2]. To this end nanosize magnesium oxide with various physiochemical properties have prepared by wet chemical routes from hydrolysis of magnesium chloride (MgO-1) and magnesium methoxide (MgO-2) [3-4], and after characterization with X-ray powder diffraction (Fig. 1), measurement of particle size and surface area have been employed as catalysts for the reduction of cyclohexanone into cyclohexanol in isopropanol at 82 °C. Result showed that the nanosize magnesium oxide obtained by various methods are effective catalysts for the reduction of cyclohexanone into cyclohexanol. Among several type of nanosize magnesium oxide, the one prepared from hydrolysis of magnesium methoxid showed higher yield. Results showed that the nanosize MgO prepared from air hydrolysis of magnesium methoxide and subsequent calcination is more effective catalyst for reduction of cyclohexanone into cyclohexanol. The effect of calcination temperature and also recycled catalyst on the yield of reaction has been investigated. Apparently, higher calcinations temperature resulted to decrease of yield, which can be attributed to the condensation of hydroxyl group and decrease of surface area. The recovered magnesium oxides retain activity in reduction of cyclohexanone into cyclohexanol, but they are not effective as freshly prepared magnesium oxide.

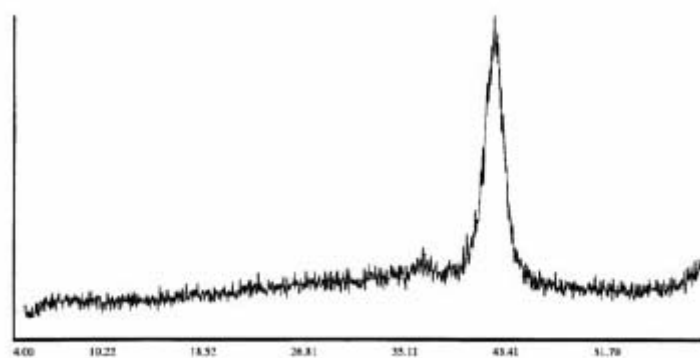


Fig. 1. X-ray diffraction pattern of MgO prepared from thermal decomposition of magnesium methoxide.

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**INVESTIGATION OF STRUCTURE AND MORPHOLOGY OF CATALYSTS
BASED ON KAZAKHSTANI ALUMOSILICATES ACTIVE IN THE CRACKING OF
HEAVY OIL RESIDUES**

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Energetic and ecological problems of processing of highly viscous oils requires design of new technological solutions. Urgent problem is use of inexpensive and accessible residual fractions from the petrochemical plants. The expediency of the processing of heavy oil fractions by oxidative cracking has been stated in [1]. In contrast to this work, which deals with the catalysts based on zeolites, the aim of [2] was the oxidative cracking of vacuum gasoils and mazuts carried out on the composites containing both zeolites and clays. The peculiarity of the proposed process is in the irreversibility of the used cheap catalyst under its low consumption. This enables one to dispense the stage of regeneration of the used catalyst, which contributes to the aggravation of ecological indices of the existing industrial processes.

The aim of the present work was to investigate the influence the nature of Kazakhstan's zeolites and clays, conditions of their activation and relative concentrations of the components which they have upon the cracking properties of catalysts in the range of reactions of destruction of hydrocarbons composing the heavy oil fractions. Chemical composition, the structure of catalysts, acidity of their active sites have been investigated and determined with the help of combined usage of XFS-spectroscopy, X-ray diffraction and IR-spectroscopic methods. It was determined, that the optimal concentration of components of activated composite catalysts does not depend on the nature of zeolites and clays composing their structure and is within the interval 14-15 % for zeolites and 86-85 % for clays.

Table I. Yield of products of oxidative cracking of heavy oil fractions from (a) “Petrokazakhstan” plant, (b) Pavlodar oil plant. The composite catalyst is prepared as the suspension containing 0.2 % of natural components ($\omega_{suspension} = 1.0\ hour^{-1}$, $\omega_{air} = 0.15\ hour^{-1}$)

C _{zeolite} , %	Yield, %mass					
	Gas	gasoil	gasoline	heavy residues	losses	total
0	1.8	0.8	25.5	71.4	0.5	100.0
10	4.2	3.5	46.8	45.0	0.5	100.0
15	4.7	5.0	74.9	14.8	0.6	100.0
20	4.4	4.4	65.2	25.3	0.7	100.0
50	4.0	4.1	55.8	35.6	0.5	100.0
100	3.7	2.9	47.0	45.8	0.6	100.0
0	0.6	0.6	66.0	32.5	0.3	100.0
10	0.7	0.6	77.5	20.9	0.3	100.0
14	0.8	0.7	79.9	18.5	0.1	100.0
20	0.4	0.4	68.8	30.2	0.2	100.0
50	0.4	0.3	63.0	35.9	0.4	100.0
100	0.3	0.2	59.7	39.3	0.5	100.0

A distinctive feature of the most active composites, according to the IR-spectroscopic studies, is the formation of crystalline zeolite phases during the process of calcination.

Table II. Phase composition of catalysts (I - without calcinations, II - calcinated) determined by the X-ray diffraction.

(a) Composites made from the Chankanai zeolite and Arkalyk clay										
Phase	Zeolite		10%		14%		20%		Clay	
	I	II	I	II	I	II	I	II	I	II
SiO ₂	3	1	5	2	6	3	4	2	7	3
(K,Na)[Si ₃ AlO ₈]	0	0	0	0	5	0	0	0	6	0
CaCO ₃	0	0	1	3	1	1	1	1	1	5
CaSO ₄	0	0	6	0	7	0	6	0	5	0
Ca,Mg(CO ₃) ₂	0	0	3	5	2	1	2	5	3	4
Mg ₂ [SiO ₄]	0	0	2	1	3	2	3	3	2	2
(Na,K,Ca)[Al ₂ Si ₁₀ O ₂₄]*7H ₂ O	1	2	8	7	9	6	7	7	0	0
parameter of the cell, A ₀ ,m ⁻¹⁰	abs	abs	abs	abs	abs	15.2	abs	abs	abs	abs
parameter of the cell, b ₀ ,m ⁻¹⁰	abs	abs	abs	abs	abs	12.06	bs	abs	abs	abs

(b) Composites of the Saryozek zeolite and Pavlodar clay										
Phase	Zeolite		10%		14%		20%		Clay	
	I	II	I	II	I	II	I	II	I	II
SiO ₂	2	2	2	2	2	2	2	2	2	2
K ₂ [AlSi ₂ O ₅ (OH) ₄]	0	0	1	1	1	1	1	1	1	1
NaAlSi ₃ O ₆	3	0	4	3	4	3	3	4	4	3
(Na,K,Ca)[Al ₂ Si ₁₀ O ₂₄]*7H ₂ O	4	3	7	6	7	6	6	7	0	0
parameter of the cell, A ₀ ,m ⁻¹⁰	abs	abs	abs	abs	abs	11.36	abs	abs	abs	abs
parameter of the cell, b ₀ ,m ⁻¹⁰	abs	abs	abs	abs	abs	7.05	abs	abs	abs	abs
parameter of the cell, c ₀ ,m ⁻¹⁰	abs	abs	abs	abs	abs	4.65	abs	abs	abs	abs
parameter of the cell, β ₀ ,m ⁻¹⁰	abs	abs	abs	abs	abs	150.3	abs	abs	abs	abs

As a result of the combined spectral studies it was observed that the necessary condition for the formation of crystalline phases building the structure of natural aluminosilicates is the characteristic balance between concentrations of natural zeolites and clays and optimal concentration of exchange cations of NH_4^+ and La. The fact, which serves as the proof of this assertion, is the absence of crystalline structure in composites of optimal chemical composition, which were not activated by the method of ion exchange in the solution of salts of the above-mentioned cations. Such being the case, exchange cations contribute not only to the acidity of active sites, but also take part in the formation of the crystal lattice of the composite.

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**GOLD CATALYSTS SUPPORTED ON HIERARCHICALLY
MESO-MACROPOROUS BINARY METAL OXIDES FOR LOW-TEMPERATURE
WATER-GAS SHIFT REACTION**

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In this presentation we try to shed some light on the relationship between textural and structural characteristics of the TiZr meso-macroporous materials, the state of gold particles and the WGS activity of catalysts prepared. We discuss the catalytic behavior of the new catalyst on the basis of their full characterization in order to unravel the role of the TiZr meso-macroporous support and possible interaction between gold nanoparticles and support.

The structural and textural properties of the meso-macrostructured single metal oxides could be improved by the introduction of secondary oxide to form the binary metal oxide composite materials. These meso-macrostructured binary oxide compositions should be significant for the use as advanced functional materials, especially in the catalysis applications. Titania- and zirconia-based mixed oxides are of great importance due to their multiple applications, including catalysis and solid-oxide fuel cells. Moreover, gold catalysts supported on single mesostructured oxides have excellent and as-yet unexplained properties for water-gas shift reaction (WGS) [1, 2]. The aim of this study is preparation of new gold-based catalyst supported on meso-macrostructured binary oxide compositions and study of its catalytic behavior in the WGS. The support of this new catalytic system is a binary oxide composition, including titania and zirconia (TZ), with a hierarchically bimodal meso-macroporous structure. The support was prepared through the surfactant templating technique combining with the use of mixed alkoxide solutions. The binary metal oxide material obtained has a homogeneous distribution of the components and the attractive structural properties of large pore volume and high specific surface area [3]. Such hierarchical porous material should be significant for improving catalytic efficiency due to the presence of a secondary metal oxide and structural control, and capable as catalyst or catalyst support. Gold catalysts were

synthesized by deposition-precipitation of gold hydroxide on meso-macroporous mixed metal oxide support. The support and catalysts were characterized by XRD, SEM, HRTEM, N₂ adsorption analysis and TPR measurements. No crystalline phase could be detected by XRD in the TZ support, indicating a homogeneous mixing of the Ti and Zr components in these materials. This suggests that the segregation did not occur, and meso-macrostructured TZ were formed with (Ti,Zr)-O₂ species, a real solid solution of TiO₂ and ZrO₂, rather than discrete TiO₂ and ZrO₂ nanocrystallites. After calcination at 500 °C the bicrystalline phases of tetragonal ZrO₂ and anatase with low crystallinity were observed. The meso-macrostructures can be retained after calcination, as revealed by SEM and TEM images. There are no visible differences in the X-ray patterns after deposition of gold. The absence of characteristic lines of gold at $2\theta = 38.2$ and 44.4° could be attributed to fine dispersion of gold nanoparticles on the surface of TiZr. The gold particles with size below 4 nm are homogeneously dispersed on the mixed metal oxide support. The pore sizes of the TZ were slightly enlarged after calcination. The BET surface areas and the pore volumes of the calcined TZ are larger than those of the calcined pure titania or zirconia, indicating the higher thermal stability of the TZ meso-macroporous materials. A significant effect of gold loading on the reducibility of the Au/TZ was found by H₂-TPR. The catalytic behavior of the gold catalysts was evaluated in WGS at a wide temperature range (140–300 °C) and at different space velocities and H₂O/CO ratios. The influence of gold content and particle size on the catalytic performance was investigated. The CO conversion of the new catalyst was compared with that related to the gold catalysts supported on mesoporous ZrO₂ and TiO₂. A high degree of synergistic interaction between titania and zirconia was observed. Gold catalysts supported on the Au/TZ exhibited significantly higher catalytic activity. New TZ support has been found to be of much interest as potential supports of gold-based catalysts for WGS reaction.

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**ACTIVITY OF BIS(TRIPHENYLPHOSPHINE) NICKEL DIBROMIDE/ZINC
CATALYTIC SYSTEM IN POLYMERIZATION OF METHYL METHACRYLATE
AND STYRENE**

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The catalytic system based on nickel(II) halides and zinc dust was proposed for accomplishing the controlled polymer synthesis under mild temperature conditions. Some features of kinetics for styrene and methyl methacrylate polymerization in the presence of the binary catalyst $\text{NiBr}_2(\text{PPh}_3)_2 + \text{Zn}$ were studied. An influence of catalyst composition on both copolymer content and molecular weight of the polymers was estimated. An original scheme for chain growth in the presence of the metal-complexed catalyst was proposed.

It was established that catalytic systems based on bis (triphenylphosphine) nickel dibromide, zinc dust in the presence of iodobenzene were capable of initiating effectively the polymerization of styrene and methyl methacrylate (MMA) at temperature ranged from -5 to +70 °C.

The scheme of initiation derived from the experimental results is based on the reduction of nickel (II) to nickel(0) complexes with zinc. Consequently, phenyl radicals generated from the decomposition of $\text{PhNiI}(\text{L}_2)$ complexes actively initiate the polymerization. The growing radicals accumulating in the media reversibly add to a nickel atom. Thus, the reversible interaction of these radicals with nickel(I) adduct prevents from bimolecular termination, and spontaneous propagation of molecular weight with conversion resulted in the control of polymer chain growth at radical initiation.

The polymerization was found to proceed without autoacceleration in the presence of the nickel catalyst, the molecular weight growing with conversion. In addition, the rate of styrene polymerization was higher than that for MMA in contrast to polymerization in the presence of AIBN when reverse phenomenon is observed – the rate of styrene polymerization is considerably slower than that of MMA.

During MMA polymerization in the presence of the metal-complexed catalyst studied a linear dependence of molecular weight on conversion is observed, that is one of the specific features of the controlled polymerization.

The study of influence of halogen nature in phenylhalide results that activity of the system in polymerization falls in the row $\text{PhI} > \text{PhBr} > \text{PhCl}$. On the contrary, the nature of the

halogen in $\text{NiX}_2(\text{PPh}_3)_2$ does not exert any influence on the yield of polymer, that is indirectly approves the proposed mechanism, since abstraction of a halogen atom from the nickel complex with zinc occurs on the first step, and low valent nickel intermediates lead the polymerization.

The following molar ratio of the monomer and catalyst/ initiator components $[\text{Monomer}]:[\text{NiBr}_2(\text{PPh}_3)_2]:[\text{PhI}]:[\text{Zn}]=1:0.05:0.1:0.08$ was selected for polymerization of vinyl monomers that was resulted from experimental data. When concentration of the initiator (Ph-I), the nickel complex and zinc dust were diminished, the rate of polymerization decreased. On the contrary, on addition of 5 mol.% of zinc iodide (as the Lewis acid) in the polymerizing mixture, the rate of the reaction increased.

It was shown that the metal-complexed catalyst exerts a strong influence on the dependence of copolymer composition on the monomer mixture content. For instance, the copolymer is enriched with styrene in overall the curve of the composition and relative ratio of styrene considerably grows ($r_{\text{MMA}}=0.45$, $r_{\text{Sty}}=1.70$) in the presence of the nickel system, while using the classical initiators (AIBN or peroxides) the curve of composition is S-shaped, relative ratios of both monomers being less than unity ($r_{\text{MMA}}=0.46$, $r_{\text{Sty}}=0.5$).

Study of kinetics of styrene copolymerization with MMA in the presence of the nickel system showed that the rate of the reaction decreases upon introduction of methacrylic monomer to the reaction mixture.

This work was supported by the Russian Foundation for Basic Research (grant No. 05-03-32688).

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**FUNCTIONAL NANOCOMPOSITE MATERIALS BASED PEROVSKITE- AND
FLUORITE- LIKE STRUCTURES: STRUCTURE, PROPERTIES AND
APPLICATION**

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Functional materials are the new emerging materials systems that consist of advanced subsystems. The important requirement in preparations of materials is to control the structural and compositional evolution for achieving superior properties. Solid oxide fuel cell (SOFC) where process is based on material properties is one of a number of applications. Development of inexpensive cathode material – constituent of full cell – with the required performances is an important problem to solve for the intermediate temperature SOFCs. Nanocomposites comprised of fluorite-like oxides (good ionic conductors) and perovskites (electronic conductors) appear to be promising for these applications due to combination of needed for cathode material properties and an efficient preparation technique - mechanochemical treatment (MC) followed by short annealing. Their structure and principal properties were studied in presented work.

Functional materials are the new emerging materials systems that consist of advanced subsystems. Such materials are distinctly different from structural materials, and their physical and chemical properties are not the same as initial components have. They cover the wide range of organic and inorganic substances. Our work focuses only on oxide functional materials, namely perovskites and fluorites. The important requirement in preparations of materials is to control the structural and compositional evolution for achieving superior properties. The creation and development of hyperfunctional materials are undoubtedly the essential tasks in many fields of science and technology such as life science, transportation, microelectronics, medical treatment, safety engineering and energy including fuel cells engineering [1].

Solid oxide fuel cell (SOFC) combining catalytic fuel oxidation with energy production is one of new types of chemical reactors where process is based on material properties. They don't need such expensive catalyst, as platinum (fell cells with proton-exchange membrane). Nevertheless practical application of SOFCs is still limited by materials science-related problems that lead to insufficient power/volume ratio, high costs and high operation temperatures (~ 1000 °C). So, development of inexpensive cathode material – constituent of

fuel cell – with the required performances (high mixed ionic-electronic conductivity, stability under working condition and compatibility with other parts of fuel cell, anode and electrode) is an important problem to solve for the intermediate temperature SOFCs.

Nanocomposites comprised of fluorite-like oxides (good ionic conductors) and perovskites (electronic conductors) appear to be promising for these applications due to combination of these needed for cathode material properties [2]. A low cost of these materials required for the practical application can be ensured by using industrially available inexpensive mixed oxides of lanthanides LnO_x ($\text{Ln}=\text{Ce}(51\%)+\text{La}(26\%)+\text{Pr}(5\%)+\text{Nd}(12.8\%)+\text{Sm}(1\%)$) and an efficient preparation technique - mechanochemical treatment (MC) of their mixture with simple transition metal oxides in high power planetary ball mills followed by short annealing [3]. The most apparent advantage of this method is the absence of wastewaters that is very important from the ecological point of view

This work aims at development of inexpensive nanocomposite cathode materials with high oxygen mobility for application in IT SOFC using low cost LnO_x and MC preparation route.

According to XRD all synthesized samples consist of two phases: doped CeO_2^* with the fluorite-like and LnMeO_3 ($\text{Ln}=\text{La, Nd}$; $\text{Me}=\text{Mn, Co, Fe}$) with the perovskite-like structures. HRTEM revealed the nanocomposite particle structure of prepared samples: particles (the average particle size is nearly 450 nm) consist of domains (domain size is in the range of 50-100 nm) with perovskite and fluorite structures.

According to H_2 TPR the increase in calcinations temperature leads to a small change in the total hydrogen consumption for Ln-Co-O and Ln-Mn-O composites and to decrease for Ln-Fe-O composite.

According to CH_4 reduction rates in H_2 and CH_4 of Ln-Me-O nanocomposites are higher than that observed for individual perovskite and for pure or doped fluorite-like phases [4,5]. Moreover, syntheses-gas was formed during the reduction CH_4 of some samples (Ln-Mn-O, Ln-Fe-O, Ln-Co-O with the stoichiometry $\text{La}:\text{Me}=1:1$, annealed at $1100\text{ }^\circ\text{C}$). It means that these nanocomposites can be also used in membrane processes.

The highest mixed ionic-electronic conductivity was revealed for Ln-Co-O material.

Compatibility of Mn-containing nanocomposites preliminary supported as thin layers on the surface of single-crystalline corundum disc (a) or porous thin stainless-steel foils (b) was studied. Since the thermal expansion coefficient of both corundum and stainless steel is close to that of Sc-doped ceria ($\sim 9\text{-}11 \times 10^{-6}$).

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Hence, prepared and searching nanocomposite materials are promising for practical application in different cases and needed for subsequent investigations.

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**SYNTHESIS OF CATALYSTS ON THE BASIS OF VANADIUM OXIDES AND
SOME METALS OF IV AND VI GROUPS OF THE PERIODICAL SYSTEM FOR
OXIDATION AND AMMOXIDATION OF ALKYLAROMATIC COMPOUNDS INTO
ALDEHYDES, CARBOXYLIC ACIDS AND NITRILES**

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Catalytic properties of a number of oxides of metals of IV and VI groups of the Periodical System and of the chemical compounds, which they form with V_2O_5 , in oxidation and ammoxidation of alkylaromatic compounds have been studied with the purpose of determination of their role in the formation of catalytic properties of the modified vanadium-oxide catalysts. This information has offered a possibility to orient oneself in the choice of the composition of a multi-component oxide system in the process of searching of the routes for synthesis of an efficient catalyst of oxidation and ammoxidation of alkylaromatic compounds.

The work presents a study of the routes of synthesis of efficient catalysts with a pre-specified set of chemical compounds and crystalline modifications of oxides, based on the investigation of chemical and phase compositions of a number of multi-component catalysts from vanadium (V) oxide and oxides of the metals of IV and VI groups of the Periodical System. Vanadium (V) oxide surpasses significantly many metal oxides by its catalytic activity in oxidation and ammoxidation of alkylaromatic compounds. That is why upon the modification of vanadium (V) oxide by the additions of metal oxides, the role of the latter consists in the formation of chemical compounds with V_2O_5 , stabilization of definite crystalline modifications of the components of the oxidic system, and an effect upon reactivity of vanadium pentoxide. All this gives grounds to consider this multi-phase system, formed upon the synthesis of catalysts, as an active "carrier", the composition of which can be regulated, and in so doing to produce an effect upon activity and selectivity of a vanadium-oxide catalyst.

There has been studied an influence of Ti, Sn, Mo, Cr, W, Zr oxides and some of their chemical compounds with V_2O_5 upon thermal dissociation of vanadium (V) oxide, the rate of which is connected with V_2O_5 reactivity, and can be considered as a measure of activity of the modified vanadium-oxide catalysts. It has been shown that by the degree of influence upon the rate of V_2O_5 dissociation the oxides are arranged in the following row: TiO_2 (anatase) > WO_3 > TiO_2 (rutile) > Cr_2O_3 > SnO_2 > MoO_3 > ZrO_2 .

THE INFLUENCE OF SUPPORT KIND (Fe_2O_3 , TiO_2 , Al_2O_3) ON THE ACTIVITY OF GOLD SUPPORTED CATALYSTS IN CARBON MONOXIDE OXIDATION BY OXYGEN OR WATER VAPOUR

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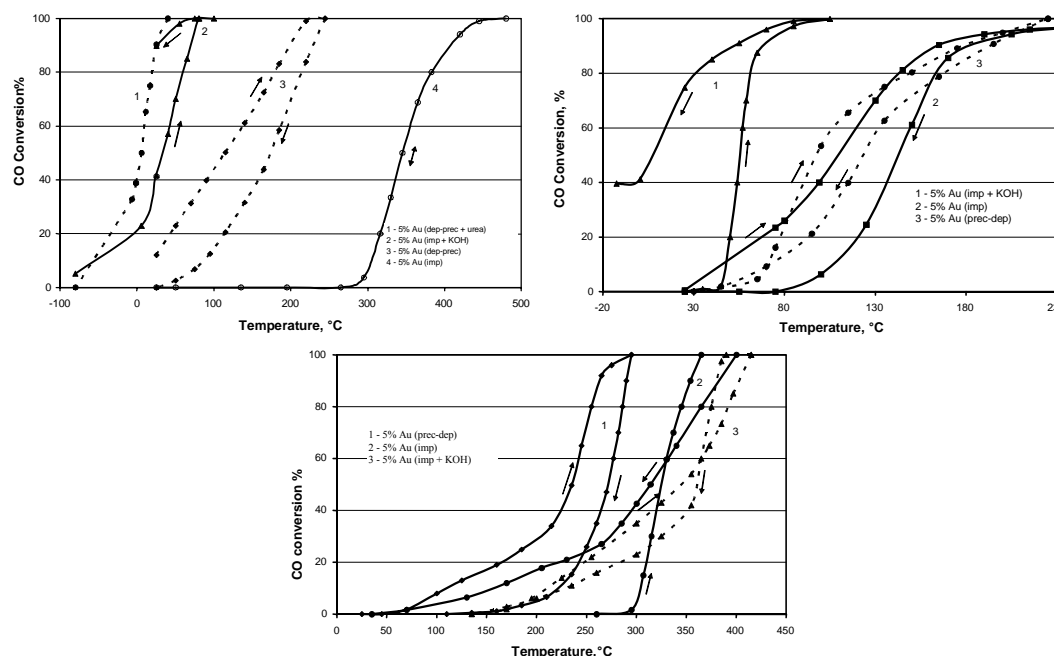
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The influence of preparation method on physicochemical properties of supported gold catalysts were studied. Effect of pretreatment conditions on catalyst activity were examined. The activity tests in CO oxidation by oxygen or water were carried out. The influence of hydroxyl groups, potassium additives and chlorine ions on catalytic behavior was investigated

The main subject of this paper is the comparison of three supported gold catalysts 5%Au/ Fe_2O_3 , 5%Au/ TiO_2 and 5%Au/ Fe_2O_3 prepared by different methods: impregnation, coprecipitation and deposition-precipitation methods and their activity were compared in two reactions CO oxidation by oxygen and water gas shift (WGS). Physicochemical properties of catalysts were determined by BET, XRD, TPR, TOF-SIMS, TG-DTA-MS and SEM techniques. As supports commercial alumina oxide (FLUKA 507C) and titania oxide (Degussa P25) were used. Iron (III) oxide was prepared from aqueous iron (III) nitrate solution. Catalysts were dried at 60°C and calcined 4h in air at: 200. 400 and 600°C.

The order of support activity was as follow: $\text{Fe}_2\text{O}_3 \cong \text{Al}_2\text{O}_3 > \text{TiO}_2$. The considerable shift toward ambient temperatures was achieved for gold supported catalysts and the order was following: $\text{Au}/\text{Fe}_2\text{O}_3 > \text{Au}/\text{TiO}_2 > \text{Au}/\text{Al}_2\text{O}_3$, being the same as the reducibility of oxides used as supports for deposited gold active phase. The influence of preparation method on catalyst activity is as follow: coprecipitation>precipitation-deposition> impregnation. The most active gold/iron oxide catalysts, even below 0°C appeared those obtained by precipitation-deposition method. The high activity of $\text{Au}/\text{Fe}_2\text{O}_3$ catalysts does not depend significantly on the precipitation agent except in the case of not efficient ammonia solution. Even for poorly active impregnated $\text{Au}/\text{Fe}_2\text{O}_3$ catalysts the addition of KOH leads to highly active catalytic system which achieve 100% CO conversion at room temperature. The supported gold catalysts dried at 60°C appeared highly active and stable during seven days test. Thus, high degree of catalyst surface hydroxylation is a prerequisite condition of high catalyst activity especially when catalyst surface is covered with high concentration of potassium. Probably

crucial role play peroxide ions O_2^- involved in CO oxidation by not dissociating oxygen molecules. The increase of the calcination temperature (in the range 60-600°C) decreases the catalytic activity of gold supported catalysts in the CO oxidation reaction by oxygen, due to their dehydration and gold sintering. The reduced by $NaBH_4$ gold/iron oxide supported catalysts seems resistant for overheating up to 500°C. Despite to many literature data chlorine ions did not appear any poison for Au/support catalysts up to molar ratio $Cl/Au = 8$ and the inhibiting effect was observed for higher molar ratio causing a rapid drop of catalyst activity. The influence of support kind on the activity of supported gold catalysts in WGS reaction can be described by following order: $TiO_2 > Fe_2O_3 > Al_2O_3$. The ineffective catalyst appeared Au/Al_2O_3 which showed rather insignificant activity above 400°C, whereas the TiO_2 supported catalysts showed WGS activity above 100°C.



The influence of preparation method on CO conversion degree for Au/support (Al_2O_3 , TiO_2 , Al_2O_3) catalysts in carbon monoxide oxidation by oxygen.

Conclusions: The prerequisite conditions of the highly active Au/support catalysts are:

1. high degree of gold dispersion
2. the reducible character of support surface $Au/Fe_2O_3 > Au/TiO_2 > Au/Al_2O_3$
3. high degree of the surface amorphization
4. presence on the surface the strong base hydroxyl groups and O_2^- ions favored by K^+ ion addition

Acknowledgements: The partial financial support of this work by the Polish Scientific Research Council (Grant No. PBZ-KBN-116/T09/2004 (No. K124/1B/2005) is gratefully acknowledged.

IN-SITU XRD STUDY OF VMoNbO CATALYSTS FORMATION. INFLUENCE OF THERMAL TREATMENT CONDITIONS

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In-situ and ex-situ XRD study of active phase formation in VMoNbO catalysts during the thermal treatment in air, in medium with low oxygen content and in helium have been performed. According to the data obtained genesis in oxidative conditions goes through the same irreversible steps. On the first step layer-type compounds, disordered in slabs, appear. Subsequent thermal treatment leads to crystallization of phases. Conditions of thermal treatment influence on the temperature range of active phase existence and on the structure of decomposition products. Calcination in helium leads to significantly different phase composition due to partial reduction of Mo and V by ammonia ions.

Oxide V-Mo-Nb catalysts hold the great promise for low-temperature oxidative transformations of ethane into ethylene, acetonitrile and acetic acid [1-3].

It was found that mixed VMoNb oxide with composition $V_{0.23 \pm 0.03}Mo_1Nb_x$, where $x=0.20 \div 0.37$ exhibiting Mo_5O_{14} -like structure is the active phase (see Fig. 1). This structure occurs when 5+ - and 6+ cations are in the certain ratio: $Mo^{+6}/Me^{+5}=0.6/0.4$, where $Me = Mo, Nb, V$.

Present work is devoted to in-situ and ex-situ XRD study of active phase genesis in air, in medium with low oxygen content (0.3 vol. % O_2 in He) and in inert atmosphere.

In-situ and ex-situ X-ray powder diffraction was performed using $CuK\alpha$ radiation with Bruker D8 diffractometer equipped with high-temperature chamber (HTK-16, Anton Paar, Austria).

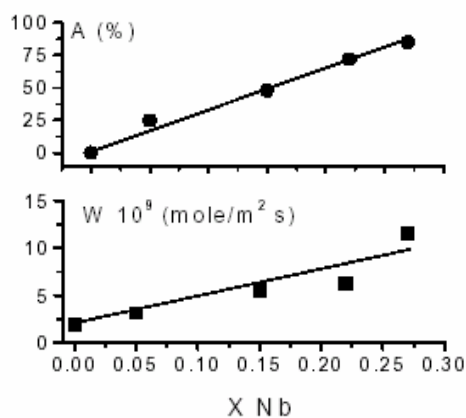


Fig. 1. Dependence of the relative amount of VMoNb compound (A), the rate of the total ethane transformation (ethane conversion is 10%), vs the Nb content (x) in the samples $V_{0.3}Mo_1Nb_x$

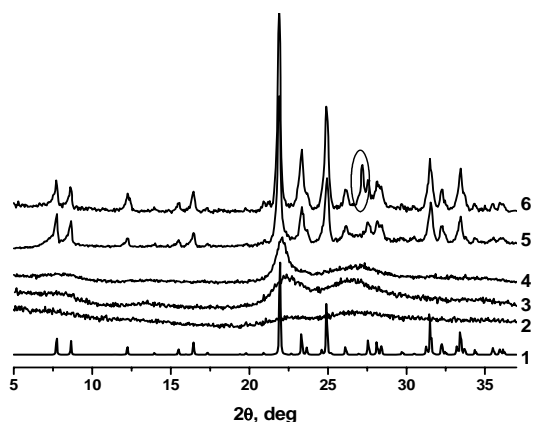


Fig. 2. XRD pattern of Mo_5O_{14} -like phase (1) and $V_{0.3}MoNb_{0.37}$ sample recorded in-situ in a high-temperature chamber in air at 180°C (2), 300°C (3), 500°C (4), 550°C (5) 600°C (6) Encircled line refers to MoO_3

According to the obtained data, formation of active phase during thermal treatment in oxidative conditions goes through the same irreversible stages.

On the first step of current phase formation at 300°C layer type compounds with interlayer distance along c – axis $\approx 4,00\text{\AA}$ occur. This interlayer distance is typical for Mo-, V-, Nb-containing oxygen octahedra connected by shared corners along the [001] direction. Furthermore, at the first step of genesis cation distribution in octahedral network in ab - plane is not uniform.

Further increasing of temperature leads to homogenization of chemical composition and crystallization of phases depending on chemical composition of the catalysts and thermal treatment conditions. For instance, in the case of low content of Nb in the catalyst ($V_{0.3}Mo_1Nb_{0.05}O_x$) mainly MoO_3 and V_2MoO_8 oxides form. On the other hand, if ratio Mo/Me (Me = Nb+V) is close to 0.6/0.4 only Mo_5O_{14} – like phase appears.

Oxidative properties of thermal treatment medium influence on the existence range of triple phase. When calcination is carried in medium with low oxygen content at 500°C lines, which correspond to V-, Nb- substituted Mo-oxide with Mo_5O_{14} - like structure, appear. Nevertheless, when calcinations is carried in air at the same temperature only three halo at $2\theta = 8^\circ, 22^\circ$ и 26.5° are observed.

Decomposition of triple phase starts at 600°C. Moreover, structures of decomposition products depend on calcinations medium. When calcination is carried in air, additional line, which corresponds to MoO_3 , appear (see Fig. 2). After calcination in medium with low oxygen content, two lines attributed to Nb_6MoO_{18} oxide emerge.

Calcination in inert atmosphere leads to significantly different phase composition. Ammonia cations, which appear due to decomposition of precursors, act as reducing agents. Thus after calcinations in helium at 550°C Mo^{4+}/V^{4+} solid solutions with rutile-like structure occur along with poorly crystallized Mo_5O_{14} -like phase.

We acknowledge the financial support of RFBR (project 07-03-00203).

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**DEHYDROGENATION OF PROPANE TO PRODUCE PROPENE ON CHROMIUM
LOADED HYDROXYAPATITE (Cr(x)/CaHAp)**

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The direct catalytic dehydrogenation of propane is a selective way to produce propene. It is frequently performed using chromia supported on various oxides such as TiO₂, ZrO₂, Al₂O₃.... The aim of the present work is the synthesis, the characterisation and the investigation of the catalytic activity of chromium loaded hydroxyapatite (Cr(x)/CaHAp) in propane dehydrogenation without oxidants. Cr(x)/CaHAP catalysts were prepared by the coprecipitation method. Stoichiometric amount of ammonium phosphate solution was added dropwise to a boiling solution of Ca²⁺ containing Cr³⁺ as additives. The pH was maintained at 9 during the precipitation. The resulting mixture was refluxed for 3h, filtered then washed and dried at 100 °C for 12 h. The Amount of Cr³⁺ loaded during the precipitation varied from 1 to 10 wt% of Cr. The synthesised compounds were characterised by IR, XRD and UV-visible spectroscopy. IR showed bands characteristic of calcium hydroxyapatites. The XRD confirmed the absence of chromium phosphates and the UV-visible spectroscopy showed the presence of Cr³⁺ and Cr⁶⁺ ions in the samples. Propane dehydrogenation over Cr(x)/CaHAP in absence of oxidant in the feeding stream was studied at 550 °C. The results showed that the propene is the primary product. The best performances were obtained with the catalyst containing 10 wt% Cr.

**CYCLOALUMINATION OF α,ω -DIOLEFINS CATALYZED BY Cp_2ZrCl_2 – NOVEL
ROUTE TO MACRO CYCLIC COMPOUNDS**

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The interaction between 1,5-hexadiene and EtAlCl_2 (1:2) in the presence of Mg as an acceptor of halogenide ions and Cp_2ZrCl_2 catalyst (10 mol %) in THF at $\sim 20^\circ\text{C}$ led to 1-ethyl-3,4-di(but-3-enyl)-aluminacyclopentane (**1**), 2,7-diethyltetradecahydrodialuminacyclopenta[a,e]cyclooctene (**2**) with two symmetrically annulated to cyclooctane ring aluminacyclopentane fragments and 2,7,12-triethylecosahydro-1H-trialuminacyclopenta[a,e,i]cyclododecene (**3**) with three symmetrically annulated to cyclododecane ring aluminacyclopentane fragments.

Cycloalumination of 1,7-octadiene with EtAlCl_2 (two-fold excess) under the reaction conditions (Cp_2ZrCl_2 (10 mol %), THF, 20°C , 8 h) resulted in 1-ethyl-3,4-di(hex-5-enyl) aluminacyclopentane and cyclododecane with two symmetrically annulated aluminacyclopentane fragments.

The tested 1,9-decadiene and 1,11-dodecadiene come into the cycloalumination reaction with EtAlCl_2 catalyzed by Cp_2ZrCl_2 to produce selectively *trans*-3,4-disubstituted aluminacyclopentanes in ~ 40 – 45% yield.

In accordance with previously reported work [1], stereoselective cycloalumination of α -olefins with EtAlCl_2 in the presence of Mg and Cp_2ZrCl_2 catalyst was found to afford *trans*-3,4-dialkylsubstituted aluminacyclopentanes.

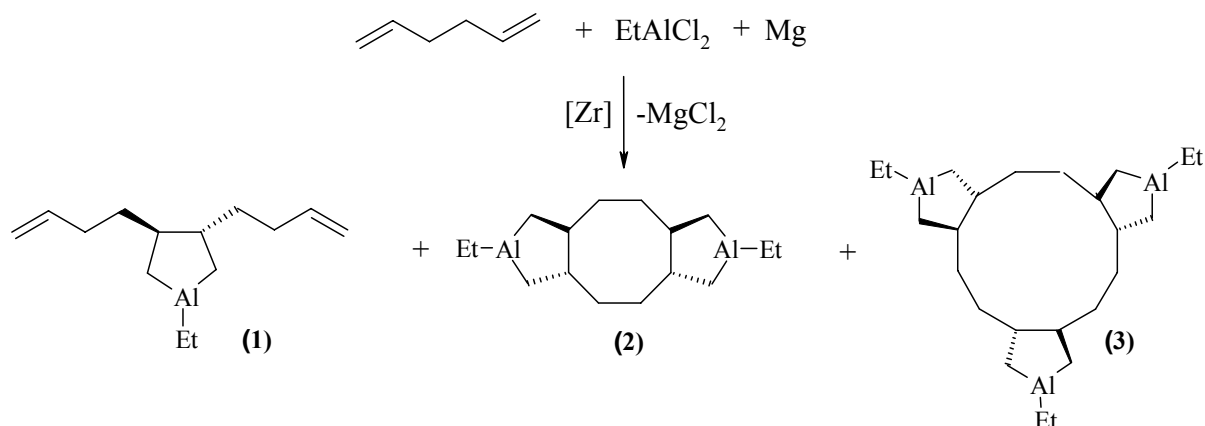
We now discuss the new cycloalumination reaction of α,ω -diolefins with EtAlCl_2 in the presence of catalytic amounts of Cp_2ZrCl_2 and activated Mg giving aluminacyclopentanes and carbocycles with annulated aluminacyclopentane fragments.

It was stated that the interaction between 1,5-hexadiene and EtAlCl_2 (1:2) in the presence of Mg as an acceptor of halogenide ions and Cp_2ZrCl_2 catalyst (10 mol %) in THF at $\sim 20^\circ\text{C}$ led to 1-ethyl-3,4-di(but-3-enyl)aluminacyclopentane (**1**), 2,7-diethyltetradecahydrodialuminacyclopenta[a,e]cyclooctene (**2**) with two symmetrically annulated to cyclooctane ring aluminacyclopentane fragments and 2,7,12-triethylecosahydro-1H-trialuminacyclopenta[a,e,i]cyclododecene (**3**) with three symmetrically annulated to cyclododecane ring aluminacyclopentane fragments. The influence of catalyst concentration, the starting reagents ratio, temperature and duration of the reaction onto yield and formation selectivity of mono- (**1**), three- (**2**) and tetracyclic (**3**) organoaluminium compounds (OAC) is discussed (Scheme).

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Cycloalumination of 1,7-octadiene with EtAlCl_2 (two-fold excess) under the reaction conditions (Cp_2ZrCl_2 (10 mol %), THF, 20 °C, 8 h) resulted in 1-ethyl-3,4-di(hex-5-enyl)aluminacyclopentane and cyclododecane with two symmetrically annulated aluminacyclopentane fragments.

Unlike 1,5-hexadiene and 1,7-octadiene, 1,9-decadiene and 1,11-dodecadiene come into the cycloalumination reaction with EtAlCl_2 catalyzed by Cp_2ZrCl_2 to produce selectively *trans*-3,4-disubstituted aluminacyclopentanes in ~ 40–45 % yield.



While proceeding the cycloalumination reaction of α,ω -diolefins with EtAlCl_2 in the presence of Cp_2ZrCl_2 minor amounts of the hydroalumination and aluminacyclopropanation products (5–18 %) were detected as well.

It was shown that under the effect of stoichiometric amounts of allylchloride and Pd-containing catalysts generated *in situ* cyclic OAC transform into cyclobutanes. Demetallation of cyclic OAC by elemental sulfur was found to yield the related polycyclic thiophanes.

The probable cycloalumination mechanism for α,ω -diolefins under the effect of catalytic amounts of Cp_2ZrCl_2 is discussed. The generation of zirconacyclopentane intermediates with subsequent transmetalation by EtAlCl_2 to give the related cyclic OAC is proposed as the key step of the reactions involved.

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ETHYLENE OLIGOMERIZATION TO LINEAR α -OLEFINS IN THE PRESENCE OF CATALYTIC SYSTEMS BASED ON THE ZIRCONYL CARBOXYLATES

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Linear α -olefins have found wide application in various areas of petrochemical synthesis. They are used for the copolymerization with ethylene, production of linear low density polyethylene, linear alkylbenzene, in manufacturing of surfactants, corrosion inhibitors, highly effective lubricant oils, oxoalcohols, α -olefin sulfonates, additives to oils, etc. Among ethylene oligomerization catalysts obtained on the basis of transition metals the zirconium-containing catalytic systems are more perspective ones providing α -olefins synthesis with high selectivity. However, the known zirconium-containing catalytic systems are not technological, do not show high selectivity towards the most important fractions of α -olefins, such as C₄, C₆-C₁₀, C₈-C₁₈ and are sensitive to impurities and a moisture.

It has been established for the first time, that the zirconyl carboxylates of structure ZrO(OCOR)_nCl_{2-n} and Zr₂O₃(OCOR)_nCl_{2-n}, where R-alkyl C₃-C₁₀ or aryl, n=1 or 2 in combination with activators – alkyl aluminium chlorides are active catalysts for ethylene oligomerization to linear α -olefins.

In the present work the investigation results of ethylene oligomerization in the presence of above catalytic systems have been reported. It was shown that in the case of using catalytic systems based on zirconyl carboxylates, molecular weight distribution (MWD) of ethylene oligomers is similar with distribution observed in the presence zirconium tetracarboxylates, i.e. has character of Schulz-Flory distribution. There have been studied the influence of various modifiers on catalyst activity and MWD of ethylene oligomerization products. It was found, that modifiers of donating type, such as ethers R₂O, where R-alkyl C₁-C₁₀ or aryl, at the molar ratio of an ether to zirconium, equal (1-3):1 change the MWD character from Schulz-Flory type to Puasson and the yield of C₈-C₁₈ fraction reaches 75-80 % on consumed ethylene. In the case of modification of indicated catalytic systems by esters the ethylene oligomers' MWD has not the Schulz-Flory character and the main products of ethylene oligomerization are C₄-C₁₀ oligomers with the yield more than 90 %.

It has been concluded that the deviation of oligomerization products composition from statistical distribution of Schulz-Flory type is caused by multi-site character of used catalytic systems.

**PROPERTIES OF ALUMINA FORMED FROM HYDRATED UNDER MILD
CONDITION TSEFLAR™ TREATED GIBBSITE**

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Physical, chemical and mechanical properties of alumina, made from rehydration product of the TSEFLAR™-treated gibbsite/hydrargillite (CTA HG), were studied with X-ray analysis, TA, EM, BET and IRS. Alumina granules were prepared by extrusion of plastic paste prepared from as prepared hydroxides after calcination at 550 °C/4 hours. Alumina formed from rehydration product of the TSEFLAR™-treated hydrargillite (CTA HG) was nearly totally γ -alumina (hydration in acid media), and nearly totally η -alumina (hydration in ammonia solution and water). Granules characterized with mono, bi or three size pore distribution (depending on hydration conditions), rather good strength, high specific surface area and moisture capacity were prepared.

Thermal activation of gibbsite (HG) is known to be a method for production of highly reactive amorphous $\text{Al}_2\text{O}_3 \times n\text{H}_2\text{O}$. Hydration of such product is a basis of wasteless manufacturing the pseudoboehmite-structured hydroxide. Thermal decomposition of HG using a TSEFLAR™ installation is a new way to implement the thermal decomposition process [1]. Product obtained is hydrated at room temperature and atmospheric pressure in water and aqueous ammonia to form eventually the stable bayerite-like hydroxide structure [2]. In an acid solution at room temperature and atmospheric pressure, amorphous and pseudoboehmite-like hydroxides are formed [3]. Hence TSEFLAR™ is a new wasteless and energy saving method for preparation of different hydroxides under mild conditions and, consequently, different alumina oxides.

The main goal of this paper is the investigation of physical and chemical properties of aluminas formed from different hydroxides including properties of alumina granules.

The samples were characterized using such techniques as XRD (including the mode with the synchrotron radiation-SR), DTA, BET, IRS, SEM and TEM.

η , γ or $\gamma + \eta$ aluminas with X-ray particle size 3-4 nm were revealed by XRD in the samples prepared by decomposition of hydroxides at 550 °C, 4 h. According to X-ray analysis, alumina formed from amorphous hydroxide (hydration in acid media) was nearly totally γ -alumina, and alumina formed from bayerite - like hydroxide (hydration in ammonia solution and water) was nearly totally η -alumina. The cell parameters of the prepared

aluminas are in the range of 0.7913-0.7922 nm which is typical for low temperature aluminas. Specific surface area was in the range 250-310 m²/g (depending on used electrolyte).

All hydroxides and aluminas may be shaped as granules by extrusion of plastic pastes. After their calcination at 550 °C/4 hours granules characterized with different phase composition, porosity, strength, specific surface area depending on preparation conditions were prepared. Granules prepared from hydroxides (even from bayerite-like hydroxide) were characterized with mono, bi or three size pores (depending on used electrolyte for paste preparation) and rather good strength: $P_o = 17-50 \text{ kg/cm}^2$. Their specific surface area was in the range 300-400 m²/g, moisture capacity - 0.5-0.8 ml/g, packed density - 0.64-0.75 g/ml. Granules prepared from hydroxide and oxide (1:1) were characterized with higher strength (up to 85 kg/cm²), specific surface area was in the range 260-350 m²/g, moisture capacity - 0.4-0.65 ml/g, packed density - 0.45-0.55 g/ml.

For alumina prepared from hydrated in acid Tseflar treated gibbsite an unusual acid –base properties were revealed by IRS using CO probe molecule.

Hence series of different aluminas with different physical, chemical and mechanical properties can be prepared using Tseflar treated gibbsite (by TSEFLARTM technology).

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**SYNTHESIS AND CHARACTERISATION OF DOPED APATITE-TYPE
LANTHANUM SILICATES WITH A HIGH OXIDE ION CONDUCTIVITY AND
NICKEL/LANTHANUM SILICATES CERMET COMPOSITES**

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Apatite-type lanthanum silicates have been prepared with a variety of synthesis methods such as sol-gel, Pechini and mechanochemical activation followed by sintering. These methods allow to obtain the apatite phase at 900-1200 °C that confirmed by XRD and IR. Synthesized samples have been studied by ²⁹Si NMR spectroscopy, oxygen isotope exchange method and electrical conductivity measurements. Ni/lanthanum silicate cermets have also been prepared with different techniques and investigated as catalysts for methane steam reforming reaction.

The scope of the more efficient and environmental friendly power generation as compared to traditional thermal energy conversion has attracted considerable interest to fuel cells [1]. The development of solid oxide fuel cells (SOFCs) is a perspective direction in this area particularly due to the possibility of internal reforming of methane and other fuels directly on the anode. The main problems limiting large scale practical application of SOFC based on well-known electrolytes - yttria-stabilized zirconia (YSZ) are high operating temperatures (~1000 °C) to ensure required ionic conductivity of YSZ and deactivation of the Ni-based anodes as a result of carbon deposition during a direct hydrocarbon conversion [1, 2]. High operating temperatures cause serious problems concerning cell life, and its reducing to 600–800 °C greatly improves cell reliability. In order to realize the intermediate temperature SOFCs, ionic conductors which have a high conductivity at lower temperatures are greatly desired.

Recently, rare earth silicates with apatite-type structure have been found to exhibit a good ionic conductivity at intermediate temperatures [3, 4]. However, the conventional solid state method of apatite-type lanthanum silicate synthesis requires too high sintering temperatures (~1500 °C) which makes optimization of their synthesis methods highly important.

In the present study doped lanthanum silicates with the general formula $\text{La}_{10-x}\text{A}_x\text{Si}_{6-y}\text{B}_y\text{O}_{26\pm y}$ (A = Mg, Ca, Sr, Ba; B = Al) have been prepared using different

synthesis methods such as sol-gel (SG), Pechini (Pch) and mild mechanochemical activation (MA) followed by sintering. The synthesized samples have been characterized by XRD, IR and ^{29}Si NMR spectroscopy, TG/TGA.

According to the thermal analysis of gels synthesized by Ph method, organic precursors are exothermally decomposed at 200-600 °C to give carbonates as shown by XRD and IR. The formation of the apatite structure accompanied by a broad exothermal effect starts above 830 °C. In fact, after sintering at 900 °C during 2 h, the samples synthesized by both the Pch and SG methods are mainly composed of an apatite-type lanthanum silicate. For the systems prepared by Pch method, the effect of the heating rate and MA of the precursors on apatite phase formation was revealed. The samples obtained via MA followed by annealing for 6-8 h at 1200 °C contain pure lanthanum silicate of the apatite type.

For Ba and Mg-doped lanthanum silicates synthesized by MA method, the conductivity was measured in the temperature range from 300 to 750 °C. The electrical measurements for samples with a residual porosity reveal a low activation energy and rather high ionic conductivity ($6.9 \cdot 10^{-4}$ - $1.1 \cdot 10^{-4}$ S/cm at 500 °C) of the systems in agreement with the literature [4]. The data of oxygen isotopic exchange revealed that these systems possess a high lattice oxygen ion mobility as well as a high rate of heteroexchange.

Ni/lanthanum silicate based cermets prepared via impregnation, modified Pch and ball mixing methods were tested in methane steam reforming (SR). Catalytic activity was measured using a flow reactor at 600-800 °C. The flow rate of the 7%CH₄-7%H₂O in He reaction mixture was 10 l/h, contact time was 0.77 s. The SR activity of the sample obtained by the impregnation was shown to be poor due to severe coking. Cermets synthesized by modified Pch method and ones doped with the complex oxides of perovskite structure insure a sufficiently high activity in SR. Moreover, promoted systems have a higher stability to coking as compared with unpromoted samples. A higher activity and stability of cermets could be provided by a high Ni dispersion (helps to hinder the carbon formation) and the presence of oxide promoters with a high lattice oxygen mobility which promote elimination of the deposited surface carbon.

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HYDROGEN BINDING IN THE REDUCED COPPER CHROMITE CATALYST: INELASTIC NEUTRON SCATTERING STUDY

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Homogeneous catalytic hydrogenation of C=O bond of ketones in the presence of metal cations in “protonic medium” is well known [1]. This reaction can be performed heterogeneously too. Perfect copper chromite, CuCr_2O_4 , acquires the catalytic activity in acetone hydrogenation after being reduced in H_2 at 250-350 °C [2]. However, it remains rather inactive in the CO conversion to methanol, unlike CuZnAl oxide catalyst which is active in both processes. The reason of so striking difference in mechanisms of heterogeneous catalytic hydrogenation of ketones to alcohols and CO to methanol are still debated in literature.

Neutron diffraction studies of the CuCr_2O_4 evolution under reductive treatments made it possible to formulate some specific features of the copper reduction in CuCr_2O_4 [3]. According to that study, the reduction of copper cations located in T_d positions of the spinel structure isn't accompanied by escape of the water molecules. Instead, hydrogen is oxidized giving H^+ , which substitute Cu^{2+} cations in crystallographic position e of the spinel structure (green tetrahedrons in Fig. 1). Moreover, a significant amount of hydrogen is absorbed in the crystallographic position c (“forbidden” octahedrons, milk-white in Fig. 1). Thus, the reduced copper chromite can be considered as Cu^0 particles over the surface of a solid solution of copper chromite and chromic acid, i.e. “solid protonic medium”. So, a certain analogy may be drawn between heterogeneous catalytic reactions and homogeneous processes in liquid phase.

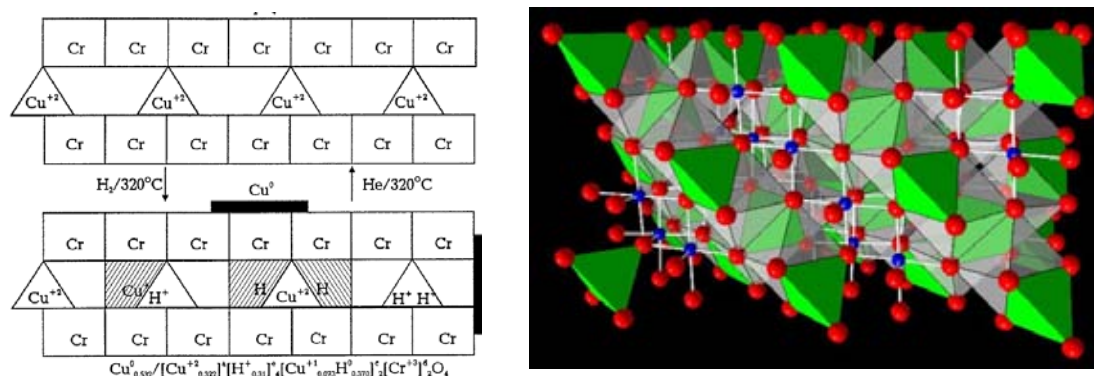


Fig. 1. (left) The schematic representation of the reduced copper chromite structure according to the neutron diffraction data of [3]; **(right)** The spatial pattern of the absorbed hydrogen locations in e (green T_d) and c (milk-white O_h) structural positions of spinel structure.

Here, we report the first study of the interaction energy of hydrogen atoms with the other elements of the reduced ideal copper chromite performed by inelastic neutron scattering (INS), which was performed in the Institut Laue-Langevin (ILL) in Grenoble, France. The samples of CuCr_2O_4 were prepared by decomposition of the co-precipitated mixed hydroxycarbonate of Cu and Cr in flowing Ar at 650 °C. The samples were placed in aluminum cells, with the wall thickness 1.0 mm. Fig. 2 shows the experimental INS spectra of two samples: treated in Ar and after reduction at 300 °C in hydrogen. The latter sample was sealed under hydrogen medium. Two features at 119.5 and 25 meV in Fig. 2 are accounted for by the hydrogen, absorbed by the chromite sample. The first value significantly exceeds the expected binding energy of hydrogen to metallic copper (ca. 90 meV) and thus may be attributed to the protons located in the T_d (e) positions of spinel. It is noteworthy, that we observe no splitting of this band at 25 K, which means no tetragonal distortion of the spinel structure in the reduced state. The initial CuCr_2O_4 structure is tetragonally distorted due to the Jahn-Teller effect; however, the reduction of Cu^{2+} and substitution of protons for copper cations results in the distortion removal. This supposition is supported by experimental changes in the chromite lattice phonons in the 50-80 meV: being splitted into triplet for the sample treated in Ar, it approaches to a singlet band after the reduction. The band at 25 meV may be tentatively attributed to the weakly bound hydrogen absorbed in the forbidden octahedrons (c).

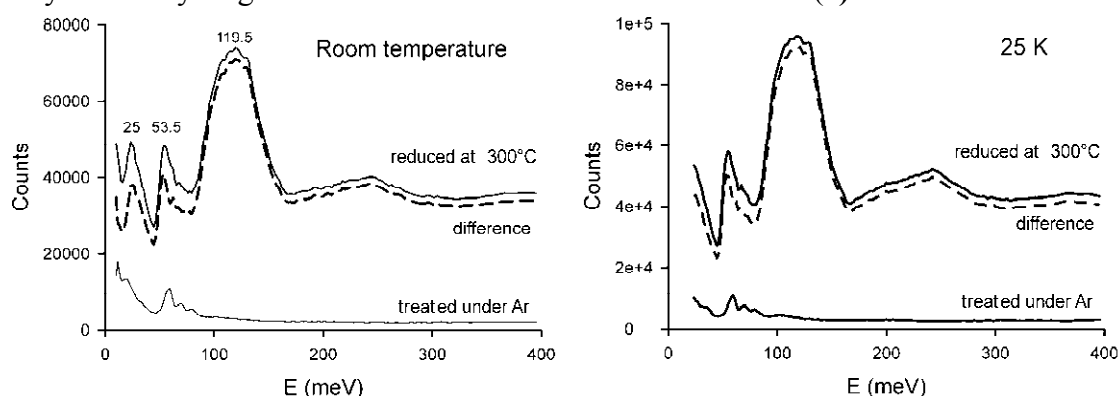


Fig. 2. The experimental INS data of the initial and the reduced copper chromite. The data are obtained at room temperature (left) and at 25 K (right).

The INS data confirm the conclusions of the earlier studies on the way of the CuCr_2O_4 structure evolution under reduction in H_2 . The binding energies of hydrogen species in the spinel structure of reduced copper chromite are measured. The obtained data can be used for elucidation of the mechanism of the catalytic C=O bond hydrogenation over copper chromite.

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**FISCHER-TROPSCH SYNTHESIS OVER THE BIMETALLIC CATALYSTS,
BASED ON THE DOUBLE COMPLEX SALTS OF TRANSITION METALS**

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Studying the possibility of preparation of bimetallic Fe-Ni, Fe-Co, and Co-Cu supported catalysts by thermolysis of double complex salts (i.e. those consisting of a complex of one metal as the anion and another complex of another metal as the cation) has shown that thermolysis of $[\text{Ni}(\text{NH}_3)_6]_3[\text{Fe}(\text{CN})_6]_2$, $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{CN})_6]$, and $[\text{Co}(\text{NH}_3)_6]_2\text{C}_2\text{O}_4[\text{Cu}(\text{C}_2\text{O}_4)_2]_2$ composition with aluminum hydroxide results in formation of alumina supported metallic particles of 15-40 nm in size. Decomposition of complexes proceeds in several consecutive exothermic stages. When using the above mentioned Ni-Fe and Co-Fe double complexes, bimetallic particles are formed with the mean size of 15-16 nm, having fcc and bcc structure, correspondingly. Catalytic properties of the obtained supported catalysts were studied in the Fischer-Tropsch synthesis at atmospheric and elevated pressure up to 20 bar.

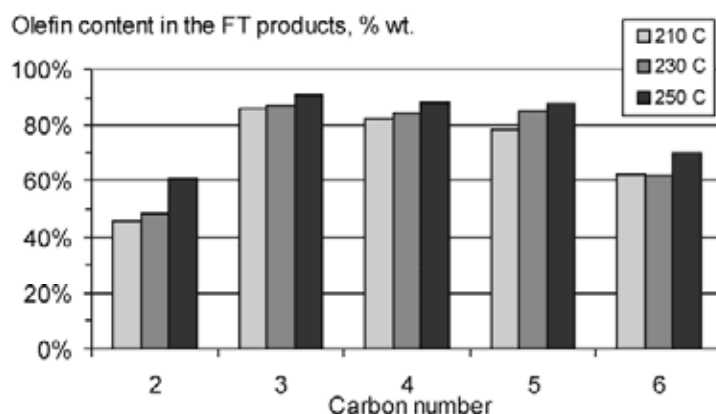


Figure 1. The experimental olefin contents in the gaseous Fischer-Tropsch products; catalyst catalyst CoFe/Al₂O₃; P = 1 bar, H₂:CO:N₂ = 6:3:1; CO conversion extent 15-20 %.

Catalytic properties of alumina supported bimetallic Fe-Co particles with bcc structure (prepared by thermolysis of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{CN})_6] + \text{Al}(\text{OH})_3$ composition) differ from those described in literature for CoFe bimetallic catalysts. The most significant difference is drastic decrease in the specific catalytic activity with respect to secondary processes of olefin

hydrogenation. This peculiarity reveals itself in extremely high selectivity of the Fischer-Tropsch process with respect to olefins (see Figures 1 and 2). Anomalous syngas temperature dependence of selectivity to olefins is also worth to mention.

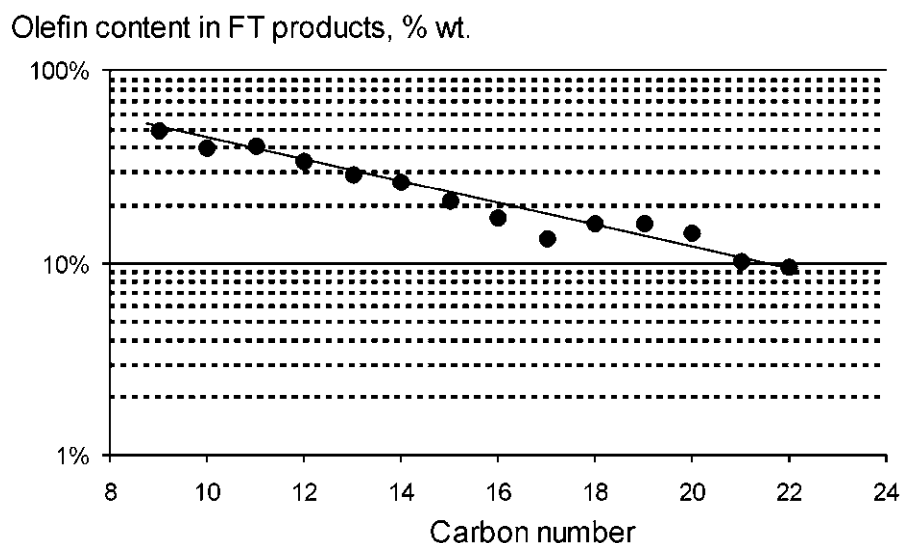


Figure 2. The experimental olefin contents in the condensed Fischer-Tropsch products; catalyst catalyst CoFe/Al₂O₃; P = 1 bar, T = 210 °C; H₂:CO:N₂ = 6:3:1; CO conversion extent 15-20 %.

Increasing the process pressure to 10-20 bar leads to dramatic change in catalytic properties of the studied CoFe catalysts. Among the most important changes is dramatic diminishing the selectivity to olefins and the rate of the secondary WGS process. The plausible explanation of the observed pressure effect on the catalytic properties of the studied CoFe catalysts is the impact of the reaction mixture to the structure and physico-chemical properties of the surface of the active component particles.

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**LIQUID PHASE OXIDATION OF CYCLOHEXANE IN THE PRESENCE
OF Au/SILICALITE CATALYSTS**

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A study of Au catalysts in cyclohexane oxidation by dioxygen showed that Au catalyst converts cyclohexyl hydroperoxide (CHHP), which forms in the reaction, to ketone and alcohol with selectivity close to 100 %, and has no significant effect on the rate of cyclohexane oxidation. An increased gold content in the samples increases the activity in CHHP decomposition and decreases the selectivity for side products formation.

Liquid-phase oxidation of cyclohexane is the most difficult step in the polyamide production. Cyclohexanol and cyclohexanone are the target products, and CHHP is the main intermediate. Without catalyst, up to 30% of the initial cyclohexane is converted to side products. Such a low selectivity is caused mainly by the free radical mechanism of CHHP decomposition.

Attempts to use heterogeneous catalysts for the liquid-phase oxidation of cyclohexane have not produced a commercially feasible process [1]. In recent years, research efforts in this field were focused on gold catalysts [2]. Of particular interest are results of the work [3], in which cyclohexane was oxidized on Au/NaY catalysts. However, the lack of blank runs (without catalyst) and the chromatographic measurement of CHHP concentration cast some doubt on the reliability of these results.

Our study was aimed at elucidating the role of Au/silicalite catalysts in the liquid-phase oxidation of cyclohexane. The catalysts were prepared by the Deposition–Precipitation method. Gold content in the samples was varied from 0 to 3.9 wt.%. Cyclohexane was oxidized in a passivated Parr reactor at temperature 170 °C and pressure 900 kPa; air was passed at a constant rate through cyclohexane containing 0.5 wt % catalyst, the reactor contents were periodically sampled.

Figure 1 shows the results of a blank run and runs in the presence of catalysts. One may see that the rates of cyclohexane oxidation with and without catalyst are very similar. In the presence of the catalyst the CHHP concentration is significantly lower and what is even more important the selectivity of cyclohexane conversion to side products decreases at conversions

4% and higher. Apparently the catalyst is involved only in CHHP decomposition and does not affect the process of cyclohexane oxidation.

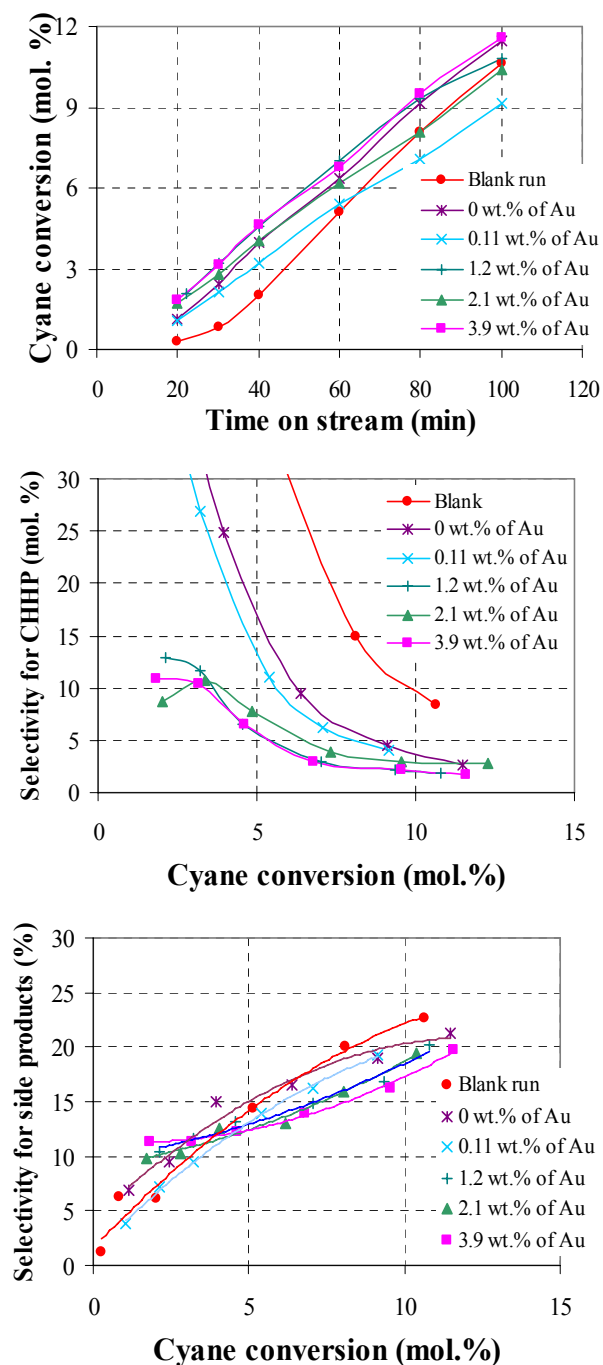


Fig. 1. Effect of Au content in Au/silicalite catalysts on performance of cyclohexane oxidation by molecular oxygen. (Reaction conditions: 70 ml of C_6H_{12} , 0.5 wt. % of catalyst, air stream 75 cc/min, stirring rate 600 rpm).

As Au content in the catalysts increased their activity in CHHP decomposition also increases, achieving a plateau at the Au concentration about 1.2 wt %. As the fraction of CHHP decomposed over the catalyst increases, the selectivity for side products formation decreases. It means that CHHP decomposition over the catalyst proceeds with a higher selectivity than thermal or non-catalytic CHHP decomposition. Independent experiments performed in a flow reactor demonstrated that gold catalyst decomposes CHHP with selectivity close to 100 %. Therefore, the main role of Au/silicalite catalysts in cyclohexane oxidation consists in highly selective CHHP decomposition to ketone and alcohol.

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**INVESTIGATION OF CATALYSTS FOR NITRIC OXIDE AND NITROUS OXIDE
ABATEMENT IN THE TAIL GAS FROM NITRIC ACID PLANTS**

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At present, nitric acid plants are to be the main man-caused sources of the nitric oxide emissions and, particularly, of the nitrous oxide – N_2O . Basing on the literature information, at the pilot plant, operating on real gas flows of the nitric acid plant, there have been prepared and investigated six types of catalysts, designed for decomposition and reduction of the nitric oxides by ammonia. The special attention has been paid to the catalyst ability for the nitrous oxide abatement.

The Russia has ratified the Kyoto Protocol, in the addendum of which there have been specified six the most dangerous greenhouse gases. The nitrous oxide, which is also considered to be the ozone damaging gas, has been included in this number. The most significant man-caused sources of the nitric oxides – NO_x , ($NO + NO_2$) and N_2O are nitric acid plants.

Generally, NO_x abatement in the tail gases from such plants has been made through their catalytic reduction by ammonia, but for all that, N_2O has not been reduced. Nowadays, all around the world, there are made trials in search of efficient ways of its decomposition and reduction.

The Foreign researchers have cited several works [1-4], indicating the possibility of N_2O decomposition. However, as a rule, they have been made on the laboratory scale, using the simulated gas flows.

At the moment, all the abatement methods are divided into three types: primary, secondary and tertiary. The primary ones cover the making of the selective catalytic systems for ammonia oxidation, not producing N_2O , the secondary ones – the making of the catalytic systems, decomposing N_2O immediately in the ammonia oxidation reactor, the tertiary ones – N_2O reduction after NO_x absorption stage, i.e. virtually jointly with the nitric oxide abatement from the tail gases at temperatures 220-280 °C.

We demonstrated [5], that existing in Russia the nitric acid plants: UKL-7, combined lines 1/3, 5 ata, have been equipped by ammonia oxidation catalytic packages, producing from hundreds to tenth portions of N_2O volume percentage, i.e. the primary methods have not yet been realized.

The secondary methods are being in the active development, however N_2O decomposition results in NO decomposition, i.e. the extent of ammonia conversion to the target product is decreased.

From our point of view, the tertiary methods are the most prospective ones and many foreign companies are working in this direction [6].

In this paper, there are presented the results of the trials of the test catalyst batches at the pilot plant, operating on the industrial gas flows, in comparison with operation of the existing catalytic system for NO_x reduction by ammonia on the catalyst ABK-10M. There have been investigated six catalyst samples: 1 – block highly porous zirconium on support CaO ($Zr = 7,5\%$); 2 – nickel-cerium on carrier $\gamma-Al_2O_3$ ($NiO = 8,5\%$ $CeO = 2,8\%$); 3 – nickel-cobalt-zirconium, granular ($NiO = 6,5\%$; $Co_3O_4 = 7,5\%$; $Zr = 1\%$; support $\gamma-Al_2O_3$); 4 – nickel, tablet ($NiO = 17\%$, support – potassium aluminate); 5 – copper-zink-manganese, tablet ($CuO = 36\%$, $ZnO = 23\%$, $MnO = 1,5\%$, support – potassium aluminate); 6 – block highly porous palladium on support $\gamma-Al_2O_3$ ($PdO = 0,4\%$).

It has been determined, that at different temperature conditions and also at different portions of ammonia, delivered for the reduction, the majority of the catalysts can decompose NO_x as well as produce nitric oxides (I, II, IV). So, on copper-zink catalyst, within the temperatures $190-250\text{ }^\circ\text{C}$, NO_x reduction by ammonia takes place, and at the temperature increasing from 250 to $340\text{ }^\circ\text{C}$ NO_x the concentration increasing can be observed on the reactor outlet; NO_x reduction on palladium catalyst takes place within the temperatures $160 - 370\text{ }^\circ\text{C}$, and after the temperature increasing up to $530\text{ }^\circ\text{C}$ the production of NO_x is to be observed. The catalysts on the base of Zr , $NiO-CeO$ do not produce N_2O , but for all that the extent of NO_x reduction by ammonia amounts to $96 - 98\%$, corresponding MPC level on NO_x within the temperature $315 - 325\text{ }^\circ\text{C}$ and at ratio $(N_2O + NO_x) : NH_3 = 1 : (1,1 - 1,3)$.

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**THE APPLICATION OF WAXS METHOD FOR CHARACTERIZATION OF PHASE
COMPOSITION AND LOCAL STRUCTURE OF MULTYCOMPONENT HIGHLY
DISPERSED SYSTEMS**

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The method of wide-angle X-ray scattering (WAXS) in details is described elsewhere [1]. The application of WAXS method for characterization of phase composition and investigation of local structure is based on using of X-ray scattering measured in wide angle range and subjected to the Fourier transformation. The analysis is reduced to detection on radial electronic density distribution curve of coordination peaks corresponded to interatomic distances, which are typical for studied phases. This analysis could be carried out even for phases with coherent scattering regions less then 50 Å. For the proposed phase composition one may calculate model WAXS curve and compare it with one calculated from experimental X-ray diffraction pattern. Using of WAXS method and calculation of model curves gives a chance to define changes in local structure of the studied phases in comparison with the monocrystal analogue [2]. Overall model curve might be decomposed in partial ones, responded to separate fragments of the structure or certain pairs of atoms. Such information is necessary for determination of changes in local structure and defects.

X-ray diffraction patterns were obtained on high resolution diffractometer at the Synchrotron Radiation Center (Budker Institute for Nuclear Physics of the Siberian Branch of the Russian Academy of Science) with extraction of monochromatic radiation on diffraction beam from crystal-monochromator Si (1.1.1) (degree of monochromatization is about $\Delta\lambda/\lambda \sim 10^{-4}$).

The numerous examples of characterization of phase composition and local structure of multycomponent highly dispersed systems using the model WAXS curves are considered: aluminium hydroxides obtained by different technologies, highly dispersed (crystalline size about 50Å) complex oxide systems Me-Ce-O, where Me=Gd, Pr, Zr and different supported metallic catalyts.

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NOVEL CHIRAL NITROGEN CONTAINING LIGANDS FOR CATALYSTS OF ASYMMETRIC REACTIONS

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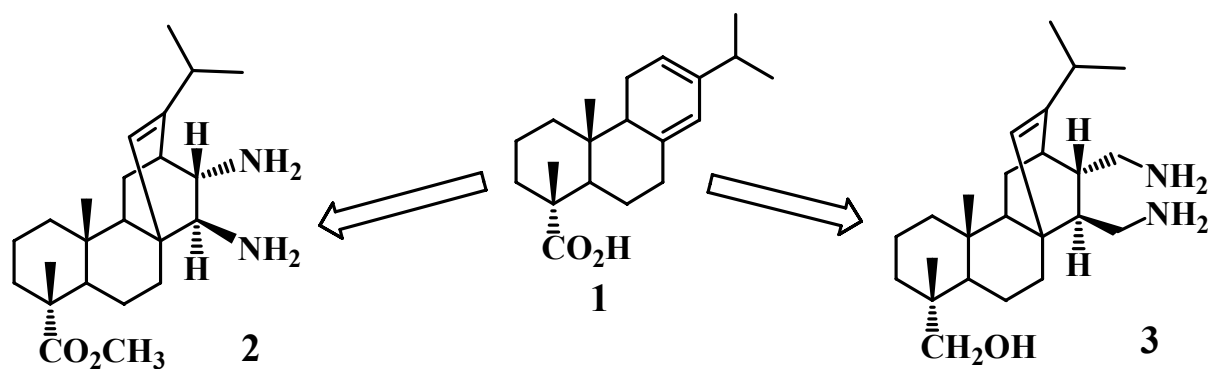
Levopimaric acid was used as a convenient chiral pool for the producing of nitrogen containing ligands for metallocomplex catalysts of asymmetric transformations. Synthesis of optically active metallocomplex catalysts of asymmetric reduction and oxidation based on new chiral diamines and azomethines has been developed.

Asymmetric catalysis is an attractive strategy of the synthesis of optically pure organic compounds and the dominant role in enantioselectivity of catalyst plays the structure of chiral ligand. Thus, design of the ligands of various structural types allows extending the field of application of asymmetric catalysis over the wide range of substrate and reactions. When preparing the ligands most attention was concentrated on the transformations of hydroxy- and amino acids, carbohydrates as well as binaphtyl, biphenyl, ferrocene derivatives. The synthesis of ligands based on steroids and terpenoids received lesser acceptance [1].

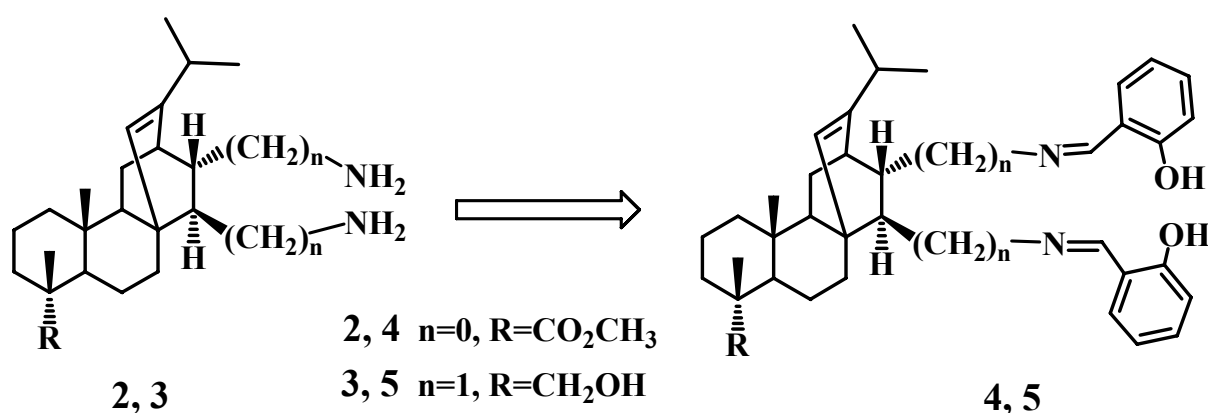
Phytogenic diterpenes have been under intensive investigation for many years. Owing to their availability and unique structures, these compounds have been widely used as starting materials for the production of highly effective drugs and chiral reagents. The use of natural terpenoids as convenient chiral pools for the synthesis of optically active elementorganic compounds is the prospective approach to the creation of wide spectrum of available chiral ligands for the catalysts of asymmetric reactions.

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

Synthesis of chiral 1,2- and 1,4-diamines (**3**, **4**) was developed starting from the adduct of levopimaric acid (**1**) with fumaric acid.



Starting from diamines (**2, 3**) chiral azomethines (**4, 5**) were prepared.



The synthesized new chiral nitrogen containing compounds was used as ligands for metalcomplex catalysts of asymmetric reduction and oxidation.

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NON-OXIDATIVE METHANE CONVERSION TO AROMATIC HYDROCARBONS ON W-HZSM-5 CATALYSTS

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The conversion of methane to aromatics in the absence of oxygen has been investigated at the reaction temperature of 750 °C over zeolite catalysts modified by W nanopowder. It has been established that the highest methane conversion per one run and maximal yield of aromatics are reached for the sample containing 8.0% W nanopowder. The W-HZSM-5 catalysts were studied by high-resolution transmission electron microscopy and energy dispersive X-ray analysis. The distribution and condition of the active species were investigated. The catalyst was deactivated in methane aromatization resulting of graphite condensation on catalyst surface. The nature of coke deposition was studied.

Recently, direct conversion of methane to higher hydrocarbons over zeolite catalysts modified with transition metal ions has attracted increasing attention [1-3]. In this connection the study into the catalyst deactivation occurring during the methane conversion reaction represent a significant research and practical interest, methane being the main component of natural and associated gases.

The activity of zeolite catalysts containing different amounts of W nanopowders was studied in the process of methane dehydroaromatization (**DHA**). The catalyst samples under study were produced via mechanical mixing of ZSM-5 zeolite (with the silicate modulus 40) with W nanopowders produced via wire electroexplosion in inert medium. The highest value of methane conversion is reached over zeolite containing 8.0% W. The catalyst (1 cm³) was placed on the quartz grid in the quartz reactor ($d_{\text{reactor}}=12$ mm) of a flow installation. The sample was heated in the helium flow to 750 °C and kept at this temperature for 20 min. Then the catalyst was treated with methane 99.9% pure at the temperature 750 °C, gas hourly space velocity 1000 h⁻¹ and a small excess pressure. The methane conversion and arene yield pass through maxima (12.1 and 9.0% respectively) at a reaction time of 100 min, and then the activity of the catalyst begin to decrease.

The study into morphology and chemical composition of W-HZSM-5 were carried out by high-resolution transmission electron microscopy (HRTEM) and Energy Dispersive X-ray

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analysis (EDX). The electron photos of the samples were obtained using JEM-2010 microscope (JEOL, Japan). Local EDX analysis was made using EDAX spectrometer (EDAX Co) equipped with a Si(Li) detector with energy resolution of 127 eV.

The catalysts operated in the reaction of methane dehydroaromatization for different period of time (10, 60 and 420 min) were studied.

It has been found that in the first stages of methane conversion the formation of tungsten carbide takes places in the catalysts studied, which is stabilized in the two forms. The first form is located on the zeolite surface as the particles less than 5 nm in size. Large particles to 100 nm are also present on the surface of this catalyst. The W particles of 1 nm and less located inside the zeolite are present on the samples worked for 60 and 420 min simultaneously with the above form of particles. The appearance of volumetric clusters and large tungsten carbide particles on the catalyst surface evidences that the redistribution of active sites comprising W occurs in the process of methane DHA both in the zeolite volume and on its surface.

The investigation of the catalyst worked for 60 min in the methane conversion has demonstrated practically complete absence of coke deposits on the zeolite surface whereas all the surface of tungsten carbide is covered with a rather dense coke layer whose thickness varies from 1.5 to 4.5 nm. This evidences that on this reaction stage the zeolite itself takes a small part in the methane conversion.

Thus, we may conclude that at the beginning of the methane conversion process the modifying element is located on the surface of the zeolite catalyst in the form of small oxide particles. Then, as the period of work increases, the tungsten carbide is formed on its surface, it partially penetrates into the zeolite volume and forms the clusters. The remaining tungsten carbide fraction is agglomerated into large particles and is located near the zeolite surface. At this active phase distribution the highest catalyst activity is observed in the process of methane conversion into aromatic hydrocarbons. Then, in the reaction course the accumulation of coke deposits occurs on the active zeolite sites and large tungsten carbide particles, which results in a gradual catalyst deactivation.

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**THE CATALYTIC ACTIVITY OF PLATINUM COMPLEXES IN
HYDROSILYLATION REACTION. THE INFLUENCE OF COMPLEX
STRUCTURE**

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The catalytic activity of mono- and binuclear platinum complexes with cyclic unconjugate dienes $[(\text{Me}_2\text{ViSi})_2\text{O}]_3\text{Pt}_2$ (**I**), $[\text{C}_{10}\text{H}_{12}\text{OEtPtOEt}]_2$ (**II**), $[\text{C}_{10}\text{H}_{12}\text{PtCl}]_2$ (**III**), $\text{C}_8\text{H}_{12}\text{PtS}_2\text{Fe}_2(\text{CO})_6$ (**IV**) in the reaction of hydrosilylation has been investigated.

The hydrosilylation of equal molar quantity of linear polymethylvinylsiloxanes and hydrosiloxanes which have different position of vinyl- and hydro group has been studied at 80 °C.

It was found that polyhydrosiloxanes with the $\equiv\text{Si-H}$ end-group show higher activity in hydrosilylation process in the presence of all used catalysts.

The comparison of rate for hydrosilylation of polymethylvinylsiloxane and polyhydrosiloxane containing functional end-groups when the conversion of the reagents changes from 10 to 60% show that activity of investigated complexes decreases in following raw: **I ~ III > II > IV**

The reactivity of vinyl compound depends on the position of vinyl group, used catalyst and hydrosilylation agent as well.

RHEOLOGICAL PROPERTIES OF BIC-42-1 PASTES

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Results of studying of rheological properties of BIC-42-1 pastes based on iron oxide and Al_2O_3 - binder are presented. Influence of the different raw materials used in technology of preparation of bulk monolith catalyst BIC-42-1 was studied. The analysis of structural - mechanical properties of pastes is made depending on the paste storage time.

BIC-42-1 monolith honeycomb catalyst is used in UKL-7 plant as a second part of two stage catalytic system (consisting of 9 platinum gauzes and nonplatinum catalyst) in ammonia oxidation process in nitric acid production [1]. A property (strength, activity, porosity) of this honeycomb catalyst was shown to be determined by raw materials used for its preparation [2] probably due to difference in their chemical interaction. This difference may also results in pastes Rheological properties (catalyst is prepared by mixing technology) according to Rebinder theory developed for pastes. Hence the main goal of this investigation is studying the Rheological properties of BIC-42-1 pastes versus used raw materials and storage.

As starting reagents an iron oxide (III), prepared by thermal decomposition of FeCl_2 (No 1), and an iron oxide (III), prepared by precipitation from FeSO_4 (No 2) are usually used for preparation of BIC-42-1 catalyst. As a binding material pseudoboehmite, made by precipitation technology (PBP), and aluminum hydroxide, made by hydration of thermal activated gibbsite (with ~50 % pseudoboehmite contents - PBTA) are used. Pastes were prepared using acetic acid water solution (dispersive media) and ethylene glycol (surfactant).

In the Z-shaped mixer (150 ml volume) 80 g of iron oxide, binding material, giving after calcination 15 g of alumina, and 5 g of alumina silicate fiber (used for better catalyst thermal shock stability) are mixed during 20 min (for homogenization). Then acetic acid solution and surfactant were added and mixed until paste is formed.

Rheological properties of as prepared pastes were studied using method developed by S.P. Nechiporenko. Data on plastic strength of pastes (prepared from different raw materials) versus pastes humidity were obtained. For the pastes with optimal humidity Rheological (the Elasticity coefficient E_1 , the elasticity module E_2 and the viscosity η) constants were determined using D.M.Tolstoy plastometer (with parallel plates). Samples of fresh paste and after daily storage (keeping) in tight container were exposed to research.

The analysis of the raw materials influence on the pastes (fresh) Rheological properties has shown, that the Elasticity Coefficient E_1 , the Elasticity module E_2 and viscosity η strongly depend on the raw materials. Thus, the Elasticity module E_2 obtained for the fresh plastic pastes prepared with PBP are is ~ 5 times higher than that for pastes prepared with PBTA. The Elasticity Coefficient E_1 has weaker sensitivity to binder than to iron oxide and is higher for pastes prepared with iron oxide No 2 as compared with iron oxide No 1. After daily storage no strong change in E_1 and E_2 values was detected for pastes with PBP, while elasticity coefficient E_1 decreased and elasticity module E_2 increased (but values stays in 3-4 time lower than that obtained in the case of PBP) for pastes with PBTA, thus revealing the change in pastes Rheological properties during storage especially strong for paste iron oxide No2-PBTA. The paste viscosity increases after storage up to 10 times, and it is lower in the case of PBP. The most significant (tenfold) growth of viscosity after storage was detected for paste prepared with iron oxide No 2 and PBTA as a binder. This viscosity parameter is the greatest.

All as prepared pastes can be molded as honeycombs. Taking into account that molding of fresh pastes for BIC 42-1 preparation usually results in cracks formation while molding of pastes after storage allows preparing of monoliths without cracks especially in the case of PBTA, one can make a conclusion about correlation between paste Rheological properties (coefficients) and possibility of preparation of monoliths without cracks. Obviously, high value of viscosity is very important and E_1 should not be of high value (lower then 50%). Probably such Rheological properties are of importance for catalyst granules strength as well [2].

Hence, for BIC-42-1 honeycomb catalyst preparation (not only for molding, but for obtaining strong honeycombs without cracks) the highest value of viscosity η is very important. The best mechanical properties were observed for the catalyst prepared from iron oxide No2 and PBTA based paste after its daily storage [2] with Rheological characteristics: elasticity coefficient $E_1=21,5\%$, elasticity module $E_2 =12,5\%$, viscosity $\eta =66\%$.

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PREPARATION AND STUDIES OF BULK URANIUM OXIDE CATALYSTS

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Uranium and uranium oxides have unique electronic structures. Uranium based catalysts can be used for a number of catalytic reactions, because of the ability of their electrons to interact with numerous organic and inorganic compounds. Uranium oxides may be used as catalysts, promoters and carriers. We have studied physicochemical properties of the samples prepared by different methods and their catalytic activity in the butane and methane deep oxidation reactions. It was shown that phase composition, structure and activity of samples depend on calcination temperature and a preparation method. Change of catalytic activity in the deep oxidation of butane and methane reactions was confirmed by temperature programmed reduction with hydrogen.

Electron structures of uranium and uranium oxides induce scientists to investigate them last years. The main field of application of uranium oxides is the nuclear industry. But at the time other branches of application of uranium compounds are known [1]. It is well known that uranium oxides are active for a number of processes of deep and selective oxidation. The uranium oxides-based catalysts were successfully tested in reactions of oxidation of volatile organic compounds such as benzene, toluene, butane, chlorobutane, chlorobenzene, trichloroethylene, cyclohexanone and butylacetate [2, 3].

This work is systematic investigation of uranium oxides for their subsequent modification and application for preparation of supported catalysts. The bulk uranium oxides were synthesized by two methods: precipitation from uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2$) solution and thermal decomposition of this salt.

The samples of deposited oxides were prepared by addition of the 25 % ammonia aqueous solution to uranyl nitrate aqueous solution with subsequent washing, filtration, drying and calcination at 300, 500, 600, 800, 1000 and 1100 °C. The samples obtained by thermal decomposition were prepared by calcination of uranyl nitrate at 300, 500, 600, 800 and 1000 °C in air. Phase composition of the samples was studied by X-ray diffraction

analysis. Specific surface areas of the samples were defined. The morphology of the samples was investigated by SEM. The samples were characterized by FTIR.

It was shown that phase composition of the samples depends on calcination temperature. The sample calcined at 500 °C consisted of β - UO_3 , which transferred to α - U_3O_8 after calcination at higher temperatures (600, 800, 1000 and 1100 °C). Specific surface area of these samples did not exceed $12.5\text{m}^2/\text{g}$.

The results of TPR investigation have shown that oxides are reduced by two steps. An increase of the reduction temperature of the samples with the same phase composition at the rising of calcination temperature was connected probably with a decrease of uranium oxides dispersion. The dispersion decrease was confirmed by results on specific surface area and morphology of the samples.

The results on investigation of catalytic activity of uranium oxides have shown that the 50 % butane conversion on the samples calcined at 600, 800 and 1000 °C was observed at 350, 370 and 430 °C, respectively. The 50 % methane conversion on the same samples was observed at 570, 590 and 660°C. It was shown that the higher the calcinations temperature, the lower the catalytic activity of uranium oxides. It can likely to be explained by a decrease of specific surface area of the samples. These data were well agreed with TPR results, where reduction temperature of the samples increased with increasing of calcination temperature.

As a result of this work, the conditions of synthesis of uranium oxides with specified properties have been defined. It will give ability to prepare uranium supported catalysts with given properties. These catalysts may be used for various catalytic processes.

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**NEW URANIUM OXIDE CATALYSTS FOR HYDROGEN PRODUCTION BY
PARTIAL OXIDATION AND REFORMING OF METHANE**

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New uranium oxide based catalysts containing different amount of uranium were synthesized, characterized and tested in the reactions of methane steam and carbon dioxide reforming, and methane partial oxidation. It was shown that introduction of uranium into Ni/Al₂O₃ catalyst can significantly improve the catalytic properties of commercial Ni-containing catalyst by an increase of hydrogen yield and a decrease of carbon formation. The uranium containing catalysts are very prospective to hydrogen production from methane and can be applied to the processes of hydrogen energy, petrochemistry and other processes.

Recent investigations in the fields of catalysis and new generation materials show that the use of uranium oxides as catalysts is very urgent today due to specific chemical and physical properties of uranium oxide materials. The most prospective peculiarity of uranium oxides is their high catalytic properties in the reactions of hydrogen or syn-gas production from light and heavy hydrocarbons by catalytic reforming or partial oxidation.

Despite the fact that chemistry of uranium containing compounds is highly studied, there is very restrictive information on catalytic properties of uranium oxide compounds.

The present work is devoted to the study of catalytic and physico-chemical properties of uranium oxides – nickel mixed catalysts in the reactions of methane partial oxidation and steam and dry methane reforming to produce syn-gas.

The alumina supported catalysts containing 10 wt.% of Ni and different uranium oxide amount (from 0 to 30 wt.%) were synthesized and tested in the reactions of methane steam and carbon dioxide reforming, and partial oxidation of methane.

It was shown that the introduction of U into Ni catalysts results in the activity increase: the higher the U content the higher the activity of the catalysts in all studied reactions. The optimum catalyst providing the highest hydrogen yield is the catalyst containing 15% uranium.

Ni-U catalysts were shown to be most effective in the processes of methane reforming with CO₂ and steam. Introduction of uranium oxides into nickel-alumina catalysts leads to a higher methane conversion and reaction products yields. An efficiency of the process depends on the content of uranium. The catalysts containing 30 %U are most active in the reaction of methane steam reforming. For example, at 850 °C and 45000 h⁻¹ on 10%Ni/Al₂O₃ (an analogue of the commercial catalyst) the methane conversion was 40 % and hydrogen yield 23 %, whereas methane conversion and hydrogen yield in the reaction of methane steam reforming on the 10%Ni/30%U/Al₂O₃ catalyst were 77 and 42 %, respectively, under the same conditions. In the reaction of methane reforming with CO₂ an introduction of 30 %U into the catalyst leads to practically total elimination of coke formation during the reaction. The carbon yield is 0.4 % at 850 °C, while on the industrial catalyst analogue the carbon yield is 14 % at 850 °C. Base on the project results, the catalyst 10%Ni/30%U/Al₂O₃ can be recommended as an optimal catalyst for the methane reforming with steam and CO₂.

In the reaction of partial methane oxidation to syn-gas the similar effect of improvement of catalytic properties of the catalyst by introduction of uranium oxides was observed. The optimal composition of the catalyst for methane partial oxidation process was determined to be 10%Ni/15%U/Al₂O₃. The methane conversion on this catalyst is 85 % and the hydrogen yield is 80 % at 800 °C and GHSV=5000 h⁻¹, whereas under the same conditions the methane conversion is 60 % and the hydrogen yield is 40 % on the catalyst containing no uranium.

As a result of the present research, it was shown that uranium oxide containing catalysts are more prospective for hydrogen production from methane and can be applied to the processes including a technological stage of hydrogen generation from methane: hydrogen energy, petrochemistry, fuel cells development and so on.

This work was performed under the ISTC project No. 2799p.

**URANIUM OXIDE CATALYSTS FOR DEEP OXIDATION OF
CHLORINATED ORGANIC COMPOUNDS**

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Deep oxidation of chlorobenzene and trichloroethylene on uranium oxide and mixed uranium – transition metal oxide catalysts supported on alumina was studied. An influence of temperature, space velocity and concentration of oxidized organic compounds and reaction products on effectiveness of the process was studied.

Uranium oxides are very attractive for catalysis due to unique chemical properties of uranium and uranium containing compounds. Uranium has a variety of oxidation states, which can slightly be changed. The U-O system has a number of polymorphous modifications and solid solutions. There are a set of transient composition compounds and metastable phases. At least 10 uranium oxides and 14 modifications of different composition are cited in the literature.

One of the prospective applications of uranium oxide catalysts is a use of them for deep catalytic oxidation of VOC including chlorinated organic compounds. Recent data obtained by G.J. Hutchings et al. show that uranium oxide catalysts are very stable to chlorine poisoning in comparison with traditional noble metal or transition metal oxide catalysts.

In the present work, oxidation of chlorobenzene (CB) and trichloroethylene (TCE) by air on 5%U/Al₂O₃ and 15%U/Al₂O₃ catalysts was studied at the temperature range 200-550 °C, space velocities 10000-70000 h⁻¹ and chlorinated compound concentration up to 11 g/m³.

It was shown that the 5%U/Al₂O₃ and 15%U/Al₂O₃ are the catalysts of deep VOC oxidation at 450-500 °C. Selectivity to CO₂ was 98-100 %. Molecular chlorine and other toxic chlorine containing compounds formation in the reaction products were not observed. Oxidation of a mixture of benzene and CB on 15%U/Al₂O₃ at 300-550°C was not influenced by CO₂ concentration in the initial reaction mixture.

Deep oxidation of CB vapors by air on mixed uranium-transition metal (Cr, Mn, Co and Cu) oxide catalysts was studied. It was shown that CO₂ selectivity was 100 % at 450-500 °C. Addition of uranium oxides to mixed oxide catalysts lead to a significant increase of the catalytic activity.

The activity of uranium oxide catalysts containing transition metal oxides increases in the following series: Cu/U/Al₂O₃ < Co/U/Al₂O₃ < Mn/U/Al₂O₃ < Cr/U/Al₂O₃.

The conversion of CB on mixed uranium - transition metal (Cr, Mn, Co and Cu) oxide catalysts at 500 °C was shown to decrease at an increase of CB concentration in the reaction mixture from 0.5 to 5.0 g/m³.

The mixed uranium – transition metal oxide catalysts were shown to exhibit high activity and high stability in the reaction of chlorinated VOC oxidation. A very slight decrease of CB conversion, about 4-5%, was observed during an operation of the catalysts at 500°C for 40 hrs. Chlorine consumption by the uranium oxide catalyst was shown to be lower than 0.2% of total amount of chlorine feed into the reaction.

Initial and spent catalysts were characterized by a number of physico-chemical methods including XRD, S_{BET}, FTIR etc. It was shown that an operation under reaction conditions leads to change of phase composition and textural properties of the catalysts.

This work was performed under the ISTC project No. 2799p.

**THE INFLUENCE OF SYNTHESIS PARAMETERS ON THE REAL/DEFECT
STRUCTURE OF PURE CERIA AND ZIRCONIA**

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Effects of the synthesis parameters (method of preparation, aging procedure etc.) on the real/defect structure of pure ceria and zirconia samples prepared from cerium nitrate and zirconyl chloride were considered. Structural features of these oxides were characterized by XRD analysis, EXAFS, IR and Raman spectroscopy. SAXS and UV-Vis spectroscopy were applied to reveal defects.

Dispersed pure ceria and zirconia attract a great attention as catalysts or supports for metal/oxide catalysts of red-ox/acid-base reactions as well as important components of complex catalysts [1-2]. It is well known that synthesis procedures affect formation of zirconia polymorphs (monoclinic, tetragonal or pseudocubic) while ceria retains a cubic fluorite structure for all preparation methods [1]. In this work combination of methods (XRD, EXAFS, IR and Raman spectroscopy, SAXS and UV-Vis spectroscopy) was applied to elucidate structural features (including defects) of pure oxides prepared from available cerium nitrate and zirconyl chloride salts. For traditional precipitation route, effect of pH and temperature of precipitation and/or aging, UV irradiation of precipitates on the real structure was considered. For the polymerized complex method (based upon formation of the chelate complexes of metal cations and complex esters) the ratio of reagents was systematically varied.

For nanocrystalline ceria, defects appear to be mainly located in vicinity of domain boundaries. For samples prepared via polymerized complex method, these boundaries could retain the structural features of nonstoichiometric Ce_nO_m oxides characterized by different Ce-O distances with residual amount of Ce^{3+} cations.

The genesis of zirconias real structure prepared via precipitation route depends considerably on the parameters of synthesis due to structural flexibility of freshly precipitated amorphous zirconium hydroxide. A short -time UV irradiation was found to favor formation of the monoclinic phase at rather low temperatures, perhaps, via affecting bonding of hydroxyls and /or water molecules in the coordination sphere of Zr cations in tetrameric $Zr_4(OH)_n(H_2O)_m^{z+}$ complexes in an amorphous hydroxide. Prolonged aging of the amorphous

precipitate at 100 °C favors formation of highly hydroxylated tetragonal phase, which could be assigned to a pronounced polymerization of tetrameric complexes at aging via known mechanism of “olation” and “oxolation” with participation of terminal and bridging hydroxyls leading to generation of sheet-like and rod-like polynuclear oxohydroxo species. Variation of the polymerization degree of tetrameric species and their stacking/ordering in the structure of a hydroxylated precursor seem to determine the relative content of monoclinic and tetragonal phases in zirconia samples calcined at moderate (up to 600-700 °C) temperatures. In dehydroxylated samples of monoclinic phase, pronounced distortion of the coordination sphere of Zr cations is reflected in UV-Vis spectra as absorption in the range of $\sim 31,000\text{ cm}^{-1}$ not present in spectra of cubic or tetragonal samples.

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EFFECT OF PARTICLE SIZE ON CATALYTIC PROPERTIES OF SULFATED ZIRCONIA

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Detection and examination of particle size effect of sulfated zirconia in Pt/SO₄²⁻/ZrO₂ as isomerization catalyst are carried out. It is shown, that sulfated zirconia with the smallest particle size (70-90 Å) has a maximum catalytic activity in n-hexane isomerization.

Catalysts based on sulfated zirconia (SZ) are very effective for different acid-catalized reactions of hydrocarbons including such industrial processes as oligomerization of alkenes, alkylation of isobutane, isomerization of alkanes. Therefore studying of preparation methods and structure of these systems has a certain scientific and practical interest. The general aim of this work is to determine correlation between the particle size of sulfated zirconia and its catalytic activity.

Regulation of SZ particle size was provided by varying the synthesis conditions: concentration of ZrO(NO₃)₂ solution (50-320 g ZrO₂ per litre); pH of precipitation (8-11) and aging time (0-7 days) of ZrO₂·xH₂O; sulfate loading (0-13 wt% SO₄²⁻); calcination temperature (500-650 °C).

Sulfate loading has the strongest impact on the dispersion and catalytic properties of SZ. Calcining of ZrO₂·xH₂O without sulfur produces low dispersion ZrO₂ with crystallite size about 200 Å, consisting mainly of monoclinic phase and having no catalytic activity. Increasing the sulfate level to 3-4 wt% leads to the formation of SZ with 80-90 wt% tetragonal phase and particle size less than 100 Å. This structure remains the same from 3 to 9 wt% of SO₄²⁻ content. Maximum catalytic activity in isomerization of n-hexane is achieved in this interval. Further increasing of sulfate content leads to amorphization of the system and decreases its dispersion and catalytic activity.

While calcining SZ in the temperature range between 500 and 650 °C crystallite size differs only in 20 Å. At the same time catalytic activity grows continuously from zero level to almost equilibrium conversion of n-hexane. Thus, influence of calcination temperature of SZ is related not to the regulation of its dispersion but to the thermal decomposition of the surface sulfate species, leading to the formation of active sites of the catalyst.

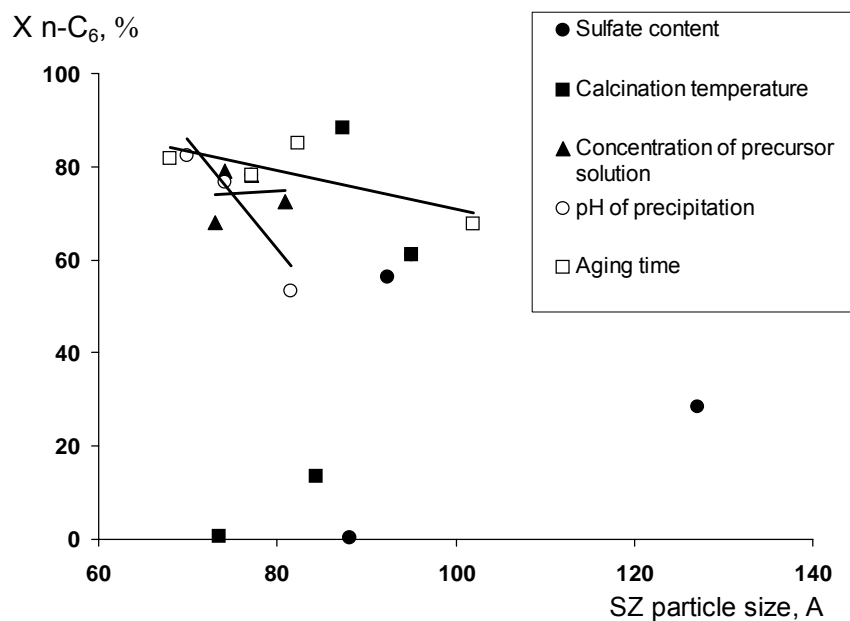


Fig. 1. Influence of particle size of SZ depending on the way of its regulation on n-hexane conversion

As can be seen from Fig. 1, varying the conditions of precipitation of $ZrO_2 \cdot xH_2O$ influences the particle size of SZ, which is formed in tetragonal modification due to further sulfation and calcination. As the crystallite size of material decreases the conversion increases. The smallest particle size which provides maximum activity of n-hexane isomerization catalyst is 70-90 Å.

**SYNTHESIS OF THE SILVER-COBALT MIXED OXIDE CATALYSTS USING
MOLTEN NH₄NO₃**

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Several silver-cobalt mixed oxide catalysts were synthesized using NH₄NO₃ under different conditions. Massive catalyst AgCoO₂ prepared by decomposition of nitrates in molten NH₄NO₃ possesses significant activity in the temperature range 200-400 °C. Catalysts supported on γ-Al₂O₃ show better activity as compared with the massive one. The most catalytic active sample was 5 % AgCoO₂/γ-Al₂O₃ prepared by wet impregnation of γ-Al₂O₃ with aqueous solutions of Ag, Co and ammonium nitrates and decomposition using microwave radiation.

Nowadays, one of the most important problems in catalysis is CO oxidation. Usually, mixed oxide systems and supported noble metals are used in this process as catalysts. The best results are achieved on gold containing catalysts, but taking in to account the price of gold the cheaper solution for industry should be found. Catalysts containing silver are almost unstudied, due to early papers showing them to be less active than gold containing ones [1]. However, recently group of authors [2] have shown theoretically using *ab initio* DFT calculations that silver in nanoparticle state are more active than gold. Also there are some recent experimental proofs of catalytic activity of supported Ag [3] and Ag-Co mixed oxides [4].

Some silver-cobalt mixed oxide catalysts were prepared in this work using molten ammonium nitrate. The composition of catalysts and synthesis conditions are presented in table 1. All catalysts were calcined at 600 °C (2 h) and were studied in CO oxidation reaction (gas mixture composition: 4.0 vol. % CO, 2.1 vol. % O₂, 93.9 vol. % He; gas rate was 10000 h⁻¹). The catalytic measurements results are given in table 1 as values of temperatures of 50 % and 100 % carbon monoxide conversion.

According to data presented in table 1 and fig. 1 samples B and C shows almost no activity in CO oxidation. On our opinion it is connected with interaction of silver and cobalt with silica gels surface. Massive catalyst A possesses significant activity in the temperature range 200-400 °C. Difference in temperatures of 50 % and 100 % conversion for samples A and D, E, F probably originated from small specific surface area of AgCoO₂ and perhaps from the formation of CoAl₂O₄ which is also active in CO oxidation. The most active sample was F which was prepared using microwave radiation. Most likely quick heating of the nitrate

mixture by microwave radiation leads to quick decomposition of nitrates which leads to the formation of smaller particles of active component comparing to conveniently prepared samples. Therefore, microwave radiation treatment instead of ordinary heating results in the formation of catalysts with higher specific surface areas of active component and as a result with higher catalytic activity in CO oxidation reaction.

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Table 1. Catalysts composition, synthesis conditions and the results of CO oxidation over Ag-Co mixed oxide catalysts prepared.

catalyst	AgCoO ₂ content	support	synthesis	T _{50%} , °C	T _{100%} , °C
A	100 wt. %	—	decomposition of silver and cobalt nitrates in molten NH ₄ NO ₃	288	400
B	5 wt. %	macro-porous silica gel SiO ₂ – 185 m ² /g	coimpregnation of the support with aqueous solutions of silver, cobalt and ammonium nitrates	550	> 650
C	5 wt. %	fine-porous silica gel SiO ₂ – 320 m ² /g		370	> 570
D	5 wt. %	γ-Al ₂ O ₃ – 185 m ² /g		200	430
E	5 wt. %	γ-Al ₂ O ₃ – 185 m ² /g	wet impregnation of the support with aqueous solutions of silver, cobalt and ammonium nitrates	224	448
F*	5 wt. %	γ-Al ₂ O ₃ – 185 m ² /g		155	260

* – decomposition using microwave radiation

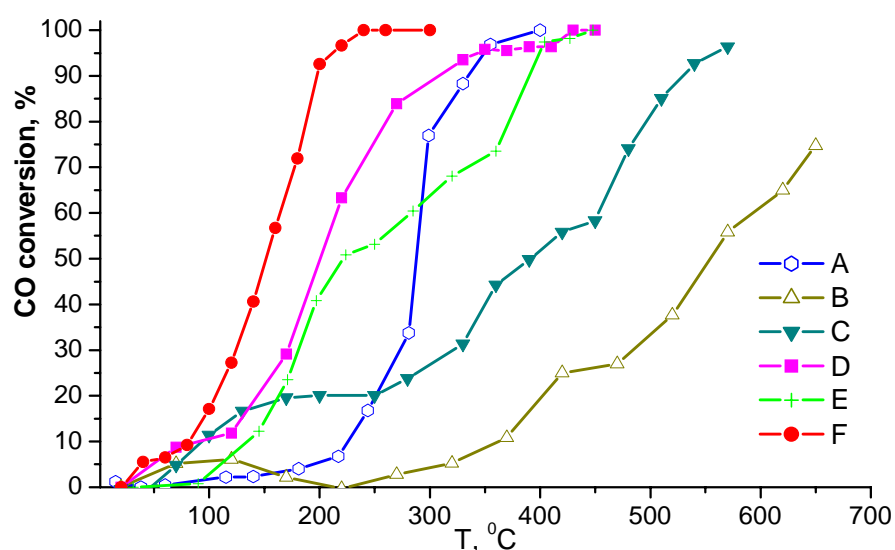


Fig. 1. Catalytic activity of samples A, B, C, B, E, F prepared in CO oxidation reaction.

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**CATALYTIC ACTIVITY OF OXIDES OF TUNGSTEN AND MOLYBDENUM,
REDUCED BY HYDROGEN IN PRESENCE OF PLATINUM METALS AND
CESIUM, IN REACTIONS OF SMALL MOLECULES OXIDIZATION**

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We have shown that H₂ reduced WO₃ and MoO₃ with Pt(Pd) and/or Cs⁺ additives exhibit high catalytic activity in the reaction of H₂, CO and CH₄ oxidation. It has been found that main catalysts component formed during reduction are hydrogen bronzes caused high surface area and considerable activity and of the composite catalysts. Deactivation of the catalysts occurs because of the bronze destruction at high-temperature regimes.

Oxides of transitional 3d- and 4d-metals (V₂O₅, MoO₃, WO₃) with small admixtures of Pt or Pd at reduction by hydrogen able to form compounds belonging to the class of hydrogen oxide bronzes H_xV₂O₅, H_xMoO₃, H_xWO₃ [1-4]. In contrast to pure oxide, the bronzes formation on the surface and bulk increase considerably catalytic activity of resulted composites in different heterogeneous catalytic processes, for example in the reactions of isomerisation and conversion of hydrocarbons [5]. Formation of oxide bronzes occurs due to the effect of the spillover of hydrogen adsorbed on Pt and Pd, from the metal to the proper oxide [1,2]. It is considered that Pt and Pd play the role of catalysts of reduction of the oxides. Besides, the platinum metals are the most active catalysts of many reactions, for example, of hydrocarbons combustion, oxidization of CO and H₂, hydrocarbons hydrogenation. Additions of salts of alkaline metals to catalysts diminish energy of oxygen binding with the surface of catalyst [6], that promote the catalytic activity increase. Potential of high active catalytic systems in the processes of complete oxidization and their stability in reaction mixtures containing oxygen excess is practically unexplored. In this work the results of examination of catalytic activity in the reactions of complete oxidization of small molecules (H₂, CO and CH₄) of oxides of tungsten and molybdenum partly-reduced with H₂ in presence of Pd or Pt, and also Cs⁺ are reported. Influencing of parameters of the reduction (temperature and time) on catalytic properties of the composite systems were studied. Also stability of the composite systems was examined at high temperatures in gas mixture with excess of oxygen, and compared with the activity of traditional Pt or Pd of catalysts supported on γ-Al₂O₃.

Catalysts were prepared by the impregnation on moisture capacity and further were reduced with hydrogen. The oxides of tungsten and molybdenum (Reakhym, 99.999 % mass.

and 99.995 % mass.) were saturated with solutions of H_2PtCl_6 or PdCl_2 in order to obtain 0.5 % mas. of metal in the sample composition. The catalysts samples were dried at 393 K and were reduced with hydrogen (mixture 10 % H_2 in Ar) during 1 h at 673 K. For the joint introduction of Pt(Pd) and Cs^+ catalysts were saturated with solution of CsJO_3 accounting on 0.05 % mass. Cs^+ in the catalyst. These samples were dried at 393 K and reduced in a stream of hydrogen-argon mixture (10 % H_2) during 1 h at 673 K. To compare the catalysts with standards, Pt(Pd)/ $\gamma\text{-Al}_2\text{O}_3$ with 0.5 % mass. of metals were prepared. Treatment with hydrogen of these catalysts was conducted for the standards just as for Pt(Pd)/ MoO_3 and Pt(Pd)/ WO_3 . Composition, specific surface (S) and temperature of achieving certain degree of the conversion ($T_{20\%}$, $T_{40\%}$, $T_{100\%}$), are listed in a table.

Table. Temperatures of certain conversion degree of H_2 , CO and CH_4 (%) in K on the catalysts of oxidation.

Sample	$T_{20\%}$	$T_{40\%}$	$T_{80\%}$	$T_{10\%}$	$T_{30\%}$	$T_{100\%}$	$T_{10\%}$	$T_{20\%}$	$T_{35\%}$
	H_2 oxidation			CO oxidation			CH_4 oxidation		
0.5%Pt/ Al_2O_3	298	307	330	460	478	486	755	768	800
0.5%Pd/ Al_2O_3	310	318	336	448	470	478	750	770	785
WO_3	475	556	-	660	768	-	-	-	-
MoO_3	526	610	-	715	805	-	-	-	-
0.05% Cs^+ / WO_3	408	450	550	628	685	-	-	-	-
0.05% Cs^+ / MoO_3	486	550	-	625	738	-	-	-	-
0.5%Pt/ WO_3	273	286	302	362	410	432	615	640	698
0.5%Pd/ WO_3	273	293	310	383	425	442	623	642	670
0.5%Pt/ MoO_3	273	286	302	390	450	463	630	658	693*
0.5%Pd/ MoO_3	273	292	310	400	442	455	634	645	680*
0.5%Pt·0.05% Cs^+ / WO_3	273*	283	294	350	400	420			
0.5%Pd·0.05% Cs^+ / WO_3	-	273	288	360	418	430			
0.5%Pt·0.05% Cs^+ / MoO_3	273	280	290	390	442	448			
0.5%Pd·0.05% Cs^+ / MoO_3	273*	283	297	388	435	442			

* Note: temperature was determined for 30% conversion.

In the reactions of gas-phase oxidization for reaction mixtures (1% H_2 (CO, CH_4) and 20 % O_2 in inert gas (Ar, He)) it is observed that introduction of Pt(Pd) in TO_3 ($T = \text{Mo}, \text{W}$) results in increasing of S in 5-6 times, addition of Cs^+ to these catalytic systems results in the further S increase. The trioxides possess low activity in oxidization of H_2 and CO, but in methane complete oxidization they are quite inactive. Hence after reduction with H_2 , the catalytic activity of systems containing Pt(Pd) in these reactions increases considerably as compared to Pt(Pd)/ $\gamma\text{-Al}_2\text{O}_3$. For the reaction of CO oxidization considerable extent of temperature region of low-active state of catalyst with $X < 20\%$ and lowering of the temperatures of reaction beginning on 100–120 K as compared with Pt(Pd)/ $\gamma\text{-Al}_2\text{O}_3$. the

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synergetic phenomenon are characteristic for the complex catalytic systems, *i.e.* non-additivity of catalytic activity at introduction of Pt(Pd) or pair of Pd Pt(Pd) and Cs⁺ in the trioxides. The temperature of beginning of methane complete oxidation shifts approximately on 140 K lower as compared with Pt(Pd)/ γ -Al₂O₃, but at temperature increase to 700 K the activity decreases and becomes equal to one of standard catalysts. In the XRPD spectra of catalysts containing 0.5 mass. % Pt(Pd) was observed intensive diffraction peaks of WO_{2.9}, H_xWO₃ and Mo₄O₁₁ and H_xWO₃, the catalysts with Cs⁺ contain Cs_xWO₃ and Cs_xMoO₃. Study of surface layer composition of catalyst by XPS was conducted on the example of samples of WO₃ with supported Pt or Pd and Cs⁺. It was shown by XPS that the binding energy of W 4f_{7/2} is of 35.9–36.0 eV, and degree of W oxidization are < +6. Correlation of W : O in the surface layer of catalysts is ranged from 1:3 to 1:2.7, that confirms existence of oxygen vacancies on the catalysts surface, and also well co-ordinates with results of XRPD. The binding energy of electrons of Pt 4f_{7/2} and Pd 3d_{5/2} shows that Pt and Pd degree of oxidization is near to 0. The binding energy of Cs corresponds to the charge state of cesium (+1) and testifies formation of Cs_xWO₃. XRPD and XPS studies of the catalysts worked in H₂ oxidation hydrogen showed that phase composition and valence of catalysts components did not change in a surface layer. According to XRPD results, the catalysts worked in CO oxidation does not contain evident quantities of H_xTO₃ (T = Mo, W). Thus in a line with WO_{2.9} and Mo₄O₁₁, that were registered in the catalysts before the reaction, the phases of WO_{3-x} (0.1 < x < 0.28) and MoO_{3-x} compositions are appeared (x = 0.12–0.2). Treatment of the catalysts in the O₂ excess reaction mixture at temperatures higher 700 K results in 1) oxidation of active in the catalysis hydrogen oxide bronzes and in 2) formation of WO_{2.9} and Mo₄O₁₁ containing vacancies on oxygen the latest originate high catalytic activity. Thus, it was determined that hydrogen bronzes as H_xTO₃ (T = Mo, W), formed at H₂ reduction of the trioxides in presence of the platinum metals, are active not only in the mixtures containing H₂ excess, but also in the O₂ excess mixtures used for complete oxidization of small molecules. However, operational temperatures of these processes are limited by a range from r.t. to 700 K where the systems work the best.

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CATALYTIC SYSTEMS BASED ON SILVER-CONTENT SOL-GEL COMPOSITES FOR THE ALCOHOL PARTIAL OXIDATION

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New catalysts for alcohol partial oxidation processes have been prepared by sol-gel method. It was shown that the method of active component introduction into silica-phosphate matrix affects the catalytic activity of the sol-gel composite systems. Catalytic activity of these systems is higher than that of polycrystalline Ag and supported silver catalysts. Silica-phosphate matrix prevents the sintering of silver nanoparticles under the action of reaction mixture.

During a long time the scientific interest of our laboratory is lying in the field of selective oxidation of alcohols on different types of catalysts such as oxide systems, massive and supported IB subgroup metal catalysts. In the present time the *focus of our investigations* directs to elaboration of novel catalytic systems on the basis of silicate-phosphate matrix prepared by sol-gel method. Active component in the developed sol-gel catalytic systems is nanoscale Ag metal particles.

In the present work the method of novel catalysts synthesis has been elaborated. The scheme of the catalyst formation has been proposed on the basis of the results obtained by using of the complex of physical-chemical methods (UV-VIS, XRD, IR, TEM) to investigate the prepared materials during the preparation procedure and after treatment in catalytic process. The systems obtained are network structures in which the porous space is filled by liquid-like polyphosphate phase. Under the action of both gaseous hydrogen-content mixture and high temperature (200 - 400°C) nanoscale silver particles are formed on the catalyst surface and subsurface region of silicate grains. Metal ions diffusion from the bulk to the surface of sol-gel catalyst is provided with the polyphosphate phase which forms ion-conduct channels in sol-gel composite structure.

The catalytic systems prepared are characterized by the high catalytic activity in the process of the ethylene glycol selective oxidation into glyoxal. Taking into account that the content of metal particles in sol-gel catalyst doesn't exceed 5 % mass, the efficiency and thermal stability of novel sol-gel catalyst are significantly higher in comparison with traditional polycrystalline Ag catalyst.

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To detail the mechanism of active surface formation, the experiments directed to study the catalyst surface behavior under the action of oxidative-reduce reaction mixtures have been carried out. The catalyst surface active centers undergo a number of transformations. Firstly it is oxidized by oxygen, then reduced by alcohol-containing reaction mixture and reactivated again. The state of catalyst surface after the consecutive cycling treatments by oxidizing (O_2 in He) and reducing (H_2 in Ar) reaction mixtures in the temperature-programmed regime have been investigated by UF-VIS spectroscopy. It has been shown that the freshly prepared catalyst is predominantly characterized by ion state of silver. The appearance of Ag clusters has been observed under the reducing treatment during the TPR experiment. The consecutive oxidation of the catalyst surface during TPO experiment leads to the returning of silver to predominantly ion state. TPR-TPO cycling experiments have shown the steady reversible behavior of catalytic systems.

Thus, the main properties of catalytic system such as reversibility and stability have been determined. The active surface has two equal forms of silver - metal clusters and ions.

Acknowledgement

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**PHASE ANALYSIS OF MULTIELEMENT CATALYSTS AND OTHER
SUBSTANCES AND MATERIALS BY STOICHIOGRAPHIC METHODS**

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The elaboration of theory and application of the stoichiographic method of differential dissolution (DD) is presented. The method is able to determine both stoichiometry and amounts of crystalline/amorphous phases with constant or variable composition when they exist in multielement and heterogeneous mixtures. The main feature of DD is to be reference-free technique when analysis of unknown phase composition samples is carried out without resorting to standard reference phases.

Factors such as selectivity and efficiency determining the separative ability of the DD processes are analyzed when dissolution of mixtures is realized under a flow dynamic regime directly in stoichiograph. The following factors are taken in account: the volume and linear rates of the solvent flow, the concentration variation of active components in the flow, the dissolution rate of the phases and washing out of the solutions formed from reactor. New approaches to collection and determination microphases appearing in inorganic multielement heterophase solids as by-products or as special additions are discussed.

DD analysis is performed by means of special apparatus, stoichiograph, using ACP AES as a detector-analyzer. The technique shows high selectivity and sensitivity and performs rather simply and quickly single operations and analysis as a whole.

Some fresh examples of phase analysis of various materials and preparative separation of phase mixtures are given which were very important for understanding of the phase formation processes of various composite catalysts and other materials of complex nature.

A great variety of multielement systems with crystalline and amorphous phases of constant or variable composition have already been analyzed by this technique. For each system the optimal dissolution procedure was determined, for which composition and concentration of active components in the differential solvent as well as their variation with temperature and in time were found. To realize the dynamic regime of DD, the stoichiographic titration was most commonly used that provided the required selectivity and efficiency of the dissolution processes for each the system. For many systems the use of DD

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referee-free analysis was about the only possible because of the phase composition of samples tested was practically unknown *a priori*.

DD being used for studying processes of phase formation for catalysts and other materials of complex nature detected all compositional variations of samples exposed to thermo-mechanical-chemical treatments, aggressive mediums or modified by some additives. Detection of amorphous and spatially inhomogeneous phases of varying composition in some heterogeneous catalysts has been made possible due to DD. Catalyst prepared mechanically, being often amorphous and non-detected by diffraction methods, were the subject of much experimentation by the DD method.

The phase composition was determined ever for composite sorbents of high degree of dispersion. The sorbents formed by salts of alkaline, alkaline-earth metals and copper were located in pores of silicogels, γ -Al₂O₃, and carbon materials of different nature. In this case a specific interaction between the salts and the matrix surface were detected.

Unique procedure was developed to separate effectively nanoparticles of MnFe₂O₄ from amorphous matrix of the K-Al-borate glasses. This made possible to study real composition and real structure of the nanoparticles and to find ways of strict controls over them.

Other examples of DD analysis applied to various subjects are also shown in order to support theoretical theses of the method and to demonstrate its unique ability to be useful even in seemingly intractable problems.

This work is supported by RFBR (grant 05-03-32236).

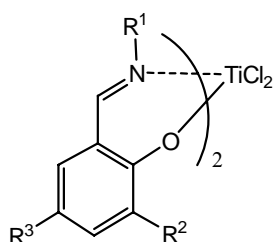
**EFFECT OF THE LIGAND SUBSTITUENTS IN PHENOXY-IMINE-TiCl₂
COMPLEXES UPON THEIR CATALYTIC ACTIVITY IN ETHYLENE
POLYMERIZATION**

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The effect of substituents at imine nitrogen and in the ortho-position of the phenoxy group in the ligands of 6 bis(phenoxy-imine)titanium dichloride complexes upon their



- (1) $R^1 = C_6H_5$, $R^2 = t-Bu$, $R^3 = t-Bu$,
- (2) $R^1 = C_6H_{11}$, $R^2 = t-Bu$, $R^3 = t-Bu$,
- (3) $R^1 = C_6H_5$, $R^2 = t-Bu$, $R^3 = Me$,
- (4) $R^1 = C_6H_{11}$, $R^2 = t-Bu$, $R^3 = Me$,
- (5) $R^1 = C_6H_5$, $R^2 = cumyl$, $R^3 = Me$,
- (6) $R^1 = C_6H_{11}$, $R^2 = cumyl$, $R^3 = Me$

ethylene polymerization behavior is studied. The polymerization was carried out using the catalyst in amount $\sim 1-2 \mu\text{mol}$ and methylalumoxane (MAO) cocatalyst at ethylene pressure 0.3 MPa, temperatures from 30 to 70 °C and Al:Ti molar ratio 250-500. For all catalyst systems ethylene polymerization kinetics was studied within at least 60 min.

For complexes (1)-(4) containing small substituents $R^2 = t-Bu$ and $R^3 = Me$ the polymerization kinetics is found to be predominantly determined by the nature of the cyclic substituent R^1 at the imine nitrogen. The structure of this substituent can affect the temperature range of the maximum catalyst activity.

However, for the complexes (5) and (6) bearing a bulky substituent in the ortho-position of the phenoxy group ($R^2 = cumyl$) the cyclic substituent at the imine nitrogen R^1 does not affect the polymerization kinetics.

Molecular, structural and thermal properties of the obtained polyethylenes are characterized.

The analysis of obtained data suggests the conclusions regarding a combined effect of the substituents in the phenoxy groups and imine nitrogen upon the optimum temperature range of bis(phenoxy-imine)titanium based catalyst performances and their activity at ethylene polymerization.

THE EFFECT OF NOBLE METAL (Au, Ag, Ru) ADDITION ON PHYSICOCHEMICAL PROPERTIES OF BI-OXIDE SUPPORTED (Ni Fe) CATALYSTS FOR PARTIAL OXIDATION OF METHANE AND METHANOL SYNTHESIS

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This project examines the effect of binary support: MgAl_2O_4 , FeAlO_3 , ZnAl_2O_4 , Al_3CrO_6 , NiAl_2O_4 and active phase: Au, Ag, Ru - Fe, Ni on physicochemical properties of metal/support catalysts and their activity in partial oxidation of methane and methanol synthesis. The formation of spinel type structure in case of all binary supports was proved. The role of noble metal addition on the reducibility of mono- and bi-oxide phases was established.

This work is focused on the role of noble metal additives on the physicochemical properties and the activity of bimetallic catalysts Au, Ag, Ru - Fe, Ni supported on binary oxide (MgAl_2O_4 , FeAlO_3 , ZnAl_2O_4 , Al_3CrO_6 , NiAl_2O_4) in partial oxidation of methane (POM) and methanol synthesis (MS). Supported bimetallic systems represent a considerable part of heterogeneous catalysts, which have been used in various reactions important in the chemical, petrochemical and oil industry. In comparison to monometallic systems the bimetallic catalysts showed better activity and stability in hydrocarbon conversion. The addition of noble metal improves the bimetallic catalyst activity due to modification of electron properties. Further modifications of the oxide support change its morphological and textural parameters.

Catalyst preparation: The binary oxides were prepared by co-precipitation method. As starting compounds an aqueous solutions of nitrates of Mg, Cr, Al, Fe, Zn were used and the appropriate mixtures of hydroxides were co-precipitated with aqueous ammonia solution with suitable molar ratio of $\text{Al/Mg}=2$, $\text{Al/Cr}=3$, $\text{Al/Fe}=1$, $\text{Al/Zn}=2$ and $\text{Al/Ni}=2$. The samples were dried and calcined in air at 700°C for 4 hours. The active phase were deposited from solutions of nitrates of Au, Ag, Ru, Fe, Ni by impregnation method. The load of metal was 5%(Ni, Fe)-2%(Au, Ag, Cu) respectively. The catalysts **were characterized** by TPR_{H_2} , low-temperature N_2 adsorption, and XRD methods. The catalytic activity measurements in POM and MS reactions were carried out in a flow quartz reactor systems with chromatographic analysis and under pressure in HDT (Germany) reactor system coupled with the mass spectrometer.

Results and discussion: The results of specific surface area measurements for supports and supported metal catalysts showed that alumina oxide had the highest specific surface area (230 m²/g). An addition of the other oxide lowers the specific surface of bi-oxide support to 60 %. The XRD phase composition studies showed a well defined spinel like structure in all binary oxides. Only the Al₂O₃ monooxide support had amorphous character. A metal phase was only detectable in case of monometallic gold supported catalysts probably due to the considerable metal sintering. Reduction effects were established for Al₃CrO₆ and FeAlO₃ supports. An overall reduction degree was below 15 % in the case of Al₃CrO₆ and below 20 % in the case of FeAlO₃. The addition of ruthenium moves the reduction effects toward lower temperature in case of reducible supports as well as in case of dispersed nickel/iron oxides used as active phase. The addition of gold changes only the reducibility of iron containing catalysts (especially for the reduction step $Fe^{3+} \rightarrow Fe^{2+}$). In the case of the catalysts supported on non-reducible support all reduction effects were attributed to the reduction of the appropriate oxide of the active phase. The most active catalysts in POM reaction appeared Ru-Au/ Al₂O₃ with 100 % of the methane conversion at 650 °C. Nickel supported catalyst was less active (100 % methane is achieved at 700-850 °C). Iron catalysts showed rather poor activity about only 20 % CH₄ conversion at 900 °C. Gold addition does not change the activity a lot but increases the stability and decreases the degree of carbon deposition. In the methanol synthesis all catalysts show comparable activity but the selectivity to methanol was different, and the catalysts containing zinc oxide were the most selective to methanol. Nickel doped catalysts mainly catalyze the methane synthesis process. The introduction of gold insignificantly increases the activity, but considerably decreases coke formation .

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THE INFLUENCE OF PREPARATION CONDITIONS ON PHYSICOCHEMICAL PROPERTIES AND CATALYTIC ACTIVITY OF Ni-Au/Al₃CrO₆ CATALYST IN PARTIAL OXIDATION OF METHANE

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The physicochemical properties and catalytic activity of 5% Ni/Al₃CrO₆ and 5% Ni-2% Au/Al₃CrO₆ catalysts were examined in dependence of preparation conditions (temperature treatment, pH, kind of precursors, presence of chlorine contents). Bimetallic 5% Ni-2% Au/Al₃CrO₆ catalysts were more active and more stable than monometallic 5% Ni/Al₃CrO₆. An addition of gold improves resistance of carbon deposition. However introduction of chloride ions AuCl₄⁻ during impregnation step can influence on poisoning active center of nickel-gold catalysts in partial oxidation of methane (POM).

The strong interest in gold is due to its potential applicability in many low-temperature reactions of CO oxidation [1], selective NO_x reduction, water-gas shift reaction and its successful using in high-temperature process, for e.g. hydrocarbon oxidation [2]. The gold addition to Ni, Fe catalyst changes their crystalline network. This modification of surface causes the abatement of methane dissociative adsorption and coke formation that improve stability and life time of catalysts [3]. The last researches show that nickel-gold alloying on the surface can be a good method to controll dilution of active nickel sites which take part in dehydrogenation of CH₃ species.

The aim of this work is to determine the influence of preparation conditions on physicochemical and catalytic properties of mono and bimetallic 5% Ni-2% Au/Al₃CrO₆ catalysts.

The Al₂O₃, Cr₂O₃, Al₃CrO₆ supports were prepared by precipitation and co-precipitation (Cr(NO₃)₃·9H₂O and Al(NO₃)₃·9H₂O) by ammonia aqueous solution. All supports were dried and calcined at 700°C/4h/air. 5%Ni and 5%Ni-2%Au catalysts were prepared by wet impregnation method, sequential impregnation (precursors: Ni(NO₃)₂·6H₂O, HAuCl₄ and Ni(NO₃)₂·HNO₃, Au(NO₃)₃·HNO₃). Catalysts were dried and calcined at 400 °C/4h/air.

The physicochemical properties of catalysts were investigated by TPO-TPRH₂, BET, XRD, TOC analysis. The activity tests in partial oxidation of methane were carried out in a flow quartz reactor in the temperature range 25-900 °C with GC analysis. The 24 h activity

tests in POM reaction and TOC measurements were carried out to determine carbon deposition and stability of catalysts.

The calcination temperature of mono and bimetallic catalysts (400, 900 °C) did not influence on CH₄ conversion in POM (Fig. 1). An increase of nickel content from 5% to 10% Ni caused decrease of CH₄ conversion to lower temperature (800 °C). The activity of mono Ni and bimetallic Ni-Au catalyst in POM was similar to each other, but gold addition to nickel catalyst reduces carbon formation and improves their stability. 5%Ni-2%Au/Al₃CrO₆ and 5%Ni/Al₃CrO₆ catalyst were the most active in POM reaction.

Various precursors were used to prepare catalysts. A reducibility for them was examined (Fig. 2). 5%Ni-2%Au/Al₃CrO₆ was prepared by means of conventional HAuCl₄ solution. This catalyst showed strong reducing effect at about 270 °C and weaker at 500-600 °C (profile F). The catalyst prepared with Au(NO₃)₃·HNO₃ precursor (profile A) had a reducible peak at lower temperature, which was probably caused by lack of chlorine ions on active centres.

The effect of calcination temperature on reducibility of 5%Ni-2%Au/Al₃CrO₆+HCl is presented by profile C, D, E. The increase of calcination temperature moved the TPR effect to higher temperature. This behaviour was connected with the sintering of active phase as well as support.

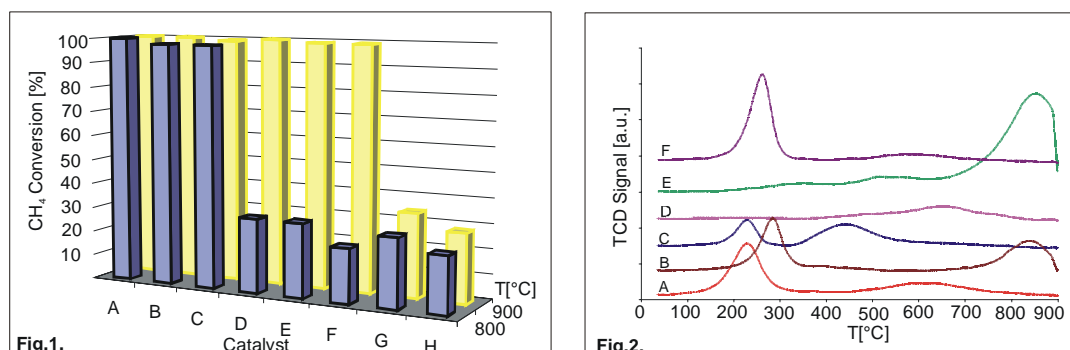


Fig 1. CH₄ conversion at 800 and 900°C for 5%Ni/Al₃CrO₆ (Tcalc = 900°C)-A, 5%Ni-2%Au/Al₃CrO₆ (Tcalc = 400°C)-B, 5%Ni/Al₃CrO₆ (Tcalc = 400°C)-C, 10%Ni-2%Au/Al₃CrO₆ (Tcalc = 400°C)-D, 10%Ni/Al₃CrO₆ (Tcalc = 400°C)-E, 5%Ni-2%Au/Al₃CrO₆ (Tcalc = 900°C)-F, Al₃CrO₆ (Tcalc = 900°C)-G, Al₃CrO₆ (Tcalc = 400°C)-H catalysts.

Fig 2. TPR_H profiles after Tcalc = 400: 5%Ni-2%Au/Al₃CrO₆(HNO₃)-A, 5%Ni-2%Au/Al₃CrO₆(HNO₃)(sequential impr.)-B, 5%Ni-2%Au/Al₃CrO₆(HNO₃)+HCl-C, after Tcalc = 700°C: 5%Ni-2%Au/Al₃CrO₆(HNO₃)+HCl-D, after Tcalc = 900°C: 5%Ni-2%Au/Al₃CrO₆(HNO₃)+HCl-E and 5%Ni-2%Au/Al₃CrO₆(HAuCl₄)

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**PREPARATION EFFECT ON THE STRUCTURE AND CATALYTIC PROPERTIES
OF SULFONIC ACID FUNCTIONALIZED SILICA MESOSTRUCTURED
CELLULAR FOAMS**

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Structural and catalytic properties of sulfonic acid functionalized silica mesostructured cellular foams (MCF) were prepared using different procedures and precursors of sulfonic groups. Catalytic activity tested in the esterification of butanol with acetic acid was found to decrease in the order MCF-et-ph-SO₃H > MCF-ph-SO₃H > MCF-propyl-SO₃H. The catalysts can be used repeatedly without loss of the activity during several cycles. Structural stability of materials after few catalytic cycles appeared to be excellent.

Porous materials functionalized with sulfonic acid groups are promising solid acidic catalyst which attract much attention because they overcome the traditional drawbacks of the use of liquid acids such as difficulties in separation, corrosiveness, formation of toxic wastes and hazards in handling.

In this work we compare the catalytic and structural properties of functionalized silica mesostructured cellular foams (MCFs) obtained by direct incorporation via co-condensation or post-synthesis grafting with three precursors: mercaptopropyltrimethoxysilane, phenyltriethoxysilane, 2-(4-chlorosulfonyl phenyl)ethyltrichlorosilane. The oxidation of thiol to sulfonic groups was carried out using 30 % aqueous solution of H₂O₂. Phenyl groups were sulfonated by 20 % of oleum or by chlorosulfonic acid. Typical structure parameters of pure silica MCFs were: specific surface area (S_{BET}) 600-650 m²/g, mesopore volume (V_p) ca. 2.4 cm³/g, pore diameter of spherical cage (d_s) ca. 24 nm, and of connecting windows (d_w) 12 nm. Samples obtained by grafting well preserved the cage-like structure of the original MCF. Only specific surface area decreased to 350-550 m²/g, whereas pore volume decreased by about 0.5 cm³/g and pore diameters by 2-4 nm. Direct incorporation of functional groups resulted in materials with small mesopores (3-6 nm) and pore volume of about 0.8-1.0 cm³/g.

Thermal stability of SO₃H-MCFs, determined by thermogravimetric method, appeared to increase in the order MCF-propyl-SO₃H < MCF-ph-SO₃H < MCF-et-ph-SO₃H. Decomposition of the first sample begins at about 523 K whereas the last one is stable up to 673 K.

The acidity, measured by two cycles adsorption of ammonia and temperature-programmed desorption of NH_3 , was the highest for MCF-et-ph- SO_3H .

Catalytic activity of materials was tested in esterification of butanol with acetic acid in a stirred batch system at 348 K. The molar ratio of acetic acid:butanol was 1:1. Directly, before using catalysts were dried at 473 K. The amount of catalyst used in the reaction was 1 wt%. Products of reaction were analyzed by a GC HP 5890 Series II with a TCD detector. GC and ^1H NMR analysis confirmed that no by-products were formed.

The highest conversions of acetic acid (ca. 70 %) after 6 h were obtained for samples functionalized with -et-ph- SO_3H groups (Fig. 1A), which is in accord with the measured acidity. The catalyst can be used repeatedly without significant loss of the activity during several catalytic cycles (Fig. 1B). We have found that the amount of the functional groups in the range of 1 or 1.5 mmol/g has no affect on the catalytic activity of materials.

Only a small decrease in surface area was observed after six catalytic cycles, while the values of pore volume and pore size were quite well preserved.

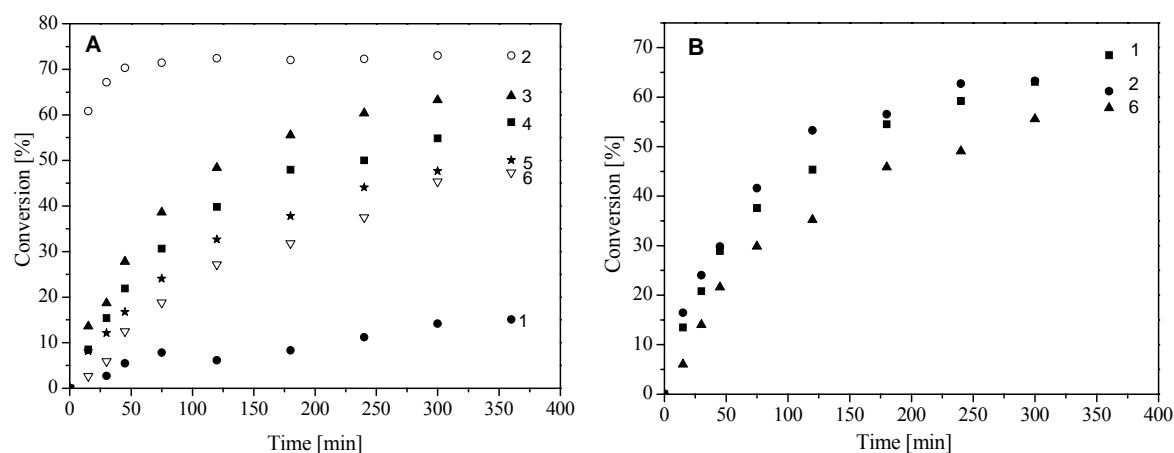


Fig. 1. Conversion of acetic acid vs. time. A: 1 – without catalyst; 2 – H_2SO_4 ; 3 – MCF-et-ph- SO_3H ; 4 – MCF-ph- SO_3H (a); 5 – MCF-ph- SO_3H (b); 6 – MCF-propyl SO_3H ; sulfonation by chlorosulfonic acid (a), oleum (b). B: after 1, 2 and 6 catalytic cycles for MCF-et-ph- SO_3H .

HYDROGENATION OF NAPHTHALENE ON SUPPORTED NOBLE METALS CATALYSTS

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The hydrogenation of naphthalene has been studied on platinum metals supported on oxides and zeolites under hydrogen pressure 0.5-6.0 MPa and temperatures 220-320 °C. The effect of nature and acidity of support, hydrogen pressure, temperature, presence of dibenzothiophene on conversion of naphthalene, yields of tetralin and decalin, activity, selectivity and stability of catalysts has been studied. Pt-Pd/Al₂O₃ catalysts has been developed and tested for diesel fuel with polyaromatics content 50-55 %. After the tests the contents of polyaromatics compounds became 10 %.

The hydrogenation of aromatic molecules of the diesel fraction is of interest both from scientific and industrial point of view. A decrease in the aromatics content of diesel fuel (presented in diesel fuels by phenanthrene, naphthalene, tetralin) will result in an increase in the number of cetane. It is well known that platinum metals catalysts have excellent hydrogenation properties at moderate pressures. But these catalysts are easily poisoned by sulfur-containing compounds in fuels (especially produced from high-sulfurous oils of Kazakhstan). However, it is also well known that complete sulfur removal is not possible. In this aspect it is very important to develop the highly effective, selective and stable against sulfur containing compounds catalysts on the basis of platinum metals. To develop the noble metal sulfur-resistant catalysts it has been proposed the addition of a second noble metal to the catalyst, i.e. bimetallic catalysts, typically Pd–Pt, but also Re, Rh, etc.

The catalysts on the basis of platinum metals were prepared by impregnation of supports with solutions of different salts and organometallic compounds. Alumina, silica, aluminosilicate and several zeolites (ZSM-5, MCM-41 and Y) were used as supports. For the catalysts characterization XRD, TEM, BET, TPD, XPS methods were used. Hydrogenation reaction has been studied at temperatures 220-320 °C and hydrogen pressure 0.5-6.0 MPa.

Naphthalene was investigated for hydrogenation as model compound and diesel fuel as real mixture of polyaromatic hydrocarbons. The products of hydrogenation of naphthalene are - tetralin and (cis- and trans-) decalin and products of ring-opening process - alkylaromatics and alkylcycloalkanes.

The effect of nature and acidity of support, hydrogen pressure, temperature, presence of sulfur containing compound (dibenzothiophene) on conversion of naphthalene, yields of tetralin and decalin, activity, selectivity and stability of used catalysts has been studied. It must be noted that on zeolite supports the yield of products of ring-opening processes much more than on oxide supports. So for ring-opening process mixed supports (oxide+zeolite) were used. Used supports for platinum metals catalysts showed decreasing effect on catalytic activity and sulfur tolerance in following sequence: $\text{Al}_2\text{O}_3+\text{A} > \text{ZSM-5} > \text{Y} > \text{Al}_2\text{O}_3 > \text{Al}_2\text{O}_3\text{-SiO}_2 > \text{MCM-41} > \text{SiO}_2$, where A – oxides of IIA-III A groups elements.

Pt, Pd, Rh and Ru metals were prepared both in monometallic and bimetallic forms.

Monometallic catalysts showed good activity in hydrogenation of aromatics, among them Pt was the best catalyst. Bimetallic catalysts present the better effectiveness in naphthalene conversion and yields of products than monometallic ones. Among bimetallic catalysts Pt-Rh-catalysts showed the highest activity and selectivity for naphthalene hydrogenation but high sulfur tolerance have Pd-Pt catalysts.

Catalysts activity and stability were tested in the presence of dibenzothiophene which was added to aromatic compounds before the reaction (maximal content 100 ppm).

The most active and stable catalyst Pt-Pd/ $\text{Al}_2\text{O}_3+\text{A}$ was tested in reaction of hydrogenation of diesel fuel with polyaromatics content 50-55%. After the tests the contents of polyaromatics compounds became 10%. Besides sulfur content also reduced from 1.5 to 0.1%.

STUDY OF MULTICENTER NATURE OF SUPPORTED ZIEGLER-NATTA TYPE CATALYSTS OVER DATA ON MOLECULAR WEIGHT DISTRIBUTION AND COMPOSITION HETEROGENEITY OF POLYOLEFINES

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One of the most important problems in olefin polymerization over highly active supported Ziegler-Natta (ZN) type catalysts is the regulation of polymer structure and molecular mass distribution (MMD). It is known that supported ZN catalysts are heterogeneous on the reactivity of active centers (multisite catalysts). However the nature of the heterogeneity remains unclear so far.

In this work the heterogeneity of active centers of supported titanium magnesium (TMC) and vanadium-magnesium catalysts (VMC) was studying based on the data on the composition and distribution of polyolefins fractions. Separation of polyethylene (PE) and ethylene- α -olefins copolymers onto narrow fractions ($M_w/M_n=1-2$) was done with new modern equipment (TREF prep.mc2). Based on detailed analysis of polymer narrow fractions by GPC and IR-spectroscopy the quantity and distribution of the different types of active centers in TMC and VMC were established. The parameters affecting on the distribution of active centers in these catalysts have been determined.

**STUDY OF METHANE DEHYDROAROMATIZATION ON IMPREGNATED
Mo/ZSM-5 CATALYSTS IN RECYCLE CONDITIONS**

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The study of methane dehydroaromatization over a series of impregnated Mo/ZSM-5 catalysts is performed in flow and recycle conditions. It is shown that if methane dehydroaromatization is carried out in recycle conditions the benzene formation rate is essentially improved. The oxidative treatment conditions of carbonized Mo/ZSM-5 catalysts providing stable operation of the catalysts under multiple reaction-oxidative treatment cycles have been selected.

During the past few years methane has been often seen as perspective source to produce valuable chemicals [1]. But it is a very stable organic molecule and new approaches of effective activation for profitable utilization of methane are needed. Mo/ZSM-5 catalysts provide high activities in methane dehydroaromatization, which is the alternative way of methane conversion to aromatic hydrocarbons and hydrogen [2].

The methane dehydroaromatization is characterized by a not great single-pass conversion. Earlier we have shown [3], that the maximum catalytic activity (CH_4 conversion $\sim 14\%$) and benzene formation selectivity (70 %) were observed for the samples with 2-5 % Mo. The activity and selectivity were improved when Si/Al in H-ZSM-5 zeolite was changed from 45 to 17. To increase overall methane conversion we performed multiple recycling of CH_4 with separation of aromatic product. It is shown that if the reaction is carried out in recycle conditions the benzene formation rate ($\text{mgC}_6\text{H}_6/\text{gcat}\cdot\text{h}$) is essentially improved. The benzene yield is increased when the circulating factor is increased.

The main problem for methane dehydroaromatization on Mo/ZSM-5 catalysts is the formation of carbonaceous deposits which block the active surface of the catalysts and lead to their fast deactivation. Thus, the dependencies of the concentration and condensation degree (C/H ratio) of the carbonaceous residues on the catalyst synthesis conditions (Mo concentration = 1-10%, Si/Al ratio in the initial H-ZSM-5 = 17-45) and reaction conditions (feed flow rate = 405-1620 h^{-1} , methane concentration = 90-98 %, reaction temperature = 720-780°C) have been investigated. The oxidative treatment conditions of carbonized Mo/ZSM-5 catalysts providing stable operation of the catalysts under multiple reaction-oxidative treatment cycles have been selected.

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**CATALYTIC OXIDATION OF ORGANIC SUBSTANCES BY POLYMER-
ANCHORED AMINO ACID DERIVED TRIDENTATE LIGAND COMPLEXES OF
VO(IV) AND Cu(II)**

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A synthetic strategy was developed for covalently anchored 3-formyl salicylic acid on to chloromethylated polystyrene cross-linked with 5% divinylbenzene. Treatment of this chelating resin with two amino acid, DL-alanine and L-isoleucine form a Schiff-base tridentate ligand (abbreviated as PS-Hfsal-ala and PS-Hsal-isol). The polymeric ligands contain tridentate ONO donor sites were treated with a solution of $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$, $[\text{VO}(\text{acac})_2]$, to form the corresponding metal complexes on the support. The metal complexes abbreviated as PS-[VO(fsal-ala)], PS-[Cu(fsal-ala)], PS-[VO(fsal-isol)] and PS-[Cu(fsal-isol)]. Structure of these immobilized complexes have been established on the basis of scanning electron micrographs, spectroscopic (Infrared and electronic), thermo gravimetric and elemental analyses studies. The catalytic oxidation of p-chloro toluene and cyclohexene were investigated using these complexes as catalyst in presence of eco friendly oxidant H_2O_2 . Reaction conditions have been optimized by considering the concentration of oxidant, amount of catalyst, volume of solvent and temperature. Under optimized condition p-chloro toluene gives a maximum 13.34% conversion with four products, cyclohexene 98.6% conversion with four and two product respectively. In situ neat complexes of all the metal has been prepared to compare the spectral properties and catalytic activities. Recycling studies indicate that the catalyst can be recycled four times without any significant loss in their catalytic potential.

**THE ROLE OF SURFACE VANADIA SPECIES IN BUTANE DEHYDROGENATION
OVER VO_x/Al₂O₃**

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The dehydrogenation of butane has been studied over a series of VO_x/Al₂O₃ catalysts. Through the use of a broad range of techniques the activity and selectivity of the catalysts has been related to vanadium and aluminium species present on the catalyst surface. The catalysts have been investigated throughout the reaction cycle: fresh catalyst, calcination, reaction and regeneration. It is shown that isolated VO_x species are highly efficient with respect to coke formation. An understanding of the role played by different surface species will facilitate the development of catalysts of higher activity and selectivity.

Vanadium catalysts are an important class of industrial materials, showing high selectivity in a number of reactions including the selective dehydrogenation of butane to butenes and butadienes [1, 2]. This reaction is of key industrial importance in, e.g. producing the precursors for synthetic rubber manufacturing. Accordingly a large number of studies have been conducted on this, and related systems. Despite this there remains significant debate and controversy in the literature as to the basis of this selectivity. Our work aims to understand the origin of catalyst activity and selectivity, to both molecular species and to coke formation. In particular the role played by different surface vanadium species and the reaction conditions which result in their formation has been investigated, with the ultimate aim of tailoring catalysts to achieve high activity and 100 % selectivity.

A number of different techniques have been employed through the collaborative effort of three institutions. These include catalytic reactor studies, TEOM, TPO, TGA, TPR and XRD in addition to UV-vis, ¹³C-, ⁵¹V- and ²⁷Al-MAS NMR and Raman spectroscopies, see e.g. [3]. Raman spectroscopy has been used, for the first time, to quantify the vanadium species present in a number of VO_x/Al₂O₃ catalysts differing only by their vanadium loading. In this work catalysts with loadings of 1, 3.5 and 8 wt.% vanadium (1V, 3.5V and 8V respectively) have been studied. Additionally, the Al sites present have been characterised by ²⁷Al MAS and ²⁷Al MQMAS NMR.

Knowledge of the surface VO_x species present allows for correlations to be made with conversion and selectivity data. In particular, isolated VO_x species have been determined to be more effective than polyvanadate species in catalysing coke formation, while polyvanadates are more effective in the formation of butenes. The dehydrogenation reaction, and subsequent regeneration of the catalysts, result in transformations in the nature of the surface VO_x species. These changes have been investigated by techniques including solid-state NMR, Raman and UV-vis spectroscopy. It is seen that under operating conditions vanadium is in a 3+ oxidation state. Figure 1 shows the influence of catalyst loading (and therefore speciation) on selectivity.

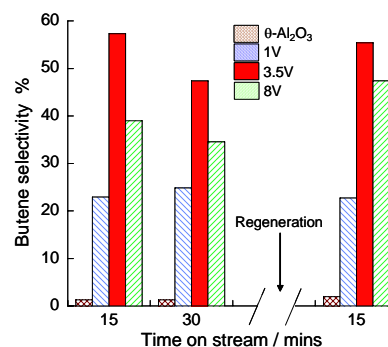


Fig. 1. Butene selectivity as a function of time on stream.

The influence of reaction conditions on selectivity, in particular to coke formation, has also been investigated. ^{13}C CP-MAS NMR studies (figure 2) of catalysts operated at different temperatures indicates the role played by the different surface VO_x species in dictating coke formation as a result of their differing reducibility. Overall, under appropriate conditions,

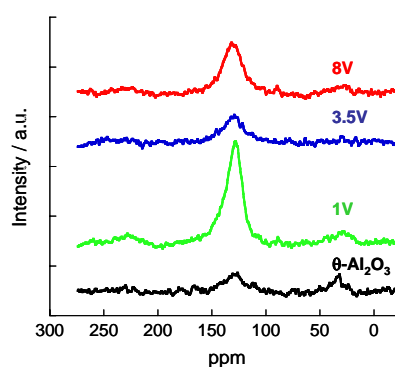


Fig. 2. ^{13}C CP-MAS NMR of coked $\text{VO}_x/\text{Al}_2\text{O}_3$ catalysts.

1V has the greatest tendency to form carbonaceous deposits. Additionally, insights into the mechanism of coke formation have been gained through the application of techniques such as Raman spectroscopy. TPO studies have also provided insight in this area e.g. much of the harmful, i.e. deactivating, coke formed is seen to consist of small molecular-like species which can be removed by oxygen treatment at room temperature. The majority of the polyolefinic/aromatic coke which is detected is located on inactive vanadium or support sites.

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IMMOBILIZATION OF ORGANOMETALLIC CATALYSTS ON ZEOLITES FOR DEVELOPMENT OF FUNCTIONAL POLYMERIZATION-FILLED POLYOLEFINS

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An immobilization of organometallic catalysts on the surface allows one to intensify the process of olefin polymerization, regulate directly the molecular weight characteristics, structure and stereoregular composition of products, and to develop the polymer composites by the monomer polymerization upon the catalytically activated supports. With the use of synthetic (type of ZSM-5) and natural zeolites, the zeolite (H₂O)/AlMe₃/Zr-cene and zeolite (H₂O)/AlEt₂Cl/VOCl₃ catalysts were developed. With application of these catalysts the new polymerization-filled composite materials with functional properties were developed.

An immobilization of organometallic catalysts on the surface allows one to intensify the process of olefin polymerization, regulate directly the molecular weight characteristics, structure and stereoregular composition of products, and to develop the polymer composites with functional properties by the monomer polymerization at the catalytically activated supports. For the preparation of immobilized zirconocene and vanadium catalysts the zeolites – synthetic (type of ZSM-5) and natural, were used as the supports. For fixation of the pre-catalysts (Cp₂ZrCl₂, Et[Ind]₂ZrCl₂ and VOCl₃) the alkylaluminumoxanes synthesized on the support surface were used. Such alkylaluminumoxanes were obtained by an earlier elaborated method [1] in the reaction of the partial hydrolysis of AlMe₃ and AlEt₂Cl with the internal water of zeolites: Na-form of ZSM-5 (Si/Al=42), NH₄ZSM-5 (Si/Al=34), HZSM-5 (Si/Al=17 and 34), NaY (Si/Al=5) and natural zeolites. They form the heterogenized complexes with Zr-cenes which are active in ethylene and propylene polymerization in the absence of other organoaluminium cocatalysts.

The peculiarities of olefins polymerization on zeolite(H₂O) /aluminiumalkyl/pre-catalyst [2,3]:

- The nature of the zeolite support influences the activity of the heterogenized Zr-cene catalysts. The most active catalysts were obtained on NaY and HZSM-5 (Si/Al=17) supports.
- Ethylene and propylene polymerization on the zeolite supported catalysts proceeds with a positive temperature coefficient. The apparent activation energies of ethylene and

propylene polymerization on zeolite (H₂O)/AlMe₃/Et[Ind]₂ZrCl₂ catalyst were found to be 32 and 48 kJ/mol respectively; in the case of ethylene polymerization with zeolite (H₂O)/AlMe₃/Cp₂ZrCl₂ – 20 kJ/mol; with vanadium catalysts - 40±2 kJ/mol.

- The specific activity of the zeolite supported Zr-cene catalyst in olefin polymerization versus the content of the Zr-cene shows a maximum.
- The reaction order of ethylene and propylene polymerization with respect to the concentration of the monomer changes from 2 to 1 as the concentration of the monomer in the reaction zone increases.

The developed immobilized catalysts were applied for the creation of filled polymer composites with method of polymerization filling. The method has no alternative for obtaining the composites with ultrahighmolecular polymer matrix and ultrahighfilled polymers. On the base of UHMWPE and natural zeolites, the composite material with high wear resistance, low coefficient of friction and high impact was synthesized. The material can be used in elements working in the conditions of friction under high load [4].

For solution of ecological problems, connected with the cleaning of water from nuclides, heavy metals, ammonia and petrochemical products, the organomineral sorbent – ultrahighfilled composite based on the dust fractions of natural zeolite (zeolite content of 95-97 wt %) and UHMWPE, was developed. Sorbent can work as the ion-exchange filters in static and dynamic conditions [5].

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**SYNTHESIS AND STUDY OF CATALYSTS FOR OLEFIN POLYMERIZATION
PREPARED WITH USE OF THE COMPOUNDS OF TITANIUM IN THE VARIOUS
OXIDATION STATES AND MgCl₂–CONTAINING SUPPORT**

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Nowadays an actual task is search of modification methods and new compositions of the supported Ziegler-type catalysts, allowing more widely and precisely to control molecular structure of polymers.

In this work we have investigated the influence of oxidation state of titanium and the effect of alkoxy -groups introduction in the composition of titanium compounds on catalytic properties of MgCl₂-supported catalysts in ethylene polymerization and ethylene - α - olefin copolymerization.

For preparation of supported titanium - magnesium catalysts (TMC) of various compositions preliminary soluble compounds of the titanium in various oxidation states: η^6 -arene-Ti²⁺Al₂Cl₈, Ti³⁺Cl₃• nDBE , Ti⁴⁺(OEt)_nCl_{4-n} have been synthesized and analysed by EPR and C¹³-NMR methods.

TMC have been prepared by adsorption of these compounds on various magnesium – containing supports. The data on oxidation states of titanium in these catalysts after interaction with the carrier and aluminiumorganic cocatalysts have been obtained with the use EPR and ESXA methods.

These catalysts are investigated in homopolymerization of ethylene and copolymerization of ethylene with α - olefin; the data on the effect of titanium compounds composition and Mg-containing support composition on activity, regulation of molecular weight of PE by hydrogen, copolymerization ability, molecular- mass distribution of polymers are obtained.

**THE EFFECT OF THE SUPPORT ON THE PERFORMANCE OF Co/Al₂O₃
CATALYST IN FISCHER-TROPSCH SYNTHESIS**

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The Co/Al₂O₃ catalysts of Fischer-Tropsch synthesis are efficient in producing heavy hydrocarbons. Catalytic properties of such systems depend on the nature of the precursor (gibbsite, boehmite, bayerite) used to produce the support.

To examine the effect of the nature of the aluminum compound on the performance of the Co/Al₂O₃ catalyst, the gibbsite, boehmite and bayerite based samples (30%Co/Al₂O₃) were tested in Fischer-Tropsch synthesis. The catalytic results were compared with phase composition of Al₂O₃ support as indicated by the XRD study.

The Al₂O₃ support was prepared by calcining aluminum hydroxide (gibbsite, boehmite, bayerite). The 30%Co/Al₂O₃ catalysts were prepared by triple impregnation of the support by Co(NO₃)₂·6H₂O water solution. Hydrocarbon synthesis was carried out in a fixed-bed reactor at atmospheric pressure. Before synthesis all samples were pre-reduced in hydrogen flow.

The XRD study showed that the nature of aluminum hydroxide (gibbsite, boehmite, bayerite) has a marked effect on the sample phase composition. In particular, boehmite based samples contain much more γ -Al₂O₃, than gibbsite based support, in which most of alumina occurs as amorphous phase. Results obtained by XRD correlate with catalytic data described below.

The catalytic tests confirmed that aluminum hydroxide structure in 30%Co/Al₂O₃ catalyst support influences the yield of C₅₊ hydrocarbons. The C₅₊ hydrocarbons yield decreases in a row: gibbsite (105 g/m³) > boehmite (96 g/m³) > bayerite (86 g/m³). The C₅₊ hydrocarbons selectivity varied insignificantly (85-90 %). All samples are characterized by lower methane selectivity (4-7 %). SF alpha values for all samples were 0.95-0.97. Fractional composition of liquid hydrocarbons depends on the aluminum precursor nature. For the gibbsite-based catalyst the contribution from C₁₉₊ fraction was essentially higher than in the case of the boehmite and bayerite based samples.

Hence, the nature of aluminum hydroxide in 30%Co/Al₂O₃ catalyst influences both the activity and selectivity of the catalyst in the hydrocarbon synthesis from CO and H₂. The

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highest C₅₊ yield (105g/m³) at the lowest methane selectivity (4%) was obtained for the catalyst prepared from gibbsite. In addition, all Al₂O₃ based samples are characterized by high selectivity to target products and low methane formation.

**THE ACIDIC CATALYSIS IN REACTION OF 2,3-DIOXOPYRROLO
[2,1-a]ISOQUINOLINE'S DERIVATIVES WITH N-NUCLEOPHILES**

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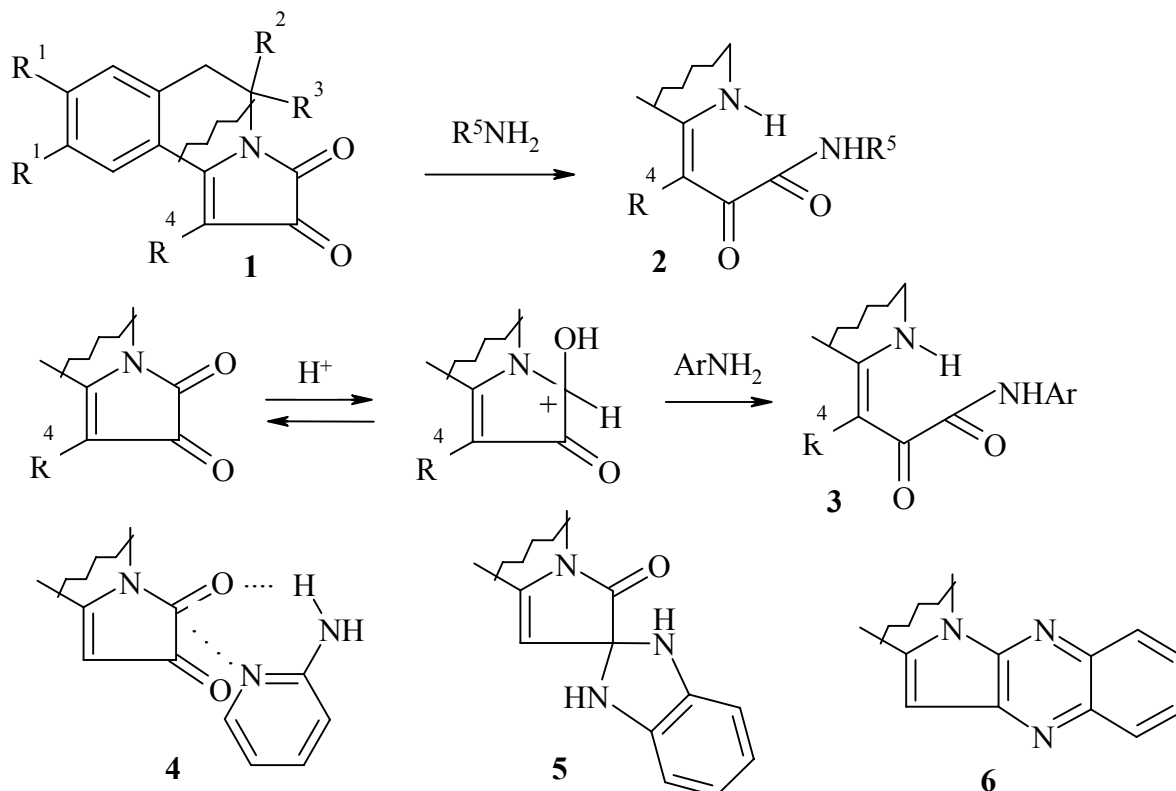
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It has been shown that way for the reaction between 2,3-dioxopyrrolo[2,1-a]isoquinolines with N-nucleophiles depends on nucleophile's structure and presence of acidic catalyst. Thus, ammonia, aliphatic amines and nitrogen-containing α -heterylamines react in absence of acids. The interaction with less active nucleophiles such as aromatic amines needs refluxing in AcOH.

The reaction with o-phenylenediamine in presence of HCl yields benzimidazoline's spiro-derivatives meanwhile products of this reaction in AcOH are condensed quinoxalines. Nucleophiles such as hydrazides and thiosemicarbazide react without cleavage of pyrrole's ring even in presence of acids.

The acidic catalysis in chemistry of carbonyl compounds is of great significance. The reaction of compounds **1** ($R^1 = H$; $R^2, R^3 = \text{Alk}$, $R^4 = H, \text{Alk}, \text{COAr}, \text{CON} = \text{etc.}$) with N-nucleophiles usually proceeds with opening of pyrrole's cycle forming amides **2**. The conditions of reaction depends on nucleophile's structure and presence of acidic catalyst. For



example, ammonia and aliphatic amines react in absence of acids forming amides **2**. The interaction with less active nucleophiles such as aromatic amines leading to amides **3** needs

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refluxing in glacial acetic acid, so this reaction proceeds via cationic intermediate. Nitrogen-containing α -heterylamines (α -aminopyridine, α -aminothiazole etc.) reacts in absence of catalyst which may be explained by forming of cyclic intermediate **4**.

The reaction with o-phenylenediamine in presence of HCl yields benzimidazoline's spiro-derivatives **5** meanwhile products of this reaction in glacial acetic acid are condensed quinoxalines **6**. Nucleophiles such as hydrazides and thiosemicarbazide react without cleavage of pyrrole's ring even in presence of acids. This fact probably may be explained by other molecule's orientation and other energy of activation consequently.

HYDROGEN-RICH GAS PURIFICATION FROM CARBON MONOOXIDE

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In order to provide a wide application of the proton exchange membrane fuel cells (PEMFC) technology, reduce cost and improve characteristics of PEMFC-based power plants, it is necessary to create a compact and economic fuel processor for deep cleaning (to 20 ppm) of converted fuel from carbon monoxide. Fuel processor comprises fuel reformer, water gas shift reactors (HTS and LTS WGS) and reactor of fine CO removal. The purpose of our study was to increase the efficiency of the last two steps. We suggest to apply a reactor with optimal temperature profile in the catalyst's bed for one stage WGS and preferential CO methanation process for fine cleaning up of fuel gas from CO. The obstacle of preferential CO hydrogenation consists in the presence of about 20 vol. % of CO₂ along with 1 vol. % of CO.

Highly effective (active and stable in a wide temperature range, 380-210 °C) Cu- containing catalyst for WGS has been developed. With the aim to provide the temperature control in the catalyst's layer the thermal conductive catalyst plates (TCP) based on the developed catalyst for compact WGS reactors have been prepared and studied. High thermal conductivity of 2.5–5 W(m K)⁻¹ can be achieved, while the effective catalytic activity of TCP is even higher than that of the commercial size catalyst grains. In the TCP reactor WGS the fuel gas containing 12 % of CO can be processed in one stage at GHSV of above 6000 h⁻¹ down to 1 % of residual CO. The TCP shape and the way of arrangement have been optimized.

Highly active and selective in kinetic field nickel-containing catalyst NM-1 was developed for CO preferential methanation. Special form - permeable composite material (PCM) - has been prepared on the base of NM-1 catalyst (PCM-NM-1), providing the fine fuel gas purification to CO concentration 10-20 ppm in the wide range of GHSV from 6000 to 17000 h⁻¹ with the selectivity of above 0.5.

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**OPTIMIZATION OF SYNTHESIS PROCEDURE OF AEROGEL VO_x/MgO
CATALYST FOR OXIDATIVE DEHYDROGENATION OF LIGHT
HYDROCARBONS**

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The modified aerogel technology for the synthesis of VO_x/MgO catalyst has been developed. Surface area of aerogel V-Mg-hydroxide samples was found to be as high as 1000-1100 m²/g, regardless to concentration of vanadium introduced. It was suggested that the high-dispersed V-component is evenly distributed on surface of MgO as amorphous vanadate. Catalytic tests in ODHP reaction revealed that the aerogel VO_x/MgO samples are 1.5-2 times more active as compared with similar catalysts prepared by mechanical mixing and impregnation methods.

The selective oxidation of light hydrocarbons to valuable intermediates via catalytic oxidative dehydrogenation (ODH) is of great interest for petrochemical industry and has been studied extensively. The ODH reaction is believed proceed by mechanism in which adsorbed alkane reacts with lattice oxygen and the reduced oxide interacts with adsorbed, dissociated oxygen. VO_x/MgO system is well known as an efficient catalyst for oxidative dehydrogenation of short chain alkanes (ethane, propane, butane). The most widely used methods for preparation of VO_x/MgO catalysts are coprecipitation of V- and Mg-salts and impregnation of MgO support with diverse V-precursors. For impregnation method, the rather high butadiene-1,3 yields were obtained for VO_x species supported on nanocrystalline aerogel MgO-AP (Autoclave Prepared) support as compared with conventional metal oxides [1, 2].

In the present work, the new approach for the synthesis of nanoscale aerogel VO_x/MgO catalysts has been suggested. In short it includes formation of Mg(OCH₃)₂ via reaction of Mg with methanol, dilution with toluene, addition of vanadium isopropoxide, gel formation by hydrolysis, supercritical drying of resultant suspension, and conversion of aerogel V-Mg-hydroxide into VO_x/MgO via heat treatment under vacuum at 500 °C overnight and ultimate calcination in air at 550 °C for several hours. It was found that the developed aerogel technology allowed us to synthesize the mixed V-Mg-hydroxides with a surface area as high as 1000-1300 m²/g. The interim stage of vacuum dehydration of V-Mg-hydroxides was applied to convert the aerogel V-Mg-hydroxides into VO_x/MgO catalysts with a final surface area of about 350 m²/g, which is superior to analogues found in literature [1-3].

During the stage of combined hydrolysis of V-Mg-alkoxides it was found that the gelation time increases as V loading in sample grows. At V concentrations > 15 wt.% the gelation does not occur. From the other hand, in case of adding vanadium isopropoxide to a as-formed $\text{Mg}(\text{OH})_2$ suspension, it was possible to obtain V-Mg-hydroxide gel within the wide range of V concentrations. Drying of these V-Mg-gels in supercritical conditions resulted in formation of aerogel V-Mg-hydroxides with a surface area of 1000-1100 m^2/g , regardless to concentration of introduced vanadium. Synthesized aerogel V-Mg-hydroxides are characterized by quite narrow pore size distribution, with a maximum near 4 nm. The direct heat treatment of V-Mg-hydroxides in the temperature programmed regime in air leads to formation of aerogel VO_x/MgO catalysts with surface area of 350-430 m^2/g , even if the ordinary used vacuum dehydration step is just skipped.

Synthesized aerogel VO_x/MgO samples were studied by the set of physico-chemical methods. The absence of V_2O_5 phase was suggested for all examined samples. By XRD and FTIR data, the formation of poorly crystallized orthovanadate phase was assumed, although XANES and Raman-spectroscopy data do not evidence this assumption. As follows from TEM images, the aerogel VO_x/MgO samples are characterized by quite uniform distribution of active component throughout the MgO support. According to SEM data, the secondary structure of aerogel V-Mg-hydroxides and VO_x/MgO samples is represented by 2-5 μm sized platelets with a thickness of 0.1-0.4 μm .

Aerogel VO_x/MgO catalysts were studied in comparative ODHP tests along with reference samples prepared on the basis of nanoscale MgO-AP support by mechanical mixing and impregnation methods. At all other parameters kept the same, the aerogel VO_x/MgO samples turned out to be significantly more active as compared with similar catalysts prepared by conventional ways. It was also shown that the replacement of O_2 by N_2O in the ODHP reaction gives the considerable benefit in selectivity towards C_3H_6 , however the yield of propylene does not change. This is as well accompanied with more intensive process of coke formation on the surface of aerogel VO_x/MgO catalysts.

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SIGNIFICANT ENHANCEMENT OF PROPENE SELECTIVITY IN PROPANE DEHYDROGENATION ON Pt/ γ -Al₂O₃ BY ADDITION OF TIN

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We report propane dehydrogenation on Pt/ γ -Al₂O₃ catalyst containing various amounts of tin at different H₂/propane ratios and temperatures. In all cases propene selectivity enhances with the tin content. A sharp increase in the selectivity at 0.25 and 0.70 wt% tin contents are observed at H₂/propane ratios of 0.8 and 1.5, respectively. In most cases the propane dehydrogenation activity decreases with the tin content, however, a maximum activity is observed at tin content of 0.5 wt% for H₂/propane molar ratio of 0.4.

Introduction

The propene produced in steam crackers or FCC units alone does not satisfy the growing demands for propene. Therefore, there is a great interest in catalytic dehydrogenation of propane to propene [1]. The dehydrogenation is carried out at high temperature and low pressure to overcome thermodynamic limitation. At such conditions coke is produced extensively leading to deactivation of the catalyst [2]. Nobel metals, especially platinum, are key ingredients in most dehydrogenation catalysts. Usually a second metal (Sn, Ag, Ge, Pb) and/or alkali metals are incorporated into the catalysts, to decrease the deactivation rate and/or enhance the propene selectivity. Supported Pt–Sn catalysts have shown lower deactivation rate and high selectivity for dehydrogenation reactions [3].

Experimental

γ -Al₂O₃ with 130 m²/g area (Axen) was sequentially impregnated with aqueous solutions of H₂PtCl₆ and SnCl₂, and then dried and calcined at 550°C for 3 h. The catalysts were characterized by ICP elemental analysis, BET area measurement, TPR and TPD. 1.0 g of the catalyst was reduced in situ in a fixed-bed quartz tube reactor of ID = 12 mm. Propane and H₂ flows adjusted by mass-flow controllers were mixed and passed over the catalyst bed at different temperatures. The reactor effluents were analyzed on an online gas chromatograph (Agilent 6890N) for C₁-C₅ saturated and unsaturated hydrocarbons.

Results and Discussions

Fig. 1a and 1b, respectively, show the propane conversion and propene selectivity with respect to tin contents of the Pt/ γ -Al₂O₃ catalysts at different H₂/propane molar ratios. At

higher H_2 /propane ratios of 0.8 and 1.5 generally the propane conversion decreases with the tin content. However, at the ratio of 0.4, the propane conversion shows a maximum value at tin content of 0.5 wt%. Fig. 1b indicates that in all cases the propene selectivity enhances with the tin content. A sharp increase in the selectivity for H_2 /propane ratio of 0.8 is observed, when 0.25 wt% tin is added to $Pt/\gamma-Al_2O_3$ catalyst. The sharp selectivity enhancement for H_2 /propane ratio of 1.5 is moved to the tin content of about 0.5-0.75 wt%. It is proposed that a charge transfer from atomic orbitals of platinum to that of tin may weaken the interaction of platinum with hydrogen favoring the dehydrogenation reactions [4].

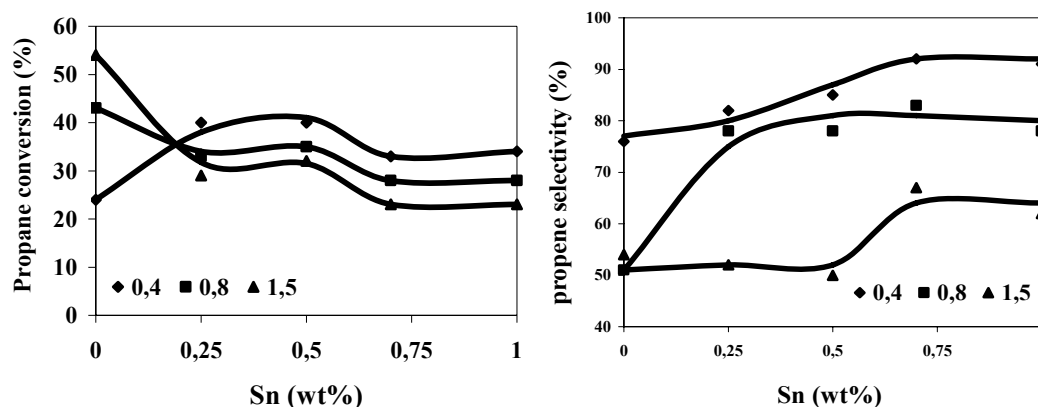


FIG. 1a and 1b: Propane conversions and propene selectivities as a function of tin contents of $Pt/\gamma-Al_2O_3$ catalyst at different H_2 /propane molar ratios for propane dehydrogenation at 575°C.

Fig. 2a and 2b respectively represent the variation of propane conversion and propene selectivity with temperature at different tin contents of the $Pt/\gamma-Al_2O_3$ catalyst. $Pt/\gamma-Al_2O_3$ catalyst with no tin shows the highest propane conversions at low temperatures and lowest propene selectivities in all cases. Propene selectivity sharply enhances when 0.25 wt% tin is added to the catalyst. Further addition of tin gradually increases the selectivity.

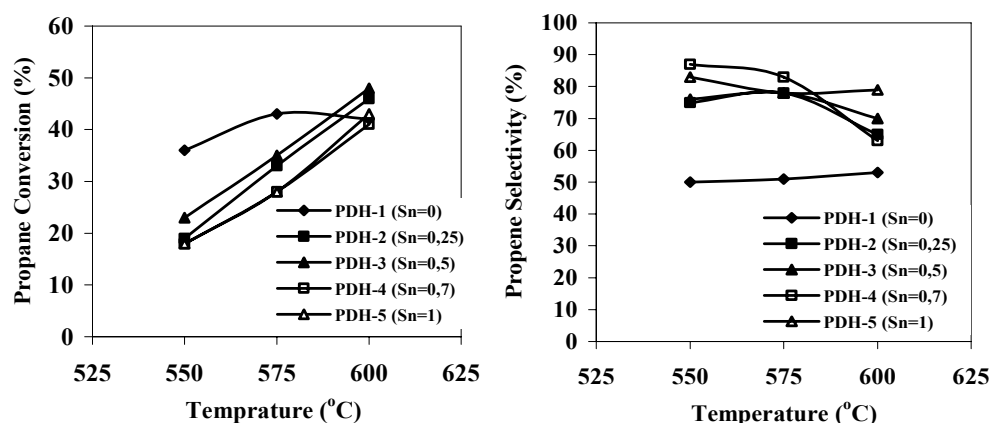


FIG. 2a and 2b: Propane conversion and propene selectivity as a function of temperature at different tin contents. The H_2 /propane molar ratio is 0.8.

Conclusions

In propane dehydrogenation on Pt/Al_2O_3 , propene selectivity sharply enhances when 0.25 wt% tin is added to the catalyst. Further addition of tin gradually increases the selectivity. In

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most cases the propane dehydrogenation activity decreases with the catalysts tin content, however, a maximum activity is observed at tin content of 0.5 wt% for H₂/propane molar ratio of 0.4.

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NANOSTRUCTURED MATERIALS BASED ON ZIRCONIA

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Nanostructured materials based on zirconium oxide are of great interest due to variety of their polymorphism, chemical and physical stability, and ion conductivity. That determines possible applications of those materials as catalysts for red-ox processes, particularly, for fuel cell applications. Properties of zirconia-based materials could be regulated by incorporating small quantities of cations with charge 2+ or 3+. Particularly, that stabilizes low temperature cubic or tetragonal phases which are characterized by high dispersity. We investigated zirconium oxides obtained by two methods:

- Treatment of the ittrium modified zirconium hydroxide by the pulse-microwave followed by calcination at different temperatures (300-1000 °C)
- Hydrothermal synthesis of zirconia followed by calcination at temperatures up to 1000 C.

Obtained oxides were characterized by transition electron microscopy (TEM), X-ray diffraction (XRD), small-angle X-ray scattering (SAX), BET, and vacuum thermogravimetry of NH₃ and CO₂ with stepwise heating regime.

For ittrium stabilized ZrO₂ it was shown that increasing calcination temperature up to 400 C leads to crystallization of non-sintered particles of tetragonal phase. Further increase of temperature causes formation of nanostructured systems.

A mild calcination at 500 °C of zirconia, obtained by hydrothermal synthesis, leads to formation of pure tetragonal phase. At further temperature increasing up to 600-650 °C the (111) “cubic” reflection reappears in XRD patterns. Modeling of XRD patterns revealed that this phenomenon could be explained by polysynthetic (001) twinning.

Functional properties of active centres of nanosize zirconia samples were characterized in the CO oxidation. It was found, that nanosized zirconia obtained at 1000°C demonstrates the highest activity in the CO oxidation. Obviously this effect is related to structural properties of zirconia, formed under the microwave treatment.

**SYNTHESIS OF ALCOHOLATES OF METALS – PRECURSORS OF CARRIERS
FOR HETEROGENEOUS CATALYSTS**

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Methods of sol-gel technology were used for the synthesis of oxides of Ce, La, Al, Zr, Mg, Cu, Co, Ni, Ba, Cr, Y. We have studied chemical and phase compositions of the derived products and their textured characteristics. We compared synthesized samples with their market analogues and studied potential application for the production of heterogeneous catalysts.

Using of alcoholates of some metals as precursors of carriers for heterogeneous catalysts is rated today as the promising trend in the catalyst production.

The present work is providing the physicochemical properties of individual and compound oxides of Ce, La, Al, Zr, Mg, Cu, Co, Ni, Ba, Cr, Y. As initial re-agents for receiving of alcoholates of metals served carbonates, acetates and nitrates, which were exposed to interaction with separate alcohols and with their mixtures: isopropyl, n-butyl, octyl, isoamyl, etc. With the hydrolysis of individual or compound alcoholate of alcoholic solutions, were accordingly derived individual or compound oxidation systems, which were dried and calcinated according to the given mode.

We studied chemical and phase compositions, specific surface with the low-temperature adsorption method (BET), porosity of synthesized samples, dimensional particle spectrum.

For the study of thermo stability, the oxidation systems were subjected to thermal shock (at 1100 °C/4 hours) and the subsequent research of the specific surface and porosity.

We carried out the comparative analysis of features of synthesized material with their market analogue. The results indicate the future promising potential application of sol-gel method for deriving of oxidation systems as carriers of heterogeneous catalyst.

**ELECTROCATALYTIC REDUCTION OF NITROBENZOIC ACID ON
CATALYSTS – METALS OF s- AND d-GROUPS**

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The researches of electrochemical and electrocatalytic reduction process of nitrobenzoic acid to aminobenzoic one on the cathode activated by skeletal and electrochemical powders catalysts – the metals of s-(Cu, Zn) and d-groups (Ni, Fe, Co) were carried out.

Due to the wide practical application of aminobenzoic acid (in quality components of aromatic substances, dyes and medicinal preparations) much attention is given to development of the most effective methods of its synthesis. The aminobenzoic acid is a product of hydrogenation of nitrobenzoic acid (OH-C₆H₅-NO₂, **1**).

The experiments on reduction of *para*-isomer of **1** were conducted in electrocatalytic cell on the copper cathode (surface area 0,05 m²) activated by skeletal and electrochemical powders catalysts (0,25 g) – the d- and s-metals (Ni, Zn, Cu, Co, Fe); at a current density of 2 kA/m², temperature 30 °C. The anolyte quality of 20 wt % solution of NaOH (60 ml), catholyte of 2 wt % solution of NaOH (60 ml), the quantity of **1** - 1,49 g (0,0089 mol) calculated on the Faradey law by absorption 600 ml of hydrogen were used. The results are given in Table.

Table. Comparative results of reduction of nitrobenzoic acid on various catalysts

Catalyst	W _{av.} , ml H ₂ /min	Consumption of H ₂ , %	η, %
Without the catalyst	5,48	79,8	85,4
Ni sk.	6,6	100	94,5
Cu sk.	6,3	100	90,4
Zn sk.	6,75	100	97,8
Co sk.	6,35	100	87,9
Fe sk.	5,5	90,8	79,8
Cu el.p.	6,6	97,2	98
Zn el.p.	6,6	100	97,1

W_{av.} – the average rate of process (50 % of absorption of hydrogen pays off for the period);

η – operating ratio of hydrogen.

According to the data electrochemical reduction proceeds not up to the end and with lower rate and operating ratio of hydrogen, than in processes with the use of the catalysts. Compare the activity of skeletal catalysts, the process of hydrogenation on skeletal iron proceeds with the least intensity, and with greatest - on Zn and Ni catalysts. As a whole, the rate of electrocatalytic reduction of **1** grows in a line of skeletal catalysts: Fe < Cu < Co < Ni < Zn. Among the used electrochemical powder catalysts zinc shows the larger activity, than copper. For electrocatalytic reduction of **1** it can be recommended the Reney nickel, which is convenient in employment and shows high catalytic activity.

**HIGH-TEMPERATURE XRD INVESTIGATIONS OF $\text{La}^{3+}_{1-x}\text{Sr}^{2+}_x\text{FeO}_{3-\delta}$
PEROVSKITES**

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Samples under study were prepared by mechanochemical method with prior mechactivation of mixture of simple oxides and following annealing. Morphotropic phase transition from orthorhombic to cubic modification for $\text{La}^{3+}_{1-x}\text{Sr}^{2+}_x\text{FeO}_{3-\delta}$ ($0 < x < 1$) solid solutions is observed. Two phases compositions from region of morphotropic phase transition (RMPT) $x=0.3, 0.4$ are monophasic at high temperature. For composition with maximal strontium content $x=0.8$ at high temperature in vacuum disintegration is observed.

Complex oxides with perovskite-related structures imply a huge family of chemical compounds with ABO_3 chemical formulae. Although exhibiting relatively simple basic structures, they show fascinating diversity at physical and chemical properties revealing different applications as magnetic and electronic devices and adsorbents encapsulating radioactive wastes [1]. Perovskites of different compositions have been intensively investigated also as promising for catalysts for the ecologically interesting chemical processes [2] and materials for novel technologies for the energy conversion [3].

It is well-known that structural modification of perovskite-type solid solution depends on oxygen content. Therefore increasing of temperature can result in structural transformation due to losing of oxygen and following vacancies ordering. However, such structural transformations are often reversible and samples return into initial state after cooling down in air. So, the main purpose of this research is an in situ investigation of perovskite-related solid solutions, especially, samples from RMPT, in region of high temperatures.

$\text{La}^{3+}_{1-x}\text{Sr}^{2+}_x\text{FeO}_{3-\delta}$ samples were synthesized from simple oxides (La_2O_3 , SrO , Fe_2O_3) by mechanochemical method including prior mechanical activation of mixture of reagents for 3 minutes and subsequent annealing during 10 h at 1200 °C.

Main experiments were carried out using synchrotron radiation station in channel with high resolution ($\lambda \sim 1.5407 \text{ \AA}$) and in channel equipped with high temperature chamber ($\lambda \sim 0.368 \text{ \AA}$). The samples were also investigated by X-ray diffractometer D8 (Bruker, Germany)

with CuK α radiation ($\lambda \sim 1.5418 \text{ \AA}$). Vacuum high temperature experiments were carried out using HTK-16 (Anton Paar, Austria) XRD chamber.

According XRD data obtained at room temperature for this series of samples morphotropic phase transition from orthorhombic ($0 \leq x < 0.3$) to cubic ($0.4 < x < 1$) modification is observed. Composition $x = 1$ is two-phase with perovskite and brownmillerite phases. According to XRD data for compositions $x=0.3, 0.4$ strong broadening of diffraction peaks is observed. Using high resolution synchrotron diffraction data for these samples it was observed splitting of diffraction peaks. These samples are two-phase with orthorhombic and cubic perovskite modifications. High resolution electron microscopy data revealed microdomain structure for used samples.

Heating in air of these samples ($x=0.3, x=0.4$) leads to narrowing of diffraction peaks and disappearing of orthorhombic modification peaks according to synchrotron diffraction data. Hence, samples are monophases at high temperature. The temperature of structural transformation decreases with increasing of strontium content. Disappearing of orthorhombic peaks at high temperatures for compositions $x=0.3, x=0.4$ is determined by polymorphous phase transformation from orthorhombic to cubic modification probably due to formation of oxygen vacancies. Hence one can make a conclusion that two phase composition and a disordered microdomain structure of samples from RMPT detected at room temperature is a result of disintegration of a high temperature homogeneous solid solution under cooling down.

Heating in air of sample with composition $x \sim 0.8$ does not lead to structural transformations. Both at room temperature and at $1200 \text{ }^\circ\text{C}$ the structure is cubic. During heating in vacuum the monophase solid solution transforms into phase probably with lower oxygen content. Cooling down in vacuum does not change the structure and results in formation of near-surface disordered and regular perovskite phases according to HREM data. Heating of this transformed sample in air leads to structural changes into initial state according to XRD diffraction data. In such a way, for samples with strontium content 0.3, 0.4 and 0.8 it is obvious that oxygen plays an important role in structure stabilization. Transformation of samples with composition $x=0.8$ at high temperature in vacuum needs following investigations.

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**ACTIVITY AND MECHANISM CHANGES FOR UNSATURATED HYDROCARBONS
HYDROGENATION AT THE PRESENCE OF Ni CATALYSTS DUE TO CARRIER
MODIFYING BY HETEROPOLYCOMPOUNDS OF TUNGSTEN, THE
OPPORTUNITIES OF THE NEW CONTACTS USE IN INDUSTRY**

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It was earlier shown [1-3], that low-percentage Ni-catalysts (2-6 mass. % Ni) on alumina, modified by heteropolycompounds of tungsten HPC (W), have the abnormal high activity (on 1 g of Ni) and selectivity in the reactions of unsaturated and aromatic hydrocarbons hydrogenation and also in the hydrogenation of ketenes and aldehydes.

It is established, that at a variation of the carrier porous structure or the Ni/HPC ratio and also of the HPC nature in the modified Ni catalysts changes their hydrogenation activity and selectivity flexibly [4,5].

In the present work it is shown how it is possible to reach the activity optimization for the new modified Ni catalysts in the hydrogenation of olefins (heptene, nonene, i-butene) and aromatic hydrocarbons (benzene, toluene).

We have carried out the experiments to establish, how the alteration of the modifier HPC structure at the molecular level (namely – the transition from simple HPC(W) to mixed HPC (Mo, W) or substitution of another HPC), has influenced at the activity and selectivity of Ni-catalysts and has created the new active surface of them in step.

This way is of use for olefins hydrogenation and the best modified Ni- catalysts of this type with special HPC(Mo, W) have the optimal activity like Pd – Ni-catalysts or more of its. The interest fact is that additional introduction Pd (< 0.03 %) at the HPC modified Ni catalyst does not influence in any way at the hydrogenation activity of these samples.

In case of the aromatics hydrogenation the insignificant additives of Pd to the modified Ni-catalyst provide to creation of more high active samples, though the variation of the HPC structure also results in active Ni- catalysts differing by mechanism proceeding from the olefins hydrogenation.

The properties of the catalysts with various modifiers and model samples surface were investigated with the help of some physicochemical methods (method of FTIR-spectroscopy on spectrometer Perkin Elmer 2000, method of PMR spectroscopy on spectrometer WL-112 (Varian), DTA, TGA etc.).

The analysis of the received data has shown that HPC on alumina drifting is accompanied by its interaction of OH-groups with H₂O molecules included HPC with additional connections formation and change of carrier acidity and formed the new active surface. Introduction of Ni results in the deformation of HPC on catalyst surface and Ni reduction degree strongly depends from surface properties and HPC nature.

So far as the modern technologies require more effective and less expensive hydrogenation catalysts the new modified Ni-catalysts creation are on the right lines. Application of these contacts for motor fuels ecological and service characteristics improvement by hydrofining of different origin raw hydrocarbons (hydrodearomatization, hydrostabilization) is demonstrated their efficiency/5/.

The studies of the modified Ni catalysts with content 3-4 mass. % Ni showed that their catalytic activity is essentially more than industry Ni-Cr-catalysts with 50-60 mass. % Ni in the entire range of relative volume velocities and approximately corresponds to very expensive Pt- and Pd-containing catalysts.

Further elaboration of new modified Ni hydrogenation catalysts and their application to hydrofining processes are in progress, but their activity optimization and the creation of new types of that catalysts have to be designed only by development of novel scientific approaches to the preparation of supported catalysts and by the use of new physicochemical techniques of their investigation.

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OLEFINS HOMO- AND COPOLYMERIZATION IN THE MEDIUM OF LIQUID PROPYLENE WITH METALLOCENE CATALYTIC SYSTEMS

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Propylene homo- and copolymerization with ethylene and higher α -olefins with high effective metallocene catalysts with different type of symmetry were studied. Isotactic, syndiotactic, hemiisotactic and stereoblock PP were produced. Metallocene catalysts produced copolymers propylene-ethylene with a tendency to alternating or random comonomer incorporation in the polymer chain. The distinct feature of propylene copolymerization with higher α -olefins on isospecific metallocene catalytic systems in propylene medium – the proximity of comonomer relative reactivity ratios ($r_1 \sim r_2 \sim 1$) that indicates ideal nature of copolymerization processes in studied conditions. Polypropylene modification with insignificant comonomer content allows to change mechanical properties of copolymers dramatically.

The highly effective homogeneous metallocene (MC) catalytic systems opened new opportunities for synthesis of different polymer materials with unique properties. New catalysts have allowed to control microstructure, molecular weight characteristics and synthesizing almost of all kinds of stereoregular polymers. Metallocene systems have a single active centers and allow to obtain copolymers with uniform distribution of comonomers.

The number of MC differ in symmetry type (C_1 , C_2 and C_s), the nature of bridge and ligands were studied in processes of propylene polymerization and propylene and α -olefins (C_2 - C_8) copolymerization in a medium of liquid propylene. Homo- and copolymerization in bulk of propylene allows obtaining metallocene polymers with ultimately high yields and high molecular weights.

Polymerization was carried at 30-80 °C with the use of different cocatalysts - polymethylalumoxane (MAO) or with partial replace of MAO by (*iso*- C_4H_9)₃Al. The influence of the metallocene structures, the polymerization temperature, the comonomer nature on the activity, molecular weight characteristics, stereoregularity, thermophysical and mechanical properties of polymers will be regarded.

The stereospecificity of polymer produced with MC is closely related to the symmetry of the ligands attached to the active transition metal. MC catalytic systems allowed synthesizing of all kinds of PP stereoisomers: isotactic, syndiotactic, hemiisotactic and stereoblock PP with high activity. Depending on the type of a metallocene used one may produce polymers from amorphous structure to the samples that have up to 85 % crystallinity degree. High monomer concentration at polymerization in bulk results in different influence on PP regularity in dependence of metallocene type. For MC C_2 - and C_s - symmetry the increasing of propylene concentration lead to increasing of PP stereoregularity. At the same time for MC C_1 -symmetry the increasing propylene concentration lead to decreasing of PP stereoregularity.

Metallocene produced propylene-ethylene copolymers have a tendency to alternating or random comonomer distribution in the polymer chain, in contrast to the heterogeneous catalysts which have a tendency to form the long crystallizable ethylene sequences.

Propylene copolymerization with higher α -olefins - 1-butene, 1-hexene and 1-octene in liquid propylene medium in presence of homogeneous MAO-activated high effective isospecific C_2 -symmetry *ansa*-zirconocene and propylene copolymerization with 1-octene in presence of silica supported metallocene catalyst activated by *iso*-Bu₃Al has been studied. General kinetic characteristics of propylene/higher α -olefin copolymerization were evaluated. In contrast to earlier investigations in toluene [1] we found for the copolymerization in the liquid propylene medium the proximity of comonomer relative reactivity ratios ($r_1 \sim r_2 \sim 1$) that indicates ideal nature of copolymerization processes in studied conditions [2]. The thermo-physical and mechanical properties of synthesized copolymers were investigated. Polypropylene modification with insignificant comonomer content (1-6 mol. %) allows to change mechanical properties of copolymers dramatically. For the 1-octene copolymers a stronger influence of the comonomer on the thermal and mechanical properties of the polymer was found. The use of metallocene catalysts provides obtaining of copolymers with the properties combining high strength and relatively high elongation at break.

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**CATALYST AND PROCESS FOR PRODUCTION OF ULTRAHIGH MOLECULAR
WEIGHT POLYETHYLENE**

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Ultrahigh molecular weight polyethylene (UHMWPE) is polymer with molecular mass more than 1 million; due to this very high molecular weight this polymer differs greatly from usual grades of polyethylenes. It possesses very high impact resistance and abrasion resistance, excellent sliding properties and chemical resistance and has thus been ranked as one kind of very promising engineering plastic.

It is necessary to use the special modifications of the supported catalysts specified for production of UHMWPE by slurry ethylene polymerization. These catalysts should produce the UHMWPE as powder with optimal morphology (average particle size within the range 60-200 μm , narrow particle size distribution and high bulk density, preferably not less than 400 g/L), with molecular mass within the range $(1\div 8)\times 10^6$ and high yield (more than 10 kg per g of solid catalyst or more than 300 kg per g of Ti).

We have elaborated three modifications of the supported titanium-magnesium catalysts ICT-8-20 to produce with very high yield the different grades of UHMWPE with different average particle size and different molecular mass. These catalysts are produced on the pilot plant at “Katalizator” company and used for production of UHMWPE on the pilot plant in “Tomskneftechim” plant.

More detail data on the catalyst and UHMWPE production will be presented and discussed in this report.

SYNTHESIS AND CHARACTERIZATION OF Pt/Al₂O₃ CATALYSTS PREPARED BY SOL-GEL METHOD

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The Pt/MoO₃-Al₂O₃ samples were prepared by sol-gel method. The prepared samples were characterized by BET surface area measurements, XRD, TEM, TPR-H₂, TPD-NH₃ and IR-spectroscopy techniques. The catalytic activity of obtained samples was tested in toluene hydrogenation reaction in the absence and the presence of H₂S. The influence of Mo-precursors introduction to the alumina sol during the synthesis was investigated. It was demonstrated that the addition of Mo-precursor after alumina sol peptization leads to formation of more active and stable to sulfur poisoning Pt/MoO₃-Al₂O₃ catalyst then in the case of impregnation procedure.

INTRODUCTION

The sol-gel procedure is a novel forward-looking method of catalyst preparation, especially for synthesis of multi-component systems. As the sol-gel catalysts were prepared from a homogenous solution containing both the metal and support precursors; they demonstrated a higher dispersion [1, 2], a homogeneous component distribution [3] and a higher thermal stability to sintering [4, 5] comparing with wet-impregnated catalysts. Also in conventional impregnated catalysts the active components locate mostly on the surface of the support, while sol-gel catalysts can provide various distributions of active component over support.

The aim of this study was to investigate the catalytic behavior in toluene hydrogenation of Pt/MoO₃-Al₂O₃ samples prepared by sol-gel method and to evaluate the sulfur resistance of these. Deactivation of Pt by poisoning with sulfur compounds is still the serious industrial problem and development of preparation methods for sulfur tolerant Pt-containing catalysts is a big challenge.

RESULTS AND DISSCUSION

In the present work, the alumina-supported Pt-Mo catalysts were synthesized by the addition of molybdenum precursor to the alumina sol before and after sol peptization by a nitric acid. The introduction of Pt precursors was performed by the following impregnation. The reference catalyst was prepared by sequential impregnation of commercial alumina with Mo- and Pt-containing salts.

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The properties of the samples were characterized by BET surface area measurement, transmission electron microscopy (TEM), X-ray powder diffraction (XRD), thermo-programmed reduction with H₂ (TPR-H₂), thermo-programmed desorption of NH₃ (TPD-NH₃) and IR-spectroscopy.

The surface area of MoO₃-Al₂O₃ systems obtained by sol-gel synthesis was slightly higher than for commercial Al₂O₃, while pore size and pore volume was lower. The Mo precursor introduction into the sol after its peptization (Pt/MoO₃-Al₂O₃-2 sample) led to more uniform pore size distribution than in the case of addition before peptization (Pt/MoO₃-Al₂O₃-1 sample).

The XRD data demonstrated that after sol-gel synthesis the MoO₃ particles were practically invisible in XRD spectra indicating rather small size of the particle or the presence of amorphous phase of molybdena. Note, that for impregnated samples the signals of MoO₃ phase were well detected by XRD analysis.

The Pt/MoO₃-Al₂O₃-2 sample has comparable activity with the impregnated catalysts, but the stability in time-on-stream is much higher for sol-gel synthesized catalyst. In contrast, the Pt/MoO₃-Al₂O₃-1 sample was inactive in toluene hydrogenation reaction.

To study sulfur tolerance of the Pt/Al₂O₃ catalysts, H₂S was added to the feed by the pulse injection of H₂S+N₂ mixture. The amount of H₂S needed for complete deactivation of Pt/MoO₃-Al₂O₃-2 system prepared by sol-gel method was 5 times higher than for conventional impregnated Pt/MoO₃/Al₂O₃ catalyst.

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**INFLUENCE OF NATURE OF HETEROPOLYCOMPOUNDS OF ANDERSON
STRUCTURES ON ACTIVITY OF Ni-Mo/ γ -Al₂O₃ CATALYSTS**

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In the present work influence of molybdenum heteropolycompounds (HPC) of Anderson structures for formation of an active phase of hydrotreating catalysts was studied. Efficiency of application of the ammonium salt of nickelmolybdic heteropolyacid and the ammonium salt of alumomolybdic heteropolyacid in the synthesis of hydrotreating catalysts is shown. The samples prepared with application HPC have shown high catalytic properties both in thiophene hydrogenolysis reactions, and in real feedstock hydrotreating process. It is shown, that the kind of heteroatoms renders significant influence on catalytic properties of catalysts.

Catalytic properties of the supported catalysts, in particular hydrotreating catalysts such as Ni-Mo/ γ -Al₂O₃, depend on morphology of an active phase. The choice of compounds, which participate in formation of an active phase, can be determining for performance of the catalyst. The most accessible and widely widespread compound for introduction MoO₃ in hydrotreating catalysts is ammonium paramolybdate (NH₄)₆Mo₇O₂₄*4H₂O (PMA). In [1] influence of the stabilizer of active components of the catalysts entered from PMA and of nickel nitrate hexahydrate Ni(NO₃)₂*6H₂O on their activity in hydrodesulfurization reactions is shown.

In the present work influence of molybdenum heteropolycompounds (HPC) of Anderson structures for formation of an active phase of hydrotreating catalysts was studied. The ammonium salt of nickelmolybdic heteropolyacid (NH₄)₄[Ni(OH)₆Mo₆O₁₈] (NiMo₆-HPC) and the ammonium salt of alumomolybdic heteropolyacid (NH₄)₃[Al(OH)₆Mo₆O₁₈] (AlMo₆-HPC) were synthesized by known techniques. The investigations of synthesized compounds were carried out by methods of Fourier transform IR data; X-ray diffraction data; and the differential thermal analysis.

Catalysts were prepared by wet co-impregnation of γ -Al₂O₃ [1] (specific surface area of 315 m²/g, apparent pore diameter of 110 Å) with mixed water solutions of active components. The catalyst synthesized on the basis of traditional PMA was a sample of comparison. The as-prepared catalysts were dried for 2 h at each of the temperatures 80, 100, and 120 °C; heated to 400 °C at a rate of 1 °C/min; and calcined for 2 h. Then, the catalyst obtained in the oxide form was subjected to sulfidation. For this purpose, the 0.25-0.5 mm catalyst fraction was

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impregnated with the sulfiding agent di-*tert*-butylpolysulfide (sulfur content of 54 wt %), placed into an individual glass reactor and sulfided under a hydrogen pressure of 1 atm for two hours at a temperature of 350 °C. The synthesized catalysts (oxide form) were extracted with water, hydrochloric acid and ammonia solution.

The catalytic activity of the test samples was determined in a pulse microcatalytic reactor unit under a hydrogen gauge pressure of 0.25 atm in the thiophene hydrogenolysis reaction over the temperature range 300-400 °C with a step 20 °C. The mass of a catalyst sample was 25 mg and the thiophene volume was 0.2 µl. The synthesized catalysts were also tested in a bench-scale flow reactor unit in the process of hydrogen treatment of real feedstock, which was a 50 : 50 mixture by volume of catalytically cracked light gas oil and the straight-run diesel fraction. The sulfur content of the feedstock was 1.09 wt %, and the amounts of unsaturated and aromatic hydrocarbons were 10.0 and 44.83 wt %, respectively. The tests were conducted at temperatures of 320, 340, 360, and 380 °C; a pressure of 4.0 MPa; a feed space velocity of 2.0 h⁻¹; a hydrogen : feedstock ratio of 600 NI/l; and a catalyst volume of 10 cm³.

As a result of the done work the efficiency of application of NiMo₆-HPC and AlMo₆-HPC in the synthesis of hydrotreating catalysts is shown. The samples prepared with application HPC have shown high catalytic properties both in thiophene hydrogenolysis reactions, and in real feedstock hydrotreating process. It is shown, that the kind of heteroatoms renders significant influence on catalytic properties of catalysts.

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**OPTICALLY ACTIVE AMMONIUM SALTS AS MODIFIERS OF CATALYSTS OF
HYDROGEN TRANSFER HYDROGENATION OF ACETOPHENONE**

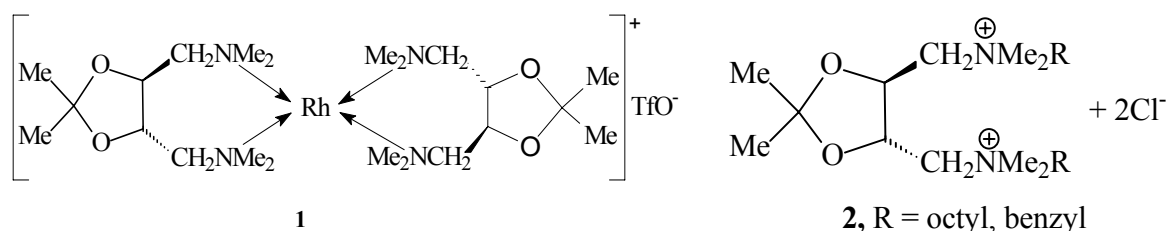
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The possibility of enantioselective hydrogen transfer hydrogenation of secondary ketones on colloidal particles formed from the cyclooctadiene rhodium(I) complexes in the presence of optically active ammonium salts derived from R,R-(+)-tartaric acids is demonstrated on the example of acetophenone.

As we have earlier shown [1] catalytic enantioselective hydrogenation of acetophenone with hydrogen transfer on individual cationic rhodium diamine complexes **1** leads to precipitation of elemental rhodium of cubic structure with the average size of particles of ca. 45 Å, which is followed by an increase of the catalyst turnover number (TON) and decrease of enantioselectivity.



The presence of elemental rhodium in the precipitates points to reduction of the transition metal under the reaction conditions to zero oxidation state that should be followed by formation of metal clusters with the size governed by the nature of stabilizers. The visually observed precipitation of rhodium black is the final stage of aggregation of smaller particles, that means that the solutions of the catalysts starting from some moment should be considered only as arbitrarily homogeneous ("quasihomogeneous").

Indeed, in the system the conditions exist, which according to the state of the art notions [2] may promote formation of ultradisperse metal particles, namely, the use of readily reducible transition metal complexes as pre-catalysts, relatively high temperature, and presence of stabilizers of nanoclusters.

We have simulated the conditions of formation of colloid metal particles by introduction of optically active quaternary ammonium salts **2** into the system.

Kinetic curves for catalytic hydrogen transfer hydrogenation of acetophenone on $[\text{Rh}((4S,5S)\text{-}2,2\text{-dimethyl-}4,5\text{-bis(dimethylaminomethyl)-}1,3\text{-dioxolane})_2]^+\text{CF}_3\text{SO}_3^-$ **1** and

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on complex $[\text{Rh}(\text{cod})_2]^+\text{CF}_3\text{SO}_3^-$ as pre-catalysts in the presence of salts **2** are shown in the Figure. In the presence of optically active quaternary salt **2** the optical yield of *S*-(-)-2-phenylethanol is higher though the conversion is lower (Table).

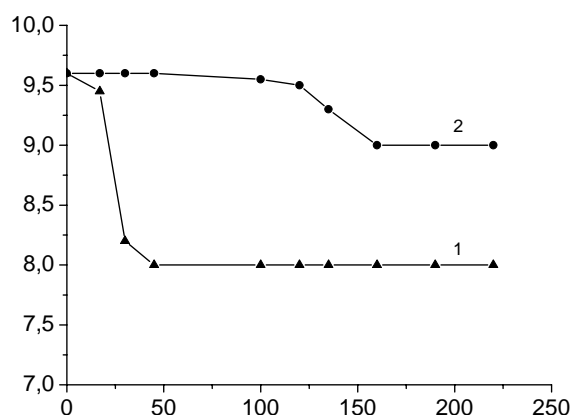


Figure. Kinetic hydrogen transfer hydrogenation of acetophenone on complex **1** (1) and on $[\text{Rh}(\text{cod})_2]\text{TfO}$ in the presence of two equivalents of **2** (R = benzyl) (2) ($C_{\text{Rh}} = 1.1 \text{ mmol/L}$, $\text{KOH/Rh} = 4$, in *i*-PrOH at $80 \text{ }^\circ\text{C}$)

Table. Enantioselective hydrogen transfer hydrogenation of acetophenone on rhodium(I) complexes in *i*-PrOH ($C_{\text{Rh}} = 1.1 \text{ mmol/L}$, $\text{KOH/Rh} = 3\text{-}5$, $80 \text{ }^\circ\text{C}$)

No.	Catalyst	Substrate/Rh	Chem.yield, %	Optic. yield, %,(conf)	TON
1	1	98	20	6, <i>S</i> (-)	52
2	$\text{Rh}(\text{cod})_2]\text{TfO} + \mathbf{2}$	80	7	16, <i>S</i> (-)	15

In both cases the reduction of acetophenone is incomplete as a result of deactivation of the catalyst with time. Apparently, the catalytic activity is due to either metal complexes prior to reduction of $\text{Rh}(1+)$ to $\text{Rh}(0)$ or $\text{Rh}(0)$ -containing particles of "quasihomogeneous" nature. With formation of larger particles the system is deactivated. The presence of optically active products in the second case proves modification of active particles by compound **2** in the chirality transfer stage, which is possible if the process is catalyzed by particles stabilized by optically active quaternary salt. Therefore, it may be concluded that hydrogenation of acetophenone with hydrogen transfer proceeds both on molecular complexes containing chiral diamines and on reduced metal rhodium particles gradually formed in the system under the reaction conditions.

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THE INFLUENCE OF FORMING CONDITIONS OF Ce-, Ag- AND Co-CONTAINING ZEOLITE SUPPORTED CATALYSTS ON THEIR ACTIVITY IN CO OXIDATION

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Catalytic activity in CO oxidation of Ce-, Ag- and Co-containing systems supported with zeolites was investigated. It was established that systems with high metal content (10wt.% Ce, 10wt.% Ag) formed at $T = 20 - 700$ °C had high activity in reaction mixture with oxygen excess (1% CO+20% O₂+79% He). The sample Ag-NaX displayed the highest activity among the investigated Ag-catalysts ($T_{\text{form.}} = 20 - 700$ °C). Optimum conditions of previous treatment of Ag-Co-NaX with low silver content were found. It was shown the Ag-Co-NaX catalysts ($T_{\text{form.}} = 20 - 350$ °C) had more high activity in comparison with 10% Ag-NaX.

Metal-containing (Ag, Au, Pt, Pd, 3d-metals) and oxide (Co₃O₄, CeO₂, CuO, MnO₂) systems deposited on ceramics, zeolites and oxides supports – Al₂O₃, TiO₂, ZrO₂ – are widely investigated in catalytic CO oxidation [1-3]. Increased attention is paid to the supported Ag-based catalysts in the connection because of their stable activity in oxidation processes. On the other hand, the investigation of zeolites as carriers for obtaining supported catalysts is perspective since their developed structure can cause a definite distribution of active components, the increasing of their content in surface layer and, consequently, activity increasing. High thermal stability of zeolites can provide for a stable activity of catalysts on their base in particular in reaction of CO oxidation.

In this paper the activity of Ce-, Ag- and Co-loaded systems supported on zeolites and formed under different conditions was investigated in CO oxidation. Co-, Ce- and Ag-loaded catalysts with high content (10 mas.%) were prepared by impregnation of granulated zeolites (size of granulas was 0,5 - 1 mm) with Ce(NO₃)₂, Co(NO₃)₂ and AgNO₃ solutions. The measure of activity was temperature of total conversion of CO (T_{100}).

The investigation showed that Ce-loaded catalysts (10 mas.% Ce) had high activity in CO oxidation – total conversion of carbon monoxide was reached in I and II cycles of catalysis for all samples. Full conversion of CO on sample 10% Ce-NaX in the I catalysis cycle was fixed at 346 °C, and it was at 328 °C in the II cycle. The activity of 10% Ce-catalysts on the base of NaA, Na,K-ERI, NaZSM-5 (SiO₂/Al₂O₃ = 37 and 69) and NaM was greatly higher – the temperature of CO total conversion on these catalysts was about 100 °C lower in comparison with 10% Ce-Na. It was established that a zeolite nature didn't noticeably influence on activity of Ce-systems (T_{100} lied in the range of 237 – 248 °C).

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In the case of investigated Ag-containing zeolite catalysts formed in temperature interval 20 – 700 °C the considerable difference in the sample activities, which depended on carrier nature, occurred for the most active (Ag-NaX) and for the least active (Ag-NaM) systems in CO oxidation ΔT_{100} amounted to 79 °C in I cycle and 99 °C in II catalysis cycle. Ag-NaX revealed the highest activity among the investigated Ag-containing catalysts ($T_{\text{forming}} = 20 - 700$ °C). The reason of activity difference for Ag-zeolite catalysts may be caused by the difference in distribution of active centers and their quantity in catalyst surface layer. According to TPR- H_2 data the degree of interaction of active phase with the surface of investigated zeolites was various – the maximum temperatures of hydrogen absorption for less active catalysts Ag-NaZSM-5 (37) and Ag-NaM amounted $T_{\text{max}} = 255 - 265$ °C; for more active samples Ag-Na,K-ERI and Ag-NaZSM-5 (69) the value of T_{max} equaled to 175 – 180 °C. Different influence of reaction environment on activity of catalysts Ag-carrier was noted – in the case of more active samples Ag-NaX and Ag-NaA the subsequent increasing of activity ($\Delta T_{100} = 23 - 25$ °C) was observed in II catalysis cycle.

The investigation of activity of 1 – 10mas.% Ag-NaX systems formed in air in temperature interval $T_{\text{form.}} = 20 - 350$ °C depending on silver content showed that the sample 3% Ag-NaX had the highest activity. The catalyst with low content of active component 3% Ag-NaX ($T_{\text{form.}} = 20 - 350$ °C) had activity comparable with the activity of 10% Ag-NaZSM-5 (37) ($T_{\text{form.}} = 20 - 700$ °C). It was established that for 10% Ag-NaX catalyst pretreatment at $T_{\text{form.}} = 20 - 700$ °C was more favorable in comparison with $T_{\text{form.}} = 20 - 350$ °C.

The investigation of Ag-Co-NaX catalysts ($T_{\text{form.}} = 20 - 350$ °C) in CO oxidation showed that the introducing of cobalt as additional active component resulted in more high activity of Ag-Co-containing catalysts in comparison of 10%Ag-NaX. It was established that influence of character of pretreatment (oxidative or reductive) on activity of Ag-Co-NaX systems was defined by the ratio of active component (Ag/Co) in catalyst.

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**NEW CATALYST OF LOW-TEMPERATURE CARBON MONOXIDE OXIDATION
FOR PURIFICATION OF AIR**

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The new catalyst for low temperature carbon monoxide oxidation was developed. It is shown on the base of X-ray diffraction data that γ -Al₂O₃ is the best support for the catalyst. The kinetics of low-temperature carbon monoxide oxidation was studied.

Carbon monoxide is one of the most common pollutants, which is emitted into the atmosphere as a product of natural phenomena (fires and volcanic eruptions), and as result of industrial and transport pollutions.

It is necessary to use respirators and air purification systems to protect peoples in extraordinary situations (fires, traffic jams). The low-temperature catalyst for oxidation carbon monoxide is functional part of these respirators and air purification systems [1-2].

This report deals with development of supported metal complex catalyst PdCl₂-CuCl₂-additives/ carrier, used for effective low-temperature carbon monoxide oxidation in the air.

A number of carriers were tested to prepare low-temperature carbon monoxide oxidation catalyst (activated coals, silica, alumina). The catalysts were prepared by the cold impregnation procedure. It was shown that alumina is the best kind of carrier for preparing of this catalyst.

The influence of alumina structure on catalytic activity of catalysts in low-temperature carbon monoxide oxidation was studied. Seven samples of industrially produced alumina were tested as carriers for above mentioned catalyst. Structure of alumina samples was studied by X-Ray diffraction method. It was shown that the highest catalytic activity was connected with γ -form of alumina structure.

The kinetics of low-temperature carbon monoxide oxidation over PdCl₂-CuCl₂-additives/ carrier catalyst was studied. The effect of partial pressures of oxygen, of carbon monoxide and of water on the reaction rate was studied by one-factor kinetic experiments. It was shown that reaction orders in oxygen (1), in water (0.8) and in carbon monoxide partial pressures

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(0.2) allowed to describe all obtained experimental data. A number of hypothetic mechanisms for carbon monoxide oxidation reaction were proposed. The part of them has been discriminated on the base of kinetics experiments. But for more details discrimination of mechanisms (mechanisms with a different order of oxygen, carbon monoxide and water interaction with active center) would be require isotope exchange experiments.

Above-mentioned data allowed us to elaborate new effective catalyst for low-temperature carbon monoxide oxidation in air [3]. This catalyst is capable to decrease concentration of CO in air from 10000÷100 mg/m³ to 20÷5 mg/m³ under very mild conditions (18-60 °C, relative humidity - 20÷98 %, up to 40000 h⁻¹).

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DRIFTS AND UV-VIS STUDY OF PHILLIPS ETHYLENE POLYMERIZATION CATALYSTS

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Formation of the $\text{CrO}_3/\text{SiO}_2$ catalyst prepared by the reaction of CrO_3 vapor with silica pre-dehydroxylated at 250-800 °C was studied by the DRIFT and DRS methods. The reactions of CrO_3 with the silica dehydroxylated at 250°, 400°C and 800 °C yielded, respectively, monocromates; mono- and dichromates; polychromates. According DRIFT (adsorption of CO) and UV-vis spectroscopy dinuclear and polynuclear Cr(II) and Cr(III) ions are formed in the $\text{CrO}_3/\text{SiO}_2(800)$ catalysts (0.07, 1.03 and 1.56 % wt. of Cr) after reducing with CO. The ligand's surround of Cr(II) ions is the main factor affecting the catalysts performance at ethylene polymerization.

Chromium-oxide catalysts (Phillips catalysts) for ethylene polymerization are known since the late 1950s. Although the catalysts have been studied intensively, numerous questions regarding the structure and composition of the surface chromium species, mechanisms by which they convert to active centers of polymerization, structure and composition of these active centers remain open and are still discussed in literature [1, 2].

Phillips catalysts are usually prepared by impregnating of silica with an aqueous solution of a chromium compound, for example, CrO_3 , chromium acetate, chromium nitrate, etc. During subsequent activation in a flow of dry oxygen or air at 400-850 °C, Cr(VI) species of various composition are assumed to form on the catalyst surface. We have studied the formation of the $\text{CrO}_3/\text{SiO}_2$ catalyst prepared by the reaction of CrO_3 vapor with silica pre-dehydroxylated at 250-800 °C was studied by the DRIFT and UV-VIS spectroscopy. It was found that CrO_3 reacts both with terminal and hydrogen-bonded Si-OH groups of silica at 250 °C to produce various chromate species and water. The latter is removed from the catalyst surface by vacuumation at 250°C. It was found the structure and composition of the surface species depends on silica dehydroxylation temperature. Monocromates; mono- and dichromates; polychromates are formed after the interaction of CrO_3 with the silica dehydroxylated at 250°, 400 °C and 800 °C yields, respectively. The catalyst activity at ethylene polymerization strongly increases with increasing dehydroxylation temperature, especially in the range of 250-400 °C. The results obtained prove di- and polychromates to be the active components of the Phillips type chromium-oxide catalysts from which the active centers are formed at interaction of the active component with co-catalyst (AlEt_3) and

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ethylene. Active centers contain the surface organo-chromium compounds with chromium ions in low oxidation states (lower than Cr(VI)).

Surface chromates (the compounds of Cr(VI)), formed after high-temperature activation of Phillips catalysts are rather easily reduced at interaction with different compounds (ethylene, carbon monoxide, aluminiumorganic compounds and etc.) Nowadays, there is a general agreement to ascribe the Cr(II) species as precursor of active site at ethylene polymerization. We have studied the influence of chromium content (0.07-5% wt. of Cr) on the state of surface chromium species and activity at ethylene polymerization of CrO₃/SiO₂(800) catalyst. According the DRIFTS and DRS data CrO₃ interact with silica, dehydroxylated at 800 °C, with formation of di- and polychromates. The Cr₂O₃ phase is formed also in the CrO₃/SiO₂(800) catalysts with Cr content more than 1% wt. The catalyst activity at ethylene polymerization strongly increases with decreasing the chromium amount.

We investigated the CrO₃/SiO₂(800) catalysts (0.07, 1.03 and 1.56 % wt. of Cr) reduced by CO. According DRIFT (adsorption of CO) and UV-vis spectroscopy dinuclear and polynuclear Cr(II) and Cr(III) ions are formed in the CrO₃/SiO₂(800) catalysts after reducing with CO. The ligand's surround of Cr(II) ions is the main factor affecting the catalysts performance at ethylene polymerization.

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NANOSTRUCTURED COMPLEX OXIDES FOR CATALYTIC COMBUSTION AND FUEL CELLS APPLICATIONS

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Mesoporous ZrO₂-TiO₂-Y₂O₃ complex oxides which have utility as electrode material in solid fuel cells (SOFCs) have been synthesized, characterized and used as catalysts for combustion of hydrocarbons. The obtained oxides were characterized by XRD, TGA, adsorption-desorption of N₂, TEM, SEM, IR and UV-Vis spectroscopy, XPS. The materials present an ordered mesoporous structure and high surface area. Stability of the porous structure is observed after calcinations at 673 K and partial breakdown of structure occurs after 873 K by crystallization of oxides. ZrO₂-TiO₂-Y₂O₃ oxides were modified with Ce, Nb or W and their role on catalytic activity in oxidation processes were edified.

The reactions that occur at the fuel-cell electrodes are obviously at least partially catalytic, so the choice of electrode materials will affect cell performance and fuel sensitivity. The electrochemical reaction is a redox process with a nonconventional oxygen source [1]. Many properties of the materials evidenced in nanotechnology involve in the solids large surface areas, regular and high porosity at the nanometer scale. In nanometer-sized particles, the ratio of the number of atoms in the surface to the number in the bulk is much larger than for micrometer-sized materials, and this can lead to novel properties.

In this paper nanostructured mesoporous ZrO₂-TiO₂-Y₂O₃ complex oxides are synthesized by surfactant-assisted preparative chemistry, characterized and used as catalysts for oxidation of volatile organic compounds. The oxides, with various titania content (8 % - 40 %), were prepared using various surfactants (Brij 30, polyoxiethylene tridecylether, block copolymer P123) as structure directing agents and precursors of oxides (zirconium chloride, titanium isopropoxide and yttrium nitrate). Urea was used as hydrolyzing agent and various promoters (CeO₂, NiCo, NiCu, NiFe) were added to increase the performances, as catalyst and anode, of the obtained materials. All the materials were prepared at room temperature by vigorous mixing of surfactants, water and precursors. The resulted gels were sealed and heated in autoclave at 253 K. The solids were filtered, washed, dried and calcined in air at 823 K.

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The obtained oxides were characterized by XRD, TGA, adsorption-desorption of N_2 , TEM and SEM microscopy, IR and UV-Vis spectroscopy. In order to understand the relation between the catalysts and the fuels the materials were thermodynamic analyzed. The materials were tested in oxidation with air of hydrocarbons (C1-C6). In order to investigate catalytic activity the catalyst was loaded in the quartz reactor and products were chromatographic analyzed. The adsorption of hydrocarbons on oxides surface was analyzed in an IR cell.

The XRD patterns of $ZrO_2-TiO_2-Y_2O_3$ powders show only the cubic phase of zirconia and, 1-2 peaks between 2θ ranging $1-4^\circ$ indicating a long-range order in the oxides. Typical SEM morphology of hierarchically nanostructured meso-macroporous materials is presented in Fig. 1. TEM images show formation of aggregates with inorganic polymers. An ordered structure is evidenced by TEM microscopy (Fig. 2).

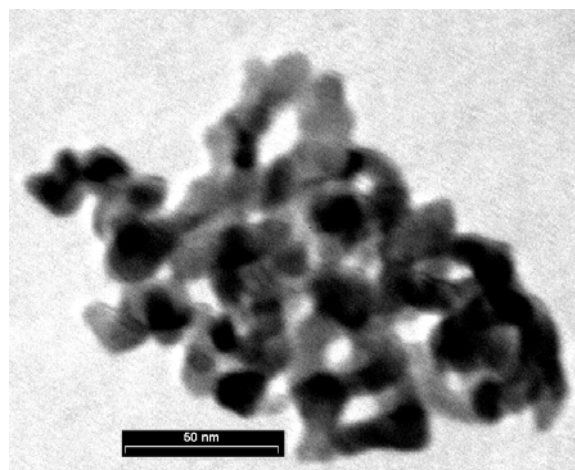
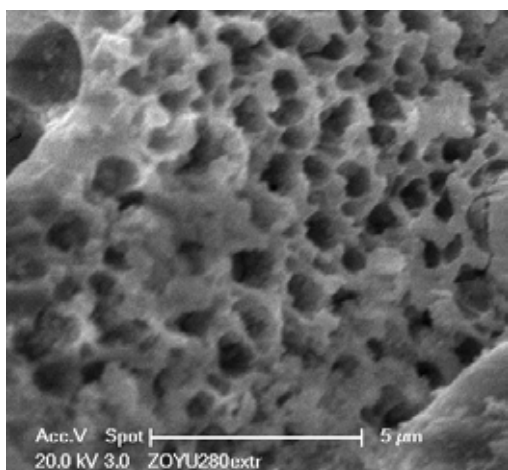


Fig. 1 SEM image of $ZrO_2-TiO_2-Y_2O_3$ oxide Fig. 2 TEM image of $ZrO_2-TiO_2-Y_2O_3$ oxide

The surface area of oxides was varied between 780-1100 m^2/g and adsorption-desorption isotherm are typically for the materials obtained with block copolymers as surfactant. Porous structure was influenced by composition and surfactant. Catalytic activity of oxide was influenced by composition and promoters. A higher activity was evidenced for oxides with ceria and/or NiCo promoters.

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**PLATINUM CATALYSTS AND THEIR ACTIVITY IN OXIDATION OF
ALCOHOLS FOR FUEL CELLS APPLICATIONS**

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In this paper we present the preparation and characterization of Pt, PtRu, PtSn and PtFe alloy colloids and the electrocatalysts obtained by their adsorption on a supporting material (Vulcan XC carbon). Mono- and bimetallic colloids were obtained by two methods. The prepared catalysts were characterized by X-ray diffraction, transmission electron microscopy and IR and UV-Vis spectroscopy. Typical TEM images of colloids show remarkably uniform and high dispersion of the metal and the alloy particles. The obtained materials were tested in oxidation of alcohols in condition of polymer electrolyte fuel cell.

Catalysts are a key element in the conversion of liquid or gases fuels in fuel cells applications [1]. Catalysis offers a variety of options for the conversion of hydrocarbons and alcohols for fuel cells. In polymer electrolyte fuel cells (PEMFC) nanostructured Pt-based alloys colloids supported on the high surface area Vulcan XC72 are the best electrocatalysts for the anodic and cathodic reactions in fuel cells. The primary advantages of catalytic processes in PEMFCs consist in the extremely low pollution.

In this paper we present the preparation and characterization of Pt, PtRu, PtSn and PtFe alloy colloids and catalysts obtained by their adsorption on a supporting material (Vulcan XC carbon). Mono- and bimetallic colloids were obtained by two methods [2, 3]. In the first method polyvinylpyrrolidone (PVP) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were dissolved in a mixture of methanol/ water (molar ratio 1/2) as solvent. The mixture was refluxed for 240 min to obtain a dark-brown homogenous dispersion. During the reaction 0.1M methanol solution of NaOH was added dropwise. Colloids with molar ratio of PVP to Me 20:1, 20:2, 30:1 and 40:1 were prepared. In the second methodant tetra octyl- and hexylammonium protected Pt(Ru, Sn, Fe) colloid were obtained by co-reduction of metal the precursors with $\text{N}(\text{oct})_4[\text{B}(\text{et})_3\text{H}]$. The colloids were supported by combining a THF dispersion of the PtMe-colloid with a suspension of Vulcan carbon in THF in such quantities to have a total of 20 wt % metal in the final catalyst. The supported colloidal nanoparticles were dried at room temperature under

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vacuum. The colloid synthesis was performed in a dry nitrogen atmosphere using dry solvents and nonhydrated salts.

The prepared catalysts were characterized by X-ray diffraction, transmission electron microscopy and IR and UV-Vis spectroscopy. All the catalysts were tested in an aqueous solution of alcohols, with a membrane /electrode assembly. The oxidized alcohols were methanol, ethanol, 2- propanol, cyclohexanol. In order to understand the relation between the catalysts and the fuels the adsorbate was analyzed by voltametry for the membrane-electrode assemblies. Typical TEM images of colloids show remarkably uniform and high dispersion of the metal and the alloy particles.

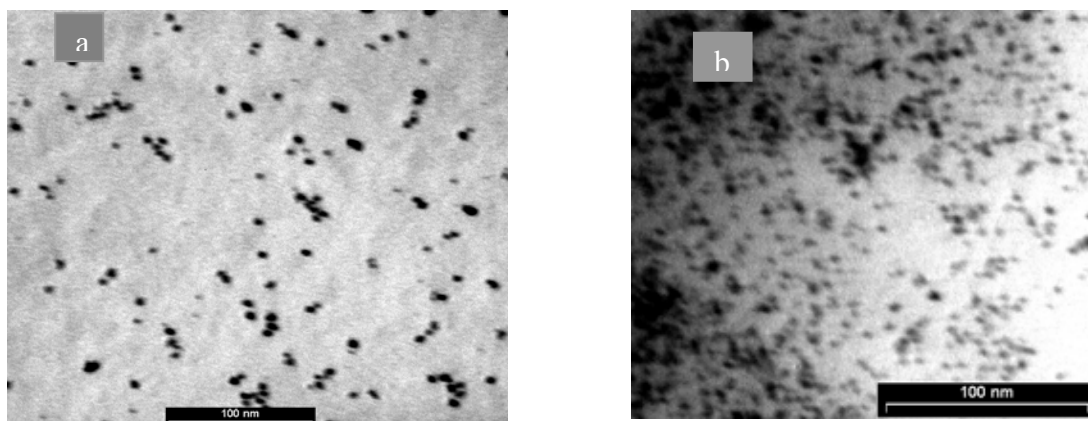


Fig. 1 TEM images of Pt (a) and PtSn (b) colloids obtained by first method

The as-synthesized PtMe/C samples display considerable crystallinity before the heat treatment. Crystallization increases with the heating time. The Pt or PtMe colloidal formation process was monitored by UV-Vis spectroscopy. The obtained spectra show gradually decreasing absorption from the ultraviolet region to 700 nm. This indicates the formation of PtMe alloy nanoparticle. The electrocatalytic tests show that Pt/C is not very active catalyst for oxidation of alcohols. Addition of the second metal enhances the activity and improves the performance of the cell. For the catalysts with colloids obtained by the first method the better performances in oxidation of methanol were obtained for PtRu/C. PtSn/C catalysts with colloids obtained by the second method are better in oxidation of 2-propanol and cyclohexanol. A high variation of performance was evidenced for PtFe/C catalysts obtained by different methods.

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**DESIGN OF STRUCTURED CATALYSTS BASED ON CERAMIC AND METALLIC
MONOLITHS FOR SYNGAS PRODUCTION VIA PARTIAL OXIDATION OF
NATURAL GAS**

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The catalysts comprised of CeO₂-ZrO₂ and LaNiO_x promoted by Pt supported on full-sized corundum and metallic monolith substrates were developed and studied in catalytic partial oxidation of methane (POM) using an autothermal reactor at transient and stationary conditions. The effect of substrates thermal conductivity, linear velocity, feed composition and inlet temperature on catalytic activity in POM was elucidated. The monolith catalysts of different types were shown to be very efficient in a wide range of contact times and stable at temperatures up to 1200 °C.

Catalytic partial oxidation of methane at short contact times is now considered as an attractive technology for the small-scale and distributed production of syngas in the stationary and mobile fuel processing [1,2]. Realization of POM at short contact times (< 0.1 sec) allows to reduce the size of the fuel processor and requires application of monolithic catalysts with a low pressure drop. The use of metallic substrates with high thermal conductivity decreases the temperature gradients within the monolithic catalysts thus increasing thermal stability during start-up. Furthermore, due to mild exothermicity, the process can be realized in the autothermal regime ensures a high yield of syngas. However, several problems associated with performance of known monolith catalysts exist. They are the insufficient thermal stability and conductivity of monolith ceramic supports, evaporation of Rh(Pt) due to high temperatures developed in the inlet part of a monolith, deactivation due to carbon build up in the outlet zone.

In this work, to solve these problems, new types of monolith supports and more stable active components were developed [2]. Here, results on design of highly active in POM and stable under high temperature operation structured catalysts based on full-sized ceramic and metallic monoliths are presented. The comparative study on performance of these catalysts with active components comprised of CeO₂-ZrO₂ and LaNiO_x promoted by Pt was performed in both transient and stationary conditions using POM autothermal reactor.

To prepare catalysts, different types of full-sized monolithic substrates were used: thin-wall corundum monoliths and metallic monoliths based on FeCrAl alloy foil or gauze. The

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surface of metallic substrates was pre-coated with a thin (~ microns) protective low-porous layer of corundum or zirconia by the unique technology of blast dusting [2]. Active components including both mixed oxides and platinum are supported by successive impregnation with appropriate suspensions or solutions followed by drying and calcination.

The monolith catalysts were tested in a tubular stainless-steel reactor. The axial temperature along the monolith was scanned at selected points by thermocouples located in the central channel. The contact time was varied in the range of 0.2-0.02 s. The feed composition was CH₄ (natural gas) - 22-29 vol.%, air – balance. Gas composition was analyzed by mass-spectrometric and GC methods.

The consumption of methane and oxygen and axial profile of catalyst temperature during start-up and steady-state reaction were found to be determined by the inlet gas temperature, contact time, thermal conductivity of substrates. For both catalysts based on corundum and metallic supports, the scan of the axial monolith temperature along the catalyst during start-up shows that ignition starts in the central or rear zone of a monolith depending on a contact time. After ignition, a zone of the maximal catalyst temperature moves towards the monolith entrance until the stationary state is attained. The time required to attain the steady state is shorter for metallic monolith catalysts as compared to ceramic ones and decreases at shorter contact times. Hence, the high thermal conductivity of metallic monolith provides fast effective transfer of heat generated in a zone of exothermic combustion along the monolith into its rear part where endothermic reforming reactions occur. Such peculiarities of metallic-based monolith catalysts are especially important for mobile fuel processors which must ensure a rapid start-up.

For the stationary state, at long contact times, a zone of the maximal temperature locates at the inlet part of monolith and, at decreasing contact time, it shifts to the rear part of monolith due to its cooling by incoming gas. In addition, for shorter contact times, the temperature gradient along the monolith declines due to contribution of the direct POM reaction having mild exothermicity as well as hindering of endothermic reforming reactions. Therefore, the monolith catalysts of different types were shown to be very efficient and stable in the POM at short contact times and temperatures up to 1200 °C. They insure a high conversion of methane and high concentration of syngas in a wide range of contact times and at high gas velocities.

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THE INFLUENCE OF CARBON ON WET PEROXIDE OXIDATION OF ORGANIC POLLUTANTS IN AQUEOUS MEDIA

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Wet peroxide oxidation of phenol and ethanol in the presence of various carbon materials (nano-diamonds (ND), onion-like carbon (OLC), graphite-like carbon Sibunit and catalytic filamentous carbon (CFC)) and/or Fe^{3+} has been studied. All carbon types were found to be low-active to oxidation of the both substrates without iron. The presence of ND inhibits as the phenol as ethanol oxidation catalyzed by Fe^{3+} . The Sibunit, OLC, CAC accelerate the ethanol oxidation. More complex effect was revealed in case on phenol oxidation.

Introduction

The combination of sorption by active carbons with destruction of the sorbate through catalytic oxidation, for example with H_2O_2 , [1] is considered promising process of purification of wastewater from toxic organic compounds. However the development of such complex processes requires clear understanding of how the presence of a carbon material affects various stages of the process.

In the literature, this problem is interpreted in three different manners. 1) The pure carbon materials can catalyze oxidation of organic substrates in aqueous solutions by hydrogen peroxide [2, 3]. 2) The presence of active carbon and adsorption of substrate on its surface increases the rate of the oxidation reaction catalyzed by transition metals [4]. 3) Point of view is quite the contrary, i.e. carbon in the solution is thought to behave as a free radical scavenger, hence, to slow down free-radical oxidation processes [5].

This work is aimed to answer the above questions. For this purpose influence of various types of carbon materials on kinetics of H_2O_2 destruction and oxidation of model substrates by hydrogen peroxide at presence of carbon materials and/or salts Fe is regularly investigated. The principal moment of our research was that we used the "pure" synthetic carbon materials free of metals impurities. The morphology and an electronic structure of these carbon materials were appreciably different.

We chose well-known reactions of oxidation of phenol and ethanol with hydrogen peroxide as model reactions. Adsorption of these substrates and kinetics of their oxidation were studied.

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Experiment

Following carbon materials have been used in this work. 1) Detonation nano-diamonds (ND) containing mainly oxygenate surface groups in total amount 0.025 mmol/g. (sp^3 -carbon material). $S_{BET} = 345 \text{ m}^2/\text{g}$. 2) Onion-like carbon (OLC) was prepared via ND thermal heating in vacuum and consisting of defective closed graphite shells enclosed each other (sp^2 -carbon). $S_{BET} = 582 \text{ m}^2/\text{g}$. 3) Porous graphite-like carbon Sibunit-4 (sp^2 -carbon). $S_{BET} = 588 \text{ m}^2/\text{g}$. This material is produced via hydrocarbons pyrolysis and therefore it contains few amount of impurities of transition metals ($C(Fe) < 0.02$ weight. %). 4) Two types of catalytic filamentous carbon (CFC) (sp^2 -carbon). $S_{BET} = 119$ and $194 \text{ m}^2/\text{g}$. Carbon morphology was characterized by TEM and nitrogen adsorption. Quantity and chemical nature of surface groups on the surface of ND were studied with IR-spectroscopy. Acid-base titration according [6] was used for estimation of amount and nature of species on the surface of Sibunit.

Phenol and ethanol oxidation was oxidized using a batch reactor with a reflux condenser at atmospheric pressure in temperature range 293-323 K. Concentration of phenol or ethanol was 0.01 mol/L, amount of carbon material was 5 g/L. The concentration of hydrogen peroxide was 0.06 mol/L for ethanol and 0.2, 0.07 mol/L for phenol oxidation, and the spent amount of H_2O_2 was made up for in the course of the reaction to provide approximately constant H_2O_2 concentration (~90-100% of the initial concentration). The concentrations of phenol and some products of its oxidation were detected by HPLC, concentration of ethanol by GC.

Results

Adsorption properties. The results obtained show ND containing only sp^3 -carbon and surface species (-COOH, -COC-, -COH, -C=O) does not noticeably adsorb neither phenol nor ethanol. Graphite-like sp^2 -carbon samples (Sibunit-4, OLC, ND) have adsorbability proportional to S_{BET} which are higher for phenol and lower for ethanol.

Catalytic activity of carbon. ND and Sibunit were found to be inactive to oxidation of ethanol in absence of iron. OLC and CFC have very low activity in this reaction. Conversion of ethanol was about 90% after 70 and 110 hours, respectively. All carbon samples have shown very low catalytic activity in phenol oxidation. 90% conversion of phenol was after 150 hours for Sibunit and 650 hours for ND, OLC and CFC.

Oxidation with Fe^{3+} & C. In case of oxidation catalyzed by homogeneous Fe^{3+} -ions the conversion ~90% was achieved after 170 min for ethanol and 30 min for phenol. Outstanding results were obtained for ethanol oxidation in presence of carbon samples. The rate of the reaction decreases in the presence of ND in the solution but increases in the presence of all

sp²-carbon samples (Sibunit, OLC, CFC). More complex effect of Sibunit, OLC and CFC was revealed in case on phenol oxidation. No influence or minor acceleration was observed for high H₂O₂ concentration (0.7 M, C_{PhOH}/C_{H₂O₂} =1/70) and t= 30⁰C. Deceleration was monitored for lower concentration of H₂O₂ (0.2 M, C_{PhOH}/C_{H₂O₂} =1/20) and t=50⁰C.

Conclusions

All types of carbon samples are inactive or low-active to oxidation of both phenol and ethanol in absence of iron. Presence of sp³-carbon slows down oxidation as phenol as ethanol catalyzed by Fe³⁺. It is possibly due to surface oxygenate species behaving as a free radical scavenger. sp²- carbon can both decelerate free-radical oxidation and to accelerate it depending on reaction conditions. Acceleration apparently is caused by ability to transfer electron due to π-conjugation in graphene layer [7].

Acknowledgements

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**ACTIVITY OF $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ SYSTEMS IN THE REACTION OF HIGH
TEMPERATURE N_2O DECOMPOSITION**

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$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ mixed oxides were prepared and tested in the reaction of high temperature N_2O decomposition. Prominent increase of activity at $x = 0.4\div 0.8$ (including the case of both water and oxygen presence in the reaction mixture) correlates well with formation of laminated structure $(\text{La}_{1-x}\text{Sr}_x)_2\text{MnO}_4$ consisting of alternating perovskite and SrO layers.

Mixed oxides with perovskite structure LaMO_3 (where M is mostly 3d-transition metal element, like Fe, Co, Mn) can be considered as very prospective systems for the high-temperature N_2O abatement due to their high thermal stability and presence of oxygen vacancies in perovskite structure, that are important sites for N_2O adsorption. Moreover, perovskites possess enhanced lattice oxygen mobility at high temperatures thus promoting active sites regeneration. Partial substitution of La or B cation with an ion of other valence giving rise to abnormal valencies of B-site cation and/or additional oxygen vacancies is an additional way to regulate both active sites concentration and lattice oxygen mobility. The main objective of this study was the elucidation of the effect of La substitution by Sr in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ on the lattice structure, texture, oxygen mobility and activity in the reaction of N_2O decomposition.

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ mixed oxides were prepared by Pechini route by mixing saturated water solutions of the nitrates of corresponding elements in necessary quantities with citric acid and ethylene glycol to obtain desired La/Sr ratio followed by heating in air, first – up to about 140-150 °C to decompose nitrates, and then - up to 900 °C or 1000 °C and kept at these temperatures for 4 h to form the perovskite. XRD, XPS and HREM have been used to characterize lattice structure of mixed oxides formed, texture of species, surface layers composition. Bulk oxygen mobility was characterized by TPR. Catalytic activity in the reaction of N_2O decomposition was measured in a plug flow reactor at 900 °C and contact time 0.001s. Inhibiting effect of H_2O and O_2 on the reaction running was checked by adding up to 10% vol. of O_2 or H_2O into the reaction mixture composing of 0.15% vol. N_2O in He.

Undoped LaMnO_3 has a structure of perovskite with close to cubic lattice and possess rather low activity with regard to N_2O decomposition (Fig.1). At low degree of La substitution by Sr ($x=0.1\div 0.2$) a perovskite with hexagonal lattice has been formed that can be characterized by enhanced activity. Reaction running over both perovskite containing lattices is strongly inhibited both by water and oxygen. At higher Sr content ($x=0.3\div 0.4$), depending on preparation conditions, both reverse transfer from hexagonal to cubic structure, and additional formation of the phase with a diffraction pattern similar to that of $\beta\text{-Sr}_2\text{MnO}_4$ [1], that was related by us to $(\text{La}_{1-x}\text{Sr}_x)_2\text{MnO}_4$, can take place. The last of them is a structure composed of alternate layers of perovskite and SrO_x and detected in parallel with perovskite phase at x range from 0.4 to 0.9. Samples containing such laminated perovskite-like phase possess high activity both in the absence of H_2O and O_2 , and in their presence. At that, surface layers composition prominently affects the activity of such samples. At highest degree of La replacement ($x = 0.9 \div 1.0$) $\text{Sr}_4\text{Mn}_3\text{O}_{10}$ has been formed. Although high active in N_2O decomposition, these samples lose their activity prominently in H_2O and O_2 presence. Dependence of samples activity on the oxygen mobility is discussed as well.

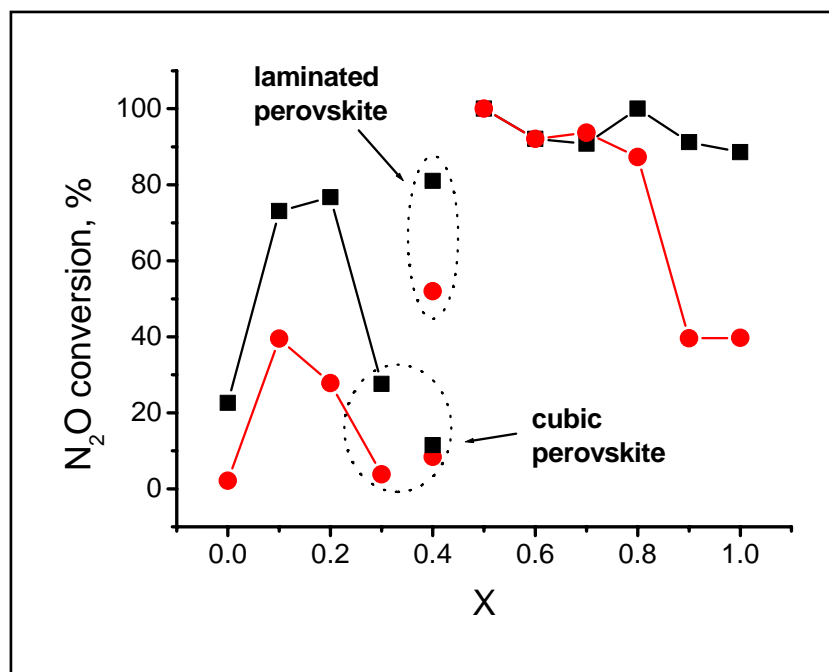


Fig.1. N_2O conversion vs La replacement degree by Sr (x) for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ series calcined at 900°C . Reaction mixture composition: ■ - 0.15% N_2O in He, ● - 0.15% N_2O + 3% O_2 + 3% H_2O in He.

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**KINETICS AND MECHANISM OF ZINC PHOSPHIDE OXIDATION IN
ALCOHOLIC SOLUTIONS OF Cu(II), Fe(III) BY OXYGEN**

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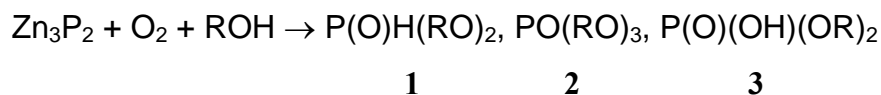
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It was found that zinc phosphide in alcoholic solutions of copper and iron chloride at 50-90 °C is oxidized by oxygen up to the phosphoric acids ethers. The kinetics and mechanism of catalytic reaction are established by methods of volumetry, redox potentiometry, GC, IR-, UV-, EPR-, NMR ³¹P-spectroscopy. The separate redox mechanisms of catalytic processes are suggested. The kinetic and thermodynamic parameters of main steps are determined.

Transition metal phosphides (FeP, Cu₃P, Zn₃P₂) exhibit low activity in organic reactions because of inertness in heterolytic transformations. Few known organic reactions of phosphides flow past at increased temperature or are initiated by a radioactive radiation.

We have shown that zinc phosphide (0,2 - 0,8 mmol) in alcoholic solutions of copper and iron chloride (2,5 - 5,0 mmol) at 50-90 °C is oxidized by oxygen (0,02 - 0,1 MPa) up to the phosphoric acids ethers – dialkylphosphites **1**, trialkylphosphates **2**, dialkylphosphates **3**.

Cat.



Cat. - CuCl₂, FeCl₃, FeCl₃/I₂; R = Et, Pr, Bu, i-Am.

The kinetic regularities of catalytic processes, structure of intermediate complexes, organophosphorus compounds (OPC), optimum conditions, mechanism of the reaction are established by methods of volumetry, redox potentiometry, IR-, UV-, EPR-, NMR ³¹P-spectroscopy, GC, quantum chemistry [1, 2].

In alcoholic solutions of CuCl₂ at 50-60 °C the reaction flows past with primary formation of **2** (85,0 - 92,8 %). Using FeCl₃ will lead to the formation of **1** (82,0 - 90,0 %). The impurities of H₂O (0,1 - 1,0 mmol) reduce the yield of **1**, **2**, promote shaping **3** (57,0 - 89,0 %). The mixed catalytic system FeCl₃/I₂ exhibits synergetic properties at 50 - 60 °C. At the ratio FeCl₃/I₂ equal 10 the maximum velocity of the reaction is observed. The main OPC will be **2** (80,0 - 90,0 %).

The redox mechanisms of catalytic processes including key steps of oxidation Zn_3P_2 by metal chlorides or I_2 with formation of OPC and regeneration of the active forms of the catalyst by oxygen are proposed. The kinetic and thermodynamic parameters of main steps are determined.

The work is executed with the support of ISTC fund (Project K-1284).

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EFFECT OF THE AlEt_3 COCATALYST ON THE INTERNAL DONOR IN SUPPORTED ZIEGLER-NATTA CATALYSTS

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The catalyst-cocatalyst interaction was studied for supported Ziegler-Natta catalysts containing EB (ethyl benzoate) or DBP (di-n-butyl phthalate) as internal donors. As the result of interaction the catalysts underwent considerable changes of its composition. It was shown by DRIFT spectroscopy, that the weak surface complexes of donors were preferably removed by AlEt_3 from surface of the catalysts. A part of removed donor adsorbs again on the catalysts surface in the form of complexes with aluminum-containing compounds.

The internal donor is an important component in supported Ziegler-Natta catalysts for propylene polymerization responsible for stereospecificity of these catalysts [1]. When used in polymerization the catalysts undergo the chemical modifications because of interaction with the cocatalyst and an external donor [2]. The AlEt_3 cocatalyst interacts with adsorbed TiCl_4 species and removes the internal donor from catalysts surface partially. Earlier we have showed the possibility to identify several types of surface EB and DBP complexes in supported Ziegler-Natta catalysts by means of IR-spectroscopy [3]. In the present study we examine the influence of the AlEt_3 cocatalyst on the chemical composition and on the state of internal donors of supported Ziegler-Natta catalyst.

Two pairs of the catalysts containing EB or DBP were prepared starting from highly dispersed MgCl_2 support or from $\text{Mg}(\text{OEt})_2$ and treated with the AlEt_3 cocatalyst. It was found, the catalysts prepared with use of MgCl_2 support showed similar changes in its chemical composition at the interaction with the cocatalyst. The content of donor and titanium decreased upon treatment with cocatalyst and aluminum containing compounds incorporated into catalyst composition. The only difference was the more profound decrease of donor content for the catalyst with EB as the internal donor. The total content of surface species (donor, titanium and aluminum compounds) markedly increased for both catalysts. In the case of the catalysts prepared from $\text{Mg}(\text{OEt})_2$ the total content of surface species increased for DBP containing catalyst only and remained the same for the catalysts with EB as the internal donor.

DRIFT study of the catalysts before and after interaction with the cocatalyst showed, that the state of donors in the catalysts has markedly changed at the treatment with AlEt_3 . The

weak surface complexes of donors were preferably removed by AlEt_3 from surface of the catalysts. In the case of catalysts containing DBP the main part of phthaloyl chloride, which forms at surface of the catalysts at its preparation, was removed by AlEt_3 . A part of removed donor adsorbs again on the catalysts surface in the form of complexes with aluminum-containing compounds.

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DEVELOPMENT OF MESOSTRUCTURED TITANIA COATINGS ON GLASS SUBSTRATES

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The aim of this work is to obtain mesoporous titania films on glass substrates. The samples will be used as substrates for active catalytic sites (bimetallic clusters) and will be tested in the heterogeneously catalyzed hydrogenation of citral to the corresponding unsaturated alcohols, which represent a broad class of industrially relevant compounds.

Mesoporous materials are such materials which have pores with size of 2-50 nm. This property allows mesoporous materials to be used as substrates for molecules and clusters immobilization as active catalytic sites. The unique characteristics of mesostructured materials, namely high pore volume and surface area combined with narrow pore-size distribution, make them particularly suitable for various fine chemical synthesis.

The goal of the present study is to develop and characterize highly ordered mesoporous titania films on a glass substrates. The titania films were prepared by using evaporation induced self-assembly method (EISA). This methodology is based on the self-assembling of structures in a presence of surface-active agents (surfactants), which play a role of template. During the synthesis of the films, fast evaporation of volatile species occurs. It promotes the formation of mesophase and polycondensation of inorganic species. Self-assembly is a complex process, which is under the control of interactions between organic and inorganic phases onto the surface. In this work Pluronic F127 ((EO)₁₀₀(PEO)₆₅(EO)₁₀₀) was used as a template and Ti(O-*i*Pr)₄ as a Ti-source. Deposition of the films was realized by a spin coating method. The pH value of initial sol was modified from 1.5 to 2 by addition of different H⁺-sources (HCl, HNO₃ and CF₃COOH) because H⁺ serves to protonate negatively charged alkoxide groups of precursor and can influence both the hydrolysis and condensation rates and the structure of the condensed product. Aging time of initial sol was varied from 8 hours to 2 weeks. Synthesis of such materials is complicated by moisture sensitivity of the required precursors, therefore it was very important to maintain a constant relative humidity level (80 %) during the synthesis.

Ellipsometric, LA-XRD, TEM, IR, contact angle measurements of titania films were carried out. Ellipsometric measurements showed that thickness of the films is affected by aging time. Superhydrophilic properties of titania after UV-treatment were confirmed by contact angle measurements. An alternative approach for surfactant removal via step-wise heating in vacuum was investigated. The successful elimination of Pluronic F127 from the as-synthesized titania films was observed after calcination at 300°C and was confirmed by IR spectroscopy.

This work is realized in the network of collaboration between Boreskov Institute of Catalysis and Eindhoven University of Technology (NWO-RFBR №060389402 project “Development of advanced mesostructured catalytic coatings on microstructured substrates for fine chemicals synthesis”).

**POSTMETALLOCENE COMPLEXES AS CATALYSTS OF POLYPROPYLENE,
POLYETHYLENE AND PROPYLENE/ETHYLENE COPOLYMER SYNTHESIS**

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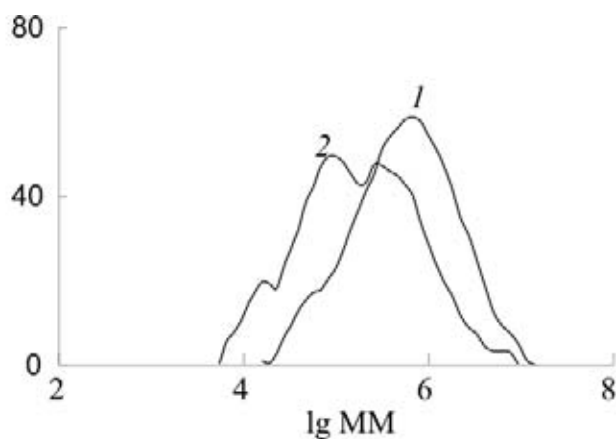
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Two dichloride titanium complexes with principal different ligands – derivatives of 1,3-dioxolane-4,5-dimethanol (TADDOL) and phenoxy-imine (FI) derivatives were synthesized and used as catalysts in propylene and ethylene homopolymerizations as well as propylene/ethylene copolymerization. The activities of the catalysts in the propylene polymerization were equal to 10 and 45 and in the ethylene polymerization - 178.5 and 2700 kg PP(PE) /mol Ti·mol C₃H₆ (C₂H₄)/l·h, respectively (50 °C, MAO as a cocatalyst). During the copolymerization the active centers of both catalysts selective polymerize the ethylene. The structural, molecular-mass, thermo-physical and mechanical characteristics of polymers were studied. It was shown that TADDOLTiCl₂ as compared to FITiCl₂ had a higher stereoregular polymerization ability.

The polymerizations of propylene, ethylene and propylene/ethylene copolymerization promoted with postmetallocene catalysts: [(4*R*,5*R*)-2,2-dimethyl- $\alpha,\alpha,\alpha,\alpha$ -tetrakis (penta - fluorophenyl)-1,3-dioxolane-4,5-dimethanol] titanium(IV) dichloride (**I**) and bis[*N*-(3,5-*tert*-butylsalicylidene)-4[bis(5-methyl-2-furyl)methyl]aniline] titanium(IV) dichloride (**II**) were investigated. The activity of **I** was equal to 10 kgPP/mol Ti·mol C₃H₆/l h (50°C, MAO as cocatalyst). Unexpectedly, the tenfold increase of Al/Ti ratio (from 88 to 940) didn't essentially influence the polymer yield.



PP synthesized with **I** at Al/Ti=90 had an extremely high MM ($M_w=1177000$) and a broad MWD ($M_w/M_n=4.8$), that confirmed unhomogeneity of active centers of the catalyst in the propylene polymerization (Fig, curve 1). The increase Al/Ti to 940 resulted in a sharp decrease of M_w to 490 000 and broadening MWD to 7.2 (curve 2).

It follows that MAO (or AlMe_3 , which is always presented in MAO solution as a trace) is an effective agent of limitation of a growing polymer chain. On the other hand the activity of **II** depended strongly on the ratio Al/Ti. For example, at Al/Ti ratio equal to 270, only traces of polymer were detected, whereas at Al/Ti ratio equal to 1600, the PP yield was equal to 45 kgPP/mol Ti·mol C_3H_6 /l h. PP prepared with **II** was a comparatively low molecular weight amorphous elastomer ($M_w=140000$, $\varepsilon_{\text{res}}=20\%$). The analysis of the PP samples by IR- and ^{13}C NMR- spectroscopy indicated that **I** had higher stereoregular polymerization ability as compared to **II** (Table).

Table. The steric pentad distribution and isotactic sequence lengths n_{iso} in the PP samples obtained with **I** and **II**

Catalyst	The steric pentad content in the PP samples, %									n_{iso}
	mmmm	mmmr	rmmr	mmrr	mrmm+ rmrr	rmrm	rrrr	rrrm	mrrm	
I	25.5	8.9	3.4	9.6	14.2	5.0	14.4	9.7	9.2	10
II	7.45	8.94	5.35	11.50	22.2	12.5	7.15	14.3	10.6	6

The activities of the catalytic systems in the ethylene homopolymerization and copolymerization of propylene with ethylene significantly higher. Thus the yields of PE obtained with **I** and **II** at 50 °C were equal to 178.5 and 2700 kg (PE)/molTi·mol C_2H_4 /l·h. It was shown that during the copolymerization the active centers of both catalysts selective polymerized ethylene. Even at a ratio of $[\text{C}_3\text{H}_8]/[\text{C}_2\text{H}_4]>10$ the resulted copolymers contained 75-85 mol% of ethylene. From ^{13}C NMR data of copolymers obtained with **II**, the copolymerization constants were estimated equal to $r_1=55.14$, and $r_2 = 0.08$. In other words, the reactivities of ethylene and propylene differed ~700 fold. As a result, the copolymers had a block character: $r_1r_2=4.6$. The presence of long ethylene sequences resulted in the formation of crystalline phase on the PE basis. However, the effect of ethylene on properties of copolymers obtained with **I** and **II** was different. In the presence of **I** the ethylene units introduced in the PP chain resulted in the decrease of MM, the degree of crystallinity and T_m of the polymer. For example, M_w and T_m of the copolymer (75 mol.% of ethylene) were equal to 550000 and 109 °C while M_w and T_m of PP obtained under similar conditions - 1180000 и 157 °C respectively. In the same time the copolymer (85 mol. % of ethylene), synthesized in the presence **II**, in contrast with the homopolymer was a higher molecular weight product and contained crystalline phase of PE ($M_w =250000$, $T_m =105$ °C). Structural, molecular-mass, thermo-physical characteristics are reflected in the mechanical properties of polymers.

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DME SYNTHESIS FROM METHANOL AND SYNGAS: EXPERIMENT AND KINETIC MODELING

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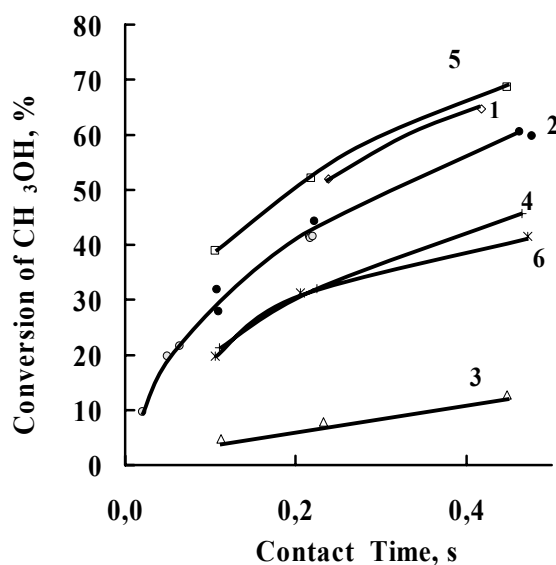
Kinetics of DME synthesis by methanol dehydration or directly by syngas processing was studied. Kinetic schemes of the process mechanism were obtained based on independent information, involving novel stages in transformations of strongly adsorbed species. Kinetic models and computer simulations were obtained on the basis of these schemes, which correlate with experimental results satisfactorily. It was shown that syngas of any composition is suitable for DME synthesis up to $H_2:CO=1:1$, including "lean" gas.

Dimethyl ether (DME) synthesis from syngas is comprised from three simultaneous reactions (macro stages): methanol synthesis (1), methanol dehydration (2), water gas shift reaction, or WGSR (3):



Accordingly, a catalyst for direct DME synthesis should be highly active in all three reactions.

Kinetics of methanol synthesis coupled with its concurrent reaction, WGSR, is studied quite well. One of the goals of this work was the study of methanol dehydration into DME



over $\gamma-Al_2O_3$ in a wide range of experimental conditions with the view to obtain a kinetic model of this reaction and finally to describe the system of reactions above. For this, 6 commercial alumina samples were tested (Fig.1); the best sample was used for kinetic studies under 0.1 MPa. It is seen that alumina provided by different companies is very different in activity.

Fig.1. Contact time dependence of methanol conversion over different $\gamma-Al_2O_3$ batches 1-6 (260 °C, 0.1MPa, $CH_3OH/N_2 = 1/1$).

For the description of methanol dehydration into DME, a mechanistic scheme involving substitution steps for strongly adsorbed species on the catalyst surface was used [1]. On this basis, a theoretical kinetic model was developed; computer simulation showed the results of calculations to be in good agreement with the experimental results. The average relative variation between calculated and experimental points was 9.9 % for 105 experiments in the range $t=220-300\text{ }^{\circ}\text{C}$, $\text{GHSV}=1-112\text{ h}^{-1}\cdot 10^3$, methanol partial pressure 0.3-1 MPa.

Kinetics of direct DME synthesis from syngas was studied over a catalyst [2] at 220-280 $^{\circ}\text{C}$, 5-10 MPa in a broad GHSV range. Kinetic model of direct DME synthesis was obtained on the basis of individual kinetic equations (1)-(3) constituting the process; newly derived kinetic model of methanol dehydration coupled with those obtained earlier [3] for methanol synthesis and water gas shift reaction allowed satisfactory description of direct DME synthesis from syngas (Fig. 2). As one of the more outstanding practical consequences of this research, it was shown that syngas of any composition is suitable for DME production, including "lean" gas (obtained by oxidation of natural gas with air) and gas with relatively low H_2 content, $\text{CO}/\text{H}_2=1:1$, for example.

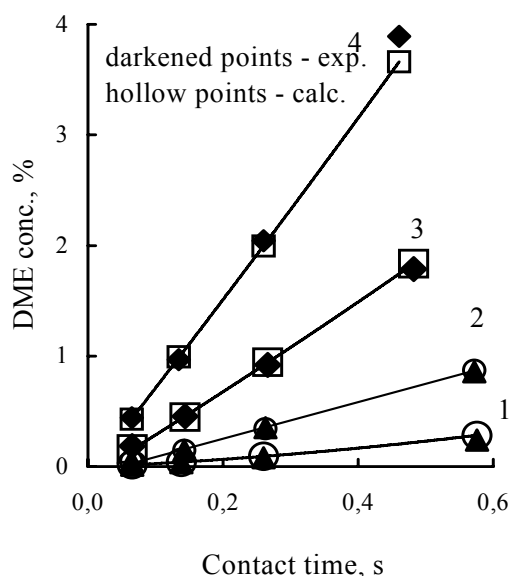


Fig.2. Checkout of the direct DME synthesis kinetic model applicability – contact time dependence of DME concentration under 5 MPa at different temperatures: 1 – 220 $^{\circ}\text{C}$; 2 - 240 $^{\circ}\text{C}$; 3 – 260 $^{\circ}\text{C}$; 4 – 280 $^{\circ}\text{C}$. Initial syngas composition: CO - 34.1; CO_2 - 2.7; H_2 - 56.3; N_2 – 2.7 (vol. %).

Acknowledgment

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**Au SUPPORTED ON CeO_2 - ZrO_2 MIXED OXIDES AS THE EFFECTIVE
CATALYSTS FOR CO OXIDATION**

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CeO_2 - ZrO_2 mixed oxides were found promising supports for *Au* nanoparticles in *CO* oxidation. $Au/Ce_{0.75}Zr_{0.25}O_2$ washed in ammonia presents the highest activity, already at room temperature. This study confirms the poisoning effect of the residual chloride on the catalytic performance of $Au/Ce_{1-x}Zr_xO_2$ catalysts. The average *Au* particle size is bigger for the catalysts containing residual chloride, as confirmed by TEM, SEM-EDS and TOF-SIMS. The activity depends on *Ce/Zr* molar ratio and increases with the increasing reducibility of the supports and catalysts, as confirmed by TPR. It indicates the role of the support properties, especially reducibility, in the creation of catalytic performance of *Au/oxide* catalysts.

Catalytic oxidation of *CO* is one of the important reactions due to its relevance in practical applications such as purification of breathing air in closed spaces, safety masks, gas sensors for the detection of trace amounts of *CO* in air, closed-cycle CO_2 lasers, automotive exhaust treatments, etc. The possibility of using supported gold nanoparticles as efficient catalysts for low temperatures reactions has attracted a lot of interest, since the pioneering work of Haruta which showed high activity towards *CO* oxidation with gold deposited on various metal oxides (1). Compared to a highly dispersed supported *Pt* catalysts, *Au* catalysts are much more active than other noble metal catalysts at temperatures below 130 °C (2).

The aim of this work was an attempt to understand the fundamental problems related to the catalysis on supported *Au* including the effect of: individual stages of the catalysts preparation, size of *Au* particles, presence of the residual *Cl* on the catalytic performance of $Au/Ce_{1-x}Zr_xO_2$ catalysts in *CO* oxidation. Special attention was paid to the specific role of support, not only as a stabilizer of *Au* dispersion and modifier of its electronic state but also as a participant in activation of oxygen.

CeO_2 - ZrO_2 mixed oxides, CeO_2 and ZrO_2 as a supports for *Au* were used. CeO_2 - ZrO_2 materials possess unique redox properties and high mobility of lattice oxygen, strongly dependant on *Ce/Zr* molar ratio. Furthermore, ceria is known to be active for the removal of post-combustion pollutants (3). It should be also noted that so far, CeO_2 - ZrO_2 systems widely studied in other applications (4), have not been examined as *Au* supports in the *CO* oxidation.

A series of $Ce_{1-x}Zr_xO_2$ solid solutions, CeO_2 and ZrO_2 was prepared by sol-gel method, based on a thermal decomposition of mixed propionates and calcined at 550 °C. The catalysts with the nominal *Au* content 2 wt. % and 5 wt. % supported on $Ce_{1-x}Zr_xO_2$ ($x = 0, 0.25, 0.5,$

0.75, 1) were prepared by the direct anionic exchange (DAE) method developed by Ivanova *et al.* (5) for Au/Al_2O_3 and next, in the cooperation with that group, adapted by us for the preparation of Au/Mg_4Al_2 (6). In order to remove the remaining Cl^- ions, part of the catalyst was washed in either warm water or 4M ammonia solution. After drying at 120 °C overnight, the catalysts were calcined under air at 300 °C for 4 hours.

The obtained systems were characterized by XRD, BET, H_2 -TPR, CO-TPR, AAS, TEM, SEM-EDS, TOF-SIMS and tested in the CO oxidation reaction, using a gas mixture containing 1.6 vol.% CO and 3.3 vol.% O_2 (He as an eluant gas).

The activity of unsupported mixed oxides was found to be dependant on Ce/Zr molar ratio. The CO conversion increases with the increasing cerium content. $Ce_{0.75}Zr_{0.25}O_2$ (Ce/Zr molar ratio = 3), with the total CO conversion at 420 °C presents the highest activity. Taking into consideration the TPR results, one can say that the sequence of the increasing activity clearly follows the sequence of the increasing reducibility of the oxides.

This study confirms the poisoning effect of the residual chloride on the catalytic performance of $Au/Ce_{1-x}Zr_xO_2$ catalysts. The average Au particle size is bigger for the catalysts containing residual chloride. All the procedures used for washing allow to decrease the average Au particle size. Depending on the washing procedure, one can observe different activities and different Au particle sizes. TEM measurements show the smallest Au particles for the series of catalysts washed in ammonia. Those catalysts were active at relatively low temperatures. The activity of $Au/Ce_{1-x}Zr_xO_2$ depends on Ce/Zr molar ratio, with a maximum obtained for $Au/Ce_{0.75}Zr_{0.25}O_2$ (Ce/Zr molar ratio = 3). The samples with the higher zirconium content were found less active. The lowest activity was observed for Au/ZrO_2 .

The presence of Au particles facilitates the reduction of the supports as indicated by the decrease in the temperature of the maximum of the reduction peak, as confirmed by TPR measurements. It suggests the activation of H_2 molecule on Au nanoparticles. The sequence of the increasing activity clearly follows the sequence of the increasing reducibility of the catalysts. It indicates the role of the support properties, especially reducibility, in the creation of catalytic performance of Au/oxide catalysts. CeO_2 - ZrO_2 mixed oxides are promising supports for Au nanoparticles in CO oxidation.

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CHLORINATED SULFOCATIONITES – EFFECTIVE CATALYSTS OF INDUCED OXIDATION OF UNSATURATED HYDROCARBONS

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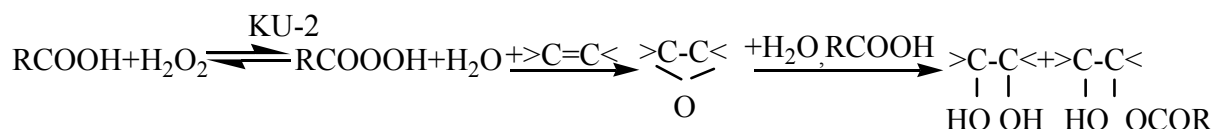
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Introduction.

Modified forms of ionites, possessing a number of advantages against homogeneous catalysts, are recently widely applied in reactions of liquid phase oxidation of unsaturated hydrocarbons [1].

In the present work we present results of study of activity of modified forms of KU-2 type cationite in reactions of induced oxidation of unsaturated hydrocarbons - octene-1, decene-1, bicyclo heptene and dicyclopentadiene in the presence of carboxylic acids and hydrogen peroxide by the circuit:



Experimental results and discussion.

Modification of H-form of cationites has been carried out under conditions of chlorine or bromine induction in the system of halogen hydric acids and hydrogen peroxide (or sodium hypochlorite) [2]. Active and stable forms of catalysts were obtained upon introduction of 2,2-9,5 mass% of chlorine in composition of cationites (Table 1).

Modification by bromine didn't give positive results, as full substitution of SO₃H groups by bromine atoms took place. With the increase of chlorine content in the macromolecule up to 9,5 mass%, cationite stability rose essentially, and its mass and activity remained practically unchanged after 3500 hours of continuous work in flow reactor.

Non-productive decay of peroxide compounds for this period was 1,3%.

Polymeric structure of sulfocationites essentially influenced their activity and stability in the reaction of oxidation of acetic acid by hydrogen peroxide in dioxane solution, formation rate constant of peroxyacetic acid is described by linear equation: $K_i = A_i C$, where K_i is rate constant; C - cationite gauntity, (mg-equiv), A_i - angle of slope of linear dependence. Catalytic activity criterion is A_i value, which characterizes yield of product for unit of active site of cationite. Rate constant of direct stage of oxidation of acetic acid by hydrogen peroxide depending upon type of modified cationites has the following values:

($K \cdot 10^6$ /mole·mg·equiv.s); KU-2x2-10,2; KU-2x6-8,24; KU-2x8-6,84; KU-2x8p-9,64; KU-2x12-4,02; KU-23-11,42, H₂SO₄-13,46.

Taking accessibility of active sites of homogeneous catalysts (H₂SO₄) 100 % as a criterion, accessibility of active sites of cationites has been estimated. In particular, accessibility of active sites of chlorosulfocationite KU-2x8 is ≈42 %. With increase of porosity of modified resins (KU 2x8 p and KU-23) accessibility of acid sites increases up to 86 %. On grinding granules of modified cationites (to 0,125 mm), their activity practically coincides with activity of homogeneous catalysts (H₂SO₄). When using chlorosulfocationite KU-2x8 containing 9,5 mass% of chlorine in reactions of induced oxidation of the above mentioned olefins, the main products of reaction within 30-50 °C range are the corresponding epoxides (68-76 %) (Table 2). At above 60 °C the rate of secondary reactions of transformation of oxirane compounds into diols and its monoacetates increases.

Table 1. Influence of work duration of modified cationites on chlorine content in oxidation reaction of acetic acid (CH₃COOH:H₂O₂=4:1; temperature 40 °C)

Catalyst work duration, hour						
Chlorine content, mass%.	KU-2x2	KU-2x6	KU-2x8	KU-2x8p	KU-2-12	KU-23
0	300	500	1500	1300	1600	1200
2,2	400	600	2500	1800	2100	1600
7,5	600	800	300	2500	2500	2100
9,5	700	900	3500	3100	2900	2800

Table 2. Influence of various factors on parameters of process of induced epoxidation of tritsiklo [5,2,1,0^{2,6}] dekadene-3,8 by hydrogen peroxide (cat. Chlorosulfocationite KU-2x8., 9,5 mass%Cl)

Initial concentration, mole·l ⁻¹			T, K	τ, min.	Conversion H ₂ O ₂ , %	Yield of mono- and diepoxide, %
H ₂ O ₂	CH ₃ COOH	diene				
1	1	1	293	420	55.8	47.3
1	1	1	303	360	70.3	62.8
1	1	1	313	300	80.0	65.0
2	1	1	313	300	73.3	65.1
2	1	1	323	240	82.1	68.0
2	2	1	323	180	90.4	76.0
1.5	3	1	313	313	95.0	63.2

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**LOW-TEMPERATURE ISOMERIZATION OF PENTANE BY SUPERACID
COMPLEXES BASED ON ALUMINIUM HALIDES**

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We have used system formed by the combination of aluminium halide with polyhalomethanes in the presence of solvent such as dihalomethane in our research of isomerisation of n-pentane as homogenous catalyst. Results evidence of possibility to realize the reaction of isomerization under mild conditions ($T = 20\text{ }^{\circ}\text{C}$, $P = 0,1\text{ MPa}$, without hydrogen).

Isomerization of n-alkanes is one of major processes of organic and petrochemistry synthesis. Isoalkanes is used as important constituent of high-octane fuel, as well as in synthesis of isoprene and isobutylene – monomers for synthetic rubber.

In isomerization of n-alkanes homogeneous and heterogeneous acid catalyst are used.

Contemporary industrial catalysts are heterogeneous bifunctional catalytic systems such as metal-carrier. Imperfections of present industrial method of isomerization over heterogeneous catalyst are high power intensity ($T = 300 - 400\text{ }^{\circ}\text{C}$, $P = 2 - 4\text{ MPa}$, presence of hydrogen) and low conversion and selectivity of one circle of the reaction.

Low-temperature isomerization is more preferable in view of thermodynamic equilibrium because it makes more favorable conditions for isoalkanes formation including highfurcated isomers with high antiknock properties. Low-temperature process provides highest possible conversion of one circle of the reaction.

We have used system formed by the combination of aluminium halide with polyhalomethanes in the presence of solvent such as dihalomethane in our research of isomerisation of n-pentane as homogenous catalyst [1]. Catalytic system displays high activity at low temperature $T = 20\text{ }^{\circ}\text{C}$ (conversion of hydrocarbon 70 %). We have varied aluminium halides and solvent's nature, ratio of catalytic system:hydrocarbon, time of the reaction. Aluminium halides nature has effect on the rate of the reaction and on formation of different products. In any case major process is complicated by cracking of alkanes. The main products of cracking are light and heavy isostructural hydrocarbons. We have found a cocatalyst the presence of which reduces yield of products of cracking and raises selectivity of the main reaction.

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EFFECTS OF THE PROPERTIES OF SO₄/ZrO₂ SOLID-PHASE CATALYSTS ON THE PRODUCTS OF R-(+)-LIMONENE DIEPOXIDES TRANSFORMATION AND REACTION MECHANISM

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We have synthesized a number of acidic SO₄/ZrO₂ catalysts with different content of the sulfate ions. It has been shown for the first time that the qualitative and quantitative composition of the reaction mixture of diepoxide limonene transformations changes by varying the concentration of acid centers on SO₄/ZrO₂.

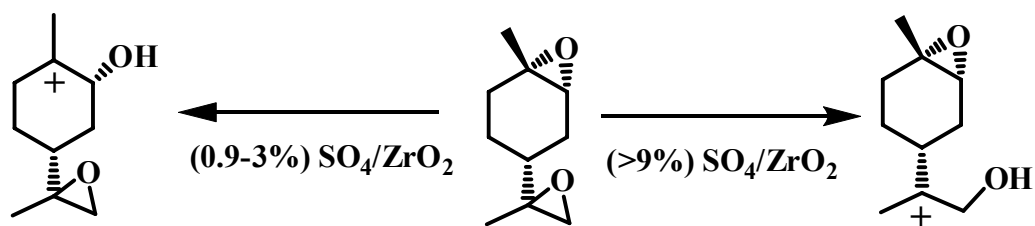
A number of acidic SO₄/ZrO₂ catalysts with different content of the sulfate ions have been synthesized. Acidic properties (Lewis and Brønsted nature) of the sulfated zirconias were investigated by new method based upon analysis of the characteristic bands of the pyridine in the DRIFT spectra after its adsorption from the solution in methylene chloride at room temperature. This method was elaborated to compare the acidic properties and activity of the catalysts in the similar conditions.

The “island” model of the sulfate centers could be proposed on the base of the data. At small addition of sulfate ions (0.9 % SO₄) they are able to form new type of Lewis centers with coordinated unsaturated Zr⁴⁺ cations. At this amount of the sulfate ions they occupy ≈ 1.5 % of the surface area. Supporting of the 3 % SO₄ could provide for the enhancement of the Lewis centers as the sulfate ions occupy only ≈ 3 % of the total area. In fact, the numbers of Lewis centers decrease and centers of the Brønsted nature appear. At higher content of the sulfate ions only Brønsted centers are determined and SSA diminishes noticeably

The transformations of limonene diepoxides on solid SO₄/ZrO₂ acids were investigated by gradually varying the acid properties of the solid catalyst. It has been shown for the first time that qualitative and quantitative composition of the reaction mixture of diepoxides transformations may change by varying the concentration of acid centers in SO₄/ZrO₂ solid acid. At a 0.9-3 % level of sulfation the dominant compounds were the products of the initial cleavage of the 8,9-epoxy group of limonene diepoxides. With the contents of sulfo groups increased to more than 9 %, the key transformations were those that started with cleavage of

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the 1,2-epoxy group. The concentration of acid centers also affects the stereochemical composition of the product mixture.



CATALYTIC ACTIVITY OF POLYMER-FERROCYANIDE COMPLEXES IN PARTIAL OXIDATION OF CYCLOHEXANE WITH HYDROGEN PEROXIDE

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Ferrocyanide complexes with different outosphere metal ions as well as the same complexes modified with polyhexamethyleneguanidine (PHMG) have been used as catalysts for hydrogen peroxide decomposition and oxidation of cyclohexane with H_2O_2 . The polymer modified ferrocyanide complexes showed higher activity and selectivity in partial oxidation of cyclohexane than corresponding inorganic complexes. The most stable catalyst for cyclohexane oxidation was $Cu_2[Fe(CN)_6]$ stabilized with PHMG.

Currently catalytic systems on the basis of metal complexes with polymer ligands are of great interest. The advantage of such systems is combinations of advantages of both homogeneous and heterogeneous catalysts. Besides, polymer-metal complexes in some kind are similar to enzymes regarding to their activity and selectivity under mild conditions. Achievement of high selectivity in partial hydrocarbon activation is a very important problem, solution of which is related to development of new catalysts including modified with polymers.

Catalyst for selective oxidation should have moderate red-ox properties so, we developed a method for synthesis of ferrocyanide complexes with polymer ligands. Polyhexamethyleneguanidin (PHMG) was selected as the ligand. Presence of nitrogen containing groups enable the polymer to form insoluble complexes. Formation of the complex between PHMG and ferrocyanide was confirmed with IR-spectroscopy method.

First, comparative activity of the polymer-metal complexes and inorganic complexes was studied in hydrogen peroxide decomposition. It was found that in acetonitrile solution intensive decomposition of hydrogen peroxide proceed over potassium ferrocyanide; however conversion of H_2O_2 was at 80 %. Copper and iron(III) ferrocyanides are less active (4 hours), but the conversion was up to 100 %. Polymer-ferrocyanide complexes have similar activity and similar conversion rate as compared to that for inorganic complexes. At the same time, polymer-ferrocyanide complexes in acetonitrile solution are more active in cyclohexane partial oxidation (Table1).

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Table 1. Oxidation of cyclohexane with hydrogen peroxide in acetonitrile over ferrocyanide and polymer-ferrocyanide complexes: $m_{\text{kat}}=0,03\text{g}$; $C_{\text{H}_2\text{O}_2} = 2 \cdot 10^{-2} \text{ M/l}$; $C_{\text{C}_6\text{H}_{12}} = 2,7 \cdot 10^{-3} \text{ M/l}$; 40°C .

Catalyst	Reaction time, h	Conversion of C_6H_{12} , %	Yield, %	
			Cyclohexanone	Cyclohexanol
$\text{K}_4[\text{Fe}(\text{CN})_6] + \text{PHMG}$	4	10,3	6,0	4,0
$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + \text{PHMG}$	4	18	9,0	8,5
$\text{Cu}_2[\text{Fe}(\text{CN})_6] + \text{PHMG}$	4	24,6	13,0	11,3
$\text{K}_4[\text{Fe}(\text{CN})_6]$	4	-	-	-
$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	4	7,8	4,0	3,5
$\text{Cu}_2[\text{Fe}(\text{CN})_6]$	4	12	6,1	5,3

In all cases of cyclohexane oxidation the products are cyclohexanone, cyclohexanol and small amount of unidentified substance.

Therefore, the polymer modified ferrocyanide complexes show rather higher activity and selectivity in partial oxidation of cyclohexane with hydrogen peroxide than corresponding inorganic complexes.

SYNTHESIS OF OXIRANES FROM RENEWABLE RAW MATERIALS COMPONENTS

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Utilization of renewable raw materials, such as industrial wood residue, offers possibilities of manufacturing of epoxy compounds of commercial value. The field of application of epoxides is rather wide. Epoxides are efficient plasticizers (modifiers, stabilizing agents and diluents) of plastics and epoxy resins as well as precursors in the synthesis of different pharmaceutical products [1]. One of the most promising processes for preparing of epoxides from raw materials is the method of phase-transfer catalysis, providing direct oxidation of different organic substrates in the presence of peroxopolyoxotungstate based catalysts [2].

The present work reports screening of substrates of different nature (unsaturated aliphatic compounds, terpenoids and coumarins) in the reaction of oxidation by H₂O₂ in a two-phase solution in the presence of methyltri-*n*-octylammonium tetrakis(oxodiperoxotungsto)-phosphate.

It was established that epoxidation of oleic and ricinoleic acids and their ethers provides 90 % selectivity with respect to epoxide.

Epoxidation of coumarins was performed using peucedanin as an example. It was oxidized to yield unstable epoxide, which transforms into ketol hydroxyoreozelon under reaction conditions.

The process of oxidation of natural terpenoids (such as betulin isolated from birch bark) results in the formation of a number of products, including epoxide, the yield of which is not higher than 30 %. By contrast, the oxidation of betulin diacetate provides 90% selectivity with respect to epoxide.

Since the above betulin derivatives exhibit antiphlogistic, antiviral and antineoplastic activity, they are of profound interest for medicinal chemistry [3].

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SELECTIVE OXIDATION OF FORMALDEHYDE OVER SUPPORTED VANADIA CATALYSTS

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The effect of nature of the oxide support on catalytic properties of 20%V₂O₅/TiO₂ (VTi), 30%V₂O₅/Al₂O₃ (VAl), 20%V₂O₅/SiO₂ (VSi) was studied for formaldehyde selective oxidation. Formic acid is the main product of formaldehyde oxidation over bulk V₂O₅ and supported vanadia catalysts. The following row of catalytic activity was determined: VTi >> VAl > VSi > V₂O₅. The highest activity of the VTi catalysts was obtained due to chemical interaction of vanadium with TiO₂ contrary to SiO₂ and γ -Al₂O₃. The effect of the support on the structure and bond strength of formaldehyde surface species was investigated.

1. Introduction

Supported vanadium oxide catalysts represent an important class of heterogeneous catalysts that are widely used in the chemical industry in various selective oxidation reaction. Catalytic properties of these catalysts are essentially depend on the nature of support.

In the present work we investigated the influence of the support nature on the selectivity / activity of the supported vanadia catalysts in the reaction of formaldehyde oxidation. The effect of the support on the structure and bond strength of formaldehyde surface species with vanadium sites was investigated.

2. Experimental

The catalysts 20% V₂O₅/TiO₂ (VTi), 30% V₂O₅/Al₂O₃ (VAl), 20% V₂O₅/SiO₂ (VSi) were prepared by the incipient wetness impregnation. The samples were dried at 110 °C and calcined at 400 °C for 4 h in a stream of air.

A Siemens D-500 diffractometer (Germany) with K α radiation was used for *in situ* X-ray diffraction (XRD) studies.

IR spectra were recorded with a Fourier spectrometer BOMEM MB-102 at room temperature. The sample (2 mg) was mixed with KBr (500 mg) and extruded to form a disk. A flow-through quartz high-temperature IR cell-reactor with the CaF₂ windows was employed for the *in situ* IR experiments.

Catalyst performance was studied in a flow circuit setup with differential reactor under atmospheric pressure at 120 °C and with constant composition of the reaction mixture (% vol): 5% CH₂O, 10 % H₂O, and 85 % air.

3. Results and discussion

The BET surface areas of the supported vanadium oxide catalysts and their corresponding surface vanadia densities (V/nm^2), and catalytic properties are presented in a Table. VSi and VAl catalysts present the mixture of phases of V_2O_5 and support (SiO_2 и $\gamma-Al_2O_3$, accordingly). VTi catalysts presents phase of anatase, modified by vanadia, and only small amounts of crystalline phase of V_2O_5 .

$HCOOCH_3$ was shown to be the main reaction product over $\gamma-Al_2O_3$ and TiO_2 . SiO_2 is inactive in formaldehyde oxidation.

Formic acid was shown to be the main product of formaldehyde oxidation under V_2O_5 , VTi and VSi samples. $HCOOCH_3$ and formic acid were the products of formaldehyde oxidation over VAl sample.

Table. Catalytic properties of the V_2O_5 and supported vanadium catalysts.

Catalyst	Phase composition	S, m^2/g	V/ nm^2 , %	t, s	X, %	S, %			$r \cdot 10^{-16}$, molec/atomV*s
						HCOOH	$HCOOCH_3$	CO_x	
V_2O_5	V_2O_5	5	-	2.8	4.6	91.8	6.8	3.1	0.04
VSi	V_2O_5 , SiO_2	129	10.1	1.3	6.6	81.7	18.3	-	0.64
VAl	V_2O_5 , $\gamma-Al_2O_3$	183	10.7	1.5	18.7	48.2	49.1	2.7	1.04
VTi	Anatase, V_2O_5 traces	94	14.0	0.3	34.6	96.2	1.3	2.5	17.8

t,s – the contact time; X – conversion ; S – selectivity; r – the reaction rate. .

The following row of catalytic activity in reaction of formaldehyde oxidation was determined: VTi \gg VAl $>$ VSi $>$ V_2O_5 . The highest activity of VTi catalysts was obtained due to chemical interaction of vanadium with TiO_2 contrary to SiO_2 and $\gamma-Al_2O_3$.

The interaction of formaldehyde and its oxidation products (i.e. formic acid and methyl formate) was studied by in situ FT-IR spectroscopy. Bidentate formates form during formaldehyde oxidation. The same formates form during formic acid adsorption on all studied supported vanadium catalysts. The effect of the support on the rate of formates decomposition and on bond strength of bidentate formates with vanadium sites was displayed.

On the base of constants rates of formate decomposition the row of stability ones may be presented: VAl $>$ VTi $>$ VSi. The effect bond strength on direction of formaldehyde conversion is observed.

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**BIODIESEL PRODUCTION FROM OLEIC ACID
USING $H_3PW_{12}O_{40}$ AND $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ AS CATALYSTS**

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Esterification of oleic acid with methanol using $H_3PW_{12}O_{40}$ (HPA) or $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as catalysts was studied. HPA proved to be a very efficient catalyst at room temperature with the possibility of being reusable. HPA can be separated from the oleic phase by repeated washing with water and precipitation with cesium carbonate. UV-visible spectrophotometry revealed that HPA was present only in the aqueous phase. XRD measurements showed that the keggin structure of the cesium salt was formed. The reaction was carried out at 25-110 °C with a (oleic acid/catalyst) weight ratio of 30-100. On the other hand $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ can be used directly as an heterogeneous catalyst with good conversions at 90° C. Liquid phase dehydration of 1,4-butanediol was employed for assessing the acidity of the catalysts..

Heteropoly compounds are used both as heterogeneous solid and as homogeneous solution catalyst (1). In this sense there is great interest in replacing hazardous liquid acids (e.g. H_2SO_4) or corrosive Lewis solid acids used in esterification reactions by other more environmentally friendly solid acids (2). Biodiesel, an alternative diesel fuel, is generally synthesized by the transesterification of natural oils or by direct esterification of free fatty acids present in larger amount of Brazilian natural plants. (3). In the present work acid-catalyzed esterification of oleic acids with methanol was studied over $H_3PW_{12}O_{40}$ in the homogeneous phase or $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as heterogeneous catalyst. The reutilization of the HPA by separation and precipitation into $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was also performed. Using 30 mg de $H_3PW_{12}O_{40}$ (HPA), a conversion of 45 % was obtained after 10 h (oleic acid/catalyst w/w \cong 100). The only observed product was methyl oleate. For higher amounts of HPA conversion of 80 % was reached (oleic acid/catalyst w/w \cong 30). $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs-HPA) was also tested as a heterogeneous catalyst. Its performance was worst than for free HPA, but also showed good activity. Using an oleic acid/catalyst w/w ratio of 30 a conversion of 30 % is observed after 10 h. Increasing the amount of catalyst, conversion of 45 % was obtained (oleic acid/catalyst w/w \cong 15). The acidity of the catalysts was estimated from data of dehydration of 1-4-butanediol. HPA showed higher conversion

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values (and also more acidity) in comparison to their partially exchanged cesium salt, in spite of some authors have postulated that the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalyst displays superacidity (4). Another possibility to re-use homogeneous HPA is trying to recover it from the reaction. The products of the esterification of oleic acid with methanol catalyzed by HPA were washed several times with water. Then oleic and aqueous phase were analyzed by gas chromatography. Oleic acid, methanol (0.021 % w/w) and methyl oleate were present in the oleic phase. Methanol, di-n-butyl ether (internal standard for chromatographic analysis) and oleic acid (0.024 % w/w) were present in the aqueous phase. The inspection of the UV-vis spectra of the oleic and aqueous phases was done in order to detect the keggin structure of HPA and revealed that HPA is only present in the aqueous phase. A Cs salt of HPA was prepared by using this aqueous phase of the product reaction. A solution of Cs_2CO_3 was added dropwise and a white precipitate of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was formed. When the precipitation was finished, the precipitate was filtered, dried at 100 °C in a oven and finally calcined at 300 °C in a muffle. The XRD spectrum of the Cs salt is similar to the spectrum of the free acid, thus confirming that the *keggin* structure of the free acid is retained in the Cs salt (5), opening the possibility of regenerate the free HPA to use it in other reactions.

Acknowledgments

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THE MECHANISM OF PHENOL OXIDATION BY OXYGEN AT THE PRESENCE OF NITROGEN OXIDES AND COBALT COMPLEXES FIXED ON HUMIC ACID

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The results of research of kinetic of phenol oxidation by oxygen at 333K in the presence of nitrogen oxides and complexes of cobalt fixed on humic acid are submitted in article. It is established, that in the presence of complexes of cobalt fixed on humic acid and nitrogen oxides it is possible to carry out oxidation of phenol in soft conditions. Fixing of mononuclear complexes on humic acid promotes destruction of an aromatic ring, reception of aliphatic aldehydes and cetones while process of oxidation at the presence of binuclear complexes of cobalt fixed on humic acid runs in formation of benzoquinone. The given system works stably. Results of this work was obtained in the frames of project NATO SfP 981438 "Phenols of industrial wastewaters:detection, conversion, degradation".

Phenolic compounds take the third place after heavy metals and mineral oil on occurrence in biosphere and ecological danger and are the basic toxic component of sewage of some manufactures.

It is found by us, that phenol in a water solution is stably oxidized in soft conditions in the presence of cobalt complexes fixed on humic acid and nitrogen oxides. Conditions at which nitrogen oxides are not come out from catalytic cycle are optimized.

Injection of sodium nitrite in a solution $\text{Co}(\text{NO}_3)_2 - \text{HA} - \text{HClO}_4 - \text{C}_6\text{H}_5\text{OH} - \text{H}_2\text{O}$ leads to increasing of redox-potential up to 100-150 mV, increasing of the rate of oxidation of phenol. The increasing of intensity of bands in IR-spectra, characteristic for NO_2 and decreasing of intensity of bands NO corresponds to increasing of the rate of absorption of oxygen and increasing of redox-potential in a solution. The given fact also confirms the assumption that autocatalytic character of oxidation is caused by generation of NO_2 as a result of reaction (1).



The basic part of process occurs at constant containing of NO_2 in a gas and liquid phase that allows to assume that catalysis of phenol oxidation is concerned with this compound.

In whole researched intervals of $\text{C}_{\text{Co}(\text{NO}_3)_2}$ the quantity of the absorbed oxygen does not change, the degree of transformation of phenol changes within the interval from 99,0 up to 87,0 %. The maximal degree of transformation of $\text{C}_6\text{H}_5\text{OH}$ is observed at the minimal

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concentration of the cobalt fixed on to humic acid though at the minimal rate of oxidation. In IR-spectra of products there are no bands, characteristic for an aromatic ring (3180-3120 cm^{-1}), appear the bands corresponding to C=O (1705 cm^{-1}) and C=C (1600-1580 cm^{-1} , 1400 cm^{-1}) a linear circuit. Videlicet an oxidizing destruction of an aromatic ring and occurrence of linear cetones proceeds with low rate of oxidation, at $C_{\text{Co}(\text{NO}_3)_2} < 5 \cdot 10^{-4}$ mole/l. The rate of oxidation sharply grows, but the mixture of o- and p-benzoquinones is formed in products at $C_{\text{Co}(\text{NO}_3)_2} > 1 \cdot 10^{-3}$ mole/l.

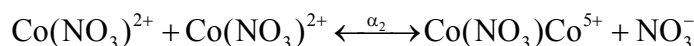
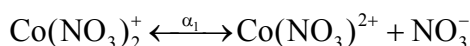
Dependence of the rate of oxygen absorption (W_{O_2} at $Q_{\text{O}_2} = 2 \cdot 10^{-2}$ mole/l) from $C_{\text{Co}(\text{NO}_3)_2}$ is described by the equation:

$$W_{\text{O}_2} = \frac{k_1 \cdot C_{\text{Co}(\text{NO}_3)_2} \cdot \alpha_1 + k_2 \cdot C_{\text{Co}(\text{NO}_3)_2}^2 \cdot \alpha_1 \cdot \alpha_2}{1 + C_{\text{Co}(\text{NO}_3)_2} \cdot \alpha_1 + C_{\text{Co}(\text{NO}_3)_2}^2 \cdot \alpha_1 \cdot \alpha_2}$$

At 60°C parameters of the equation work out:

k_1 , mole/l·min	k_2 , mole/l·min	α_1 , l/mole	α_2 , l/mole
$3 \cdot 10^{-3}$	$1,8 \cdot 10^{-2}$	$3,3 \cdot 10^2$	$5,75 \cdot 10^2$

The analysis has shown that the mononuclear and binuclear complexes of cobalt fixed on humic acid work in system.



The results in system $\text{C}(\text{NO}_3)_2 - \text{C}_6\text{H}_5\text{OH} - \Gamma\text{K} - \text{HClO}_4 - \text{H}_2\text{O} - \text{NaNO}_2$ in interval C_{HA} from $0,5 \cdot 10^{-3}$ mole/l up to $5 \cdot 10^{-3}$ mole/l at a variation of humic acid concentration are obtained. It shows that the changing of humic acid concentration does not influence on stoichiometry of reaction of phenol oxidation, but raises catalytic activity of cobalt complexes. Dependence of rate of oxygen absorption on initial concentration of humic acid is described by the equation:

$W_{\text{O}_2} = k \cdot \chi_{[\text{CoNO}_3\text{Co}]\Gamma\text{K}}$, where $\chi_{[\text{CoNO}_3\text{Co}]\Gamma\text{K}}$ - a part of an active cobalt complex fixed on humic acid.

Fixing of mononuclear complexes on humic acid promotes destruction of an aromatic ring, reception of aliphatic aldehydes and cetones while process of oxidation runs out to formation of benzoquinone in the presence of binuclear complexes of cobalt fixed on humic acid. The given system works stably. N_2O is not formed in investigated conditions, nitrogen oxides are not formed in catalytic cycle.

The mechanism of catalytic process is offered.

THERMOSTABILITY OF Pd-ZEOLITE CATALYSTS FOR DEEP OXIDATION OF HYDROCARBONS

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The adsorptive-catalytic cleaning of exhaust gases from toxic hydrocarbons supposes the presence of active combustion catalysts on the surface of adsorbents. The Pd-zeolite catalysts are perspective in this relation. The high temperatures often develop at the combustion of adsorbed hydrocarbons. So the main goal of our work was to prepare a set of Pd-zeolite catalysts and to investigate their activity after heat treatment at high temperatures. Besides it was supposed to study the influence of the introducing of known modifiers: CeO₂ and ZrO₂ in catalysts composition on catalysts thermostability. The zeolites: ZSM-5, ZSM-12, ZVN, ZVM, β – were used as supports. The last four were produced at JSC “Angarsk Plant for Catalysts Production and Organic Synthesis”¹.

The catalyst activities were measured in the methane deep oxidation with flow-circular setup and in toluene complete oxidation in flow reactor. In the last case the activity was determined as the temperature of 50% conversion of toluene.

The results are presented in the Fig. 1-3.

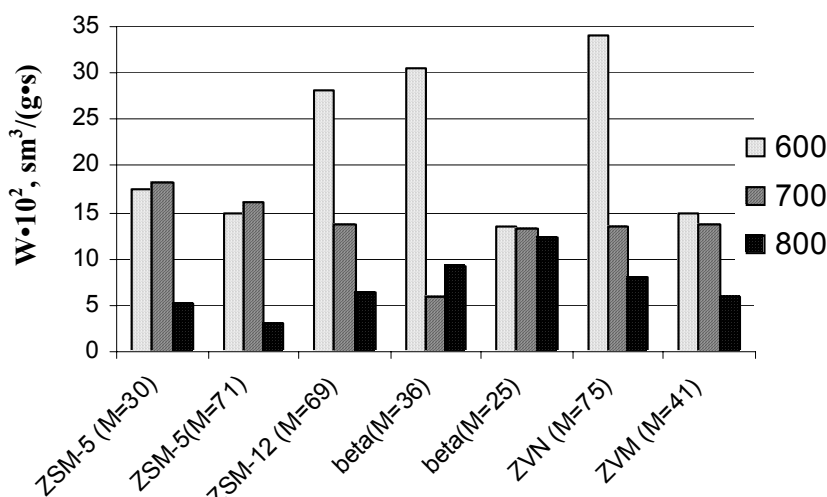


Fig.1. Catalyst activity in deep oxidation of methane (500 °C, C₀CH₄ = 0,5% vol., X = 50%)

¹ The authors express their Thanks to M.I. Tselyutina for assignment of the set of zeolites for investigation.

It is seen that the most thermostable sample is 2%Pd (mass.)/ β (with $M=\text{SiO}_2/\text{Al}_2\text{O}_3=25$). It was shown that the β ($\text{SiO}_2/\text{Al}_2\text{O}_3=25$) based catalysts with Pd content 1% and 2% mass are approximately equal in their activities and thermo stabilities. Therefore the investigation of the influence of the modification with CeO_2 and ZrO_2 was fulfilled with catalyst 1%Pd/ β . It was found that independently from the method of modifier introduction (ionic exchange or impregnation), the modification considerably increases the catalyst activities both in methane and toluene oxidation. For example, the decreasing of $T_{50\%}$ of toluene conversion is $\sim 25\text{-}35$ °C for initial catalysts (calcinated at 600 °C) if the introduction of Ce and Zr was fulfilled by ionic exchange and it is $\sim 35\text{-}50$ °C if the introduction of Ce and Zr was fulfilled by impregnation. The most active sample is 1% Pd/ 1%Zr-imp/ β (Fig. 2). But after calcination at 800 °C or after hydrothermal treatment at this temperature the activities of modified and unmodified catalysts become equal.

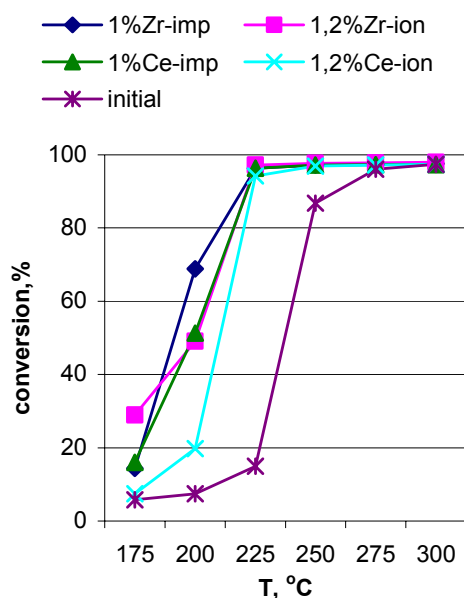


Fig. 2. Activities of initial and modified by Ce and Zr 1%Pd/ β ($\text{SiO}_2/\text{Al}_2\text{O}_3=25$) samples in toluene deep oxidation. The heat treatment temperature of catalysts is 600 °C on air.

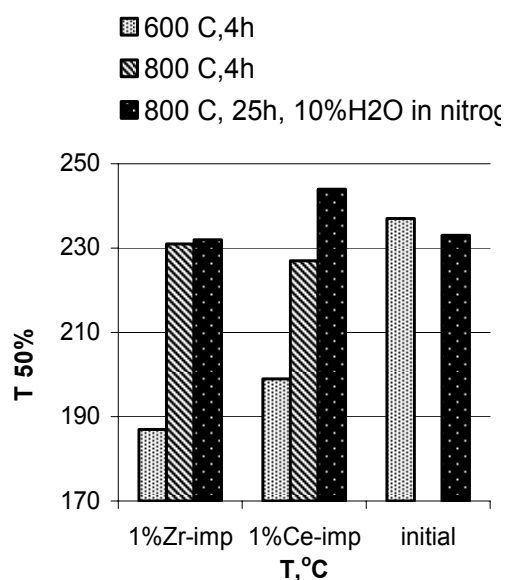


Fig. 3. Thermostability of initial and modified catalysts 1%Pd/ β ($\text{SiO}_2/\text{Al}_2\text{O}_3=25$).

The obtained results were discussed by taking into account the strong interaction of Pd with modifiers and acceptor sites on zeolite surface.

It was noted that at using β -zeolite with different modulus ($\text{SiO}_2/\text{Al}_2\text{O}_3=25$ or 11) as support the acidity of zeolite influenced on the activity and thermostability of both initial and modified catalysts.

CO OXIDATION ON CuO-CeO₂/γ-Al₂O₃ CATALYSTS PREPARED BY SURFACE SELF-PROPAGATING THERMAL SYNTHESIS (SSTS) METHOD

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The goal of this work was preparation of CuO-CeO₂/γ-Al₂O₃ catalysts by means of surface self-propagating thermal synthesis (SSTS) instead of conventional impregnation and investigation of its activity in CO oxidation reaction. CuO and CeO₂ precursors were Cu(NO₃)₂ and Ce(NO₃)₃, respectively. In the case of SSTS citric acid was used as a fuel dope along with precursors. All activity tests were carried out in temperature range 50÷150 °C. The reaction mixture consisting of CO (1% vol), O₂ (2% vol) and H₂ or N₂ as a balance was used in this study. It was observed that catalysts prepared by SSTS method show higher activity in comparison with impregnated catalysts.

This work continues the investigation in the field of catalysts preparation by active components self-propagating thermal synthesis on the surface of the various supports such as porous metal hire, honeycomb cordierite blocks, glass fiber fabric which are widely investigated in laboratory of catalytic conversion of hydrocarbons (IHP SB RAS) during last few years [1, 2].

Earlier we carried out the study of supported CuO-CeO₂/γ-Al₂O₃ catalysts, prepared by conventional impregnation method in reaction of selective CO oxidation in the presence of hydrogen in collaboration with laboratory of catalytic processes in fuel cells of BIC SB RAS. This process is very important for hydrogenous mixture cleaning before its feeding the fuel cell.

The goal of this work was synthesis of CuO-CeO₂/γ-Al₂O₃ catalysts by surface self-propagating thermal synthesis method (SSTS) and by impregnation method and investigation of its activity in CO oxidation reaction.

We used Cu(NO₃)₂ and Ce(NO₃)₃ as active component precursors and citric acid was used as a fuel dope. The samples prepared were studied by XRD and texture investigation technique. Atomic-absorptive method was used to determine the active component concentration. The activity tests in CO oxidation reaction were carried out in flow-circulation setup in temperature range 50÷150°C. The reaction mixture used for this work contains following components: CO (1% vol.), O₂ (2% vol.) and H₂ or N₂ as a balance.

It was observed that SSTS prepared catalysts are more active in CO oxidation at both reaction conditions than the impregnated ones. We suppose that the high activity of SSTS

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samples is due to high dispersion of active component and its highly defected structure which are formed during the thermal front passing through the sample.

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THE ROLE OF I-CONTAINING PROMOTER IN THE ACTIVE SILVER SURFACE FORMATION FOR PROCESS OF GLYOXAL SYNTHESIS

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The catalytic properties of polycrystalline silver, morphology and interaction of oxygen with silver surface were investigated by catalytic tests, SEM and TPD methods. An adding of ethyl iodide into reaction mixture increases both activity and selectivity owing to destruction of active centers which form oxide-like structures on the silver surface.

Pure halogens and halogen compounds are widely used as promoters in the processes of partial oxidation of organic compounds. It is known the using of halogens as promoters for metallic catalysts (in the processes of methanol oxidation and ethylene epoxidation over silver) and oxides (for example, in the process of aromatic compounds oxidation over V_2O_5). In consequence of similar conditions of methanol and ethylene glycol partial oxidation processes it was proposed that iodine-containing promoters will be favorable in glyoxal synthesis.

In the present work catalytic properties of polycrystalline silver promoted by iodoethane were investigated. It is shown, that adding of C_2H_5I into reaction mixture increases selectivity of the process about 10 – 12%, and simultaneously, decreases the yield of deep oxidation products, such as CO and CO_2 . So, it contributes to the temperature regime stabilization. Besides, the extreme dependence of glyoxal selectivity vs. C_2H_5I quantity in reaction mixture has been observed. A long-time treatment of catalyst with C_2H_5I -containing reaction mixture leads to decreasing of selectivity because of poisoning of silver surface. The active centers on the surface were reactivated by means of thermal annealing of silver in oxygen atmosphere with subsequent treatment with reaction mixture.

To detail the mechanism of promoting effect the interaction of reaction mixture consisting of oxygen and C_2H_5I with silver surface by means of thermal programmed desorption method (TPD) and silver morphology by secondary electron microscopy (SEM) have been investigated. According to TPD results, no ethyl iodide adsorption on the pure surface of polycrystalline silver was observed, and C_2H_5I chemisorbs competitively with oxygen and prevents forming of oxide-like oxygen state Ag_2^sO ($T_d^{max} = 543K$), which is

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responsible for deep oxidation of ethylene glycol to carbon dioxide. These results are in good agreement with catalytic data.

According to SEM results, adding of ethyl iodide into the reaction mixture leads to some morphological changes. It prevents the carbon deposition on the silver surface and decreases amount of «holes», because of displacement of adsorbed oxygen, which is responsible for carbon deposition on the silver surface. Besides, a long-time treatment of catalyst with C₂H₅I-containing reaction mixture leads to etching of the surface, probably, owing to silver iodide formation, which is possible thermodynamically.

Thus, an adding of C₂H₅I into the reaction mixture leads to glyoxal selectivity increasing owing to destruction of active centers which form oxide-like structures on the silver surface.

Acknowledgement

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THE BULK POROUS ELECTRODE MATERIAL WITH CONTROLLABLE GEOMETRICAL PARAMETERS OF THE STRUCTURE

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The electrode material consisting of one- or multicomponent conducting base, having a bulk porous structure with the holes uniformly allocated on all electrode surface is considered. The formation of such bulk porous structure makes it possible to achieve the substantial increase of the electrode material surface area which is accessible to electrochemical (electrocatalytic) reactions. The permeability of the electrode material for gas and liquid is also increasing. The bulk structure modifying of electrode material base can be carried out by physical and chemical methods.

During electrochemical processes which proceed with participation and formation of the gaseous products or during other electrochemical redox reactions one can choose electrode material which has the gas and liquid permeability, the substantial surface area available for an electrochemical reaction, corrosion resistance and mechanical stability. The electrode material consisting of one- or multicomponent conducting base, having a bulk porous structure with the holes uniformly allocated on all electrode surface is considered. The formation of the bulk porous structure can be carried out by the bulk structure modifying of electrode material base by the controllable manner with the use of physical and chemical methods (for instance, chemical or electrochemical etching, laser technology of the material treatment, lithography with the suitable linear precision and others). The formation of such bulk porous structure makes it possible to achieve the substantial increasing of the electrode material surface area and permeability of electrode material for the gas and liquid. Electrocatalytic activity, corrosion resistance, other necessary electrode material properties can depend not only on the base structure and properties but also on the properties of one- or multicomponent coverage with the submonolayer, monolayer or multilayer thickness. The coverage is deposited on the electrode surface after the bulk structure modifying of electrode material base. In the case of nanodispersional coverage it can be achieved the substantial additional increasing of the electrode material surface area available for an electrochemical reaction.

**PECULIARITIES OF LACTIC ACID AND METHYL LACTATE
HYDROGENATION OVER SILICA-SUPPORTED COPPER**

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In the present work general peculiarities of lactic acid and methyl lactate hydrogenation to propylene glycol over silica-supported copper were studied. Gas-phase catalytic experiments were conducted in fixed-bed reactor at atmospheric pressure. It was found, that under equal conditions methyl lactate conversion and selectivity of propylene glycol formation are higher than that for lactic acid. It was revealed, that the nature of solvent has a great effect on distribution of by-products. Pure methyl lactate hydrogenation gives less amount of by-products than that for aqueous and methanol methyl lactate solutions. It was shown, that selectivity of propylene glycol formation starting from methyl lactate increases from 78% to 98% as temperature decreases from 200 °C to 140 °C.

A catalytic method of synthesis of commercially valuable propylene glycol over the copper-containing catalysts is in progress [1] instead of currently petroleum-based one where promising starting material is a refined lactic acid obtained by fermentation of crude biomass.

The aim of this work is to study lactic acid and methyl lactate hydrogenation to propylene glycol over silica-supported copper.

For hydrogenation experiments the 17 wt.% water solution of lactic acid was used. According to gas-liquid chromatography analysis and chromatography-mass spectrometry propylene glycol and propionic acid are the main products of lactic acid conversion. It was found that 45,5 wt.% Cu/SiO₂ catalyst sample prepared by homogenous deposition-precipitation method exhibits the maximum selectivity of 1,2-propandiol formation [2]. High catalytic activity seems to be caused by great specific surface area of metallic copper [3].

It is well-known that derivatives of carboxylic acids, e.g. esters, are more reactive in comparison with carboxylic acids in reactions of hydrogenation [4]. It was revealed, that hydrogenation of methyl lactate in a water solution at temperature 200 °C, results in methyl lactate conversion to 99 % and selectivity of propylene glycol formation to 78 %. It was established, that the conversion and selectivity of propylene glycol formation decrease with increase of reagent supply. The basic by-products were propionic and lactic acids and methyl-2-methoxypropanoate.

Methanol was suggested to be used as solvent to reduce the by-products formation. It was found, that kind of solvent has not affected conversion of methyl lactate, but the number of various by-products depends on the solvent used.

A lot of experiments was carried out on hydrogenation of methyl lactate without solvent. It was observed that methyl lactate conversion was 98 % and selectivity of propylene glycol formation was 78 % at 200 °C, and the main by-products were only propionic and lactic acid. The effect of temperature on methyl lactate conversion and propylene glycol selectivity was studied. It was established, that decrease of reaction temperature leads to increase of selectivity of propylene glycol formation and reaches 98% at 140 °C.

To conclude methyl lactate is quite reactive to be used for selective propylene glycol formation in the presence of silica supported copper at atmospheric hydrogen pressure.

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**SUBSTANTIATION OF STRUCTURE OF THE CATALYST OXIDATIONS OF
PROPANE IN ACROLEIN**

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The problem of catalytic transformations of less scarce raw material - the lowest limiting hydrocarbons contained in natural, passing and industrial (torch) gases in valuable substances is considered. In particular, by the example of propane it is shown, that synthesis of catalysts on the basis of the ions accelerating reaction of synthesis acrolein with their subsequent updating by ions, accelerating reaction dehydrogenation propane has allowed to receive the structures possessing the greater activity and selectivity in comparison with a line of other catalysts, tested in reactions of one-phasic synthesis acrolein.

Because of essential increase of the prices for oil which is initial raw material for various technologies, last years interest to catalytic transformation of less scarce raw material - the lowest limiting hydrocarbons contained in natural, passing and industrial (torch) gases has considerably increased.

Heterogeneous transformation of limiting hydrocarbons can occur in directions dehydrogenation, oxidations, dimerization, condensation to education of some valuable organic connections which reception on the basis of traditional sources of raw material is economically less favourable.

Transformation of limiting hydrocarbons can pass with appreciable speed only at the higher temperatures, with low selectivity on target substances and difficult structure of reactionary gas. The successful decision of a problem is absence of laws of selection of catalysts for selective oxidation of limiting hydrocarbons, and the mechanism of reaction is investigated much less, than corresponding nonlimiting.

The most perspective hydrocarbons are ethane and propane. From them it is possible to receive ethylene, propylene, formaldehyde, acrolein and other valuable substances.

Selection of catalysts for one-phasic synthesis acrolein has not given essential results that testifies to more difficult mechanism of the given reaction [1, 2, 3]. However, if to assume, that synthesis acrolein occurs through an intermediate stage dehydrogenation propane, then the qualitative way of the further perfection is catalysts of one-phasic synthesis acrolein. Their structure should include the components accelerating a stage dehydrogenation of propane and components, oxidizing propylene to acrolein.

Synthesis of catalysts on the basis of ions W^{+3} , Sb^{+3} , Bi^{+3} , P^{+3} accelerating reaction of education акролеина with their subsequent updating by ions V^{+5} , Ni^{+2} , accelerating reaction dehydrogenation propane has allowed to receive the structures possessing the greater activity and selectivity in comparison with a line of other catalysts, tested in reactions of one-phasic synthesis acrolein.

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**DYNAMICS OF ETHANE OXIDATIVE DEHYDROGENATION UNDER
CONDITIONS OF ALTERNATING REAGENT SUPPLY OVER Pt/Al₂O₃,
Pt/ZnO/Al₂O₃ and Pt-Sn/ZnO/Al₂O₃**

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The dynamics of ethane ODH under conditions of alternating air/ethane supply over Pt/Al₂O₃, Pt/ZnO/Al₂O₃ and Pt-Sn/ZnO/Al₂O₃ was studied by on-line FTIR gas analyzer. It was found that CH₄ formation and carbon deposition (probably coke formation) are the main factors limiting the process efficiency. Modification of Pt with tin allowed us to increase significantly selectivity in ethylene by suppressing of these undesirable side-reactions.

Oxidative transformation of light alkanes (C₁-C₃) to valuable products is one of the most important directions of research nowadays. The process of ethane oxidative dehydrogenation (ODH) to ethylene is of significant industrial interest. However, there are a number of problems which limits application of this process. On the one hand, ethylene-air feed is explosive. On the other hand, there is a considerable decrease in selectivity at high ethane conversions due to total oxidation of ethane and ethylene by gas phase oxygen.

One of the promising approaches for improving selectivity of ethane ODH consists in performing reaction under conditions of alternating supply of an oxidant (air) and a hydrocarbon feed to a catalyst. At the first stage oxygen is accumulated on catalyst surface, and at the second stage the interaction of hydrocarbon with catalyst active sites and accumulated oxygen takes place. This method makes it possible to increase selectivity of ethane oxidative dehydrogenation due to a suppression of undesirable total oxidation process in gas phase. On the other hand, alternating supply of oxygen and hydrocarbon eliminates a danger of explosion of feed gas.

However a development of the effective ODH process requires a detailed study of the reaction mechanism under conditions of alternating air-ethane supply. Therefore the main focus of this study consisted in elucidation of a dynamics of ethane oxidation and formation of the reaction products under conditions of alternating supply of reagents on a catalyst.

The following catalysts were studied: Pt/Al₂O₃, Pt/ZnO/Al₂O₃, and Pt-Sn/ZnO/Al₂O₃. Zinc oxide was introduced as an oxygen storage component (OSC). A basic reaction cycle consisted of four stages: 1) catalyst treatment in air during 200 seconds for surface oxygen accumulating; 2) purging in nitrogen during 50 seconds for removing of gas phase oxygen; 3) ethane oxidation by accumulated oxygen during 400-600 seconds; 4) purging in nitrogen during 50 seconds for removing of unreacted ethane and reaction products from gas phase.

Dynamics of variations of C_2H_6 concentrations and reaction products formation were monitored by on-line FTIR gas analyzer.

Variations of ethane and reaction products (ethylene, methane, CO, CO_2) yields over Pt/ZnO/ Al_2O_3 at 500 °C are displayed in Fig. 1.

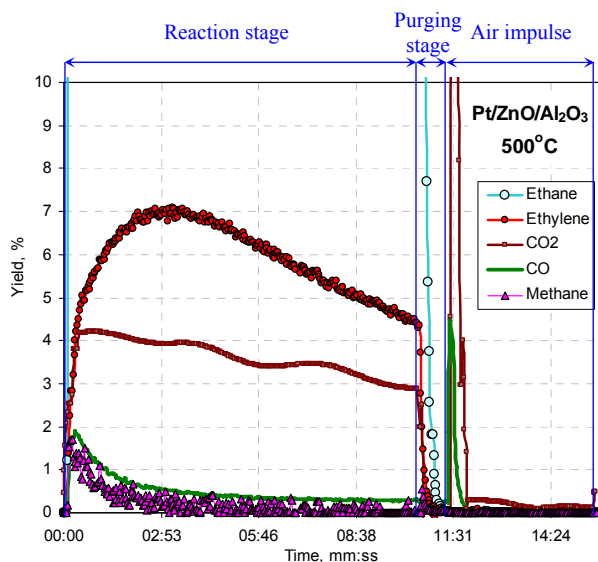


Fig. 1 Transient responses upon supplying of the Pt/ZnO/ Al_2O_3 catalyst with 600 s impulse of ethane followed by purging with nitrogen and supplying of air impulse

During the first seconds of ethane impulse a maximum formation of CO, CO_2 and methane was observed. Carbon oxides are presumably formed due to a reaction of ethane and ethylene with weakly bounded oxygen. Ethylene is dominant product of ethane oxidation and ethylene yield passes through the maximum after 2-3 minutes of the reaction. Presumably during this period “easily accessible” oxygen is consumed, and further ethylene formation proceeds via a combination of a non-oxidative dehydrogenation and oxidative dehydrogenation by oxygen diffused from the catalyst bulk. The following air impulse resulted in an intensive

(up to 25 %) CO_2 evolution due to oxidation of carbon containing deposits accumulated on the catalyst surface during C_2H_6 ODH.

Analysis of the reaction products indicates that one of the main factors limiting the process selectivity is a formation of CH_4 during the first stage of ODH, and carbon deposition of the catalyst surface (probably coke formation). It was found that modification of Pt/ZnO/ Al_2O_3 with Sn allow us to suppress undesirable side-reactions and increase ethylene selectivity significantly (Fig. 2, 3).

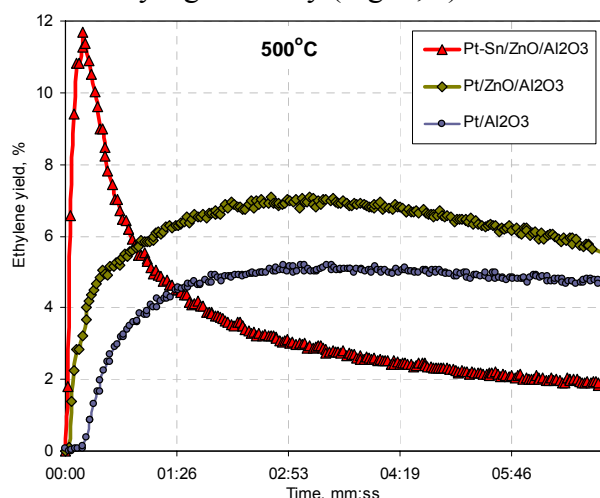


Fig.2 Variations of ethylene yield over Pt/ Al_2O_3 , Pt/ZnO/ Al_2O_3 and Pt-Sn/ZnO/ Al_2O_3

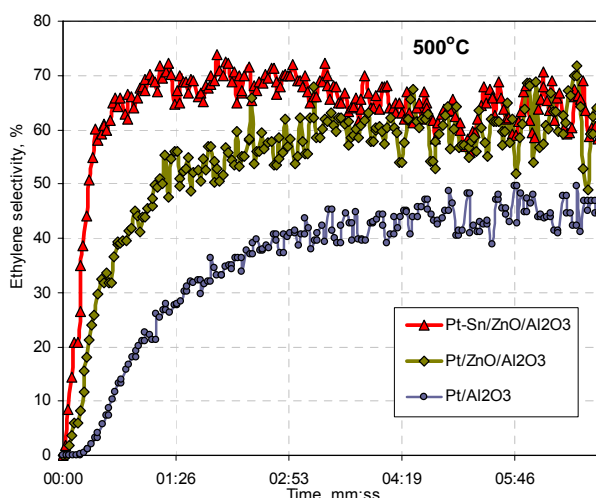


Fig.3 Variations of ethylene selectivity over Pt/ Al_2O_3 , Pt/ZnO/ Al_2O_3 and Pt-Sn/ZnO/ Al_2O_3

**INFLUENCE OF ZEOLITES STRUCTURE ON Co/ZEOLITE CATALYSTS
PERFORMANCE IN FISCHER-TROPSCH SYNTHESIS**

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The influence of zeolites nature on Co catalysts performance in hydrocarbons synthesis from CO and H₂ was investigated. The best result, i.e. the highest C₅₊ hydrocarbons yield and selectivity, was obtained for zeolite Beta-based Co catalyst. The variations in C₅₊ molecular-mass distribution is explained by contribution of hydrocracking process.

Competitiveness of Fischer-Tropsch process in comparison with traditional oil refining processes in hydrocarbon production is determined by the efficiency of the catalyst. Zeolite-based bifunctional Co catalysts represent separate interest as they combine the functions of Fischer-Tropsch catalysts and hydrocracking/isomerization. It is necessary to note that the bifunctional catalysts cited in literature are usually a physical mixture of a Fischer-Tropsch synthesis catalyst and zeolites or, alternatively, the zeolite-based Co catalysts for aromatic hydrocarbons production.

The goal of the present work is the study of influence of zeolites nature on Co catalysts performance in the hydrocarbons synthesis from CO and H₂.

The catalysts were prepared by impregnation of the zeolites with aqueous solution of Co nitrate. Used zeolites were Beta (Si/Al ratio is 40), TsVN (Si/Al ratios are 32 and 80), ZSM-5 (Si/Al ratio is 80) and ZSM-12 (Si/Al ratio is 80) in H-forms. Cobalt content was 20 wt. %. The Fischer-Tropsch synthesis was carried out in the flow-type fixed-bed reactor at 1 bar. Before synthesis catalysts were activated in hydrogen flow.

XRD study of zeolites showed that zeolites stability at thermal treatment decreased in the following order: ZSM-12 > ZSM-5 > TsVN (Si/Al ratio is 80) > TsVN (Si/Al ratio is 32) > Beta. C₅₊ yield increased in the following order: ZSM-12 < ZSM-5 < TsVN (Si/Al ratio is 80) ~ TsVN (Si/Al ratio is 32) ~ Beta. C₅₊ selectivity increased in the following order: ZSM-12 < ZSM-5 < TsVN (Si/Al ratio is 80) < TsVN (Si/Al ratio is 32) < Beta. All that means the thermal stability of zeolites correlates with catalytic properties of Co-zeolites catalysts.

The analysis of the hydrocarbons C_{5+} formed in the presence of zeolites Beta and TsVN (Si/Al ratio is 32) showed that their fractional compositions did not correspond to the molecular-mass distribution typical for products of classical Fischer–Tropsch polymerization. In these cases molecular-mass distribution had maximum at C_9 – C_{14} hydrocarbons. In other cases fractional compositions corresponded well to molecular-mass distribution of polymerization processes. This phenomenon can be explained by heavier aluminum presence in zeolites Beta and TsVN (Si/Al ratios are 40 and 32 respectively). Shift of synthesis products to the area of heavier hydrocarbons can be successfully explained by olefins formation in the result of hydrocracking of polymerization products over the acid centers. These olefins can be oligomerized, or create additional centers of chain growth.

Comparison of group compositions of hydrocarbons produced over Co-Beta and Co-ZSM-12 catalysts showed that C_{5+} isoparaffines content was two times higher over Co-Beta, than over Co-ZSM-12, while C_{5+} olefins and n-paraffines were 2–3.5 less abundant over Co-Beta, than over Co-ZSM-12. That clarifies the contribution of acid centers.

**MODIFYING INFLUENCE OF WHITE PHOSPHORUS AND PHOSPHINE (PH₃)
IN THE PRODUCTION OF NANOSCALE PALLADIUM HYDROGENATION
CATALYSTS**

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The formation, nature and properties of palladium nanoscale hydrogenation catalysts modified by white phosphorus or phosphine have been studied. It has been shown that white phosphorus and phosphine exceed significantly in magnitude of promoting effect nanoscale palladium hydrogenation catalysts with organic phosphines studied earlier. One of the reasons for promoting effect of phosphorus and phosphine at low ratio P/Pd compared with Pd-black is a dispersity increase of the catalyst consisting of palladium clusters Pd(0) and palladium phosphides of different composition.

In this paper, data on the formation, nature and properties of nanoscale hydrogenation catalysts based on palladium bis-acetylacetonate, white phosphorus and phosphine formed under molecular hydrogen are presented. It has first been shown that the usage of white phosphorus or phosphine (PH₃) as the modifiers at the stage of synthesis allows one to obtain highly effective palladium nanoscale hydrogenation catalysts whose specific activity exceeds that of nanoscale catalysts based on palladium complexes with organic phosphines [1]. An influence of different parameters on the composition and properties of the catalysts has been studied. It has been shown that the size, nature and therefore catalytic properties of formed nanoparticles depend on the ratio P/Pd. Independently of the promoter nature (P₄, PH₃, PH₂Ph [2]) the most effective hydrogenation catalyst is formed at the ratio P/Pd = 0,3. That catalyst consists mostly of the nanoparticles in 8-10 nm containing palladium phosphides of different composition (Pd₆P, Pd_{4,8}P, Pd₅P₂) and palladium in reduced state the share of which attains 30%. One of the reasons for promoting effect of phosphorus and phosphine is a dispersity increase in comparison with Pd-black formed under the similar conditions. Using the complex of the physical-chemical researches of the catalytic systems (NMR, IR-, UV-spectroscopy, X-ray diffraction, TEM) the model of active catalyst has been suggested. The general trends and distinctions in the formation and nature of the nanoparticles of palladium hydrogenation catalysts obtained in the presence of different containing phosphorus compounds have been established.

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THE MECHANISM OF COPPER COMPLEXES' CATALYTIC ACTION IN THE LIQUID PHASE THIOL OXIDATION

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The nature of mono- and polyfunctional donor compounds influences the rate of mercaptan catalytic oxidation in non-polar media in the presence of individual and heterogenized copper complexes greatly [1]. The conversion of dodecanethiol to corresponding disulfide in the *i*-octane at room temperature was studied as the test reaction. Nitrogen-, sulfur- and phosphorous-containing compounds were used as donors. Strong Lewis' bases (for example, aromatic amines and aminoalcohols) were found to inhibit the process. For instance, the mentioned compounds suppress the activity of homogeneous systems on the basis of divalent copper. The activity of heterogeneous systems decreased to a lesser degree. Aromatic amines and aminoalcohols (benzylamine, 1-phenyl-3-(*N*-methylamino)-propanol-3, 1-phenyl-2-(*N*-methylamino)-ethanol) were established by the use of UV- and ESR- spectroscopy to stabilize divalent copper ions and impede agreeably its reduction to copper thiolate — an important step of thiol oxidation. The inhibitory action of weak Lewis' bases (e.g. triphenylphosphine) can be accounted for by the univalent copper stabilization and agreeably by the deceleration of metal ion oxidation. The best donors, rising the catalytic activity of copper-containing catalysts turned out to be monoethanolamine>benzylamine>ammonia>cyclohexylamine. In the presence of the mentioned compounds in the system, containing the catalyst, dodecanethiol and the dissolver both univalent and divalent copper ions were observed.

In accordance with generally accepted mechanism on the first stage of the reaction the divalent copper is reduced copper (I) thiolate. We have established, that copper thiolate is not active in the thiol oxidation. Even after the addition of donor compounds the reaction proceeds much slower than in the case of individual copper complexes' use.

The mechanism of the investigated donors' in homogeneous systems promoting action has been considered and the comparative analysis of their role in homogeneous and heterogeneous processes has been carried out.

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ISOBUTANE - BUTENE ALKYLATION ON SULFATED ALUMINA WITH CHLORINE-CONTAINING PROMOTORS

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The catalytic properties of the samples of sulfated alumina in the reaction of alkylation of isobutane by butenes have been studied. Both the concentration of sulfate-ion and the temperature of preliminary thermal treatment were varied in this investigation. Physical and chemical properties of the samples were studied by means of DTG and IR-spectroscopy using CO molecules as a probe. It was observed that few sulfate species with different acid-base and catalytic properties are formed over support surface depending on the initial concentration of the sulphatizing agent and the temperature of pretreatment. An aggregation of the sulfate ions is occurred when its concentration exceeds monolayer quantity.

In line with the global move for environmental protection, there has been considerable improvement in gasoline materials for automotive fuels which are relatively free of environmentally harmful alkenes and aromatics. A notable example of such improved gasoline material is an alkylate containing highly branched alkane. Alkylate is an economical, clean-burning, high-octane, low volatility product.

The liquid acids HF and H₂SO₄ are the industrially used catalysts for the aliphatic alkylation. But their wide use is related with a serious problem like corrosivity and toxicity. At present there are a lot of investigations dedicated to research an alternative solid acid catalyst to replace these liquids. Since the discovery of its strong acidity, sulfated oxides (especially zirconium) have attracted much attention as a potential catalyst.

In this research the catalytic properties of the sulfated alumina has been studied in the reaction of alkylation of isobutene by butanes. It was considered for a long time that the sulfated alumina is an unpromising catalyst for the acid-catalyzed reaction due to its lowest activity in comparison with the oxides of zirconium, tin and titanium [1, 2]. However, gamma alumina shows high thermostability at the temperatures up to 800 °C and retains its phase state and surface area on the same level. On the other hand, zirconia and titanium oxide could be easily sintered at the temperature mentioned above.

Moreover, it is well known that the sulfation of crystalline oxides brings to inactive catalyst formation. That is why only amorphous oxides can be used for the preparation of the sulfated catalysts. In this view, alumina is an exception [3].

The problem of the low activity of sulfated alumina could be solved by addition of tetrachloride carbon into the feed flow. This approach allows enlarging not only the catalytic activity but stability as well. In [4], it has been shown that both activity and stability of sulfated alumina in the presence of CCl_4 additions rich the same values as for sulfated zirconia. By means of XPS it was studied that promoting action is not followed by the chemical binding of promoter with catalyst's surface.

To get the optimal catalyst composition the concentration of supported sulfate was varied by using different initial concentration of sulphatizing agent and by varying the temperature of pretreatment. Two kinds of sulfate species were observed by DTG for the samples with sulfate loading closed to the monolayer. The highest acidity observed by IR-spectroscopy of adsorbed CO and catalytic activity as well are peculiar to weak binding species. Simultaneously the most strongly binding sulfate species exhibited less catalytic activity and acidity. For the samples with low sulfate loading (less than monolayer quantity) only the high temperature pick has been observed. In the case of high sulfate loading (more than monolayer quantity) the low temperature pick became wider and overlapped the high temperature one. It allows us to conclude that the agglomeration of sulfate species could be a possible reason for a plateau in catalytic activity observed during catalyst test. The catalytic activity was practically constant for the samples with the sulfate concentration from 14 up to 20 %. Moreover, it should be mentioned that the rate of sulfate species decomposition on the sulfated samples is much higher in the presence of palladium which plays a role of hydrogenating component in this catalytic system.

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**THE DESIGN OF THE ACTIVE COMPONENTS DISTRIBUTION THROUGHOUT
THE PORES OF DIFFERENT SIZE IN CATALYSTS OF HYDROCATALYTIC
PROCESSES (OIL REFINING)**

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The present-day condition of problem of catalyst active component distribution in the supporter porous matrix is analyzed. An experimental approach for measurement of the quantity of surface centers of Pt, Pd and Mo in the pores with different size of hydrocatalytic processes catalysts on the basis of SiO₂ and Al₂O₃ is suggested. The results of the influence of preparation parameters on the active components distribution on the surface of pores with different radius are cited.

Distribution of an active component (AC) in porous structure of hydrocatalytic processes catalysts is an important characteristic because it influences on the local concentration (density) of substances fixed on certain areas of supporter surface and so determines the stability of an active phase to agglomeration. Displacement of the active phase localization in thin supporter pores can determine its accessibility for reactive molecules and also stability to deactivation by coconut sediment at plugging (blocking) of thin pores by coconut. Thus the nature of AC distribution throughout the pores with different size will influence on the retention of catalyst operating characteristics at its exploitation to a great extent.

During the preparation process of supported catalysts of hydrocatalytic processes (reforming, hydrofining) combination of diffusion and sorption processes on the soaking stage of porous matrixes of supporters by active substances controls penetration and consequently distribution of the active component not only throughout the volume of a supporter granule (this phenomenon is well-known and studied for a long time [1]). At the same time with the displacement of the active substances throughout a granule the migration of adsorbed predecessors throughout the volume of the pores with different size with the following precipitation of the active substances in them always takes place. Because of diffusion processes the appearance of differences of metal concentration in thin and large pores would be expected.

In the work the present-day condition of problem of catalyst active component distribution in the supporter porous matrix is analyzed. An experimental approach for measurement of the quantity of surface centers of Pt, Pd and Mo in the pores with different

size of hydrocatalytic processes catalysts on the basis of SiO_2 and Al_2O_3 is suggested. The results of the influence of preparation parameters on the active components distribution on the surface of pores with different radius are cited.

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PRODUCTION OF HYDROGEN VIA REFORMING OF METHANE AND METHANOL OVER STRUCTURED MONOLITHIC CATALYSTS

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It is shown that use of honeycomb structure catalysts on ceramic monoliths enables to reduce essentially the content of active components in catalyst compositions of CO₂ conversion of methane, partial oxidation and steam reforming of methanol without decrease in their productivity.

Methane and methanol belong to the most widespread feedstock for production of hydrogen and synthesis - gas. Therefore, reforming processes of C₁ organics mentioned are among strategic tasks of XXI century at transition from fundamental science to industrial technologies [1, 2].

Processes of oxidative conversion of methane (steam, CO₂) are carried out at high temperatures and proceed in diffusion mode. Depth of penetration of reaction in a granule of the catalyst does not exceed 0,25 mm and a degree of use of a surface of the catalyst is insignificant. Thus, using monolithic catalysts of honeycomb structure for these processes is considered promising. Such an approach will facilitate increasing the productivity and reducing the coking of an internal surface of the catalysts of CO₂ conversion of methane due to elimination of diffusion restrictions caused by CO₂ transportation in a zone of reaction. The structured monolithic composites offer the advantages, such as high surface-to-volume ratio, large open frontal area, low thermal mass *etc.*, for methanol reforming reactions too [2], for which Cu- and Cu-ZnO-based catalysts are considered to be the primary.

As a framework of the catalysts ceramic monoliths of honeycomb structure from synthetic cordierite (2Al₂O₃·2MgO·5SiO₂) with cell size 1,0×1,0 mm and wall thickness of 0,2 mm were used in this work.

Catalyst samples for methane conversion were prepared via impregnation of monoliths mentioned by nickel and aluminium nitrates followed by annealing. In the course of synthesis of the catalyst samples a formation of spinel NiAl₂O₄ takes place and during reduction thereof the particles of finely dispersed metal nickel stabilized in matrix Al₂O₃ are formed. Nanocomposites, synthesized by means of such a technology, are characterized by the

enhanced stability against carbonization in comparison with the granulated catalysts which is caused by maintenance of necessary balance between rates of CH₄ decomposition on metal nickel and CO₂ dissociation on border *metal - oxide* as it was reported in work [3].

To prepare the structured Cu-ZnO catalysts for methanol reforming, samples of the cordierite monoliths, initially coated with γ -Al₂O₃, were impregnated with solutions of zinc sulfate and copper nitrate followed by calcination and reduction.

As shown from the Table, granulated commercial (a sample 1) and structured (a sample 2) catalysts with nearly identical contents of an active component (about 8 % NiO) practically do not differ with respect to activity (temperature of 80 % conversion) while decrease of NiO content to 4,0 % (a sample 3) results only in insufficient decrease of the catalyst activity. However, productivity of the monolithic catalyst is almost four times higher as compared with granulated one. Moreover, productivities of the structured and granulated catalysts *per* a weight unit of nickel oxide, differ even more considerably (since in catalysts of honeycomb structure a wall thickness of the monolith is commensurate with depth of a working layer and, therefore, a higher degree of an active component's use is achieved).

Table. Activity and productivity of catalysts in CO₂ methane conversion

№	Catalyst	Temperature of 80 % conversion, °C	Productivity	
			A 10 ⁶ , mol·s ⁻¹ ·g _{cat} ⁻¹	B 10 ⁶ , mol·s ⁻¹ ·g _{NiO} ⁻¹
1	GIAP-18 (commercial)	485	12,96	1,62
2	8,2wt.% NiO/11,2wt.%Al ₂ O ₃ / cordierite	480	38,3	4,8
3	4,0wt.% NiO/11,2wt.% Al ₂ O ₃ / cordierite	488	32,0	7,2

When using Cu-ZnO/ γ -Al₂O₃-based monoliths (with no more than 15 wt. % of (Cu + ZnO) loadings) in partial oxidation and steam reforming of methanol, formation of hydrogen with a yield about 80 % and, respectively, 90 % was observed.

Thus, use of honeycomb structure catalysts on ceramic monoliths enables to reduce essentially the content of active components in catalyst compositions of CO₂ conversion of methane, oxygen and steam reforming of methanol without decrease in their productivity.

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**SYNTHESIS OF MONO- AND BIMETALLIC NANOCLUSTERS OF GOLD,
NICKEL, IRON, COBALT, PALLADIUM USING METAL-VAPOUR SYNTHESIS
WITH SOLVENTS AND ITS HYDRATION AND HYDRODECHLORINATION
CATALITIC ACTIVITY**

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Using metal-vapour synthesis (MVS) M/X (M=Ni, Fe, Co, Pd; X=SiO₂, Al₂O₃, C) and M₁-M₂/X (M₁=Au, M₂=Ni, Pd; X=SiO₂, Al₂O₃) nanocompounds grafted on various supports were synthesised. Nanocompound composition, structural and electron properties were described with TEM, XRD, XPS and atomic absorption. Sufficient nanocompounds catalytic activity (10³ - 10⁵ mole*mole⁻¹*h⁻¹) was discovered hexene-1 hydration and chlorbenzene hydrodechlorination. It is proved, that nanocompound catalytic activity depends on several characteristics: nature, size, morphology and concentration of grafted on support metal particles.

In this work grafted mono- and bimetallic M (M=Au, Fe, Ni, Co, Pd, Au-Pd, Au-Ni and Au-Fe) nanoparticles were synthesised using MVS. M/X nanocompounds were obtained by impregnation of supports (X=γ-Al₂O₃, SiO₂, activated charcoal) with toluene and triethylamine metal organosols. According to SEM and XRD data, average size of grafted Au particles were 3-5 nm (coating with Au-Et₃N organosol) and 30-40 nm (coating with Au-toluene organosol), average size grafted Fe, Co, Ni, Pd particles were 10-100 nm (coating with amine organosol) and 2-6 nm (coating with toluene organosol).

Nanocompound catalytic activity was determined towards hexene-1 hydration (1) and chlorbenzene hydrodechlorination (2) reactions. It was found, that activity of iron, nickel, cobalt containing catalysts were about 10⁵ mole*mole⁻¹*h⁻¹ - towards (1) and about 0,6*10⁵ mole*mole⁻¹*h⁻¹ of palladium and 0,1*10⁵ mole*mole⁻¹*h⁻¹ для nickel and gold-nickel containing catalysts towards reaction (2). On the contrary, catalysts containing pure gold were less-active – at most 10³ mole*mole⁻¹*h⁻¹.

It is shown, that activity of grafted catalysts depends on metal nature and concentration, catalyst preparation conditions. It is shown, that palladium containing catalysts are most-active, nickel and gold-nickel containing catalysts are slightly less-active. Catalysts containing pure gold were low-active.

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HYDROGEN PRODUCTION BY METHANE DECOMPOSITION ON NICKEL CONTAINING CATALYSTS MODIFIED BY COPPER, IRON OR PALLADIUM

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The using of bimetallic Ni-Cu, Fe-Ni, Ni-Pd catalysts for hydrogen production by means of methane decomposition in the temperature range of 600-850 °C was experimentally analyzed. The influence of catalyst's mixture and process' temperature on maximum yield of hydrogen and nano-fibrous carbon during the period of complete deactivation of catalyst was studied. The conditions corresponding to maximum yield of hydrogen were determined. It was demonstrated that this index depends on peculiarities of stage's going of process' starting. The maximum yield of hydrogen amounting to 285 g (855 g of carbon) per 1 g of catalyst was get using the 45%Ni-45%Pd-10%SiO₂ catalyst under the process' temperature of 800 °C and 50 hours of stable work.

Hydrogen is known to be very prospective energy carrier with low effect on the environment. For example, as a fuel for H₂-O₂ fuel cells. Today, all advanced countries of the world work on the development of fuel cells. One of the main problem of industrial implementation of fuel cells is a development of autonomous hydrogen sources, which are free from carbon monoxide. At the present time industry gets hydrogen by steam reforming of natural gas, but during this process hydrogen becomes polluted by carbon monoxide, which is poison for fuel cells. The necessary purification is a technically and commercially complicated problem. As an alternative method the process based on methane catalytic decomposition on carbon and hydrogen can be considered. In this process the formation of carbon monoxide is impossible at all, because of the absence of oxygen in the initial reactants.

The analysis of thermodynamic limitations of the decomposition of methane process shows, that the high concentration of hydrogen in the gas mixture can be obtained only at the temperature higher than 600 °C. Usually, nickel-based catalyst is used for methane decomposition, but it can't work stably for a long time at the high temperatures. That's why there is a necessity in searching for another catalyst systems for methane decomposition process, which have higher stability in work under high temperatures. The analysis of literature shows that one of the prospective directions in solving of this problem is connected with the development of bimetallic catalysts.

The main part of this work was devoted to studying of bimetallic Ni-Cu, Fe-Ni, Ni-Pd systems in the process of catalytic pyrolysis of methane under temperatures of 600-850 °C.

PP-II-130

Evaluation of Ni-Cu, Fe-Ni and Ni-Pd catalysts' activity was studied using the method of the temperature-programmable reaction. For determining of stability resource experiments were held.

It was determined that optimal temperature range for Ni-Cu-(10wt. %) Al_2O_3 catalysts is about 600-700 °C. According to data obtained, increasing of the copper in the catalyst from 8% wt. to 20% wt. leads to the increasing of catalyst's stability and maximum yield of hydrogen. The best result showed the 70%Ni-20%Cu-10% Al_2O_3 catalyst, which had worked stably during tens of hours at the temperature of 700 °C. Methane conversion was 60 %. Optimal temperatures for getting hydrogen during the methane decomposition using Fe-Ni catalysts are in the range of 700-750 °C. The variation of Ni content in the catalysts allowed to determine that the maximum yield of hydrogen can be obtained using catalysts of 60%Fe-15%Ni- Al_2O_3 . This catalyst works effectively at the temperature of 750 °C, providing the methane conversion on the level of 60 %.

Conversion, provided by Ni-Pd-10% SiO_2 catalysts increases in the range of 600-850 °C. Catalysts of Ni-Pd-10% SiO_2 content are able to maintain a high level of methane conversion under temperatures of 800-850 °C. The biggest yield of hydrogen was 285 g (855 g of carbon) per 1 g of catalyst for the 45%Ni-45%Pd-10% SiO_2 catalyst at the temperature of 800 °C. The time of stable work was 50 hours.

It was revealed the starting stage of the process decomposition effects the stable work of the catalyst. In the case of feeding of methane to a reactor after heating of reduced catalyst in the argon medium under 800 °C, the catalyst deactivates quickly. And the catalyst stability is much higher in the case of process' starting on the catalyst in the sphere of methane at the low temperature and further increasing of the process temperature to 800 °C.

Results obtained shows that examined catalysts are very attractive to us under the high temperatures and allow to get a mixture with high concentration of hydrogen.

**CATALYTIC HYDROALKOXYCARBONYLATION OF OLEFINS IN THE
PRESENCE OF THE PHOSPHIN-PALLADIUM COMPLEXES**

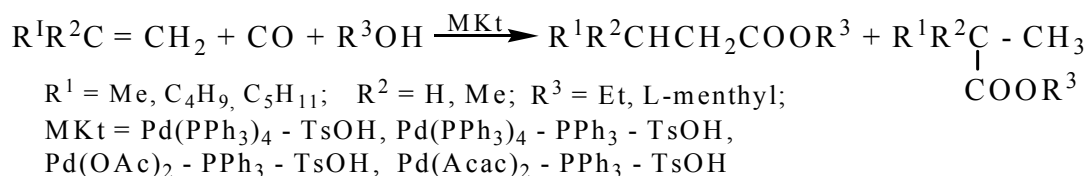
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Hydroalkoxycarbonylation of olefins with carbon monoxide and alcohols under conditions of homogeneous catalysis with transition metal complexes allows facile one step synthesis of practical useful carbon acid esters. Many of them have biologic activity and are constituents of drugs. Menthyl isovalerate is the main active component of validol medicine. Ethyl α -bromisovalerate is one of main active components in the widely used korvalol medicine.

We investigate the catalytic activity of a series of two and three – component systems on the basis of halogen-noncontaining palladium phosphine complexes. The high catalytic activity in olefine hydroesterification at low pressure of carbon (II) oxide (≤ 2 MPa) of the systems Pd(Acac)₂-PPh₃-TsOH, Pd(OAc)₂-PPh₃-TsOH, Pd(PPh₃)₄-TsOH and Pd(PPh₃)₄-PPh₃-TsOH was demonstrated. The reaction were performed in a stainless-steel autoclave in the absence of solvent. The autoclave at room temperature was charged with a catalytic



system and alcohol. The autoclave was hermetized, purged in duplicate with carbon monoxide for deaeration and charged with olefin, after which required carbon monoxide pressure was effected, and stirring and heating were started. The reaction products were isolated by fractional distillation.

The yields of the target products were 67-83%. The regioselectivities in linear reaction products of 1-hexen(1-hepten) hydroetoxy-carbonylation and isobutene hydroetoxy-(menthoxy)carbonylation were 83-88 and 100%, respectively. High regioselectivity (100%) in isobutylene hydroalkoxycarbonilation is not surprising and seems to be characteristic of isobutylene.

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Optimal conditions were determined for hydroethoxycarbonylation and hydromethoxycarbonylation of isobutylene in the presence of catalytic system Pd (Acac)₂-PPh₃-TsOH: T=100 °C, P_{co}=2MPa, τ = 4-5h; the optimal [ROH]:[i-C₄H₈]:[Pd(Acac)₂]:[PPh₃]: [TsOH] ratio is 434:550:1:3:12 and 434:550:1:7:12, respectively.

The most probably is a hydride mechanism. Evidence for this proposal comes from the observation of an exceptionally strong effect of the TsOH addition which, being a proton donor, facilitates formation of the primary active hydride complex HPd(PPh₃)₃ of the catalytic cycle.

NANOSTRUCTURED METAL-POLYMERIC CATALYSTS

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Polymers which contain complexes or metal nanoparticles may be used as the catalysts in a variety of organic reactions as they combine the advantages both of homogeneous (high activity and selectivity) and heterogeneous (easy recovery from the reaction mixture and a possibility of regeneration) catalysts. Catalytic properties of such systems may be changed by varying the type of polymeric matrix and characteristics of complexes or metal nanoparticles. This study is aimed to the development and investigation of novel metal-polymeric systems which are catalytically active and selective in synthesis of vitamin intermediates and medicinal preparations.

Traditional catalysts may be simply separated from the reaction mixture and regenerated. But they have relatively low activity and selectivity, because of the low surface area. High content of noble metal results in the high cost price. Besides, traditional catalysts are often needed to be modified, which results in the low quality of target product.

In the previous studies, phthalocyanine and fullerene metal complexes were found to be effective in the reactions of catalytic hydrogenation. Cumulative theoretical and experimental experience led to create the nanostructured metalpolymeric catalysts. So, various nanostructured matrices and polymers, which are able to control nanoparticle morphology and could be applied as supports for catalytic applications, were investigated.

The methods of nanoparticles formation in nanostructured polymers were combined into the groups depending on the medium:

- i. nanoparticle formation in amphiphilic block-copolymers (polyethylene oxide-block-poly(2-vinylpyridine) (PEO-P2VP) and polystyrene -block – poly(4-vinylpyridine) (PS-P4VP) were chosen);
- ii. formation of metal nanoparticles in polyelectrolyte systems (polydiallyldimethyl ammonium chloride (PDADMAC) and biopolymer chitosan (CS) were investigated as the examples of cationic polyelectrolytes);
- iii. metal nanoparticles formation in cavities (pores) of a polymeric matrix (hypercrosslinked polystyrene (HPS) was investigated).

PP-II-132

Catalytic properties of the synthesized nanostructured composites were studied in selective hydrogenation of long-chain acetylenic alcohols, enantioselective hydrogenation of ethylpyruvate to (R)-ethyl lactate and in direct oxidation of D-glucose, L-sorbose and phenol.

For all the organic reaction studied, optimal catalytic system providing the selectivity of 98.0-99.5% was chosen.

Kinetic investigations and data of physical-chemical analysis (NMR, XPS, XRD, TEM, AFM, FTIR, BET) of catalytic systems and substrates showed that the interaction of active component of the catalyst with the solvent, support, modifier and substrate was taken place. It was confirmed that selective hydrogenation and oxidation take place via multiligands reaction complex. Substrate activation occurs by transfer of electron density from active component of the catalyst.

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**THE EFFECT OF THE SUPPORT ON THE PERFORMANCE OF Co/CoAl_xO_y
CATALYST IN FISCHER-TROPSCH SYNTHESIS**

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Fischer-Tropsch synthesis is a complex catalytic process that includes many successive and competing reactions and leads to formation of a various hydrocarbons from syn-gas. Heavy hydrocarbons are preferably formed in the presence of Co based catalysts. Catalytic properties of such systems depend on the support phase composition, which is determined by the nature of initial compounds and preparation conditions. Alumina based Co-catalysts are efficient in producing heavy hydrocarbons with undesirably high methane formation. To combine high yields of heavy hydrocarbons with low selectivity to methane the mixed oxide based Co catalysts were developed. The present work is aimed at the investigation of influence of Co/CoAl_xO_y catalyst support on yield and selectivity to high molecular weight hydrocarbons formed from CO and H₂. Catalytic results are supplemented by the XRD study of phase composition of CoAl_xO_y support and 20%Co/CoAl_xO_y catalysts.

The CoAl_xO_y support was prepared by calcining mechanical mixture of cobalt precursor (nitrate, acetate, basic carbonate, oxide) with aluminum hydroxide. The 20%Co/CoAl_xO_y catalysts was prepared by double impregnation of support by Co(NO₃)₂·6H₂O water solution. Hydrocarbon synthesis was carried out in fixed-bed catalytic reactor at atmospheric pressure. Before synthesis all samples were pre-reduced in hydrogen flow.

The XRD study showed that the nature of cobalt precursor and aluminum hydroxide (gibbsite, boehmite, bayerite) influenced sample phase composition. In particular, boehmite based samples contain much more γ -Al₂O₃, than gibbsite based support, in which most of alumina occurs as amorphous phase. For all samples the main spinel phase detected was Co₂AlO₄. Results obtained by XRD correlate with catalytic data described below.

Catalytic tests confirmed that cobalt precursor nature in 20%Co/CoAl_xO_y catalyst support has an influence on yield and selectivity to C₅₊ hydrocarbons. The C₅₊ hydrocarbons yield varied in a row: basic carbonate (127 g/m³) > nitrate (110 g/m³) > acetate (97 g/m³) > oxide (83 g/m³). The highest C₅₊ hydrocarbons selectivity was also reached for cobalt basic carbonate containing sample (91% vs. 84-85% for other catalysts). It should be noted that all

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samples are characterized by significantly lower methane selectivity (4-6 %), than that of previously described analogs (10-20 %) [1-3]. Fractional and group composition of liquid hydrocarbons was nearly independent of cobalt precursor nature. SF alpha value was 0.92-0.95 for all samples.

Investigation of the influence of aluminum hydroxide structure in 20%Co/CoAl_xO_y catalyst support on C₅₊ hydrocarbons yield and selectivity showed, that the highest yield (127 g/m³) and selectivity (91%) was obtained with the support prepared from gibbsite. Corresponding values for boehmite (107 g/m³ and 80 %) and bayerite (90 g/m³ and 87 %) were lower. Methane selectivity changed in a row: gibbsite (4 %) < bayerite (7 %) < boehmite (10 %). All samples are characterized by high SF alpha value (0.89-0.93).

Hence, the nature of cobalt precursor and aluminum hydroxide in 20%Co/CoAl_xO_y catalyst influences both activity and selectivity of the catalyst in hydrocarbon synthesis from CO and H₂. The highest C₅₊ yield (127g/m³) and selectivity (91 %) at lowest methane selectivity (4%) were obtained for the catalyst the support of which was prepared from gibbsite and cobalt basic carbonate. In addition, all CoAl_xO_y based samples are characterized by high selectivity to target products and low methane formation. The results of this work are covered by the RF patent №2279912.

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ALTERNATIVE APPROACH TO DESIGN OF SUPPORTED VPO/SILICA CATALYSTS

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The deposition of catalyst active phase on support permits to increase a mechanical strength of catalyst, specific surface area and improves a porous structure of the sample and etc. However, the number of publications described the synthesis of supported VPO catalysts active in reactions of paraffins transformations is limited. The deposition of active mass on support by traditional methods e.g. impregnation, precipitation, grafting, CVD don't permit to obtain the systems with catalytic properties comparable to bulk catalysts. The main reason of this fact is the formation on support surface vanadium (IV, V) phosphate phases instead of hemihydrate vanadyl hydrophosphate ($\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$) precursor of catalyst selective in oxidation processes.

The alternative method of the synthesis of supported VPO/silica catalysts was developed in this work. The method includes three basic stages:

i) Preparation of silica aerogel with the homogeneously-mesoporous structure by hydrothermal method from the fume silica A300.

ii) Barothermal modification of surface of prepared aerogel by different organic compounds. The citric acid, salicylic acid, oxalic acid, 1,4-butandiol, benzyl alcohol and 1-butanol were used as the modification agents. It is necessary to note that some of these compounds are used as reducing agent in traditional synthesis of bulk VPO catalyst. The hexamethyldisiloxane which adds the hydrophobic properties to surface was used also.

iii) Simultaneous barothermal synthesis of active VPO phase and its deposition on support. The modified support, V_2O_5 , H_3PO_4 and organic medium (1-butanol) were loaded to autoclave and process of synthesis was carried out at 170 °C.

The prepared samples were studied by means of XRD, DTA, SSA, porosimetry, IR-spectroscopy methods. Also, the activity of VPO/ SiO_2 catalysts in oxidative dehydrogenation of propane was determined.

It was established that developed method of catalyst synthesis permits to prepare the supported crystalline phase $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. The nature of modification agent regulates the ratio of crystallographic planes I_{001}/I_{200} of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. It is well-known, that the

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reactions of selectivity oxidation take place on basal plane whereas the lateral plane of crystal favours to oxidative dehydrogenation processes. It is necessary to note that proposed method allows preparation of the samples with high specific surface area 50 - 150 m²/g and attractive pore structure (d = 20 - 70 nm).

The catalytic tests of prepared supported catalysts in oxidative dehydrogenation propane show that obtained samples demonstrate the better catalytic properties than bulk VPO catalysts.

**THE LOW-TEMPERATURE CATALYTIC OXIDATION OF VARIOUS
SUBSTRATES BY OXYGEN IN THE PRESENCE OF NITROGEN OXIDES AND
THE COMPLEXES OF TRANSITION METALS**

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Nitric acid very frequently is used in the industry of organic synthesis at oxidation of organic compounds. Disadvantage of nitric acid is the evolution of sample quantity of nitrogen oxides. The similar effect is observed at oxidizing metals manufacturing from sulphidic ores. Practical interest is represented with recycling in such processes nitrogen(III-V) oxides not as oxidizers, but as catalysts of substrates oxidation by oxygen. It is shown, that at the presence of transition metal complexes and nitrogen(II, IV) oxides it is carried out low-temperature oxidation of a lot of substrates by oxygen. The reactions kinetic is investigated by modern methods (IR-, UF- spectrophotometry, GL-chromatography, redox-potentiometry, volumetry), quantum-chemical characteristics of the intermediate particles participating in reactions calculated by NDO method. The scheme of the mechanism is offered.

Study of the processes kinetics specified in table 1, has shown, that oxidation rate of various substrates by oxygen is described by the kinetic equation (1):

$$W_{O_2} = \frac{k_2 \cdot C_{NO} \cdot C_{O_2} \cdot k_1 \cdot C_S \cdot C_{NO_2}}{k_1 \cdot C_S + k_2 \cdot C_{NO} \cdot C_{O_2}}, \quad (1)$$

where S – a substratum reacting with oxygen, k_1 and k_2 – rate constants of reactions (2, 3):



Table 1 – Low-temperature (40-60 °C) oxidation of various substratum by oxygen at presence nitrogen oxides and complexes of transition metals

Process	Catalysts	k_1 , mole/l·s	k_1 , l ² /mole ² ·s
$C_6H_5OH + O_2 \rightarrow C_6H_4O_2$	NO, NO ₂ , CuCl ₂	$7 \cdot 10^{-2}$	$9,3 \cdot 10^6$
$2H_2S + O_2 \rightarrow 2H_2O + 2S$	NO, NO ₂ , I-	$8,3 \cdot 10^{-1}$	$8,7 \cdot 10^6$
$2(C_6H_5)S + O_2 \rightarrow 2C_2H_5OH + 2S$	NO, NO ₂ , I-	$5 \cdot 10^{-2}$	$8,6 \cdot 10^6$
$C_6H_4Cl_2 + O_2 \xrightarrow{H_2O} C_6H_5O_2 + 2HCl$	NO, NO ₂ , CuCl ₂	$1,3 \cdot 10^{-1}$	$8,8 \cdot 10^6$
$C_6H_6 + HBr + O_2 \rightarrow C_6H_4Br_2 + H_2O$	NO, NO ₂ , Co(NO ₃) ₂	$8,6 \cdot 10^{-3}$	$8,7 \cdot 10^6$

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The analysis of the data of table 1 leads to the conclusion, that the value of k_2 practically does not depend on the nature of substrate and is close to value k_2 of the reaction (3) described in a literature. The value k_1 depends on medium acidity, on the nature of a substratum and the nature of a complex of transition metal.

The received results allow us to assume that reactions (2, 3) are two slow stages of oxidation of substrates by oxygen in presence of nitrogen(II, IV) oxides. In the result of protonization oxidative ability of NO_2 is increasing in relation to substrates. The introduction of the transitive metal complex promotes the activation of a substratum.

CATALYTIC PROPERTIES OF LAYERED OF CLAYS

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Nowadays considerable attention has been given to the development of new functionally active sorbents, supports, and a new class of catalysts based on clay minerals. These materials possess unique structural and catalytic properties due to the capacity adjustable of surface acidity and nature of cation.

High-surface-area pillared clays (PILC) were prepared from naturally occurring montmorillonites by exchanging interlayer ions with various cation species such as H⁺, Na⁺ and Al_{13-x}Fe_xO₄₀⁷⁺ (x = 0÷2). Clay nanocomposite (CCn) was obtained based on a synthetic smectite-type clay and MgO incorporated via surfactant stabilization to produce [1]. The obtained PILCs and CCn were characterized by far FT-IR and DR-UV-vis spectroscopy, ESR, ²⁷Al NMR, scanning electron microscopy and N₂ adsorption. Acidities of PILCs were studied by IR spectroscopy both analysing the band due to OH-vibrations and following the adsorption of carbon oxide. It was shown that the nature of pillaring agent determines texture characteristics and surface acidity.

Na-PILC, Al₁₃-PILC and CCn were used for supported of cobalt(II)-tetraphtalocyanine (Pc(SO₃Na)₄). According to DR-UV-vis spectroscopy, ESR, XRD and N₂ adsorption data the state and amount of Pc(SO₃Na)₄ supported depend on intrinsic character of supports. Catalytic activity of these materials was investigated in cyclohexene oxidation with H₂O₂ and *tert-butyl*-hydroperoxide, and in aerobic oxidation H₂S. It was shown that aggregation and crystallization of Pc(SO₃Na)₄ molecules on the surface bring to decreasing of catalytic activity. Pc(SO₃Na)₄ dimeric form exhibits a higher catalytic activity than that of Pc(SO₃Na)₄ monomeric form.

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**THE FORMATION OF PALLADIUM NANOSCALE HYDROGENATION
CATALYSTS UNDER THE ACTION OF LITHIUM ALUMOHYDRIDE**

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The nature and properties of palladium nanoscale hydrogenation catalysts based on $\text{Pd}(\text{acac})_2$ and LiAlH_4 have been studied. It has been shown that $\text{Pd}(\text{acac})_2$ reduction with LiAlH_4 is accompanied by the side process of decomposition to give palladium aluminides. The reasons for an abrupt increase of the catalyst specific activity and its extreme type of dependency on the storage duration of LiAlH_4 in THF solution have been found.

The catalysts of Ziegler type demonstrate an activity in different processes of organic synthesis most known of which are as follows: olefin and diene polymerization; isomerization; carbonylation and hydroformylation; oligomerization; coupled diene telomerization as well as hydrogenation of unsaturated compounds including asymmetrical hydrogenation. Along with conventional coreagents of these systems viz organoaluminum compounds, the alumo- and borohydrides of alkaline metals are widely used as reductants as well.

In this paper formation and properties of palladium nanoscale hydrogenation catalysts formed in the course of $\text{Pd}(\text{acac})_2$ reduction by lithium alumohydride have been considered. It has been shown that along with $\text{Pd}(\text{acac})_2$ reduction by lithium alumohydride a side process of the catalytic decomposition of the formed alane occurs that leads to palladium aluminides of different composition. That fact is probably the main reason for relatively moderate activity of the discussed catalytic system in the alkene hydrogenation ($30 \text{ mol substrate (g-at Pd min)}^{-1}$) compared to earlier studied palladium nanoscale catalysts formed under the action of AlEt_3 [1]. An influence of different parameters on the properties of palladium hydrogenation catalysts has been studied. It has first been found that the properties of $\text{Pd}(\text{acac})_2 - \text{LiAlH}_4$ catalytic system depend on the duration of LiAlH_4 in THF solution storage under inert atmosphere. An abrupt growth of the catalyst specific activity (more than by a factor of 7) has been observed. By the method of NMR ^{27}Al spectroscopy it has been established that such a phenomenon is connected with a slow LiAlH_4 partial hydrolysis and oxidation to give "aluminoxanes". The latter undergo side process of the catalytic decomposition resulting in palladium aluminide and hydrogen formation to a lesser degree than LiAlH_4 . In addition, might arise as stabilizer of palladium nanoparticles.

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EFFECT OF Zr ON THE OXIDATION STATE OF Pd AND CATALYTIC ACTIVITY OF THE SOL-GEL PREPARED Pd/Al₂O₃-ZrO₂ CATALYSTS

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The catalytic properties of Pd-only catalysts supported in Al₂O₃-ZrO₂ have a dependence on the concentration of ZrO₂. It is shown that by controlling the support characteristics it can be improved the catalytic activity for the CO oxidation. CO adsorption shows a clear influence of the ZrO₂ concentration over the oxidation state of palladium and the physical properties of the supports.

Introduction

The palladium-only three-way catalyst has been developed by the catalytic industry to achieve better elimination of the cars exhaust gases, especially during the cold-start [1]. This type of catalysts has substituted advantageously the Pt-Rh or Pd-Rh catalysts in the catalytic converters, since it has been found that under close-loop operation conditions palladium can meet the properties of the bi or three-metallic catalysts. Some challenges remain in the optimization of these catalysts, as, diminishing the concentration of palladium, improving the thermo-stability, reducing NO_x in presence of oxygen excess, improving the selectivity to nitrogen, etc. With the aim of design improved palladium-only catalysts, we started a study of preparation of mixed oxides of Al₂O₃ with additives of La₂O₃ [2], ZrO₂ [3] and CeO₂ [4] using the sol-gel technique. In this work the effect of zirconia over the properties of the catalysts of Pd supported in Al₂O₃ will be addressed.

Results and Discussion

Mixed Al₂O₃-ZrO₂ supports were prepared with different ZrO₂ concentrations (1.6, 4.7, 8.0, 12.2, 20.8 and 44 wt %), using the sol-gel method. The solids were calcined at 650 °C, and then impregnated with a palladium chloride solution to give a concentration of 0.3 wt% of palladium. The surface areas were determined by N₂ adsorption, finding a maximum area for the catalyst containing 4.7 wt% of ZrO₂. CO adsorption monitored by infrared spectroscopy was one of the techniques used to characterize the properties of the Pd surface. It was observed that different species of CO adsorbed are formed both on the support and on the palladium, depending on the ZrO₂ concentration and the pretreatment conditions. CO species

adsorbed linearly on Pd^{1+} and Pd^{2+} were identified on the oxidized catalysts. Being in the samples with 1.6 and 8 wt % ZrO_2 where more Pd^{1+} could be stabilized.

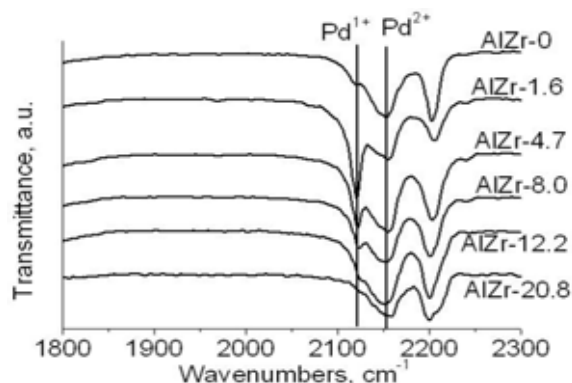


Figure 1. IR spectra of Pd/Al₂O₃-ZrO₂ samples pretreated in O₂ at 550 °C. CO adsorbed at -120 °C.

CO oxidation was used as a model reaction. The comparison of the different catalysts was done by ramping the temperature up and down. A typical set of curves is shown in the figure 2 for the catalyst 0, 8 and 44 wt % ZrO₂. It is seen that activity increase for the 8 wt % sample, compared to the 0 % sample. Then for high zirconia contents, 44 wt %, the activity goes down significantly. The above results can be explained by the combination of chemical and physical changes induced by the addition of zirconia to support, changes including average Pd particle size and its oxidation state.

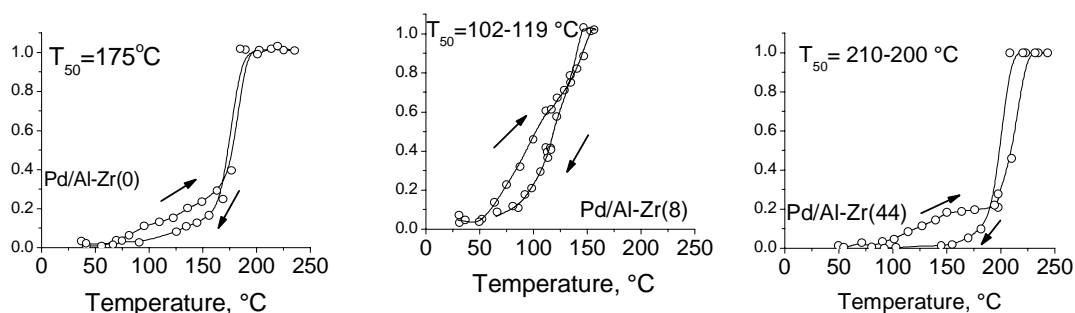


Figure 2. CO oxidation curves for Pd/Al₂O₃-ZrO₂(0, 8 and 44).

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THE NATURE OF ACTION OF THE EFFECTIVE IN THE TRANSFORMATIONS OF UNSATURATED HYDROCARBONS CATALYST SYSTEMS ON THE BASE OF BIS-ACETYLACETONATE PALLADIUM AND BORON TRIFLUORIDE ETHERATE

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For the catalyst systems on the base of Pd(Acac)₂, Acac — acetylacetonate, and BF₃OEt₂, including the case of their modification by PR₃, direct participation of unsaturated hydrocarbons in the process of bond Pd—H formation in the active species of HPd(L, L'_n)BF₄ composition is determined, where L — the molecule of an unsaturated hydrocarbon, L'=L or PR₃, n=1; 2, the structure fragment BF₄ can be bonded to Pd via F atom in a charge transfer complex or in the form of an ion pair with retain of the coordination number by 4. The considering systems are characterized by high selectivity (up to 94—100 %) and activity in processes of position isomerization of α-alkenes, styrene dimerization, telomerization of butadiene with diethylamine, polymerization of norbornene.

For the first time the catalyst systems on the base of palladium β-diketonates and molecular complexes of BF₃ with oxygen containing hydrocarbons (diethyl ether, ethylacetate, methanol, phenol and others) were described in [1, 2] as catalysts for the dimerization of propene and oligomerization of ethylene. Later such systems, and also systems modified by PR₃ in test experiments showed high selectivity (up to 94—100 %) and activity in processes of position isomerization of α-alkenes, telomerization of butadiene with diethylamine, styrene dimerization, additive polymerization of norbornene and its derivatives. On the first stage of the investigation it has been established that nature of β-diketonate ligands at palladium and oxygen containing hydrocarbons at BF₃ doesn't show considerable influence on the catalytic properties of the discussing systems. Therefore in the next stage of the investigation the catalyst system Pd(Acac)₂+BF₃OEt₂ was chosen to be basic as the most informative. On the base of aggregate experimental data obtained mainly in the 2000—2006 [3—11] on studying by IR, UV, NMR and X-ray structure analysis spectroscopy of the products of interaction of the components of the discussing system, in the presence of PR₃, hexene-1, propene, butadiene, phenylacetylene, and also data on testing of functioning in the processes of unsaturated hydrocarbons conversion active species by catalytic poisons and modifying additives, it has been drawn a conclusion that for the considering systems the active complexes (AC) are transition metal hydrides of HPd(L, L'_n)BF₄ composition, where L

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— the molecule of the unsaturated hydrocarbon, $L'=L$ or PR_3 , $n=1; 2$, the structure fragment BF_4 can be bonded to Pd via F atom in the charge transfer complex or in the form of ion pair with retain of the coordination number by 4. In the AC bond Pd—H forms with the direct participation of the unsaturated hydrocarbons, playing also the role of independent and necessary component of the catalyst system. The generating AC are square planar structures, in which free places for the coordination of the substrate molecules and PR_3 are located in the trans-position to each other and the cis-position to Pd—H bond. The fourth coordination place in the AC located in trans-position to Pd—H bond is occupied with structure fragment BF_4 , in the charge transfer complex of $HPd(L, L')F \cdot BF_3$ type. If the substrate can replace BF_4 to second coordination sphere, the formation of the ionic type complexes is possible, e.g. $[HPd(L, L'_2)]^+BF_4^-$, where $L'=PR_3$ are located in the trans-position to each other and the cis-position to Pd—H bond. Transformation of these complexes into the AC is foregone by $trans \leftrightarrow cis$ regrouping of PR_3 in the coordination sphere of Pd in the AC.

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CYCLOHEXANE OXIDATION OVER POLYGALACTURONANE STABILIZED COPPER COMPLEXES

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Copper complexes with polygalacturonan active in catalytic reaction of cyclohexane oxidation with hydrogen peroxide in mild conditions were synthesized. Yield of products depending on reactants ratio and catalyst were studied. The structure of the copper complexes was studied with EPR, IR and electron microscopy methods.

Hydrocarbons are an important source for petrochemical and chemical industries. Such important products as alcohols, aldehydes, ketones and fatty acids can be produced by oxidation of saturated hydrocarbon which are the basic components of oil and natural gas.

Catalytic oxidation of hydrocarbons with oxygen and hydrogen peroxide over polymer-immobilized metal complexes is similar to enzymatic reactions and carried out with high selectivity at low temperatures over small amount of catalyst. However, polymer matrix can hinder access of the reagents to the active sites. To improve properties of such catalysts, thin-layer polymer-immobilized copper complexes were supported on alumina. Polygalacturonane (PGU) was used as matrix for metal fixation because natural polymers are often applied as supports for many biological and biochemical application. PGU is a polysaccharide with high adsorption capacity.

The prepared catalysts as well as unsupported metal/PGU complex and trivial heterogenous Cu/Al₂O₃ were compared in cyclohexane oxidation with hydrogen peroxide under mild conditions. The supported polymer-metal complex showed the best catalytic activity. Conversion of cyclohexane was 47.7 %. Lower yields of oxygen-containing products over Cu-PGU complex can be explained by limited access to the active sites (Cu ions) located inside polymer globules. Copper leaching from Cu/Al₂O₃ was observed in the process of cyclohexane oxidation. The yield of cyclohexanone over 10 %Cu/PGU/Al₂O₃ was five times higher than that for 8,3 % on 10 %Cu/Al₂O₃. The yield of cyclohexanol over the same catalyst was increased 10 times from 1.2 % to 12 %.

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In the presence of 10 % copper PGU complex supported on alumina optimum cyclohexane:H₂O₂:catalyst ratio is formed which provides maximum accumulation of the products.

Thus, immobilized copper complexes supported on inorganic oxide are active catalysts for cyclohexane oxidation under mild conditions. Interaction of Cu ions with carboxyl groups of PGU and formation of polymer-metal complexes was confirmed by IR and EPR spectroscopy methods.

Mo AND W HETEROPOLYACID-CONTAINING HYDROTREATING CATALYSTS

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Results of synthesis of Al-Ni-Mo hydrotreating catalysts modified by heteropolycompounds (HPCs) of molybdenum and tungsten of 12 lines and their tests during hydrotreating processes of diesel fraction are given. It is shown, that application of HPCs of molybdenum instead of ammonium paramolybdate at synthesis of Al-Ni-Mo catalysts increases their HDS degree and hydrogenation activity. Additives of tungsten also increase HDS degree and hydrogenation activity of catalysts. However influence of a nature of compounds of tungsten on hydrogenation activity is more complicated.

Heteropolycompounds (HPCs) recently began to be applied more often in synthesis of heterogeneous catalysts for various petrochemical and oil refining processes. HPCs are used in preparation of isomerization catalysts, hydrogenation catalysts and hydrotreating catalysts. As a rule, authors used individual chemical compounds or their mixes for the characteristics of catalytic properties of the synthesized catalysts. Tests of catalysts for real raw material meet extremely seldom.

In the present work results of synthesis of Al-Ni-Mo of hydrotreating catalysts modified by HPCs of 12 lines and their tests in hydrotreating processes of diesel fraction [1] are given.

For synthesis of catalysts of 12 lines molybdenum HPCs were used: $H_4[Si(Mo_{12}O_{40})] \cdot nH_2O$, $H_3[P(Mo_{12}O_{40})] \cdot nH_2O$, $H_3[P(VMo_{11}O_{40})] \cdot nH_2O$ and $(NH_4)_x[V(Mo_{12}O_{40})] \cdot nH_2O$. Catalysts were prepared by a method of impregnation of the carrier with subsequent drying and calcination. At the first stage compounds of molybdenum were rendered, on the second – compound of nickel. For comparison the catalyst with the use of ammonium paramolybdate (PMA) was synthesized by a similar method.

Next part of research is devoted to modifying of catalysts by 12 lines HPCs tungsten. Catalysts were prepared by a method of consecutive impregnation of the carrier with solution of tungsten compounds and a solution of nickel nitrate with intermediate drying. As the carrier it was used calcinated alumina, content of MoO_3 8 wt %. Content of WO_3 was 6 wt %. As compounds of tungsten were used ammonium paratungstate (PTA), $H_4[Si(W_{12}O_{40})] \cdot nH_2O$ and $H_3[P(W_{12}O_{40})] \cdot nH_2O$.

The synthesized catalysts were tested in a bench-scale flow reactor unit in the process of hydrotreating of diesel fraction. The tests were conducted at temperatures of 340, 360, 390,

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and 410 °C; pressure of 3.5 MPa; a feed space velocity of 2.5 h⁻¹; a hydrogen : feedstock ratio of 450 NI/l.

For initial fraction and obtained hydrogenates contents of sulfur and polycyclic aromatic compounds (PCAC) was determined, it have allowed to determine HDS and hydrogenation activity of catalysts.

As a result of the done work application of H₄[Si(Mo₁₂O₄₀)]*nH₂O, H₃[P(Mo₁₂O₄₀)]*nH₂O, H₃[P(VMo₁₁O₄₀)]*nH₂O instead of PMA at synthesis of Al-Ni-Mo catalysts increases HDS degree and hydrogenation activity was shown. As an example in figure diagrams of dependence of HDS degree from temperature of process for catalysts on the basis of PMA (№ 1), H₄[Si(Mo₁₂O₄₀)]*nH₂O (№ 2), H₃[P(Mo₁₂O₄₀)]*nH₂O (№ 3), H₃[P(VMo₁₁O₄₀)]*nH₂O(№ 4) are given.

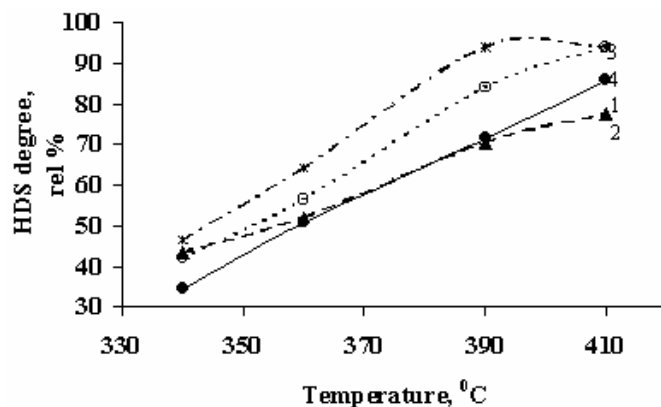


Fig. HDS activity of Al-Ni-Mo hydrotreating catalysts

Additives of tungsten increase HDS and hydrogenation activity of catalysts. Replacement of PTA on H₄[Si(W₁₂O₄₀)]*nH₂O and H₃[P(W₁₂O₄₀)]*nH₂O raises HDS activity of catalysts in all the investigated interval of temperatures. Influence of a nature of tungsten compounds on hydrogenation activity is more complicated. Additives of tungsten in all cases raise activity also, but PTA shows the best results, than H₄[Si(W₁₂O₄₀)]*nH₂O, and H₃[P(W₁₂O₄₀)]*nH₂O shows very high activity only in the field of low temperatures.

Thus, the use of HPCs for synthesis of Al-Ni-Mo hydrotreating catalysts allows to increase their HDS degree and hydrogenation activity in relation to PCAC diesel fraction.

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**HYDROCARBON CONVERSION CATALYSTS BASED
ON MESOPOROUS $\text{Ti}_{0.03}\text{Si}_{0.97}\text{O}_2$**

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Catalytic properties of mesoporous titanium-silicates modified by Ce, Co, Ni, Ru, Zn are investigated in the following model reactions: benzene and toluene hydrogenation, hydrodesulfonation of cyclic S-containing compounds, and hexene-1 oligomerization. It is proved by FT-IR, XRD, BET, SEM, TEM, and AFM methods that catalysts synthesized are uniform, highly porous, weakly crystallized, nanostructured systems. Metal-modified titanium-silicates of interest are demonstrated to have high activity in above mentioned model reactions even in mild conditions. Conclusion is drawn about future trends of development on their basis the modern, highly selective catalysts for petrol component production in accordance with modern ecological demands.

The development of new class of heterogeneous, highly porous and highly effective catalyst of polyfunctional action on the basis of mesoporous silicates will allow solving one of the relevant petrochemical problems to refine low-octane hydrocarbon (HC) raw material for yield enhancement of high quality petrol components. Recently, there is performed a number of works in Institute of Petrochemical Synthesis, RAS, to develop a method of production of mesoporous metal-silicate system, as perspective carriers and catalysts for petrochemistry; the results presented constitute a part thereof. A catalyst series modified by one to three metals (Ce, Co, Ni, Ru, Zn) was synthesized on a basis of mesoporous (3-9 nm) $\text{Ti}_{0.03}\text{Si}_{0.97}\text{O}_2$, following by further investigation on a number model reactions such as hydrogenation of aromatic HC, hydrodesulfonation of cyclic S-containing HC and oligomerization of olefin HC. The morphology and texture of the silicates synthesized and catalysts on the basis there are tested by FT-IR, XRD, BET, SEM, TEM, and AFM methods; product compositions of catalytic processes were determined by GLC, NMR, FT-IR, and GC-MS methods.

Gas phase hydrogenation of benzene (1) and toluene (2) was accomplished with catalysts having general formula $\text{Ru}_x\text{Ni}_y\text{Ti}_{0.03}\text{Si}_{0.97}\text{O}_{2+\delta}$, ($x=0-0.02$, $y=0-0.2$) on flow-through apparatus (100-250 °C, 1 atm, 5.5-6.0 h⁻¹, HC/H₂=0.2-0.4). Conversion in test temperature range was 65-85 %. It is to be noted the yield of gaseous C₁-C₄ products is sharply increased at temperatures >150 °C. Main feature in both cases however was quantitative formation of aliphatic HC C₉₊ (1) и C₁₀₊ (2) with iso-structure (signals in the range of 0.7-1.9 ppm).

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Liquid phase hydrogenation of benzene was accomplished with the same series catalysts at a room temperature and 1 atm. Only one $0.5\text{Ni}_2\text{O}_3\cdot\text{Ru}_{0.04}\text{Ti}_{0.03}\text{Si}_{0.97}\text{O}_{2+\delta}$ catalyst revealed evident activity in so mild conditions. The conversion was $10(\pm 0.4)\%$, and the primary hydrogenation product was cyclohexane. It is interesting, however, that $\sim 1\text{wt}\%$ of raw benzene was partly hydrogenated to cyclohexene.

Hydrodesulfonation. The petroleum S-containing components are presented essentially by sulphides (65-90 %) and thiophenes (10-23 %); this fact predetermined the choice of model compounds for desulfonation capacity tests of catalysts formed. Thus, 2-propyl(S1)- and 3,4-tetramethylenethiolanes (S2), and also thiophene (S3) were selected, being dissolved in hexane (0.8-1.2 wt%). The selected concentration was close to 200 ppm of sulfur that correlated with their content in typical fractions, intended for petrol delivery. The test was performed on a quartz flow-through reactor provided with an immobile catalytic layer of $3.3\text{Ni}_2\text{O}_3\cdot 0.1\text{TiO}_2\cdot 3.2\text{SiO}_2$ ($S=140\text{ m}^2/\text{g}$) at temperatures 80-200 °C (1 atm., 7.1 h^{-1} , $H/S=1.5/1.0$). The catalyst was established to display high desulfonation capacity at temperature 80 °C (Table). It is to be noted that catalyst further displayed isomerization ability at a temperature close to 150 °C and higher. Thus, there were up to 20-26 wt % of $\text{C}_6\text{-C}_7$ iso-HC in the case of S1 in the reaction products.

Table. The hydrodesulfonation efficacy on $3.3\text{Ni}_2\text{O}_3\cdot 0.1\text{TiO}_2\cdot 3.2\text{SiO}_2$

Temperature , °C	Conversion, %			Efficiency, $\text{g}_s/(\text{g}\cdot\text{atom}_{\text{Ni}}\cdot\text{h})$		
	S1	S2	S3	S1	S2	S3
80	-	97	-	-	0.565	-
100	100	97	83	0.575	0.565	0.399
120	-	97	-	-	0.565	-
150	100	98	100	0.575	0.575	0.481
200	100	98	100	0.575	0.576	0.481

Oligomerization of olefines. To improve the yield of liquid products there is a need to use oligomerization catalysts for low molecular olefin HC. A temperature 150-400°C and pressure 10-40 atm. are common conditions for this process. In this case hexene-1 was selected as a model HC, which oligomerization was accomplished in a liquid phase (temperature 60°C and pressure 1 atm.) on $\text{Zn}_{0.012}\text{Co}_{0.012}\text{Ce}_{0.012}\text{Ti}_{0.03}\text{Si}_{0.95}\text{O}_{2+\delta}$. The hexene-1 conversion was 85-91% and correlated with conversion rate $0.65\text{-}0.70\text{ mol}/(\text{g}_{\text{cat}}\cdot\text{h})$. The

selectivity of the hexene-1 oligomerization had shown to change in time by composition analysis data for reaction mixture over 8 h: the selectivity diagram passes through the maximum for C₁₂. To the end of 8-th hour the oligomerization products were C₉-C₁₂ ($\Sigma C_{13+} \leq 1$ wt%) with normal or iso-structures in the ratio C₉:C₁₀: $\Sigma C_{11,12}$ =35:30:35. The process runs obviously by polymerization-depolymerization mechanism.

Thus, it is demonstrated herein that mesoporous titanium-silicates, modified by Ce, Co, Ni, Ru, Zn, are promising for development on their basis the modern, highly selective catalysts for petrol component production in accordance with modern ecological demands.

The authors thank Prof. A.N. Ozerin, Drs E.S. Obolonkova and A.S. Merekalov for SEM and AFM analyses.

**CATALYTIC ACTIVITY OF DIFFERENT GOLD SPECIES IN HIGH-SILICATE
AND LOW SILICATE Au-MORDENITES**

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It was disclosed for Au/zeolites that not one, but several active sites can be reactive in CO-oxidation on the same catalyst. Au³⁺ cationic species does not show the activity under studied conditions. Gold nanoparticles (1.5-5 nm) are characterized by activity at high temperature. Gold clusters ($\leq 0,7$ nm) display activity in low-temperature region, but only after sample pretreatment in He at 500 °C. The clusters lost the activity during reaction probably due to oxidation and can be reactivated by He treatment while nanoparticles are stable to redox treatment at high temperature. Received data can explain the contradiction concerning the nature of active sites existing in the literature.

An intensive study of gold in catalysis for last decade was stimulated by discovery of unique activity of gold nanoparticles at low temperature for several reactions such as CO oxidation [1]. However, the origin of this unusual behavior of gold remains still under debate. A number of gold active sites were proposed: gold-support interface [2], the second layer of gold atoms from the support [3], gold nanoclusters with nonmetallic electronic properties due to a quantum-size effect [4], Au³⁺ ions [5], etc.

The effect of multiplicity of Au active sites in one catalyst and their activation under different conditions was revealed in our previous studies [6-9]. In this work the data about active sites for high-silicate and low-silicate zeolites will be considered, and how the data about the nature of active sites could explain discrepancy in the literature [10].

AuM206 sample was prepared by ion exchange procedure of protonic mordenite (TOSOH Corporation, Japan, SiO₂/Al₂O₃ molar ratio (MR) = 206) with aqueous [Au(NH₃)₄](NO₃)₃ complex at room temperature. Samples were dried at room temperature for 24 hours. Au/zeolites were studied by different physicochemical methods to reveal the active sites in CO oxidation.

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XPS, XRD and UV-Vis DRS studies showed that the ionic Au³⁺ precursor is decomposed partially at room temperature with formation of gold clusters which according to data of NMR of adsorbed ¹²⁹Xe are stabilized inside the zeolite channels. Sample reduction with hydrogen or their calcination in air at temperatures above 100 °C leads to: (i) reduction of cations Au³⁺, (ii) formation of nanoparticles with the size 1-10 nm detected with TEM and optical spectroscopy on the external surface of zeolites, (iii) stable preservation of clusters even at temperatures higher than 300 °C.

Catalytic tests in CO oxidation showed difference in reactivity of different gold species. Analysis of catalytic, DRS, XPS, NMR of ¹²⁹Xe and TPR results allowed to assign the active sites in low temperature region to gold clusters, stabilized inside the zeolite channels. The sites active at high temperature were assigned to small nanoparticles. Partially charged gold clusters are the most active in catalytic CO oxidation among gold species incorporated into zeolites. Nanoparticles are stable while clusters are characterized by low stability particular in the atmosphere of oxygen. Received data could partially explain the discrepancy in the nature of gold active sites described in literature. Various research groups could work under different conditions activating different active sites in the same catalyst.

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**INFLUENCE OF ZIRCONOCENE PRE-CATALYST DESIGN AND ACTIVATOR
NATURE ON CATALYTIC PROPERTIES OF HETEROGENEOUS
METALLOCENE CATALYSTS IN OLEFIN POLYMERIZATION**

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The heterogeneous metallocene catalysts on the base of zirconocenes of different design (*rac*-Et(Ind)₂ZrCl₂; *rac*-Me₂Si(Ind)₂ZrCl₂; *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂; *rac*-[1-(Flu)-2-(5,6-Cp-2-Me-Ind)Et]ZrCl₂) and methyl- and isobutylaluminoxanes synthesized on the montmorillonite surface by the reaction of the partial hydrolysis of AlR₃ (AlMe₃, Al*i*-Bu₃, Al*i*-Bu₂H) by the support mobile water (MMT-H₂O/AlR₃) were elaborated. It was shown that the catalytic properties of heterogeneous MMT-H₂O/AlR₃/Zr-cene catalysts (kinetics, activity, stereospecificity) depend on the design of zirconocene pre-catalyst (nature of η -ligands and substitutions in η -ligands, symmetry type) and the aluminoxan nature.

The homogeneous metallocene catalysts give the exclusive possibilities for the synthesis of the new polyolefin materials with the unique properties, which depend on a nature and design of the catalytic system components. However, a progress in the industrial production of polyolefins, in many respects, is associated with the creation of heterogeneous metallocene catalysts and their application in the slurry and gas-phase industrial processes.

The development of the heterogeneous metallocene catalysts on the base of zirconocenes of different design and the investigation of the influence of the support surface, the nature of pre-catalyst and activator on the catalytic properties of these catalysts in ethylene and propylene polymerization were the aim of this work. The *ansa*-zirconocene compounds with the different types of bridges, η -ligands and substitutions in the ligands (*rac*-Et(Ind)₂ZrCl₂; *rac*-Me₂Si(Ind)₂ZrCl₂; *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂; *rac*-[1-(Flu)-2-(5,6-Cp-2-Me-Ind)Et]ZrCl₂) were used. The methyl- and isobutylaluminoxanes synthesized *in situ* on the surface by the reaction of the partial hydrolysis of AlR₃ (AlMe₃, Al*i*-Bu₃, Al*i*-Bu₂H) by the mobile water of support montmorillonite (MMT-H₂O/AlR₃) were applied as the activators of the *ansa*-zirconocene pre-catalysts.

The thermal destruction of the methyl- and isobutylaluminoxanes synthesized on the surface and commercial MAO in the solid state was studied by the method of the mass-spectrometric analysis of the products evolved at the temperature-programmed desorption

from the surface of sample for the investigation and comparison of these aluminoxan composition and structure. It was shown, that the most part of alkylaluminoxane molecules is bonded with the support surface by the donor-acceptor interaction, with the retention of the most reactivity CH_3 -groups. Such groups are necessary for the alkylation of transition metal at the formation of catalytic complexes. The differences in the thermal behavior of the surface methyl- and isobutylaluminoxanes were found, which were, obviously, connected with the differences of their steric and electronodonor properties. These properties, apart the others, define the behavior of aluminoxanes as metallocene activators-cocatalysts in olefin polymerization. The investigation of the ethylene and propylene polymerization in the presence of elaborated $\text{MMT-H}_2\text{O/AlR}_3/\text{Zr-cene}$ catalysts showed that $\text{MMT-H}_2\text{O/AlR}_3$ are the high-effective activators for zirconocenes. They do not demand the use of the commercial MAO or the other aluminumorganic cocatalysts. It was revealed the dependence of the catalytic properties of investigated heterogeneous systems (kinetics, activity, microstructure of the synthesized macromolecules) on the design of zirconocene pre-catalyst (nature of η -ligands and substitutions in η -ligands, symmetry type) and the aluminoxan nature. Isobutylaluminoxane synthesized on $\text{MMT-H}_2\text{O}$ formes with all investigated *ansa*-zirconocenes more active in propylene polymerization catalytic complexes, than methylaluminixane in $\text{MMT-H}_2\text{O/AlMe}_3$. The stereospecificity of $\text{MMT-H}_2\text{O/AlR}_3/\text{Zr-cene}$ catalysts depends on the composition and the type of symmetry of zirconocene compound and does not depend on the activator nature. The data concerning the influence of catalytic complex immobilization on the stereocontrol of polymer chain propagation in the process of propylene polymerization were obtained. The character of this influence depends on the zirconocene structure. Thus, the immobilization of C_2 -symmetric *rac*- $\text{Me}_2\text{Si(Ind)}_2\text{ZrCl}_2$ on the $\text{MMT-H}_2\text{O/AlR}_3$ surface leads to the increase of the catalyst stereospecificity in the comparison with the compatible homogeneous system. In the case of C_S -symmetric *rac*-[1-(Flu)-2-(5,6-Cp-2-Me-Ind)Et]ZrCl₂ immobilization the catalyst stereospecificity decreases. At the same time the immobilization of the stereospecific catalyst on the base of C_2 -symmetric *rac*- $\text{Me}_2\text{Si(2-Me-4-Ph-Ind)}_2\text{ZrCl}_2$ leads only to the slight decrease of the heterogeneous system stereospecificity.

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THE USE OF METAL NANOPOWDERS IN ZEOLITE CATALYSIS

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At present many metals or their oxides synthesized in the form of nanopowders (NP) are widely used in different areas of science and technology. The application of zeolite catalysts, containing metal NP, opens up new opportunities in the ennobling of low-octane gasoline fractions. NP obtained by gas condensation of metal vapor in inert gas and introduced into zeolite matrix are characterized by higher catalytic activity in the reactions of oil processing as compared with similar powders formed via electric explosion.

The use of high-silica ZSM-5 zeolites modified by metal nanopowders (NP) makes it possible to produce polyfunctional catalysts simultaneously accelerating several reactions in a single process. The change of surface structure determines the character of its interaction with reagents, the nature and reactivity of adsorbed particles and, finally, the activity and selectivity of NP in heterogeneous catalysis.

The increased demand for motor fuels under the simultaneous toughening of their quality specifications as well as the involvement of the oil stock with high content of n-alkanes and sulfur compounds in the processing have predetermined the research field.

In this connection, the aim of this work was to study the availability of obtaining of high-octane gasolines from the oil straight-run fractions and gas condensates over high-silica zeolites of pentasil family, modified by copper, ferrum, nickel, zinc and platinum NP.

The study performed has shown that the zeolites containing nano-particles obtained by the method of gas condensation of metal vapours in a volume of an inert gas demonstrate the greatest catalytic activity in the process of ennobling of straight-run gasolines. The addition of NP to zeolites promotes the reduction of reaction temperature, so allows the process under milder conditions that causes in its turn the time of stable catalyst action to increase. As a result the decrease of the cracking reactions rate leads to the rise in the yield of the desired product.

Thus, a unique microstructure of metal NP gives them some novel properties as compared to the conventional metals and chemical compounds. The features of nano- and microgeometry and a high specific NP surface propose new possibilities for the creation of active and selective catalytic systems to be used in the process of oil refining. The presence of the dimensional effects in the electron and structural characteristics of the nanopowders means that their reactivity changes with the decrease in particle size.

THE INFLUENCE OF THE ACIDITY CHARACTERISTICS OF A COBALT CATALYST ON THE FISCHER-TROPSCH SELECTIVITY

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The incorporation of strong acid sites by the addition of promoters has a large influence on the Fischer-Tropsch selectivity of a cobalt catalyst. Strong acid sites increases the rate of double bond isomerisation, decreasing the rate of re-adsorption of olefins and re-incorporation during chain growth leading to a decrease in the chain growth probability.

The Fischer-Tropsch synthesis is the catalytic conversion of synthesis gas, a mixture of hydrogen and carbon monoxide, yielding long chain hydrocarbons. Desired products in the Fischer-Tropsch synthesis can be low and intermediate molecular weight olefins, liquid hydrocarbons (C₅₊) and/or linear C₂₀₊ hydrocarbons. Methane is an undesired product of the Fischer-Tropsch synthesis. Therefore, the methane selectivity should be decreased with an increase in the Fischer-Tropsch chain growth probability.

Some literature on CO hydrogenation indicates that molybdenum oxide and vanadium oxide used as a promoter may be beneficial for the selectivity of a cobalt based catalyst by decreasing the methane selectivity and increasing the chain growth probability.¹⁻⁷

An alumina support was modified with molybdenum and vanadium in attempt to create molybdenum and vanadium oxide layer covering the alumina surface. Cobalt was added to the modified support by impregnating precipitated nano-size cobalt hydroxide particles.

The incorporation of molybdenum oxide and vanadium oxide in the formulation of a cobalt-based Fischer-Tropsch catalyst introduced strong acidic sites as determined by density functional theory calculations (DFT) and NH₃-TPD in combination with the iso-propanol test reaction.

DFT calculations showed that an increase in the strength of the acid sites decreased the activation energy of double bond isomerisation. The increase in the strength of the acid sites in the catalysts due to the addition of molybdenum oxide and vanadium oxide thus led to an

increased the rate of double bond isomerisation. The rate of re-adsorption of olefins decreases with an increase in internal olefins leading to a decrease in olefins being reincorporated during chain growth decreasing the Fischer-Tropsch chain growth probability (see Figure 1).

The strength of the acid sites of the catalysts increased with a corresponding decrease in the Fischer-Tropsch chain growth probability in the following order:

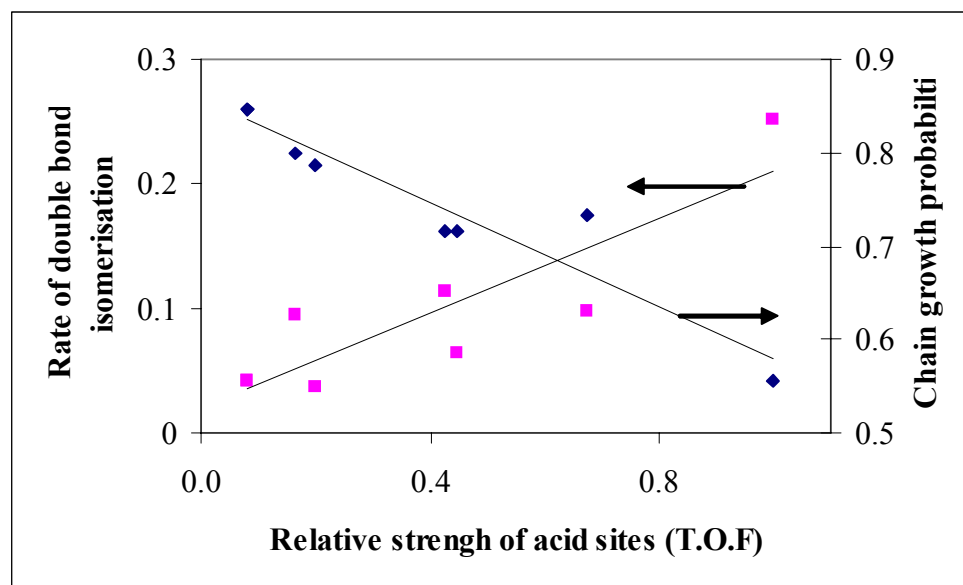


Figure 1: Influence of strength of the acid sites on the Fischer-Tropsch selectivity of the catalysts tested at 220°C and 20bar

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CHARACTERISATION OF NEW GOLD CATALYSTS SUPPORTED ON MIXED OXIDES FOR THE WATER GAS SHIFT AND PREFERENTIAL CO OXIDATION REACTIONS

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HRTEM and FTIR characterisation on three new gold catalysts supported on mixed oxides for WGS and PROX reactions are here reported. Two of these are supported on mixed ceria-titania oxides, with different ceria loading (20 % and 50 %), the other is supported on mixed ceria-zirconia oxides. The catalytic data on WGS reaction show that the addition of ceria has a positive effect, on the activity of these new samples, probably due to the presence of new gold species.

1. Introduction

Catalytic systems containing highly dispersed gold have received great interest from both experimental and theoretical points of view. Due to their high catalytic activity, particularly in CO oxidation at low temperature (1, 2), they are regarded as promising candidates for H₂ production, through methanol decomposition and water gas shift (WGS) reactions, and purification, through preferential CO oxidation (PROX). The nature of the support on which gold is dispersed plays a crucial role in determining the catalytic activity. In particular, the ceria supported systems are very stable and exhibit a high activity for the WGS reaction (3) over a wide temperature range, at different space velocity and H₂O/CO ratios (4).

Our study, recently performed, on the two gold catalysts supported on mixed ceria-titania oxides, with different ceria loading (20 %, AuCe_{0.2}Ti_{0.8}, and 50 %, Au_{0.5}Ti_{0.5}), has shown that the addition of ceria to titania has a beneficial effect on the stability and on the activity in WGS reaction (5). In order to get a quite deeper interpretation of the positive effect of ceria, TEM and FTIR characterisations have been undertaken on another new gold catalysts supported on mixed CeO₂-ZrO₂ oxides (50 % ceria loading.). All the catalysts were prepared by deposition-precipitation method and subsequent calcination at 670 K, to generate strong contact between the metal and the oxide support. The effect on the gold dispersion and on the catalytic activity of different preparation of the supports before the deposition has also been investigated.

2. Results and discussion

The analysis of HRTEM and FTIR measurements points out a quite different morphology and structure of the samples.

HRTEM measurements on Au/ CeO₂-ZrO₂ have shown a large interdispersion of the two oxides; the same result was obtained, by HRTEM analysis, on the AuCe_{0.5}Ti_{0.5} catalyst. In this sample, in addition to the large interdispersion of ceria and titania, substoichiometric phases as Ce₆O₁₁ are also present. On the AuCe_{0.2}Ti_{0.8} the two oxides, ceria and titania, are easily recognizable (ceria appears darker than titania) and they do not give rise to a solid solution or to a new mixed phase. The diffraction fringes show highly defective oxide phases in both cases.

FTIR spectroscopy of adsorbed CO revealed on the three new gold catalysts, in addition to the usual bands related to CO weakly bonded to the metallic gold step sites and to the uncoordinated support cations, a new absorption band, at 2166 cm⁻¹, never observed before on pure Au/TiO₂, Au/CeO₂ and Au/ZrO₂. This band is completely irreversible to the outgassing at room temperature, giving an evidence of a strong bond between the CO and the involved adsorption sites. On the basis of its frequency and its behaviour it has been assigned to cationic gold clusters [6, 7] stabilized on the structural and/or electronic defects.

The activity in the PROX reaction in presence of CO, O₂ and H₂ has been studied in situ by FTIR. CO₂ production is very fast, and the large intensity of the related band indicates a high activity also in the presence of an excess of hydrogen.

The catalytic data on WGS reaction will be also reported; they show that these new gold/mixed oxide catalysts have an higher activity than the simple Au/TiO₂, Au/CeO₂ and Au/ZrO₂ ones.

The catalytic activity, towards WGS as well as PROX will be discussed considering the evidenced surface sites.

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**STUDY ON THE REGULARITIES OF THE FORMATION OF Pt/C
ELECTROCATALYSTS FOR PEMFC**

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We have studied systematically the effects of synthesis parameters in precipitation method to obtain highly dispersed Pt/carbon catalyst. Influence of the reducers, alkali agents, temperature, the molar ratios of the reagents as $\text{H}_2\text{PtCl}_6/\text{Na}_2\text{CO}_3$ and $\text{H}_2\text{PtCl}_6/\text{NaOOCH}$, and regimes of their dosing on dispersion of the platinum catalysts were investigated. The dispersion of the platinum catalysts was found to depend on both metal content on the support surface unit and the chemical state of the latter. Effects of chemical modification and surface admixtures of the support surface, the addition of an extraneous electrolyte on the catalyst dispersion were studied. On the basis of the experimental data, possible mechanism of the formation of the Pt/C catalysts was proposed.

Proton exchange membrane fuel cell (PEMFC) is a highly attractive power source for mobile and stationary applications due to its high power density at low temperatures (55–95 °C) and its compact design. The electrocatalysts containing large amounts of platinum are important component of the fuel cells. Mainly they are obtained by precipitation method. However, most of applicable methods require scarce reagents, organic solvents or highly dilute water solutions, those are not suitable for a large-scale production of the catalysts. This paper presents an attempt of working up a simple and technological method of the preparation of 10-50% (wt) Pt/C catalysts, which consists in precipitation of platinum onto the carbon surfaces by the hydrolysis of platinum chloride complexes in the presence of alkali and reducing agents.

A set of 15%Pt/C catalysts were prepared by traditional hydrolytic methods including sequential addition of aqueous solutions of the alkali (NaOH or Na_2CO_3) and the reducer ($\text{C}_2\text{H}_4(\text{OH})_2$, H_2CO , HCOONa or N_2H_4) into the carbon slurry in H_2PtCl_6 solution at 75 °C. Furnace blacks and Sibunit carbons with S_{BET} of 20-400 m^2/g were used as the supports. The dispersion of the supported platinum was measured by the pulse CO chemisorption method. It was shown that NaOOCH and Na_2CO_3 are the most promising as reducing and alkaline agents which lead to the highest dispersion of the supported Pt particles.

Main parameters of the Pt/C preparation procedure were optimized: among them are temperature, the manner of preparation of the carbon suspension in H_2PtCl_6 solution, the

molar ratios of the reagents as $\text{H}_2\text{PtCl}_6/\text{Na}_2\text{CO}_3$ and $\text{H}_2\text{PtCl}_6/\text{NaOOCH}$ and regimes of their dosing. Relationships between the dispersion of Pt/C catalysts prepared at “optimal” conditions and platinum loading, chemical state of the carbon surface, crystalline structure and texture of the support, and the presence of extraneous electrolytes were derived.

The dispersion of the platinum catalysts was found to depend on both metal content on the support surface unit and the chemical state of the latter. The catalyst dispersion falls with increasing areal concentration of the metal deposited onto the support. The correlation built up in logarithmic coordinates is linear (Fig. 1). In the case of chemically unmodified carbon supports, this dependence seems to be universal because it is independent on the type, specific surface area, porosity and crystalline structure of the support. With the other factors being equal, chemical modification of the support surface (chlorination, oxidation by oxygen-containing oxidants and heat-treatment in He or H_2 atmospheres) results in a decrease of the catalyst dispersion. The chemical state of the carbon surface is well known to govern its acid-base behavior. Thus, a volcano-like dependence of the catalysts dispersion on pH value of the support suspension in water can be revealed (Fig. 2).

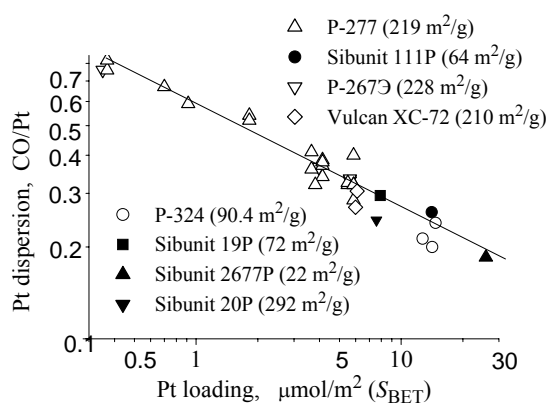


Fig. 1. Dependence of Pt dispersion on areal Pt loading for a set of Pt/C catalysts prepared on chemically unmodified carbon supports.

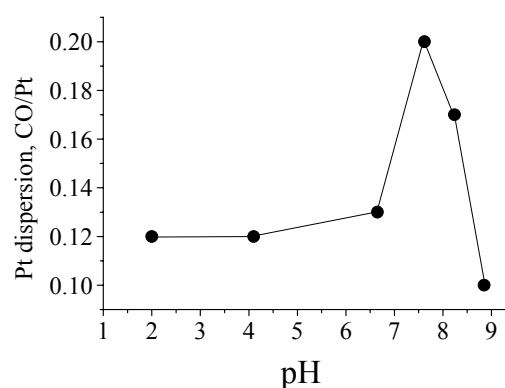


Fig. 2. Correlation between Pt dispersion in 20% Pt/C catalysts and pH values of aqueous suspensions of chemically modified carbon black P-324.

In the most cases, the addition of an extraneous electrolyte as KClO_4 , NaCl or NaNO_3 to aqueous solution of H_2PtCl_6 leads to a decrease of platinum dispersion in the final Pt/C catalysts. Analogous effects are produced by some surface admixtures (iron oxides, sulfur) inherent to carbon supports. On the basis of the experimental data, possible mechanism of the formation of the Pt/C catalysts was put forward, which included two steps of the formation of the supported platinum particles. The first of them is the origin of platinum nuclei on carbon surface during the adsorption H_2PtCl_6 , and the second is the autocatalytic growth of these nuclei in the course of catalyzed deposition of platinum from solution.

Platinum catalysts supported on novel carbon supports from the Sibunit family with BET surface areas ranging from 22 to 415 m²/g were prepared and investigated as polymer electrolyte fuel cell cathode catalysts. The highest mass specific activities at 0.85 V were achieved for the 40% (wt) and 30% (wt) Pt catalysts prepared on the basis of Sibunit carbons with BET surface areas 415 and 292 m²/g. These exceeded the mass specific activities of conventional 20%wtPt/Vulcan XC-72 catalyst by a factor of ca. 4 in the oxygen and 6 in the air feed.

Acknowledgements

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ETHANOL CONVERSION ON CKE (H-ZSM-5) CATALYSTS

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The role of HZSM-5 catalysts structural promoters, Si/Al ratio and doping metal oxides on its activity and selectivity in the process of ethanol conversion to liquid and gaseous hydrocarbons was investigated. The best selectivity to liquid hydrocarbons was reached on the catalysts, which was synthesized with hexamethylenediamine as the structure forming agent. Mechanochemical doping of CKE catalysts with gallium and iron oxides increases the catalyst life. Zirconium oxide doped catalyst shows the rapid loss of selectivity to liquid hydrocarbons. The dependence of liquid hydrocarbons selectivity from Si/Al ratio exhibit a minimum which corresponds 2 atoms of alumina per zeolite cage.

The process of alcohols conversion to liquid hydrocarbons was investigated in mid-70's mainly for methanol and the process of methanol conversion is used nowadays on industrial scale in New Zealand. Other alcohols can also be converted to the liquid hydrocarbons, but due to the high market price these processes was not developed. Recently, ethanol attracts much interest as a source of hydrocarbons production, because it can be obtained in ecology friendly way as a half-product of biomass recycling. This work is devoted to investigation of CKE (HZSM-5) catalysts structural promoters, Si/Al ratio and doping metal oxides on its activity and selectivity in the process of ethanol conversion to liquid and gaseous hydrocarbons (LHC and GHC).

CKE catalysts (Si/Al = 50) was synthesized in Tomsk State University using different structure forming agents: X-oil, alcohols fraction and hexamethylenediamine – all of them are products and reagents in nylon production cycle, and therefore cheaper than the tetrapropylammonium salts conventionally used for zeolites production. All catalysts shown a 100% activity in ethanol conversion (WHSV = 10 h⁻¹, T = 380 °C, p = 3 bar), but the selectivity to liquid hydrocarbons was very low on CKE_{X-oil} catalysts (99 % ethylene), and also on CKE_{alcohol fraction} catalyst (90 % ethylene). The catalyst synthesized with hexamethylenediamine as a structure forming agent have shown LHC selectivity near 30 % which is close to the same catalyst synthesized with tetrapropylammonium bromide (28 %). In the further work only catalysts synthesized with hexametylenediamine was used.

The influence of oxide CKE promoters was investigated for iron, gallium and zirconium oxide. The impregnation of zirconium and iron salts on CKE leads to decrease of catalyst

selectivity to LHC, moreover using 2 % Iron oxide impregnated from nitrate the process of ethanol dehydrogenation to ethylene can be done with near 100% yield. In the case of 2% ZrO₂/CKE the yield of LHC was near 10 %. Mechanochemical doping of CKE with iron and gallium contrary leads to the slight increase of LHC selectivity (37 and 38 % correspondingly) and to the increase of catalysts life.

Dependence of yields of liquid hydrocarbons from silicate module is presented on Fig. 1. It appears, that the lowest selectivity on liquid hydrocarbons has the catalyst with the silicate module 50, whereas on catalysts with silicate modules 30 and 90 higher yields are observed. Also it is interesting to note, that in comparison with other catalysts, on the catalyst with the silicate module 50 extraordinary high yield of propylene is observed. On our opinion it concerned with an arrangement of atoms of aluminium in HZSM-5 zeolite's cage.

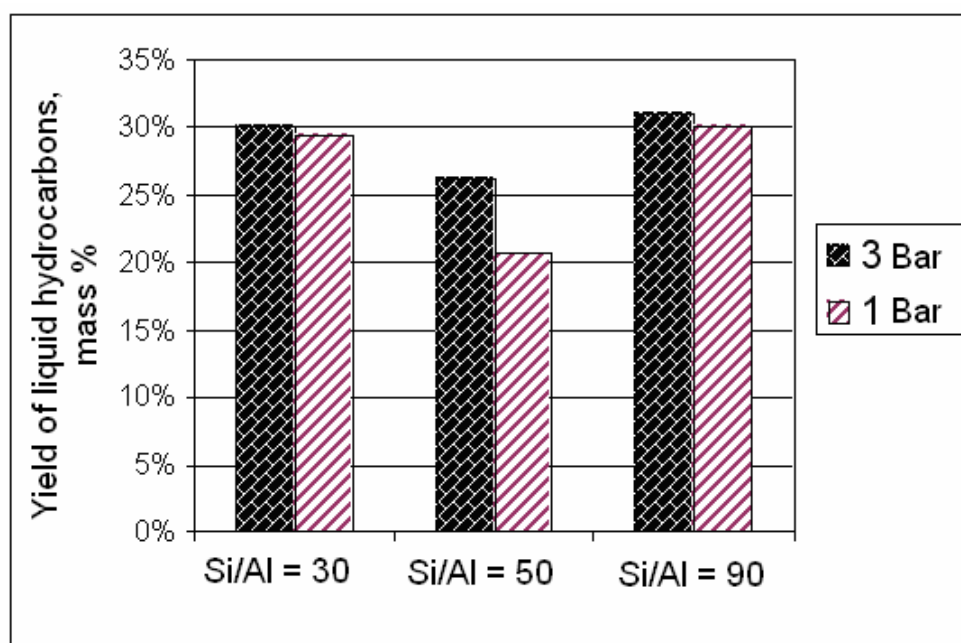


Fig.1. Yield of liquid hydrocarbons during ethanol conversion on CKE catalysts (WHSV=10 h⁻¹, T = 400 °C, reaction time - 4 hours).

It seems, when in a cell of zeolite contains two atoms of aluminium, their arrangement leads to prevail of cracking reaction of hydrocarbons C₆-C₈ on their aromatization. It is interesting to mention, that total concentration C₃-fraction + C₄-fraction in products mixture practically does not vary with growth of the silicate module whereas increasing of pressure leads to relative growth of propane/propylene production.

Thus, CKE catalysts with silicate module 30 and 90 and with mechanical promotion of gallium or iron oxide work can be used in further development of new, ecological friendly, technology – liquid hydrocarbons production from biomass derived ethanol.

CuCeZrY-BASED CATALYSTS FOR OXIDATION OF ACETONE AS A MODEL OXYGENATE OF BIO-OIL

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Catalysts for partial oxidation of bio-oil based on $\text{Cu}_x\text{Ce}_{0.7-x}\text{Zr}_{0.1}\text{Y}_{0.2}$ mixed oxides promoted by Al_2O_3 and Cr were synthesized via urea-nitrate combustion method. Structural and redox characteristics of catalysts were studied by XRD, IR spectroscopy, Differential Dissolution (DD) and H_2 -TPR methods. Catalytic tests in acetone oxidation reaction have shown that the catalysts based on CuCeZrY mixed oxides are active, alumina and chromium additives favor increasing of catalysts stability.

Catalytic steam reforming of bio-oil derived from fast pyrolysis of biomass is attractive route to generate hydrogen or syngas from which liquid fuels (gasoline, diesel) and valuable chemicals can be synthesized. The main problem in steam reforming of bio-oil which contains oxygenates (carboxylic acids, alcohols, ketones et cet.) is heavy coking of the catalysts leading to its deactivation at temperatures around 470 °C. For today no stable catalysts for this process has been found. Options to minimize coking and catalyst deactivation are: to enhance steam activation over the catalysts and to facilitate coke precursor gasification or to co-feed oxygen during bio-oil steam reforming. Thus, for efficient generation of syngas autothermal reforming (ATR) and partial oxidation (PO) are the most relevant processes. A promising approach to catalyst design is based upon materials with a high lattice oxygen mobility (for example Ce-Zr mixed oxides with fluorite-like structures [1]) promoted by Ni or Cu, since precursors of carbonaceous deposits are expected to be efficiently oxidized before oligomerization.

The objective of the present work is to design active and selective catalysts for partial oxidation of bio-oil based on $\text{Cu}_x\text{Ce}_{0.7-x}\text{Zr}_{0.1}\text{Y}_{0.2}$ (CCZY) mixed oxides promoted by Al_2O_3 (CCZYA) and Cr (CCZYA+Cr). Acetone is one of the components of bio-oil and it was chosen as a model compound in this study.

Catalysts were synthesized via the urea-nitrate combustion method [2]. Urea $\text{CO}(\text{NH}_2)_2$ was added to a mixed solution of Cu, Ce, Zr, Y and Cr nirtates in the appropriate molar ratios. Al_2O_3 powder (10-40 w.%) was added to the mixed solution with urea and then it was

steamed until a gel formation followed by calcination in air at 400 °C. Catalysts characteristics were studied by XRD, IR spectroscopy, Differential Dissolution and H₂-TPR.

For unpromoted CCZY samples, the solid solutions of fluorite structure are already formed after calcination at 400 °C and they all contain CuO phase. According to XRD, IR and DD, the samples promoted by alumina and Cr contain highly dispersed YCuO_x, Al₂O₃ of poor crystallinity and Cr₂O₃ along with a solid solution of the fluorite type. Addition of alumina and Cr leads to the significant increase of the specific surface area from 6-33 m²/g (CCZY samples) up to 170 m²/g for CCZYA and CCZYA+Cr samples.

Redox properties of the catalysts were investigated by H₂-TPR. For all catalysts, a broad peak with a maximum at 200-235 °C is observed in TPR spectra. The position of this peak depends on the copper content and presence of promoters. Thus, the peak maximum shifts from 232 °C for unpromoted catalysts to 209 °C for Al₂O₃ and Cr-containing catalysts. This peak could be assigned mainly to reduction of Cu²⁺ since the H₂ consumption increases with the copper content. However, the ratio of H₂ consumption to Cu concentration is above 1, hence, even at this relatively low temperature partial reduction of Ce⁴⁺ occurs as well. Moreover, for promoted samples, the increase of H₂ consumption is observed testifying acceleration of oxygen mobility.

The catalysts were tested in partial oxidation of acetone using a quartz flow reactor packed with a catalyst (0.25-0.50 mm fraction) diluted with quartz sand. Reaction mixture of 1% acetone + 0.5% O₂, He -balance was fed through the reactor at contact time 25 ms and increasing temperature from 25 to 880 °C with the rate 10 °C/min.

The overall system of reactions which may occur during the acetone oxidation is quite complex. For almost all catalysts, the main tendency of product distribution is similar. Formation of CO₂ due to partial acetone oxidation is observed in the temperature range of 150 to 250 °C depending on the catalyst. At 300-350 °C, H₂ and CO appear indicating that thermal decomposition of acetone competes with the oxidation. H₂ is produced faster than CO and its maximum concentration attains at lower temperatures. The steep increase of CO concentration followed by the decrease of CO₂ concentration at 600-650 °C may be attributed to the reverse water-gas shift reaction [3]. Chemical composition of the catalysts strongly influences on their performance in acetone oxidation. The start temperature of hydrogen and syngas evolution depends on the copper and alumina content, chromium additives in the catalyst. Thus, among unpromoted CCZY catalysts, for the sample with the highest copper content, the maximum hydrogen concentration reaches at the lowest temperature – 790 °C.

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For the catalysts with alumina additives, the start temperature of H₂ formation lowers to 670 °C and chromium addition to the catalyst results in further temperature decrease to 625 °C. It was shown that catalysts with alumina and chromium additives are more stable in acetone oxidation than unpromoted catalysts.

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ELECTRONIC STATE OF Crⁿ⁺ CATIONS IN CHROMIA-ALUMINA CATALYSTS

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In the current communication we shall review the electronic state of chromium cation in chromia-alumina catalyst used for thiophene synthesis. It has been shown that the Cu-Cr-Al and Mg-Cr-Al oxide catalysts have three electronic states of Crⁿ⁺ cations: isolated Cr³⁺ ions stabilized in γ -Al₂O₃ structure, isolated Cr⁵⁺ ions and associates of Cr³⁺ ions formed the fine-dispersed X-ray amorphous phase of chromium (III) or copper/magnesium chromite.

The chromium-aluminum oxide catalysts are extensively used for processes of catalytic conversion of different sulfur-containing compounds, especially: hydrogen sulfide oxidation to elemental sulfur [1], reduction of sulfur dioxide by methane or synthesis-gas [2], thiophene and its derivative synthesis [3, 4]. It has been established that the catalytic activity in mentioned reactions increases with chromium loading in the catalyst, and after preliminary sulfidizing of the catalyst. It is probable that the activity of the chromia-alumina catalysts in the mentioned processes is concerned with electronic state of Crⁿ⁺ cations.

This presentation is devoted to study of phase composition and electronic state of Crⁿ⁺ cations in chromia-alumina catalysts depending on chromium loading (0-10 wt.%) and on a presence of second metal (Cu, Mg).

The data of X-ray diffraction (XRD) and differentiative dilution analysis show that the Cu-Cr-Al and Mg-Cr-Al oxide catalysts contain a fine-dispersed X-ray amorphous phase of chromium (III) oxide and a solid solution of Cr³⁺ cations in γ -Al₂O₃ structure. At that, the solid solution of Cr³⁺ cations in γ -Al₂O₃ structure has a Cr/Al ratio equaled to 0.04 and spacing parameter similar to γ -Al₂O₃ ($a = 7.920 \text{ \AA}$), and its loading amount is not less than 80-84%. When copper is used as second metal, a formation of fine-dispersed amorphous phases of CuCr₂O₄ and Cu₂Cr₂O₄ is also observed. Whereas Mg²⁺ cations is mainly stabilized as solid solution in γ -Al₂O₃ structure ($a = 7.975 \text{ \AA}$).

According to ESR and UV-Vis spectroscopy, the Cu-Cr-Al and Mg-Cr-Al oxide catalysts contain three electronic states of Crⁿ⁺ cations. The first are isolated Cr³⁺ ions ($g_0 - 4.97$) in a distorted octahedral coordination of oxygen-containing ligands. They can be ascribe to a stabilization of Cr³⁺ cations in the γ -Al₂O₃ structure as solid solution. Associates of Cr³⁺ ions are the second state, which characterized by isotropic ESR spectrum with g_0 -1.97-1.98 and a

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linewidth 500 Oe. This state is probably attribute to the fine-dispersed X-ray amorphous phase of chromium (III) or copper/magnesium chromite. Third, an isolated Cr^{5+} ions ($g_0 = 1.97$) are observed. The ratio between Cr^{3+} associates and isolated Cr^{5+} ions depends on chromium loading and calcination temperature. The concentration of Cr^{3+} associates is raised and the concentration of isolated Cr^{5+} ions is diminished when chromium loading and calcination temperature are increased. The concentration of isolated Cr^{3+} ions is practically constant.

Although, pre-sulfiding is well known and commonly used, there is still debate regarding the optimal conditions of active sites formation. In order to explain the purpose of pre-sulfiding in thiophene synthesis we studied a chemical composition of the Cu-Cr-Al and Mg-Cr-Al oxide catalysts pre-sulfided in H_2S or DMDS. A formation of weakly and strongly fixed sulfur was observed after pre-sulfiding by both DMDS and H_2S . When DMDS was used for the catalysts pre-sulfiding, a formation of carbon-containing fragments was also observed. These pre-sulfided catalysts were characterized by the ESR signal with $g_0=2.0$ and a linewidth 5 Oe and the weight loss followed by the exothermal effect at 425-450°C observed by thermogravimetric analysis. These signals in ESR and TGA were also observed for the samples after thiophene synthesis from butane and dimethyldisulfide, and were absent for sample pre-sulfided by H_2S . Formation of the carbon-containing fragments can explain the larger catalytic activity of the samples pre-sulfided by DMDS in comparison with the samples pre-sulfided by H_2S .

It has been shown that the calcination of a spent catalyst in air at 580°C results in a regeneration of the initial electronic state of Cr^{n+} ions and removal of coke formed during reaction. Strongly bonded sulfur is removed at temperature above 800°C.

Thus, the Cu-Cr-Al and Mg-Cr-Al oxide catalysts have three electronic states of Cr^{n+} cations. Further studies are needed to evaluate their role in the catalytic activity in thiophene synthesis and reduction of sulfur dioxide by methane or synthesis-gas.

Acknowledgements

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**METAL SUPPORTED CATALYSTS ON THE BASIS OF FIBROUS CARBON
SULFOCATIONITE FOR REDUCTION-OXIDATION REACTIONS**

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Metal supported catalysts on the basis of fibrous carbon sulfocationite prepared by modification of the fibrous carbon material “carbopon” with sulfonated styrene-divinylbenzen copolymer were obtained. High activity of the synthesized catalytic systems in the reaction of CO oxidation as well as electrodes for hydrogen-air fuel cell was determined.

New types of activated carbons, such as carbon fabrics and nonwoven materials as supports of catalysts stimulate increasing interest.

In present work nonwoven material carbopon (“Khimvolokno” association, Svetlogorsk, Belarus) manufactured by carbonization of viscose fiber was used as raw material. Adsorption and structural characteristics of carbopon: fiber diameter 5-10 μm , sorption volume (by water) 0.64 cm^3/g , mean pore diameter 23 \AA , specific surface by nitrogen sorption 780 m^2/g , electric resistance – no more than 1 ohm.

On the first stage of the synthesis of the fibrous carbon sulfocationite (sulfocarbopon) raw carbopon was modified with styrene-divinylbenzen copolymer by the radiochemical method. Thereto carbopon plates were saturated with monomer mixture and placed into the canal of the RHM-gamma-20 reactor with ^{60}Co core. Output power of irradiation was 4.6 kGr/h. Copolymer loading was varied by changing of irradiation dose.

On the second stage of the synthesis a sulfonation was performed by treating of the obtained matrix with concentrated sulfuric acid (100 $^{\circ}\text{C}$, 2 h).

Series of samples of metal supported catalysts (Pt, Pd) on the basis of carbopon and sulfocarbopon were synthesized. Samples were prepared by the methods of metal deposition from hydrosol and ion exchange and were examined in the reaction of CO oxidation with air oxygen. The most active of those samples were platinum supported catalysts on the basis of sulfocarbopon, prepared by multiple ion exchanges from the aqueous solution of tetraammineplatinum chloride followed by reduction of the metal in hydrogen atmosphere after every stage of the ion exchange. In the presence of the sample 5.4Pt/sulfocarbopon (5 cycles of ion exchange – reduction) at 16 $^{\circ}\text{C}$ and space velocity of gas mixture (0.6 vol.% CO in air) comprised 600 h^{-1} , 100 % conversion of CO was reached. High catalytic activity of

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those catalysts is caused by highly dispersed platinum on the support surface (mean particle size 1-4 nm).

Platinum contained catalytic systems on the basis of sulfocarboon were examined as materials for anode and cathode of hydrogen-air fuel cell (FC). Materials of FC electrodes for its effective functioning must possess proton conductivity as well as electroconductivity. Sulfocarboon as the basis for materials of electrodes is satisfied both aforesaid demands.

Samples of materials of electrodes were prepared by means of the following methods: hydrosol impregnation, ion exchange and electric precipitation. Electrodes of the demonstrational hydrogen-air FC PEMFC Kit manufactured by Fuel Cell (USA) were used as standards. Optimal values of ion exchange capacities of sulfocarboon (0.6 - 0.7 meq/g) and optimal quantities of supported platinum (2 – 4 wt.%) were determined. The best sample of anode was prepared by multiple ion exchanges from the aqueous solution of tetraammineplatinum chloride (4 cycles) and contains 4 wt.% Pt. The most effective sample of cathode, which contains 2.3 wt.% Pt, was prepared by means of electric precipitation. Those samples are highly competitive with foreign analogues.

FORECASTING CATALYTIC CHARACTERISTICS OF THE OXIDE CONTACTS FOR HIGH TEMPERATURE AMMONIA OXIDATION

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Physical-chemical and catalytical properties of oxide catalysts systems $\text{Fe}_2\text{O}_3\text{-Me}_x\text{O}_y$, where Me - Li, Cu, Zn, Cd, Co, Ni, Be, Mg, Ca, Sr, Ba, Al, Ga, Sc, Y, La, Ce, Pb, Cr, Bi, Mn are studied in the process of high temperature oxidation of ammonia. Influence of phase and chemical compositions of the system on the physical-chemical and catalytical characteristics of oxide catalysts is shown. It is proved that the selectivity of the catalysts to nitrogen (II) oxide correlates with the binding energy of adsorbed oxygen with the surface of both simple and the complex oxide systems. It is shown that there are optimal values of the binding energy “catalyst – oxygen” for obtaining maximum value of the selectivity both increase and reduction binding energy of the oxygen with the oxide surface in the comparison with the optimal values lead to the reduction of the catalytic selectivity to NO and of the selectivity to molecular Nitrogen. Influence of the composition of the catalytic systems on the binding energy of catalyst oxygen and finally on the selectivity of oxides to the Nitrogen (II) is considered. Influence of structure factors of crystal lattices on the binding energy of adsorbed oxygen of the catalysts is shown (for example, contact - ferrites).

Mechanism and regularities of reactions of the oxidation of ammonia on simple and complex oxide catalysts [1, 2], including adsorption of the oxygen change from ammonia into surfaces N_{ads} are studied by the methods of programmed thermodesorption, massespectrometry, IRS. The recombination of two N_{ads} leads to formation of N_2 and interaction of N_{ads} with O_{ads} - to the formation and desorption of NO. It's shown that oxidation of ammonia is related to structured-sensitive processes.

Multiple-stage mechanism of reaction is used to explain the correlation of catalyst selectivity to NO with the binding energy of adsorbed oxygen and structural peculiarities of the surface of oxide systems.

Influence of chemical and structural modifiers on phase and chemical compositions is shown. Structured and catalytic characteristics of oxide systems, binding energy of adsorbed oxygen with surface contacts is shown [3]. Recommendations on the syntheses of highly selective catalysts for ammonia oxidation are given.

PP-II-153

Data obtained can be used for theoretical and practical bases for creation of efficient non-platinum catalysts for ammonia oxidation.

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**RE - CONTENTING HC OXIDATION CATALYSTS OBTAINED BY THE
AUTOCLAVE THERMOLYSIS METHOD**

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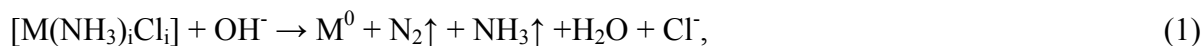
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There are some samples of catalysts containing Pt – Re and Pd – Re on the steel X18H10T prepared by the autoclave thermolysis method and the catalytic activity of these catalysts was tested.

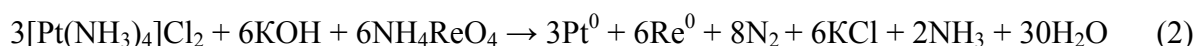
Double metal coated heterogeneous catalysts often show synergetic effect and are more active than monometallic one. Binary catalysts containing platinum and nonferrous metals as an active component are widely used. Ways of metal coating, nature of inters, technological procedures have decisive importance for obtaining the active catalyst.

For coating of metals on ceramic and metal substrates we have developed the procedure of autoclave thermolysis of complex ammine in the alkaline medium. This method is based on the irreversible process of intramolecular reduction of metal's ion - complexing intraspherical ammonia according to the equation of reaction (1):



where M = Pt, Pd, Rh, Ir, Ru etc.

In this work, we offer to broaden the autoclave thermolysis method for Re-containing systems. As a basic process, we offer to use the reaction proceeding by the following equation (2):



Samples of catalysts containing Pt – Re and Pd – Re, on the steel X18H10T were tested on the laboratory facility of the flowing type with isothermal reactor and in conditions similar to the ideal displacement mode. We have studied catalytic activity and stability of samples in the process of the deep oxidation of the model hydrocarbon (n- hexane). The composition of the reaction mixture was analyzed by gas chromatography method.

We have determined that in processes of the deep oxidation of n-hexane, the catalytic activity of Pt /Re and Pd/Re catalysts is close to the activity of Pt/Pd catalysts obtained by the autoclave thermolysis method.

CATALYTIC SYNTHESIS OF COMPOUNDS FOR ENVIRONMENT CONTROL

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The protection of useful plants with synthetic pheromones and attractants of harmful insects is characterized by absolute safety for an environment in contrast to insecticides poisoning ground and water. At hydrogenation 5,17-docosadiene on 10% Cu/ γ -Al₂O₃ modified by europium oxide (Eu 1-10 %) under hydrogen pressure 8MPa and 393K is converted to 5,17-docosadiene with 100 % yield. 5,17-docosadiene is attractant of gipsy moth which is pest of forest and fruit trees. The tests in woods of Beltswill have shown high biological activity of attractant.

Synthetic sexual pheromones and attractants of pest insects are used for revealing of pests and forecasting of their development with the purpose of definition of exact terms of protective chemical actions that reduces use of insecticides poisoning ground and water. In case of use of pheromones or attractants for pest control it is not necessary to apply the chemicals. In both cases it results in improvement of a condition of environment.

On developed 10-30% Cu/ γ -Al₂O₃-catalysts under the certain conditions of hydrogenation 5,17-docosadiene is converted into 5,17-z,z-docosadiene with 100 % yield but reaction duration is very long. In this connection the most active catalyst 10% Cu/ γ -Al₂O₃ was modified. The modifier was selected taking in account the earlier carried out quantum-chemical calculations. As strengthening of donor properties of the catalyst raises a part of giving electron transfer at adsorption of acetylene compounds and promoting to loosening the triple bond resulting to growth of activity and selectivity of its hydrogenation therefore as modifier europium oxide with strong donor properties was selected. The contents of europium in the catalyst was varied from 1 to 10 %. Catalysts were investigated by methods of XRD, BET, TPD, electronic microscopy.

On all modified catalysts under hydrogen pressure 8 MPa and temperature 393 K, 6-8 MPa and 423 K 5,17-docosadiene is converted to cis-,cis-5,17-docosadiene with 100 % yield. Reaction stops spontaneously. The rate of reaction increases and reaction duration decreases: by 5,8 times at Eu contents from 1 to 3 %; by 3,8 times on catalysts with 7 and 10 % Eu. The maximal decrease of reaction duration by 11,6 times and the maximal rate of

reaction are shown on the catalyst with 5 % Eu that correlates with results on thermodesorption of hydrogen from the modified catalysts. The catalyst with 5 % Eu is characterized by the contents of hydrogen by 2,4 times exceeding those for the initial copper catalyst. The amount of atomic and molecular hydrogen at change of europium contents passes through a maximum corresponding to the catalyst with 5 % Eu. As reaction of hydrogenation to copper is limited by activation of hydrogen it is obvious that the maximal contents of atomic hydrogen on a surface will correspond to the most active catalyst. From the data of electronic microscopy follows that at modifying by europium the tendency to decrease in number of dense of large formations is marked. But substantial increase of dispersity does not occur. It can be proposed that the increase of the contents of atomic hydrogen at catalyst surfaces occurs due to strengthening of hydrogen spillover at Eu presence. High selectivity of hydrogenation of acetylene bond on copper is connected to low heat of adsorption of olefine bond unfavourable for catalysis. The high yield of cis-olefinic compounds is provided by formation of dihydride complexes of copper type which enable to give the synchronous connection of two atoms of hydrogen to triple bond (1 *) with formation of z, z-diolefine.

5,17-docosadiene is attractant of gipsy moth which is pest of forest and fruit trees (*Lymantria Dispair*). At testing of synthesized attractant in gardens of Alatau forestry even at the lowest number of harmful insects it was found out on 5-7 butterflies in traps. In case of carrying out of tests in Beltswill woods (USA) in traps with attractant it is found 14-17 butterflies for two days and in traps with sexual pheromones (*Lymantria Dispair*) for the same time 5-14 butterflies of a harmful insect are revealed. These data shows the high biological activity of synthesized attractant.

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COPPER COMPLEXED CATALYSTS IN HARMFUL INSECTS PHEROMONES SYNTHESIS

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Stereoselective 9-hexadecyne-1-ol hydrogenation over γ -Al₂O₃ supported copper catalysts modified with polyvinylpyridine and europium and yttrium oxides have been studied. All modified catalysts at hydrogen pressure of 8 MPa and temperature 393-413 K as well as 10 MPa and 393 K present 100% yield of cis-9-hexadecene-1-ol which is used as a component of pest insect pheromones.

Unlimited use of herbicides and pesticides for plants protection leads to water and soil contamination, destroys some important types of insects. Biological methods of plant protection are the most progressive and environmentally friendly. One of them is based on use of synthetic pheromones of harmful insects. This methods action is highly specific.

Prediction of harmful insects development is made and the precise time for preventive disposal of chemicals is defined due to use of synthetic pheromones, and thus, the amount of insecticides used decreases. In both cases state of environment becomes better.

In the present paper stereoselective 9-hexadecyne-1-ol hydrogenation over copper complexed catalysts immobilized on support () through functionalized polymer ligands (polyvinylpyridine – PVP) is studied. Influence of modifiers – europium and yttrium oxides – on activity, selectivity and stereoselectivity of catalysts was examined. Catalysts were tested (analyzed) by methods of RPE, BET, electronic microscopy. Fixing of copper complexes on support was proven by IR-spectroscopy and electronic microscopy. The surface area of 10% Cu-PVP/ γ -Al₂O₃ is 77m²/g, surface area after modification by yttrium oxide (1% Y) is 74m²/g, by europium oxide (5% Eu) – 94 m²/g. By means of RPA the presence of metallic copper without supplementary atoms in its crystalline structure was shown. Presence of carbon formed during thermal treatment of the sample leads to of surface.

When polymer is added Cu(II) interacts with PVP and its particles are dispersed uniformly over the surface. Polymer chains prevent agglomeration of copper particles on support surface. According to electronic microscopy size of copper particles is 60Å. Copper is dispersed precisely along PVP chains.

The product of stereoselective 9-hexadecyn-1-ol, which is the main component of gray grain worm (*Apomea anceps*-s) pheromone and semiproduct of cotton worm - moth (*aclothia armigera*) pheromones component. 9-hexadecyne-1-ol hydrogenation over 10% Cu-PVP/ γ -Al₂O₃ under hydrogen pressure of 8 MPa and temperature 393-413K goes with total conversion of initial acetylenic alcohol and 100% cis-9-hexadecene-1-ol yield. Under 6 MPa pressure and at temperature of 393 K as well as under 8 MPa and 373 K. The process goes with less conversion. Small amount of initial acetylenic alcohol and 99,9% of cis-9-hexadecane-1-ol are present in product mixture. Increase of hydrogen pressure to 10 MPa leads to forming of hexadecanole, but the major product is cis-9-hexadecane-1-ol (99,9%). In all cases reaction stops spontaneously. Modification of 10% Cu-PVP/ γ -Al₂O₃ by oxides of europium and yttrium does not change stereoselectivity of the process. All modified catalysts at hydrogen pressure of 8 MPa and temperature 393-413 K as well as 10 MPa and 393 K present 100% yield of cis-9-hexadecene-1-ol. Increase in activity of catalysts is very small perhaps, due to small growth of hydrogen spillover during modification.

Time of hydrogenation over supported copper PVP catalyst is twice less than that of 10% Cu/ γ -Al₂O₃.

SOLUBLE POLYMERS IN DESIGN OF NANOSIZE HETEROGENEOUS CATALYSTS

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A simple method for preparation of heterogeneous catalysts with even distribution of metal nanoparticles on supports have been developed. The procedure includes: a) polymer adsorption on a carrier; and b) fixation of transition metal ions on polymer coated oxides. The developed catalysts were studied with TEM and spectroscopic methods and tested in semihydrogenation of long-chain acetylene alcohols and cyclohexane oxidation with H₂O₂ under mild conditions.

Active nanosized catalysts are formed by interaction of functionalised polymers with transition metal salts [1,2]. However, the drawbacks of macromolecule supports are diffusion limitation of the substrates to active centers often located inside polymer-metal globules and mechanical instability of such types of catalysts. These disadvantages can be overcome by supporting polymer-metal complexes on inorganic carrier. The procedure includes: a) adsorption of polymer on sorbent; and b) fixation of transition metal ions on polymer coated surface of support [2-4]. The effect of the nature of supports as well as polymer-modifiers on activity, selectivity and stability of the prepared catalysts have been studied.

Polyethylene glycol (PEG) as well as polyvinylpyrrolidone (PVPD) were found the best modifiers for preparation of nanosized Pd/oxide catalysts for semihydrogenation acetylene alcohols (Table 1). Bimetallic Fe-Cu and Fe-Mn on aluminosilicates (AL-Si) coated with N-containing polymers showed high activity and selectivity in cyclohexane oxidation with hydrogen peroxide under mild conditions (Table 2).

Table 1. Hydrogenation of 3,7,11-trimethyldodcene-1-ol over supported palladium catalysts in ethanol at 40 °C and atmospheric pressure of hydrogen

Catalyst (1% of Pd)	W·10 ⁻⁴ , mole/l·sec		TON	S _{C=C} , %
	C≡C	C=C		
Pd/ZnO	2,71	0,25	4400	91
Pd-PEG/ZnO	6,23	0,01	3800	98
Pd-PVPD/ZnO	27,97	0,04	62000	95

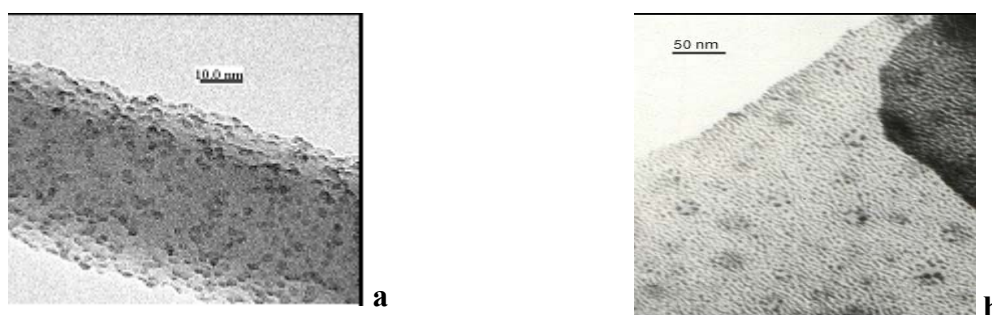
Supporting Pd on ZnO coated with polymers leads to significant improvement of the catalysts' properties. The Pd-PVPD complex showed higher activity and TON but lower selectivity in hydrogenation of 3,7,11-trimethyldodecyne to 3,7,11-trimethyldodecene to compare with Pd/ZnO and Pd-PEG/ZnO catalysts.

Table 2. The results of cyclohexane (0.3 ml) oxidation with H₂O₂ in acetonitrile (1.2 ml) on (Fe +M)/Al-Si catalysts (0.03 g), aluminosilicates

Catalyst	Conversion of C ₆ H ₁₂ , %	Cyclohexanol %	Cyclohexanone %	Ol/one ratio
10%Fe-PHMG/Al-Si	22.3	15.7	6.6	2.4
10%(Fe+Cu)-PHMG/Al-Si	47.0	14.7	32.3	0.45
3%(Mn-Fe)-PHMG/ Al-Si	47.3	38.8	8.5	4.6

Fe catalyst supported on aluminosilicate modified with polyhexamethyleneguanidine (PHMG) is less selective and active in oxidation of cyclohexane to compare with bimetallic catalysts (Table 2). The yield of cyclohexanol is higher on the Cu-Fe catalyst. Cyclohexanone with selectivity of 82 % is produced on the Mn-Fe catalysts. Cyclohexane conversion on the both catalysts are about 47 %, TON is 400-600

Figure 1. TEM image of the Pd-PEG/ZnO (a) and %(Mn-Fe)-PHMG/ Al-Si (b) catalysts



TEM study showed even distribution of the Pd nanoparticles with 2-3 nm sizes on the surface of ZnO covered with PEG (Fig.1) Pd particles of different sizes are formed on ZnO without the polymer.

Results of TEM study of the Cu-Fe and Mn-Fe catalysts on aluminosilicates (Al-Si) confirmed the decrease of metal particle sized on the surface of polymer-containing supports (Fig.1, b). IR-spectroscopy data confirm interaction of the polymers with metal ions and formation of complexes on the surface of supports.

Thus, a simple method for preparation of active, selective and stable heterogeneous catalysts with even distribution of metal nanoparticles on supports have been developed based on strong adsorption of soluble polymer on carrier and binding of metal ions with functional groups of macromolecules. The procedure is carried out under mild conditions (ambient temperature and atmospheric pressure, water as solvent).

**COPPER-CARBON CATALYST –PRODUCT OF COPPER ACETYLENIDE
EXPLOSIVE DECOMPOSITION**

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The catalytic properties of products of copper acetylenide explosive decomposition (Cu+C) have been investigated in simulated reaction of dehydration-dehydrogenation of propan-2-ol at 60 – 350 °C. An explosive decomposition of copper acetylenide led to the formation of small amorphous carbon granules and copper particles in it. It was shown, that condition of copper acetylenide explosive decomposition (on air or in vacuum) influenced the selectivity of propan-2-ol decomposition. The (Cu+C)-catalyst have revealed the high activity (85 % conversion at 60 °C) and 100 % selectivity with regard to acetone.

The copper containing catalysts are widely used both in industry and in preparative chemical synthesis. In contrast to silica and alumina, being used as support, carbon is stable to acid and base, that is essential for many chemical processes. The method of the «dry» one-stage synthesis of the copper containing catalyst on carbon support by initialisation of the copper acetylenide explosive decomposition have been developed and realized in this work.

The copper acetylenide explosive decomposition was initiated by means of heating on air (1) and by destruction in vacuum (2).

The specific surface of system (Cu+C) (way 2), measured by the nitrogen adsorption, was 120 m²/g. The catalytic properties of (Cu+C) system were investigated by the pulse microcatalytic method in dehydration-dehydrogenation of propan-2-ol. The conversion products were determined with the help of gas chromatography detection.

The (Cu+C) system, received by way (1), showed the catalytic activity in propan-2-ol decomposition at temperatures above 260 °C with the formation of propylene and acetone in practically equal yields and the total reaction conversion was not higher, than 30 %.

The (Cu+C)-system, received by a way (2), initiated the catalytic process already at 60 °C with 85 % alcohol conversion. Furthermore such type of catalysts provided 100 % selectivity

relating to acetone. With the help of XRD-research of system (Cu+C), received by way (2), it was shown, that carbon was amorphous in it and this system didn't contain copper oxides at all.

SEM-research of both systems (Cu+C) allowed us to determine that copper particles were quite spherical and their diameter distributed in range 0,5 – 20 mcm.

ONE-STEP HYDROOLIGOMERIZATION OF BUTENES INTO ISOALKANES

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Features of synthesis and properties of bifunctional (metal-acid) catalysts based on mixed oxides Al-Zr-B-O_x with palladium dispersed on their surfaces have been viewed. The possibility of using of these catalysts in one-step hydrooligomerization of butenes into isoalkanes for producing clean motor fuels has been shown.

Catalytic reactions for synthesis of C₅-C₈ isoalkanes play a key role in production of up-to-date high-octane clean motor fuels. The technologies of dimerization of C₄ alkenes into C₈ isoalkenes with further hydration attract attention of the researchers along with isomerization and alkylation processes. In that way, it is possible to get products with research octane number from 80 to 100 depending on the feed. The main drawback of such processes is two-step technology which leads to increase in capital and operating costs. In this work the possibility of conversion of butenes into isoalkanes on bifunctional Pd/Al-Zr-B-O_x catalyst by one-step hydrooligomerization has been examined.

On the first stage of this study the use of boria as anionic modifier for alumina, zirconia and their compositions has been experimentally approved. In oligomerization of butenes catalytic activity of systems, modified with boria was two times higher than catalytic activity of samples obtained with hydrochloric and phosphoric acids.

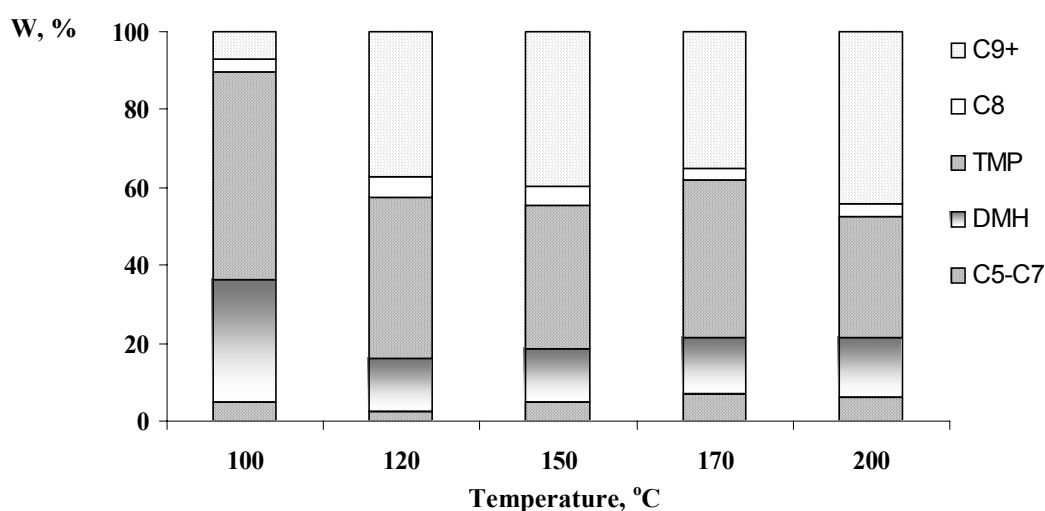


Fig. 1. Hydrocarbon type content of liquid products of hydrooligomerization (W – mass concentration; TMP – trimethylpentanes; DMH - dimethylhexanes)

At the same time, catalysts containing 4-6 wt% of boria provide 70-80 % conversion level of butenes with octenes content in C5+ products equal to 50-60 wt%. Using of sulfate species as modifiers gives the similar results. However, sulfated systems are much less stable in hydrogen and water steam conditions due to theirs reduction and hydrolysis.

Introducing of zirconia makes the number of surface acid sites of borated alumina catalysts 1.3-1.4 times higher, what is confirmed by infrared spectroscopy and catalytic tests. The most active catalysts are formed by supporting of 15 wt% of zirconia on alumina.

Testing of bifunctional borated alumina-zirconia catalysts obtained after forming on theirs surface of particles of metallic palladium in hydrooligomerization of butenes with hydrogen input showed the possibility of forming C5+ isoalkanes, similar to those, obtained in traditional alkylolation of isobutane with butenes (Fig. 1).

Supercritical conditions (150-200 °C, 40-80 atm) with respect to initial reactants (butenes) are determined as optimal for hydrooligomerization of butenes. Such conditions provide the highest activity and stability (more than 20 hours) of studied catalysts due to the extraction properties of supercritical reaction medium.

This work was supported by the Lavrentiev Grant Of Young Scientists SB RAS №72.

**DEVELOPMENT OF NON-SULFIDAZED CATALYST OF
HYDRODEOXYGENATION OF BIO-OIL**

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Biomass is a renewable alternative to fossil raw materials in the production of liquid fuels and chemicals. The European Union has set a challenge of 20 % substitution for conventional fuels in the motor vehicles by 2020. Therefore, efforts in research and development for biomass utilization have increased. The focus on the improving the properties of biomass-derived liquid fuels, which are produced by flash pyrolysis and high pressure liquefaction. The oxygen content in wood-derived crude bio-oil can be as high as 45 wt% due to mainly aliphatic and aromatic alcohols, ethers, ketones, carboxylic acids and water. These oxygenated compounds are responsible for some deleterious properties of bio-oil: high viscosity, non-volatility, poor calorific value, corrosiveness, immiscibility with fossil fuels, thermal instability and trend to polymerization on storage and transportation. Hence, the bio-oil needs upgrading to reduce the oxygen content.

Hydrodeoxygenation (HDO) allows oxygen-free compounds to be synthesized at the H_2 pressure of 1-150 atm and 200-350 °C. Sulfided hydrotreating catalysts such as $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ are commonly used for HDO. The catalyst properties such as stability and selectivity are crucial, as the interaction of oxygen-containing compounds with the catalysts can modify the sulphide structure of the catalysts. Note that alumina is an inappropriate support for the bio-fuel HDO catalysts because of their cracking and coking. Most HDO studies reported in the literature were carried out with model compounds and mixtures of model compounds rather than real bio-oil. Most attention in the field was paid to phenols and furans because of their low reactivity in HDO. In general, in the presence of sulfided $CoMo$ - or $NiMo$ -catalysts HDO of an oxygen-containing compounds proceeds at a lower rate than the hydridesulfidizing (HDS) of a sulfur-containing compound of a similar structure. The main reason for these phenomena is reduction of sulfided Co- or Ni-containing active center to the metal state followed by coke formation and the catalyst deactivation. When so, sulfur is removed from the catalysts and the target fuels are contaminated by sulfur.

The aim of our work is to develop a non-sulfided heterogeneous catalyst which would be active and stable in HDO of both model compounds and of real bio-oil under mild conditions: 250-300 °C and 1-20 atm of H₂. At first, anisole was chosen as model compound which has a low reactivity in HDO reaction. Really, the commercial sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts (obtained from Albemarle Catalyst Company) do not allow high yields of benzene and cyclohexane to be achieved under mild conditions: 250-300 °C and 1-10 atm of H₂. For example, the products of anisole HDO at 300° C and 10 atm of H₂ in the presence of sulfided CoMo/Al₂O₃ were: 41 % of phenol, 23 % of benzene, 5 % cyclohexane and ca. 30 % of methylphenols isomers. The oxidized CoMo- or NiMo-catalysts do not give, either, a satisfactory results. In the presence of oxidized catalysts at the 100 % conversion of anisole the main products were phenol (~40 %) and anisole isomerization products(~ 60 %): isomers of mono-, bi-, tri- and tetra- methylphenols.

The development of new HDO catalysts was based on two approaches:

- Design of binary active center consisted of hydrogenation metal (noble metals) and a transitional metal oxide (mostly Ni, Co, Mo, W oxides). The oxide form of transitional metal with variable valency is needed for the activation of oxy-groups of compounds – bio-oil components.
- Development of an appropriate catalyst support; alumina is an unsuccessful choice for HDO of bio-oil because of the acidic properties of alumina and high acidity of bio-oil (pH~2-3). The acidic properties of alumina promote an undesirable organics cracking and coke formation. On the other hand the real acidic bio-oil dissolve alumina during the HDO process and active component are removed from catalyst surface. So, the catalyst support has to be stable to the acid medium and to possess basic properties to inhibit the coke formation. The promising supports for HDO catalysts are carbonaceous materials, silica, modified silica and carbon-silica composites.

The said approaches allowed ~80 % yield of deoxygenated products of anisole, namely ~20 % of benzene and ~60 % of cyclohexane to be obtained under the similar (referred above) reaction conditions over the Rh based catalyst. The by-product of anisole HDO was methane. The further optimization of catalyst composition and reaction conditions will allow ~100 % of HDO - selectivity (i.e. selectivity of C-O-bond hydrogenolysis) to be achieved.

The further development of effective catalysts for bio-oil hydrodeoxygenation (HDO) will contribute to solving the problem of the finding an alternative renewable resource of hydrocarbon fuels.

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**PALLADIUM CATALYSTS SUPPORTED ON SILICON NITRIDE FOR THE
TOTAL OXIDATION OF METHANE**

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Palladium catalysts were prepared by impregnation of Pd(II) acetylacetonate in toluene solution of silicon nitride powder and were tested in the methane total oxidation reaction. A strong influence of the phase composition and the crystalline states of supports on the catalytic properties of Pd catalysts was found. Pd supported on α -Si₃N₄ is found to be the most active and stable under reaction conditions.

Transition metals catalysts, especially Pd, are very active and widely used in hydrogenation processes and total oxidation of methane. Catalysts that are used for this reaction are generally supported on different refractory materials. The high thermal conductivity of silicon nitride, especially at high temperatures, could be useful to create thermostable catalysts. The objective of this work is to study the influence of the Si₃N₄ support nature and of the chemical compounds used for preparations on the physical-chemistry and catalytic properties of the palladium systems in the total oxidation of methane.

In order to investigate the influence of the phase-structural state of silicon nitride on the catalytic properties of Pd, three kinds of silicon nitride were used as supports in this work: amorphous silicon nitride (SiN-am); amorphous silicon nitride annealed at 1450 °C for 2h under nitrogen flow (SiN-annl) and α -Si₃N₄. The Pd catalysts were prepared by impregnation of the silicon nitride supports with adequate amounts of Pd(II) bis acetylacetonate dissolved in toluene [1]. In order to determine the influence of the used solvents on the physical – chemical properties of the Pd deposited on α -Si₃N₄, two samples were prepared by impregnation of the supports using Pd (II) acetate dissolved in water and toluene (Pd/ α -Si₃N₄-wat; Pd/ α -Si₃N₄-tol). All catalysts had about the same amount of the loaded Pd (near 0.5 wt %).

It was established that the preparation of Pd catalysts by impregnation Pd(AcAc)₂ on silicon nitride supports (SiN-am, SiN-annl, α -Si₃N₄) leads to the formation of nanosized metal particles (3 – 6 nm). Palladium catalysts show different catalytic activity for the total oxidation of methane. For the as-prepared catalysts it increases with the α -Si₃N₄ content and

crystallization state of the support. This behavior can be due to the modification of the electronic states or the structure of the Pd metallic particles depending on the nature of the silicon nitride. The decrease of the catalytic activity after heating for 3h at 650 °C in presence of the reagent mixture was observed for Pd/SiN-am and Pd/SiN-annl.

The catalytic activity of Pd/ α -Si₃N₄ is strongly affected by the preparation procedure. Impregnation of silicon nitride using toluene solution of Pd acetate was the most effective []. The total conversion of CH₄ in the experimental conditions was achieved already at 400 °C. Conversely, the Pd/ α -Si₃N₄ catalyst obtained by aqueous impregnation is less active and less stable. Total conversion of methane was never obtained. In conclusion, the catalytic behavior is very different despite similar average size (4.3 – 4.9 nm) and dispersion of the active phase observed by TEM for both catalysts. To evaluate the relations between the catalytic activity and the oxi-reduction properties of the catalysts, TPD of oxygen experiments were carried out. The TPD profiles of oxygen from Pd significantly changed depending on the preparation. The desorption observed for both samples near 700⁰C is generally attributed to stabilized oxide species (PdO_x). High temperature shift of the desorption peaks was observed for Pd/ α -Si₃N₄-tol. For this active catalyst, a strong interaction between Pd and oxygen is thus evidenced. We can thus suppose that if water is used as an impregnation solvent, the surface acid-based properties of Si₃N₄ support and/or of the Pd active phase are irreversibly damaged. In conclusion, Pd supported on α -Si₃N₄, prepared by impregnation of the Pd organic compounds in toluene solutions are found to be the most active and stable under reaction conditions.

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**NOBLE METAL MODIFIED CARBON CATALYSTS FOR LIQUID PHASE
OXIDATION OF GLUCOSE**

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Introduction

Carbon materials are attractive catalyst supports in liquid phase oxidation reactions due to their enhanced stability in acidic and alkaline media, particularly, in comparison to other common support materials such as SiO₂ and Al₂O₃. Furthermore, for metal-modified carbons recovery and recycling of the expensive metal compounds can be easily accomplished by burning off the support [1]. The textural and surface chemical properties of carbon materials commonly used are not well defined, as their preparation is difficult to control. Consequently, there is lasting interest to develop innovative routes to prepare carbons with defined properties. In particular, template assisted routes turned out to be a promising method, since porous materials like silica or zeolites have been applied as solid templates preparing such carbon materials [2-4]. Firstly, the template pores will be filled with carbon precursor followed by carbonization within the template pore system. Treatment with hydrofluoric acid to remove the template yields a carbon replica. So, textural, structural and morphological properties of the template can be transferred into the final carbon material. Metal loading of carbon supports is typically performed via impregnation followed by reduction of the noble metal precursor in presence of gaseous or liquid reducing agents. Though preparation of such materials still includes many cost-intensive and above all time-consuming synthesis steps.

Thus, shortening preparation of noble metal doped materials a direct synthesis of noble metal doped carbons was applied, however, based on the template assisted route, too. At the same time, carbon supported metal catalysts were prepared by impregnation of

several carbon materials as well. The obtained noble metal modified carbon catalysts were comparatively studied in respect of their textural properties, noble metal particle sizes and catalytic behaviour. Therefore, materials were characterized by means of nitrogen adsorption at 77 K and X-ray diffraction (XRD), whereas, the selective oxidation of glucose to gluconic acid was employed as test reaction, since this reaction has been investigated and described in literature systematically [5-7]. X-ray photoelectron spectroscopy (XPS) and inductive coupled plasma optical emission spectroscopy (ICP-OES) had been applied revealing additional information about the distribution of the reactive metal component within the carbon matrix.

Experimental

Synthesis of noble metal doped carbon catalysts were performed via two different synthesis routes. On the one hand, preparation of noble metal modified carbons occurred by customary deposition of a noble metal precursor onto the carbon support, which was prepared by template assisted synthesis beforehand. In contrast, direct synthesis was realised by template assisted route whereas the noble metal precursor has been introduced in the synthesis approach already [8]. However, sucrose as carbon precursor and amorphous silica gel [9] or MCM-48 [2] as solid siliceous templates have been applied for both synthesis routes. Hexachloroplatinic acid and tetrachloroauric acid were employed as noble metal precursor salts, respectively. The liquid phase oxidation of glucose was performed under stable alkaline conditions using a semi batch reactor at 323 K with an air flow as oxidizing agent.

Results

Mesoporous noble metal modified carbon materials had been obtained no matter which synthesis pathway was employed. For both procedures low noble metal contents at the external surface and rather small particles have been found in

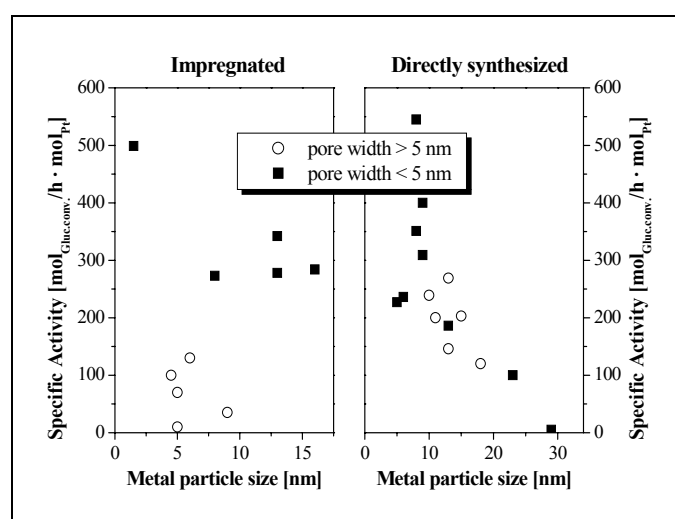


Fig.1: Effect of metal particle size (XRD) and pore width (DFT) on the specific catalytic activities of impregnated and directly synthesized platinum containing carbons

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case of Pt-doped carbons. However, for direct synthesised materials the noble metal compound is to some extent embedded in the carbon matrix, whereas, for impregnated materials Pt is located inside the carbon support pore system only. In contrast, Au-doped carbons exhibit significant differences in their surface noble metal contents in respect of the synthesis route applied. Au-impregnated catalysts showed rather small noble metal particles, predominantly occurring outside the pores of the carbon support. Differently, gold aggregates to very large particles in case of the direct synthesis route (results not shown here).

However, in case of impregnated catalysts a significant influence of the metal particle size on the specific catalytic activity was not established for Pt-particles > 4 nm, whereas a clear impact of support pore widths on the specific catalytic activity was found (Fig. 1). Catalysts with Pt-particles < 2 nm reveal the highest specific catalytic activity. Attributed to mass transfer limitations catalysts prepared from MCM-48 are less active than those catalysts made from silica gel. However, analogous Au-samples are 2-3 times more active than Pt (not shown here).

Differently, specific catalytic activity of directly synthesised Pt-carbons depends on Pt-particle sizes, whereas larger particles were found less potent oxidising glucose than smaller particles are. Significant effect of support pore widths on the specific catalytic activity could not be identified because of synthesis procedure used formation of both carbon pore system and metal particle occurs simultaneously. However, analogous Au-carbon materials tend to be inactive, due to their very large metal particle sizes (not shown here).

Acknowledgment

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POSTER PRESENTATIONS

SECTION III ENVIRONMENTAL AND INDUSTRIAL CATALYSIS



INFLUENCE OF DISSOLVED OXYGEN ON PHOTOELECTROCATALYTIC AZO DYES OXIDATION

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Influence of dissolved oxygen at different pressure on photoelectrocatalytic azo dyes oxidation is investigated. It is shown, that in the presence of dissolved oxygen the rate of photoelectrocatalytic azo dyes oxidation on TiO₂ increases due to formation of active particles upon oxygen reduction.

Synthetic dyes are extensively used for dyeing and printing in textile industries. Over 10,000 dyes with an annual production over $7 \cdot 10^5$ metric tonnes worldwide are commercially available and about 50 % among them are azo dyes. It is estimated that approximately 15 % of the dyestuffs are lost in the industrial effluents during manufacturing and processing operations. Synthetic dyes, classified by their chromophores, have different and stable chemical structures to meet various coloring requirements. The release of these colored wastewaters in the ecosystem causes aesthetic pollution, eutrophication and perturbations in aquatic life. Color is usually the first contaminant to be recognized in wastewater. Many azo dyes may be decomposed into potential carcinogenic amines under anaerobic conditions in the environment. Color removal from wastewater is often more important than the removal of soluble colorless organic substances, a major fraction of which contributes to the COD and BOD, besides disturbing the ecological system of the receiving waters.

In the present work the photoelectrocatalytic oxidation of azo dye direct black 22 at high pressure of oxygen was investigated. For the determination of concentration of dye spectrophotometer was used. Oxidation of azo dye upon photoelectrolysis under pressure of oxygen occurs not only on the anode TiO₂, but also on the cathode due to generating active particles of ions O₂⁻, HO₂⁻, radicals HO₂[·], HO[·] etc. Increasing of the oxygen pressure leads to an increase of the process efficiency. We have undertaken investigation of the dye-sensitized degradation using TiO₂ under artificial source of UV light in a shallow pond slurry reactor at laboratory scale. Effect of parameters such as UV intensity, pH, initial concentration, oxidants, aperture to volume ratio and catalyst loading on reaction kinetics were studied to optimize the process.

**DEVELOPMENT OF INFRARED CATALYTIC HEAT-GENERATING ELEMENTS
FOR ENVIRONMENT-FRIENDLY POWER PLANTS**

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Infrared catalytic heat-generating element (ICHGE) was developed based on oxidation-resistant high-porous permeable cellular materials (HPPCM) – carriers of catalytic layer. The new heat-and-energy production technology comprises ICHGE-based power plants using gaseous and liquid pollution-free fuel which, when being combusted, generates infrared radiation (IRR). IRR Fourier spectra were recorded and examined.

Economic growth determines the increase of the rate of energy consumption and necessity of introducing new generating capacities of "cluster" power engineering, together with updating of existing ones. According to Russian and foreign experience, this also ensures due level of energetic safety.

"Cluster" power engineering is based on small 30 to 250 kW isolated power plants using natural gas, equipped with micro gas-turbine and other types of engines in 2×3×2±0.5 m boxes. Establishment of high-technology production will allow to improve competitiveness of novel "cluster" power supply in the global and domestic market, avoid dependence on foreign firms and improve efficiency of allied industries.

G.M. Krzhizhanovsky ENIN, together with a number of enterprises, that is: Perm Scientific Centre of Powder Material Science, Kaluga pilot-production engine construction service (KPPES) and ZAO "Gidromashservis", performs work concerning development of catalytic power reactor – gas-fed catalytic steam-generating power reactor (CSGR) containing infrared catalytic heat-generating element (ICHGE), using two-stage turbo expander with generator for power-and-heat production.

A special-purpose oxidation-resistant high-porous permeable cellular material (HPPCM), suitable for long-term high-temperature (600 to 900 °C) performance in oxidizing atmosphere, was developed by the Scientific Centre of Powder Material Science. This material is used as a high-permeability catalyst carrier. Average pore size of HPPCM is 1.2 to 1.4 mm (34 ppi), porosity is 92 %, compressive strength is 3.5 to 5.0 MPa. Its macrostructure

and microstructure, oxidation resistance, permeability at flow rates of up to 6 m/s and deformation behavior were studied. A method for specified deformation of HPPCM plates from 12 mm to 5 mm length was developed. A pilot batch was produced, intended to be used as ICHGE.

The catalytic steam-generating power reactor (CSGR) allows to perform deep flameless fuel oxidation at reactor temperatures of less than 1000 °C, which virtually eliminates formation of nitrogen oxides NO_x , as well as of CO .

The emission spectrum of high-power selective infrared radiation (IRR) of cobalt-chromium ICHGE catalyst was examined at different temperatures of flameless methane combustion. This spectrum was recorded by means of Fourier spectrometer. The energy estimation shows that the main chromatic band of high-power IRR ($\lambda_m = 4.37 \mu\text{m}$) contains about $\frac{1}{4}$ of ICHGE integral energy Q_Σ , which corresponds to radiant surface unit power output of about 0.3 mW/m^2 , the value achieved amounting to $Q_\Sigma = 1.2 \text{ mW}$.

Due to heat-generating elements and heat-exchange surfaces being located close to each other, the furnace volume tension is by one order higher than in torch-type furnaces, which results in decrease of steam generator dimensions and reduction of its cost. Use of two-stage turbo expander (instead of an expensive turbine) as an engine allows additional cost reduction of the established kilowatt-hour of electric and heat power. Everything abovesaid allows to obtain an environment-friendly and reasonably cheap power plant, which can be used as a relatively low-power source of electric energy and heat (100 kW to 5 MW per plant) for isolated power supply of urban houses and quarters, as well as of isolated remote consumers.

**HIGH POROSITY CELLULAR METAL IN PLASMACATALYTIC GAS
TREATMENT**

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Plasmacatalytic device is developed for sterilization and purification of polluted air. Technology is based on a highly porous cellular metal (HPCM) carrier catalytic blocks and dielectric low-temperature plasma barrier or surface discharge with the use of ceramics and HPCM electrodes.

High-porosity permeable cellular metals and alloys represent a new type of structures having unsurpassed porosity, permeability and cohesion. The combination of heterogeneous catalysis and low-temperature plasma technologies (Figure 1) has allowed creation of compact high-efficiency plasmacatalytic air cleaning device. Final clearing and full decomposition of surplus of ozone occurs on an electrical heating porous nickel catalytic blocks.

It is shown, that cold plasma is stably generated on non-uniform surface of HPCM with barrier and surface discharge mechanism at voltage as low as 2000 V. Highly permeable structure of HPCM effectively dissipates heat and removes generated ozone in a gas stream. Computer simulation of heat-exchange, electric field, flow regime, temperature and pressure is carried out with the use of a finite elements method. Results of simulation have allowed to optimize a design and to improve efficiency of clearing and sterilization of air. Pre-production devices have shown high efficiency in complete decomposition of organic compounds to carbonic gas and water and can be used in air conditioning and sterilization in industrial, public and household purposes.

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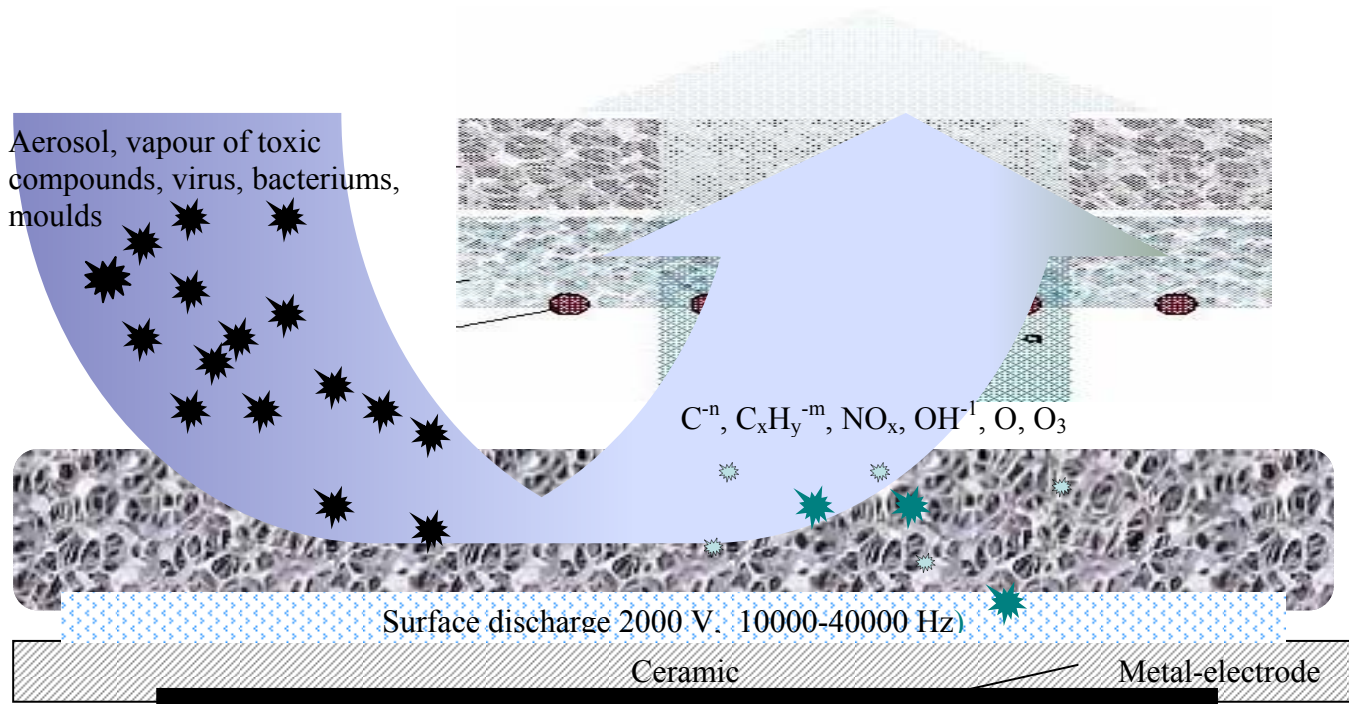


Figure 1. Principle of plasmacatalytic device based on HPCM

THE PREPARATION AND TESTING OF A MODIFIED POLYANILINE BASED ELECTRODE AS A SENSOR FOR THE DETERMINATION OF ANTIOXIDANT CONTENT

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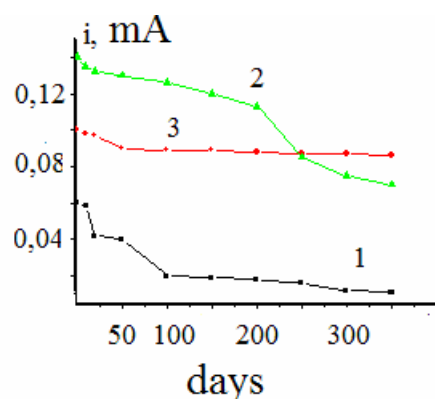
Over the past years special attention in medicine is given to free radicals formed as a result of vital activity of living organisms. The best protectors from the destroying effect of free radicals are antioxidants, a large family of biologically active compounds widely spread in nature. According to the standpoint of physicians, high everyday level of consumption of antioxidants provides the maintainance of a desired antioxidation status of organisms.

There are analytical methods to determine antioxidation activity of food¹, most of them are suitable for laboratory experiments but can hardly be used for the analysis in food production and in proximate analysis.

Thus, it seems reasonable to develop easy operating analytical devices, namely, electrochemical sensors comprising a chemically modified electrode (CME) as the main sensitive unit. The operating principle of such CME is based on the reaction of a catalytically active mediator (oxidant), which is involved in the electrode coating, with an antioxidant (reductant) at the CME/electrolyte interface followed by the regeneration of an oxidized form of a radical as a result of electron transfer to an electrode in the polymer bulk. The insertion of a modifier (catalyst) into a modified electrode allows one to enhance electrode sensitivity and provides a linear dependency of current on concentration in the tested antioxidant solutions. An organic mediator, 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid (ABTS), and an inorganic mediator, hexachloroiridate anion (IrCl_6^{2-}), were tested as mediators. Trolox, ascorbic, uric and gallic acids were used as model antioxidants. Conventional electrode material is Pt, which essentially enhances the cost of a resulting product. We developed a general approach, which consists in using metal complex catalysts² to prepare high quality polyaniline (PAn) coatings on various supports coated even by an oxide film that allows Pt to be replaced with more available and cheaper ecologically clean (pure) materials.

This work reports on the preparation and investigation of CME based on PAn, and ABTS or IrCl_6^{2-} mediators inserted into a polymer matrix. The PAn coatings were prepared on glassy carbon, tantalum and titanium electrodes using electrosynthesis. The mediator was

inserted in PAN either in the course of electrosynthesis or using the subsequent impregnation of the polymer in the mediator solution. It is important for a long operating CME that the content of the immobilized mediator would remain constant. This is, to a great extent, provided by the formation of chemical bonds between a mediator and a polymer. We showed that ABTS³ and HCl⁴ form stable complexes with aniline. The complexes were isolated and characterized by elemental and IR analyses. Therefore, one could expect that such mediators would be fixed in PAN due to the formation of chemical bonds with a polymer and, hence, the main condition for stable operation of the sensor will be met. All the CME were tested for the determination of concentrations of antioxidants at +0.7 V (Ag/AgCl) electrode potential. At this potential, as it derives from the experimental data, Ir is in +4 oxidation state and ABTS is in the radical cation form. As a result of the reaction with the antioxidant, Ir is reduced to the +3 oxidation state and ABTS is reduced to a neutral form. At +0.7 V they are oxidized to Ir⁺⁴ and ABTS⁺. Then the cycle is repeated until the antioxidant is consumed. It should be noted that an amperometric response to different concentrations of antioxidants is demonstrated by pure (without a mediator) PAN as well, though this response is noticeably weaker. The role and the necessity of a mediator in the structure of a sensor were studied during a long-term observation of three type sensors: 1) PAN; 2) PAN-ABTS; 3) PAN- IrCl₆²⁻. The sensors were stored in air for a year and their activity was controlled periodically. Ascorbic acid was used as a reference compound. Each time a new 6x10⁻³ M solution of ascorbic acid was prepared and sensor activity was tested. The data are presented in Fig.1:



The most stable sensor was found to be that based on PAN- IrCl₆²⁻, and the sensor based on pure PAN demonstrated only 14% of its initial activity by the 300th day. These data are evidence of that the mediator introduced in the sensor structure can perform not only as an active component but essentially stabilizes the performance of the sensor.

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**THE PYROLYSIS OF METHANE AT THE COMBINED ACTION OF THE
MICROWAVE–RADIATION AND MASSIVE METAL CATALYSTS**

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The mechanism of methane pyrolysis to nanodispersible carbon material and hydrogen on massive metal catalysts at influence of the microwave-radiation was considered.

The conversion of methane was carried out in a flowing wave in the presence of the microwave- category with frequency 2450 MHz. For maintenance of the category and heating of the catalyst was used the source adjustable by the microwave with the maximal capacity 1,5 kW. In process was used the combination of metallic catalysts and the influence of microwave field on catalyst and methane was studied. At influence of microwave radiation on the catalyst and methane micro categories between granules of metal were observed. It led to primary formation of ethylene, acetylene and hydrogen from methane. The endothermic reaction of formation of unsaturated C₂-compounds resulted in decrease of temperature of catalytic layer. At achievement of critical concentration of hydrogen in a reactor there was "ignition" of the plasma category, which resulted in total conversion of methane and unsaturated compounds to carbon.

The table. Parameters of process of conversion of methane in the microwave reactor

The catalyst	Conversion of methane, %	<u>Concentration H₂, %vol.</u>	Content of amorphous carbon (%)	Content of carbon nanotubes (%)
<u>TiNi</u>	<u>42.4</u>	<u>52.3</u>	<u>45.00</u>	<u>46.1</u>
<u>AlNi</u>	<u>15.8</u>	<u>28.3</u>	<u>55.00</u>	<u>33.1</u>
<u>Ni</u>	<u>79.5</u>	<u>84.9</u>	<u>21.2</u>	<u>56.5</u>
<u>Fe</u>	<u>54.5</u>	<u>69.4</u>	<u>4.04</u>	<u>78.2</u>
<u>Mo</u>	<u>77.6</u>	<u>84.6</u>	<u>64.9</u>	<u>24.9</u>
<u>Ti</u>	<u>27.9</u>	<u>43.4</u>	<u>23.1</u>	<u>40.5</u>

The rest is a graphite and ortacarbon. The maintenance C₂₌ in reactionary gases up to 8 % about.

The mechanism of pyrolysis of methane in the presence of massive metal catalysts and microwave field can be assumed: at influence of the microwave of radiation there is a heating of volume of the catalyst upon which chemical reaction of formation of ethylene and acetylene from natural gas proceeds. The formed unsaturated hydrocarbons (ethylene and acetylene) are carried by a stream of gas to the zone of an electric field of the high-temperature category in which there is a pyrolysis of unsaturated hydrocarbons up to amorphous carbon. Also an additional process is possible: on the surface of the catalyst occurs a formation of the structured carbon at heating up of the catalyst. The formed carbon is carried away from a surface of the catalyst to post-reactor space at secondary plasma-formation.

Thus, the formation of carbon and hydrogen can be presented as follows:

1. The primary accumulation of unsaturated hydrocarbons;
2. There is an accumulation in a reactionary mix of hydrogen (parallel with (1));
3. The origin of the category (it is possible, hydrogen).

Further there is an imposing two reactions:

1. The decomposition of the formed unsaturated hydrocarbons with formation of amorphous carbon in plasma of the gas category;
2. The growth of carbon nanotubes and, probably, ortacarbon on a surface of the catalyst. And the formed carbon is carried away from a surface of the catalyst to post-reactor space at secondary plasma-formation.

SYNERGISTIC PHENOMENA IN PHOTOCATALYTIC PROCESSES

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Synergistic phenomena (or effects, SE) were examined in photocatalytic reactions according to classification SE in catalysis which includes 5 categories.

Synergistic phenomena in catalysis are super-additive increase of activity, selectivity or stability of catalysts (Cat) and catalytic systems (or yield of products) during change of component composition of synergistic couple (for two component systems). It is necessary to distinguish the synergism of catalysts and synergism in catalysis in general. In the last case any compound can be a component of synergistic couple of chemical reactions: supports of a catalyst, molecules of substrates, solutions, ligands of complexes and the physical factors such as radiation, photolysis, electrochemical systems et al.

Previous classification of SE in chemistry [1] and in catalysis in particular [2] can be transferred to photocatalytic processes with some corrections. It includes the 5 categories.

1. Nature of synergistic effects (includes 3 types): a) chemical, b) physical, c) mixed or hybrid, physico-chemical [3].

2. Functional characteristics of the particles participating in SE (includes 3 classes) [4]: a) Cat1- Cat2, b) Cat-non-Cat (Cat-X), c) Non-Cat1 – non-Cat2 (X1 – X2 where X – chemical compound or physical factor, e.g. photolysis).

3. Mechanism of interaction between components of synergistic couple and components of synergistic couple with molecules of substrates, (includes 3 types) [1].

4. Hierarchy of SE origin includes 2 types [2]: a) primary SE, b) secondary SE, e.g. photocatalysis.

5. Reason of synergetic effect, (includes 2 types): a) intrinsic (internal), b) induced (external), e.g. due to photolysis.

Nature of SE in photocatalytic reactions is often chemical sometimes structural or dynamic if the partners SE are complex catalytic systems, or physico-chemical (hybrid), if the effect of super-additivity is achieved due to photo-component and catalyst or any chemical compound.

Many examples of SE in photocatalytic processes are given in the report.

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ELECTROCATALYSTS WITH LOW PLATINUM METAL CONTENT FOR ELECTROCHEMICAL SYSTEMS WITH PROTON EXCHANGE MEMBRANE

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The electrocatalysts for hydrogen electrochemical oxidation/reduction and oxygen reduction in proton exchange membrane (PEM) fuel cells and electrolyzers supported on new nano-carbon materials were synthesized. Both physical technique (magnetron sputtering of metal onto the carrier) and chemical reduction in water solution were applied for this purpose. As anode catalysts for water electrolysis the mixed oxide electrocatalysts were studied. The low-temperature technique for synthesis of these electrocatalysts was developed. The catalyst characterization was carried out using electrochemical techniques and other modern methods.

The main goal of hydrogen technologies is to solve ecological and energy problems. Development of low cost and high effective PEM fuel cells and water electrolyzers seems to be very important for this task. These electrochemical systems represent complex devices with electrocatalyst as a key component. The catalyst activity and stability determines the performances of the whole electrochemical system, and noble metal content considerably effect on its price. Usually the catalyst for hydrogen electrochemical oxidation/reduction and oxygen reduction is a platinum supported on carbon black. The carbon carrier is used in order to reduce the noble metal loading and to increase the electrochemical active surface area of the metal. The carrier's properties have a considerable influence on the catalyst performances. The primary goal of present study is to develop the catalysts supported on new carbon materials, such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs).

The special attention was focused on optimization of chemical and thermal pre-treatment of the carrier. It was shown that developed pre-treatment technique allows to increase the carbon's specific surface and to improve the precursor sorption on the carrier.

The pre-treated CNTs/CNFs were used for the catalysts synthesis. Both chemical reduction in water solution and physical (magnetron sputtering of metal onto the carrier) techniques were applied for carbon-supported catalyst synthesis. Scanning and transmission electron microscopy, X-ray analysis, thermogravimetry and mass-spectroscopy together with electrochemical researches were applied for characterization of the catalysts obtained. It was shown that CNTs-supported catalyst has higher electrochemically active surface and porosity than the catalyst with conventional carbon carrier like Vulcan XC-72. Thus, usage of CNTs as

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a catalyst carrier allows to reduce platinum loading providing the same performance of the PEM-device.

The second R&D goal is to develop the anode (oxygen evolution) catalysts for PEM-electrolysers. Since carbon materials have insufficient stability at the anode operating conditions, the mixed metal oxides were applied as a catalysts carrier.

The iridium is widely used as anode catalyst, but its activity and stability in acid solutions is not the highest ones, alternative catalysts are required. Ruthenium has better activity than iridium but it dissolves rather quickly at the electrolyser operating conditions. The usage of high active Ru or Ir together with its stabilization by means of mixed oxide compositions is offered. The main problem in this case is to find a proper synthesis technique. This technique has to be fast and cheap, and low platinum metal loading is strictly desirable. The simplest technique is to oxidize a corresponding metal alloy, but the high temperatures result in a low specific surface of the catalyst. The low temperature synthesis of solid oxide solutions of such metals as Ta, Sn, Ti and some others seems to be very useful and some of them were studied by our researches.

Mixed oxide compositions based on IrO_2 , RuO_2 , SnO_2 , TiO_2 , Ta_2O_5 have been synthesized using the new low-temperature technique. The samples were examined by the X-ray diffraction. It was shown that binary and ternary mixed oxides form a solid rutile-structured solution where ruthenium and iridium oxides determine the crystalline structure and the particle size. Electrochemical behavior of mixed oxides was tested in electrolysis cell with Nafion membrane. In particular, it was shown that ternary mixed oxide $\text{RuO}_2\text{-IrO}_2\text{-SnO}_2$ shows rather high electrocatalytic activity (comparable with activity of IrO_2) and sufficient corrosion stability. The similar results were received for mixed oxide anodes on the basis of Ta_2O_5 . It was shown that such oxides, modified by IrO_2 and RuO_2 , have considerably smaller electric resistance and higher stability.

This work has been partially supported by the Council for Grants at the President of the Russian Federation (grant No MK-4218.2006.8) and INTAS (grant No 04-83-2585).

VERY PURE SILICA FIBROUS AS PHOTOCATALYST CARRIER FOR AIR TREATMENT

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A highly pure silica fibrous (quartzel®) has been developed as carrier for photocatalysis for air treatment purpose in enclosed places. Characteristics of this material such as low pressure drop, high purity, chemical and UV resistances, high specific surface area are exposed. These advantages make of it a very good photocatalyst carrier.

Photocatalytic oxidation of organic compounds in air and water is a very attractive method for pollution abatement particularly for low levels of contamination. It gives the possibility at room temperature to reach a complete mineralization of the harmful organics to CO₂ and H₂O. The use of photocatalysis for forced air treatment in enclosed places (house, building, airplane ...) is especially attractive because volatile organic compounds (VOC) are typically found at low concentration in such area and oxygen from air is used as oxidant. VOC are not the only target for air treatment, bad odour molecules like sulphurs and micro-organisms decomposition belong to the aim of photocatalytic air treatment.

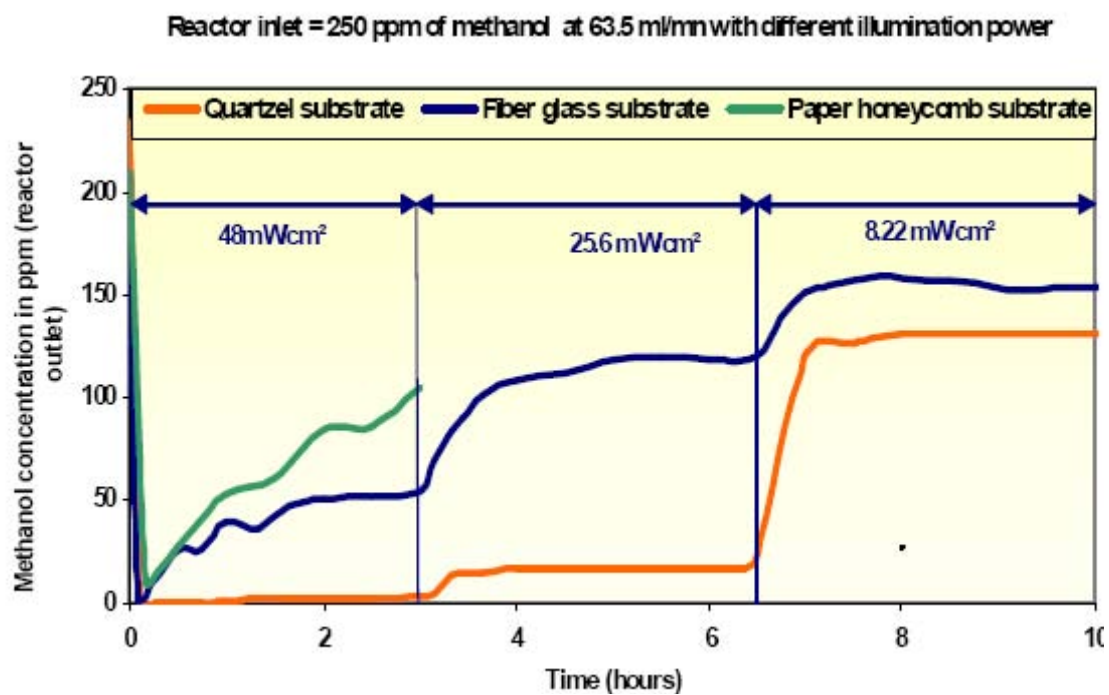
Titanium dioxide, in its anatase phase is known as the best and the most widely used photocatalyst due to its relatively high photoactivity under UV-irradiation, low cost and reduced toxicity. For a better efficiency, TiO₂ has to be dispersed within a high specific surface area.

In the case of forced air treatment the photocatalyst carrier is very important too. It has to have a pressure drop adapted to the apparatus in which it is included, the higher the volume treated, the higher the flux through the carrier is and the lower the pressure drop has to be.

Saint-Gobain has developed a very pure silica fibrous quartzel® for photocatalysis purpose. Silica fibrous conducts naturally UV light, which allows deposited TiO₂ to be active in the whole thickness of the substrate. The density of this carrier is very low consequently has a very low pressure drop then can be used in many applications with high air flux. In the same time, continuous silica fibers offer a tortuous path for the air resulting in a high probability of contact between pollutants and photocatalyst for a better efficiency.

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As example we show below the decomposition efficiency of methanol on quartzel® substrate compare with 2 other carriers for various UV irradiation intensities.



METAL CONTAINING ZEOLITES - CATALYSTS OF STEAM CONVERSION OF METHANE

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The practical approach to use clinoptilolyte of Aidag deposits as the carrier for imbibitions catalysts of steam conversion of methane is developed. Optimum conditions of reaction of steam conversion of natural gas with the purpose of syn-gas production are certain: temperature-900 °C, a volumetric ratio $\text{CH}_4/\text{H}_2\text{O}=1\div 1-3$, volumetric rate of gas mix - 425-650 h^{-1} .

One of parameters of technical progress in the developed countries is the level of capacities on manufacture of hydrogen and synthesis-gas. The main industrial way of synthesis-gas production is catalytic conversion of hydrocarbons, cheapest of which is methane.

Interest to processing of natural gas to liquid fuel and valuable chemical products, such as, methanol, formaldehyde, methyltertbutyl ether, dimethyl ether, etc., has strongly increased in connection with the rise in price of oil.

Steam conversion of methane $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$, $\Delta H = 206,4$ kJ/mole is one of perspective processes of processing of natural gas and the main industrial way of production of synthesis-gas, and is considered to be well studied /3/.

Clinoptilolyte of Aidag deposits of the Azerbaijan Republic has been used for the first time as the carrier of the catalyst of steam conversion of methane. Application of natural clinoptilolyte for obtaining synthesis-gas will allow not only to expand assortment of catalysts, but also to reduce raw, power expenses for its manufacturing.

Ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ in clinoptilolyte testifies that it can be referred to highly-siliceous zeolites of ZSM-5 type which, as it is known, find rather wide application in processes of oil processing /4/.

As an active component has been chosen traditional-nickel. The purpose of the present research was creations of effective metal containing zeolite catalysts of steam conversion of methane, studying of composition and structure of the carrier, a way of preparation and conditions of activation of contact, and also an influence of the maintenance of an active component of nickel in the catalyst.

PP-III-9

Optimum parameter of the process have been certified: temperature, volumetric speed of submission of a gas mix, influence of a ratio of initial components on a degree of conversion of methane.

Catalytic activity tests were carried out in laboratory installation of flowing type at atmospheric pressure with chromatographic analysis of products.

The highest activity was shown by samples of clinoptylolyte catalysts containing 15 % of nickel. The temperature of process was varied in an interval 750-950 °C, volumetric speed of submission of a gas mix 425-650 h⁻¹, a ratio CH₄/H₂O=1÷1-3. The degree of conversion of methane thus reached 98 %.

As a result of tests of catalysts during 300 hours it has been established, that contacts work practically without decrease in activity.

Thus, high activity and stability allows to consider Ni/clinoptylolyte catalysts comprehensible to process of steam conversion of methane with the purpose of synthesis-gas production.

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**THE INFLUENCE OF TREATMENT METHOD ON THE ACTIVITY OF
MODIFIED ZEOLITES IN PARAFFINS CRACKING**

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The paraffins are formed in the process of deparaffinisation of diesel fuel, now they are burned with heavy oils in the heat boilers. But the paraffins and paraffin products are very valuable products for synthesis of high normal α -olefins which are highly demanded in petroleum synthesis processes. The main process of transformation the paraffins into olefins is the cracking and it demands the new catalysts. We have natural zeolites of Shankanay field as the investigation object. The main mineral is acid and alkaline resistant wedge ptylotyth. The Shankanay zeolites have high concentration of Fe oxides and other admixtures.

The aim of this research is elaboration of new methods of modification the natural zeolites and studying of their activity in cracking of heavy *n*-paraffins. One of the goals is deleting the admixtures and the another is creation the active in cracking acid centers on the surface of natural zeolites. The aim contains the preparation the zeolites for using as the catalysts of *n*-paraffins cracking and also as beds of metallic catalysts. We have used technical paraffin C₂₀-C₄₀ with 52 °C melting point.

The deletion of Fe³⁺ was made by treatment the natural and deionated samples by chelate agents: ethylenediaminetetraacetic acid (EDTA) and its di-sodium salt (Trilon B).

Table – The activity of modified zeolite catalysts in cracking of hard technical paraffin at 540-560 °C and raw supply velocity 2 h⁻¹

Catalyst	Yield, % mass				Characteristics of paraffins after distillation		Conversion, %	Selectivity, %
	Liquid fraction	Gas	Cox	Non-trans	n ²⁰ _D	Bromine number		
CSM-EDTA-1	14,57	30,23	1,93	53,27	1,4437	81,40	46,73	32,52
CSM-EDTA-2	17,49	27,23	1,58	53,70	1,4400	68,50	46,30	39,11
NCSM-Na-EDTA	25,09	25,22	1,91	47,78	1,4370	85,13	52,22	49,87
NCSM-EDTA	23,45	43,35	2,40	30,80	1,4360	84,22	69,20	35,10

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Earlier we had shown that the dealkylation and dealuminisation degrees depend on temperature, duration and number of treatments, also the acid concentration and solution volume and intermediate treatment of samples. In case of using of non-modified natural zeolites the conversion is only 7,6 %

It was fixed that the dealkylated samples been modified by Kerr method in Soxhlet apparatus (NCSM-EDTA) at cracking temperature 560-580 °C the yield of olefins is relatively higher (23-28 % mass) with the selectivity 29-35 %. The bromine number of olefin fractions is 104,0 –107,9 with refractive index n_D^{20} 1,4460.

We have made the experiments for investigating the temperature influence on the conversion and yield of olefins and other products. The natural zeolite was treated by disodium salt of ethylenediaminetetraacetic acid (NCSM-Na-EDTA). The results show that this method is more effective than the previous. The yield of olefins with bromine numbers of 91,6-97,1 was reached at 560 °C and is 27,6 % mass. At 580 °C the yield of target product is 34,4 % at the conversion rate of 96,5 % mass. But the deep disintegration of raw material leads to augmentation of gas products and decreases the selectivity for target product. Therefore, the increasing of cracking temperature is not profitable.

Thus, we have identified the influence of zeolites modifying method on their activity in cracking of hard technical paraffin. The zeolites dealkylated by 1.75N hydrochloric acid and further treated by 10 % water solution of Trilon B have the best properties. The augmentation of activity is related to transformation of chemical composition of exchange complexes of natural zeolite in modified samples.

**PARA-HYDROGEN INDUCED POLARIZATION IN HETEROGENEOUS
HYDROGENATION REACTIONS**

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For the first time, it was demonstrated the creation and observation of para-hydrogen induced polarization in heterogeneous hydrogenation reactions. Wilkinson's catalyst supported on either modified silica gel or a polymer, is shown to hydrogenate styrene into ethyl benzene and to produce enhanced spin polarizations, observed through NMR, when the reaction was performed with H₂ gas enriched in the para spin isomer. Furthermore, gaseous phase para-hydrogenation of propylene to propane with two catalysts demonstrates heterogeneous catalytic conversion resulting in large spin polarizations. These experiments serve as a direct verification of the mechanism of heterogeneous hydrogenation reactions involving immobilized metal complexes and can be potentially developed into a practical tool for producing catalyst-free fluids with highly polarized nuclear spins for a broad range of hyperpolarized NMR and MRI applications.

NMR is a superior tool for investigations with catalytic reactions, because the parameters of chemical shift, coupling constant, and relaxation time yield much information about chemical structures, as well as mechanisms. However, the macroscopic magnetization generated by the nuclear spins at thermal equilibrium in magnetic field of a typical NMR spectrometer is only about 10⁻⁵ of what it could be if all spins were aligned in parallel. It is well known that correlation of nuclear spins of para-hydrogen can be utilized for MNR signal enhancement via hydrogenation of an appropriate substrate. Hydrogenation reactions play an important role in chemical industry. The fact that homogeneous catalyst is present in the reaction mixture along with products can be main disadvantage for much wider use of the homogeneous catalysts. One of the effective routes to solve this problem is immobilization of homogeneous (Wilkinson, etc) catalysts on solid supports. The main goal of this work on the one hand is synthesis different immobilized Rh(I) metal complexes and their use in hydrogenation reactions and on the other hand an attempt to establish mechanisms of reactions by hydrogenation of suitable substances with para-hydrogen. Three different kinds of heterogeneous catalysts was used: Wilkinson's catalyst supported on styrene-divinylbenzene copolymer (1); RhCl(PPh₃)₃ supported on modified silica gel, RhCl(PPh₃)₂PPh₂(CH₂)₂-SiO₂ (2), and a supported tridentate complex Rh(cod)(sulfos)-SiO₂

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(cod = cycloocta-1,5-diene; sulfos = $^-O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$) (3). Both 1 and 2 supported catalysts hydrogenate styrene when H_2 is bubbled through the sample tube containing the solution of styrene and the catalyst. More importantly, both catalysts produce clear PASADENA (para-hydrogen and synthesis allow dramatic enhancement of nuclear alignment) signals as para-enriched H_2 is bubbled through the sample at high field. The catalysts also produce ALTADENA (adiabatic longitudinal transfer engenders net alignment) signals when para-enriched H_2 is bubbled outside the magnet. In addition, 1 and 3 catalysts were very active in the gas phase hydrogenation of propylene and produced exceedingly strong antiphase multiplets and fast product formation. These results constitute the first direct confirmation of the mechanism of the hydrogenation reaction utilizing immobilized metal complexes. The clear PASADENA and ALTADENA spectral patterns confirm the preservation of the longitudinal spin order between the protons derived from the same para-hydrogen molecule, proving that the addition is, indeed, pairwise. Moreover, there can be no *a priori* certainty that an immobilized complex will produce polarization even if the chemical mechanism of the reaction remains essentially the same as in homogeneous solution. Indeed, the transfer of both hydrogen atoms of an H_2 molecule to the same product molecule is a necessary condition for the observation of PASADENA or ALTADENA. Numerous NMR and MRI applications, in particular those carried out in low and ultra-low magnetic field environments, could immensely benefit from the ability to produce polarized media (both liquid and gas phase), free of dissolved catalyst. At the same time, it was demonstrated that polarized liquid can be used to visualize geometry of different objects (micro channels, cross phantom) with enhancement factor of 10.

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NOVEL CHITOSAN-BASED CATALYSTS FOR BIODIESEL PRODUCTION FROM RENEWABLE NATURAL FEEDSTOCK

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A number of chitosan complexes with different metals (Zn, Co, Ca, Ni, Mn, Sn, Pb) were synthesized and tested as catalysts in a reaction of transesterification of tributyrine simulating the process of biodiesel production from renewable natural feedstock (triglycerides, vegetable oils). It is found that chitosan complexes are stable and effective catalysts for transformation of tributyrine into the corresponding ester. Sn, Pb, Ca-containing complexes were successfully implicated for transesterification of vegetable oils (sunflower-seed oil, olive oil).

Immobilization of transition metal complexes on the surface of polymer supports enables designing new catalysts that combine the advantages of homogeneous catalytic systems and heterogeneous ones. Chitosan, a biopolymer (poly(1-4)-N-acetyl- β -D-glucosamine) extracted by deacetylation of chitin, the component of crab shells, insects, and plant cell walls, is one of the most abundant natural polysaccharides. Catalysts on the basis of chitosan and its derivatives could be considered as good candidates for the "Green catalysis".

A number of chitosan-based complexes with different metals (Zn, Co, Ca, Ni, Mn, Sn, Pb) prepared by coprecipitation and adsorption techniques were immobilized on the surface of macroporous silica to produce the egg-shell catalysts. As we found earlier this type of catalysts possess the more developed surface and higher mechanical stability as compared with bulky chitosan complexes. The structure and stability of complexes prepared were investigated by different methods (EXAFS, XPS, IR, and SEM). Catalytic activity of heterogenized chitosan-supported ions was compared with activity of homogeneous macroligand-free samples. The influence of counter-ion (Cl^- , Br^- , CH_3COO^- , NO_3^-) on catalytic activity of the chitosan complex was also investigated. Catalytic testing revealed a good performance of all the catalysts for the reaction of transesterification, with Sn, Pb, and Ca-chitosan complexes demonstrating the best catalytic activity. Tributyrin conversion reached 95% for Pb- and Ca-containing catalysts, and 85% for Sn-sample, with selectivity 98% (60-70°C; reaction time 3-6 hrs). Sn, Pb, Ca-containing complexes were successfully implicated for transesterification of vegetable oils (sunflower-seed oil, olive oil).

VISIBLE LIGHT DRIVEN Pt/TiO₂ CATALYSTS FOR THE PHOTOCATALYTIC DEGRADATION OF 4-CHLOROPHENOL IN AQUEOUS SOLUTION

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The photocatalytic degradation of 4-Chlorophenol (4-CP) in water solution as a model reaction was investigated on Pt/TiO₂ catalysts when illuminated with visible (λ of 450 nm) light. The catalyst under study with 1 % of Pt shows higher efficiency for the photodegradation of 4-CP, comparing with that of Pt-modified P-25. The observed photocatalytic behavior of Pt-supported catalysts were found to depend on their structural arrangement.

Introduction

TiO₂ is extensively used in the photocatalytic degradation of organic pollutants due to its high oxidative power, photostability, and nontoxicity [1]. However, severe limitation of this material lies in the large band-gap (3.2 eV for bulk TiO₂) that drives the photosensitivity to the UV region responsible for only 3% of the solar spectrum. According to published results, it is obvious that doping of TiO₂ with different elements extends light absorption into the visible region [2]. Here the results of the photocatalytic testing of Pt/TiO₂ catalysts for the degradation of 4-Chlorophenol (4-CP) in water upon irradiation with visible light as well as structural peculiarities of the catalysts are described.

Experimental

Pure TiO₂ and Pt/TiO₂ catalysts with 0.5-2 wt% Pt were synthesized according to [3]. Sample of 1% Pt on P-25 (Degussa) was prepared through photoreduction of PtCl₄ solution added to the oxide support. Catalysts were studied with XRD, HRTEM, XPS. The activities were measured by the decomposition of 4-CP in concentration of 2×10^{-4} mol/L⁻¹ in water at 20 °C in the dark and after illumination for 2 hours with four Luxeon 3,4 W LED lamps (maximal 470 nm). Content of 4-CP in the reaction mixture before and after the run were determined from characteristic absorbance with on-line UV-Vis spectrometer.

Results and discussion

Fig. 1 shows that dark adsorption of 4-CP on the synthesized Pt/TiO₂ catalysts does not practically change with growth of Pt content and remains as low as 10 %. After illumination, the photodegradation of 4-CP increases from 38 up to 63 % for 0.5 and 1 % Pt, respectively, and quickly declines in the case of the sample with highest (2 %) concentration of the supported metal. For pure P-25 (Degussa) removal efficiency is lower - photodegradation of 4-CP does not rise over 13 %, whereas after its modification with 1 % Pt the photodegradation grows but achieves only 40 %.

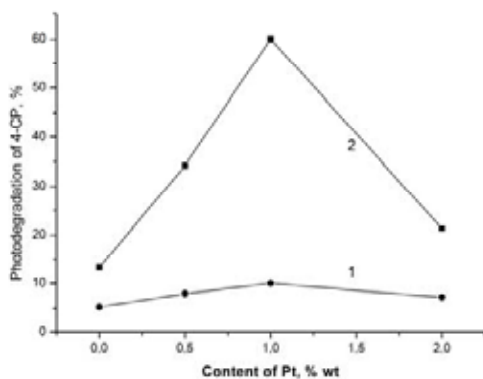


Fig. 1. Dark adsorption (1) and photodegradation of 4-CP (2) over different Pt modified titania catalysts illuminated with visible light ($\lambda=450\text{nm}$)

It seems likely that photodegradation ability of the catalysts under study is governed by their specific morphology. Pt species observed by HTREM in the Pt modified samples are mainly in the metallic state confirmed by XPS measurements, however presence of ionic Pt in 0.5 % Pt/TiO₂ sample where 0.3 nm-sized particles have been visualized could not be excluded. In the sample with higher (1 %) Pt content supported metallic particles, being mainly in size of 1.5-2 nm, stay separately from each other. At higher (2 %) content, Pt particles are about 3-4 nm in size and give rise to coalescence. In the case of 1 % Pt/P-25 Pt particles are also as small as 2 nm but show a tendency to aggregate thus covering the titania surface. Following [2], we suggest that in the sample with lowest Pt concentration metallic particles are too small to collect effectively the electrons and to accelerate the electron transfer process. In turn, highest Pt loading results in the formation of bigger particles which become negatively charged and play a role of recombination centers. For Pt-modified P-25, excessive coverage of the support surface by numerous metallic particles, though being small in size, hinders the accessibility of irradiation light to the TiO₂ and consequently reduces the number of the photogenerated electron-hole pairs that leads to the lower photodegradation ability of the catalyst. Most active photocatalyst with 1 % Pt content seems to possess optimal loading value for producing the separately located fine metallic particles with ability to attract more electrons from titania surface for more efficient charge separation.

Conclusion

Structural arrangement and photocatalytic properties of the Pt/TiO₂ catalysts in the photodegradation of 4-CP in water were found to depend on the Pt content. 1%Pt/TiO₂ consisting of isolated fine metallic particles dispersed over oxide surface shows the best catalytic behavior owing to improved charge separation rate.

Acknowledgement

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ELECTROCHEMICAL SYNTHESIS OF Mo₂C CATALYTICAL COATINGS IN MOLTEN SALTS

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The aim of this study is the development of new generations of highly active and stable catalytic coatings for the water gas shift (WGS) reaction by application of high-temperature electrochemical synthesis in molten salts. Three different methods and electrolytes were used for electrosynthesis of molybdenum carbide in the present investigation.

Electrochemical synthesis of molybdenum carbides from molten salts offers considerable advantages over other methods. For example, electrochemical methods such as Pulse Plating and Reversed Plating provide a possibility to control the structure and phase composition, the thickness of the coatings, the grain size (down to nanomaterials), porosity, smoothness, and the texture of the layer. The other advantages are: (i) relatively low synthesis temperature (973-1123 K); (ii) parameters of electrochemical depositions can be easily adapted in scaling-up synthesis; (iii) the method can be applied to the substrates with a complicated geometry (such as microstructured plates) for obtaining of uniform coatings with respect to thickness, grain size and composition of the layer; (iv) high purity of resulting coatings even with low-grade initial reactants; (v) the production costs are much lower comparing to other methods.

Electrochemical synthesis of molybdenum carbide coatings on molybdenum substrate was performed by galvanostatic electrolysis with utilization of the next molten salts systems: NaCl-KCl-Li₂CO₃ (1); NaCl-KCl-Na₂MoO₄-Li₂CO₃ (2); LiCl-KCl-Li₂C₂ (3).

Alkali chlorides (Prolabo, 99.5 wt.%) were dehydrated by continuous and progressive heating just above the melting point in a gaseous HCl atmosphere in quartz ampoules. The excess of HCl was removed from the melt by an argon flow. The salts were handled in a glove box and stored in sealed glass ampoules. Li₂CO₃ (chemically pure) and Na₂MoO₄·2H₂O (chemically pure) were dried for 24 h at 473 K. Li₂C₂ was synthesized *in situ* in LiCl-KCl eutectic melt by discharge of Li⁺ cations at the graphite cathode with cathodic current density 2 A cm⁻². Alkali chlorides were mixed in a required ratio, placed in a glassy carbon ampoule (SU-2000 type) and transferred to a sealed stainless steel retort. The latter was evacuated to a

residual pressure of 0.67 Pa, first at room temperature and then stepwise at 473, 673, and 873 K. The cell was heated using a programmable furnace and the temperature was measured using a Pt–Rh (10 wt.%) Pt thermocouple. The retort was then filled with high purity argon (U-grade: < 3 ppm H₂O and < 2 ppm O₂) and the electrolyte was melted. Li₂CO₃, Na₂MoO₄ and Li₂C₂ were added to the alkali chloride melts.

Molybdenum sheets (99.99+ wt.% Mo) of 40 mm long, 8 mm width, with a thickness of 100 μm were used in this study. Molybdenum samples were cleaned in xylene for 1 hour to remove organic contaminations from the surface and dried in an oven at 413 K. The molybdenum substrates were immersed in the melt through a special hole in the top part of the retort under inert atmosphere. Synthesis of Mo₂C on the molybdenum substrates was performed at 1123 K for 7 h with a cathodic current density of 5 mA cm⁻² for molten systems (1) and (2) and with an anodic current density of 5 mA cm⁻² for molten system (3). The glassy carbon crucible served as anode for systems (1) and (2). After experiments, the samples were washed in distilled water and alcohol and weighted.

The thickness of Mo₂C samples obtained from molten systems (1) and (3) did not exceed 2 μm, because carbides of refractory metals are formed a good barrier layer and interdiffusion coefficients of molybdenum and carbon decreased on some orders of magnitude. Joint electroreduction of MoO₄²⁻ and CO₃²⁻ ions led to the formation of Mo₂C coatings with the thickness ca. 50 μm. The morphology, roughness and specific surface area of molybdenum carbides were determined for samples obtained by different methods.

In all cases Mo₂C coatings with the hexagonal lattice were obtained. At the same time a bulk Mo₂C usually has a cubic lattice. The formation of Mo₂C with the hexagonal structure in the processes of electrochemical synthesis is due to specific conditions (electrical field, double layer, high temperature) of electrocrystallization. It was noted in our studies the similarities of the effects of electrochemical crystallization and the external high pressure.

A preliminary results on the catalytic activity of three types molybdenum carbide coatings were obtained.

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**TRANSESTERIFICATION OF VEGETABLE OIL TO BIODIESEL OVER
MgO-FUNCTIONALIZED MESOPOROUS CATALYSTS**

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This study compares the catalytic activity of MgO-functionalized mesoporous materials, synthesized using different: (i) silica supports (MCM-41, KIT-6 and SBA-15); (ii) precursor salts (magnesium acetate and nitrate); and (iii) loading methods (impregnation and in-situ coating), in the transesterification of blended vegetable oil with ethanol. The yield of selected esters (ethyl palmitate, stearate and oleate) was used as a marker to determine the most active heterogeneous catalyst for biodiesel production. Effects of support material, precursor salt and loading method on the basicity and catalytic activity of the catalyst were analyzed.

Recently, there has been an increased research activity directed at the development of heterogeneous catalyst systems to produce biodiesel. Their benefits include simplification of the separation and purification of the reaction products, easy reuse of the catalyst in the reactor, reduced corrosion problems and possibly low sensitivity to free fatty acids and water.

This study compares the catalytic activity of MgO-functionalized mesoporous materials, synthesized using different silica supports, precursor salts, and loading methods, in the transesterification of blended vegetable oil with ethanol to produce biodiesel. Mesoporous catalysts are chosen because their acidic/basic properties can be easily modified by varying their surface groups and composition, they have uniform structures and high surface areas, which are ideal as catalysts for large organic molecules and guest-host chemical supports.

Three types of mesoporous silica, namely MCM-41, KIT-6 and SBA-15, were prepared and subsequently impregnated with MgO using magnesium acetate. Another batch of SBA-15 was loaded with MgO using magnesium acetate and nitrate via in-situ coating. The morphology and basicity of the catalysts were characterized using XRD, N₂ adsorption/desorption, CO₂ Chemisorption, and SEM techniques.

The transesterification of vegetable oil was carried out in a batch reactor at 220 °C, with an oil-to-ethanol molar ratio of approximately 1:6, a reaction time of 5 hours, and a catalyst amount of ~2 wt %. While the pure mesoporous silica showed little or no catalytic activity, calcined mesoporous supports loaded with MgO were found to be active as catalysts, among which SBA-15 impregnated with MgO via magnesium acetate was the most effective. The resulting yield of the selected esters ranged from 62 % to 96 % over the MgO-functionalized catalysts when compared to a complete homogeneous transesterification catalyzed by KOH

using the same feedstock. The number of “strong” basic sites in a catalyst appeared to be a major contributing factor for its catalytic activity, demonstrating a strong correlation with the resulting ester yield ($r^2 = 0.99$). The total number of basic sites (including both strong and weak sites) was, however, found to be irrelevant to the yield under the set conditions. No correlation was established between the quantity of MgO loading on the support and its corresponding basicity or catalytic activity. This suggests that the catalytic activity of a functionalized mesoporous catalyst is strongly influenced by the type of supporting material used. From the further study of SBA-15 catalysts, the effect of the type of precursor salt used was found to be insignificant for the catalytic activity. The MgO loading method, on the other hand, determines the dispersion of MgO and accessibility of basic sites to the reactants, where impregnated catalysts turned out to be more effective than the in-situ coated ones in terms of the resulting ester yield.

Based on the current findings of this study, the MgO-impregnated SBA-15 catalyst requires further investigation to enhance the catalysis of the biodiesel production process. Its physical and chemical properties (e.g. Mg^{2+}/Si molar ratio and particle size) will be modified and experimental conditions (e.g. reaction temperature, oil-to-ethanol) will be optimized in the attempt to improve the efficiency and overall yield of the reaction. These results will be presented in the full paper.

THE TUNGSTEN TRIOXIDE LAYERS ON ALUMINIUM AND TITANIUM

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The compositions of valve metal/oxide film, containing WO_3 , MoO_3 , Nb_2O_5 , V_2O_5 , are of interest of the catalysis. The data on the formation of surface structures with WO_3 on aluminium and titanium by plasma electrolytic oxidation technique (PEO – the electrochemical oxidation by reactions caused by electric discharges) have been reported.

The compositions metal/film have been formed in aqueous solutions containing tungstate isopoly and heteropolyoxoanions (IPAs and HPAs) .

Aqueous solutions of $\text{K}_8[\text{BW}_{11}\text{O}_{39}\text{H}]$, $\text{Na}_2\text{H}[\text{PW}_{12}\text{O}_{40}]$, $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]$ with concentration of W(VI) $0.1 \text{ mol}\cdot\text{l}^{-1}$ have been used, table 1. Oxide structures have been formed during 10 min in solutions of room temperature.

Table 1. The effect of nature of tungstate HPAs on the phase composition of PEO-layers, formed on aluminium and titanium in isopoly and heteropoly electrolytes.

The electrolyte composition	pH	The phase composition of PEO-layers	
		On Al	On Ti
$\text{K}_8[\text{BW}_{11}\text{O}_{39}\text{H}]$	6.9	WO_3	WO_3
$\text{Na}_2\text{H}[\text{PW}_{12}\text{O}_{40}]$	2.0	$\text{WO}_{2.9}$ (islets)	$\text{WO}_{2.9}$ (islets)
$\text{H}_4[\text{SiW}_{12}\text{O}_{40}] + \text{K}_2\text{CO}_3$	5.7	$\text{H}_{0.23}\text{WO}_3$	$\text{H}_{0.23}\text{WO}_3$
$(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]$	6.5	WO_3	No data

Both surface structures composition and morphology depend on the pH value (Fig. 1). When IPAs and HPAs are stable ($\text{pH} < 7.5$), multilayer coral-like structures with outer layer of tungsten oxides are formed (Fig. 2). Coral-like structures are built from spherical fragments with dimensions about 300 nm. Dimensions of fragments and layers thickness may be regulated by a current density and a time of formation.

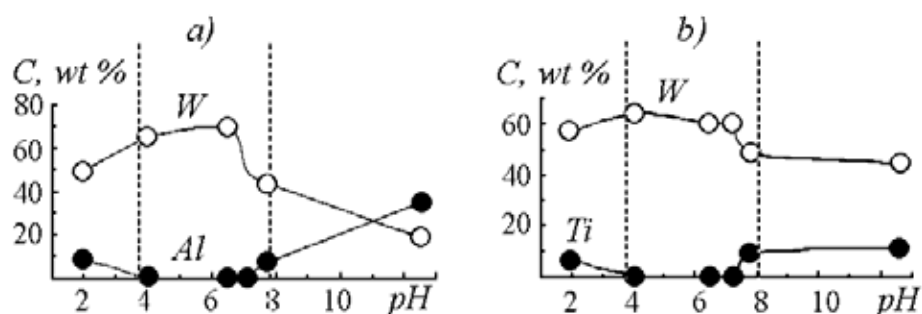


Fig 1. The effect of pH value of tungstophosphate electrolytes on the elemental composition of the coatings on aluminium (a) and titanium (b).

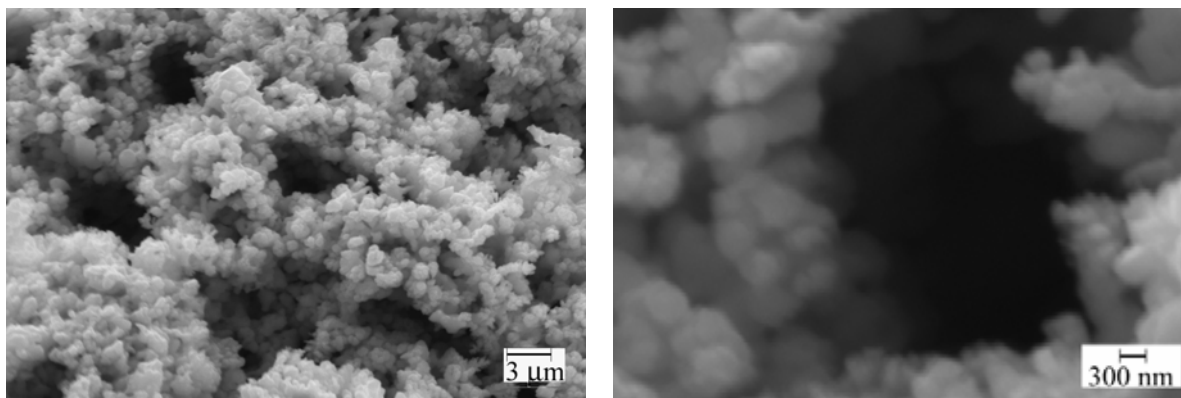


Fig. 2. SEM-images of surface layer of WO_3 on aluminium.

When HPAs are unstable ($\text{pH} > 7-8$) or the dissolution of metal by treatment increases ($\text{pH} < 2-4$), more complicated structures on aluminium are formed. The layer of $\text{Al}_2(\text{WO}_4)_3$ forms on anodic oxide film, and islets of WO_3 are located on its surface, Fig 3. The nature of heteroatom of HPAs doesn't have significant influence on the elemental composition of layers.

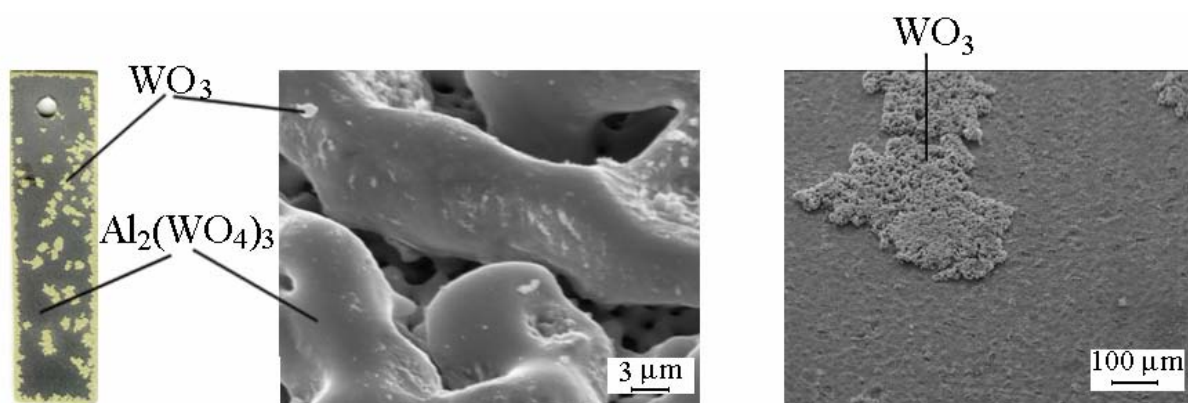


Fig.3. Images of complicated structures formed on aluminium in tungsten-containing electrolytes at $\text{pH} > 7.5$ and $\text{pH} < 4$.

When salts of transition metals are added into tungstate heteropoly electrolyte the conditions for a composed HPAs formation are created. The one-stage PEO-obtaining of complicated oxide compositions, for example $\text{Al}/\text{Al}_2\text{O}_3/(\text{WO}_{2.9}+\text{Mn}^{2+})$ and $\text{Ti}/\text{TiO}_2/x\text{TiO}_2 \cdot y\text{P}_2\text{O}_5 \cdot m\text{V}_2\text{O}_5 \cdot n\text{WO}_3$, is possible.

Thus it is shown that plasma electrochemical oxidation of aluminium and titanium in aqueous electrolytes containing isopoly and heteropolytungstates allows obtaining the compositions $\text{Al}/\text{Al}_2\text{O}_3/\text{WO}_3$; $\text{Al}/\text{Al}_2(\text{WO}_4)_3/\text{WO}_3$, $\text{Ti}/\text{TiO}_2/\text{WO}_3$ at one stage, which may be of interest for catalysis.

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PROPANE DEHYDROGENATION BY ENERGY CATALYSIS

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Dehydrogenation of propane was studied in the gas phase homogeneous process performed in a “wall-less reactor”. Reactants were activated by continuous CO₂-laser radiation, with the laser energy being adsorbed by ethylene and passed to the reaction volume. Ethylene was found to be among the main reaction products, which allows considering the process as the “energy catalysis”.

Dehydrogenation of C₂-C₃ hydrocarbons is an important field of chemical technology development. When studying propane pyrolysis, homogeneous reactions of hydrocarbons that occur in the reactor volume should be distinguished from heterogeneous processes on the reactor walls.

To study the homogeneous reactions of propane pyrolysis we used a wall-less reactor which excludes the occurrence of heterogeneous processes. The reactions were conducted in a 6.5 cm³ reactor, with the heat energy being supplied directly to the gas at atmospheric pressure using a continuous CO₂ laser with the radiation power up to 120 W at the power density up to 10⁴ W/cm². Since propane does not absorb radiation of the CO₂ laser, it was mixed with ethylene that has a strong absorption band at 10.6 μm. The reactor design ensured the gas to be bifunctional, i.e. a part of the high-dense mixture served as a heat insulator between the quartz walls, with their temperature not exceeding 125 °C, and the reaction zone, with its temperature not exceeding 1000 °C. The study was performed in a static regime.

Conversion of propane was found to depend on the time of reaction mixture contacting with laser radiation. As the contact time increased from 2 to 7 sec, propane conversion increased from 8 to 85 %. The outlet laser power was constant and amounted to 87.3 W. The ethylene and methane yields were approximately equal, ranging from 2 to 30%, whereas the yield of propylene decreased from 60 to 4 %.

Propane conversion was shown also to depend on the laser power. In the power range 49 – 91 W, propane conversion increased from 3.5 to 81.2 % at a constant contact time 4.6 sec. In the narrow range of the laser power 70 – 73 W, propane conversion had a jumping function with a sharp rise from 12 to 70 %. The maximum yield for ethylene was 26%; for methane, 31 %; and for propylene, 13 %.

The experimental data obtained on propane pyrolysis demonstrate the applicability of the CO₂-laser radiation for controlling the endothermic chemical reactions by adsorption of laser energy by ethylene as a product. Propane pyrolysis conducted under homogeneous conditions in the wall-less reactor can be considered as the “energy” catalysis.

EPOXIDATION OF RAPESEED OIL BY HYDROGEN PEROXIDE IN THE PRESENCE OF PHASE TRANSFER AGENTS

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Epoxidized rapeseed oil was obtained under various reaction conditions. Depending on the goal, the variation of technological parameters of reaction allows obtaining high value of epoxide number, high selectivity to peroxide, higher rate of reaction and low catalyst load. Catalytic system able to effective rapeseed oil epoxidation which can be used repeatedly, at least two times without loss of product quality was developed. Epoxidation was performed in the presence of peroxotungstate catalyst under phase transfer conditions.

Epoxidized oils as plasticizer-stabilizer are added to polymer in quantity of 2-3 mass % and cause an increase of its temperature and light stability and its durability. Annual production of polyvinylchloride in Russia is around 750 000 tons. Demands in epoxidized oils are primarily met by their import. One of perspective ways of using of oxidized oils is production of polyols formed by hydrolysis of epoxide groups. Polyols are widely used in manufacture of urethane resins. Epoxidized vegetable oils are mainly produced by peracid method. Reaction between organic acid (generally formic or acetic) and hydrogen peroxide yields peracid which is used as epoxidizing agent. The main disadvantage of this method is high corrosion caused by acting between quite strong acids and hydrogen peroxides.

Another method which is less used is organic hydroperoxide epoxidation. Organic hydroperoxides selectively epoxidize double bonds in presence of transition metal (usually molybdenum). This method is technologically poor acceptable because hydroperoxides are highly explosive, expensive and forms a corresponding alcohols which must be removed.

Using of hydrogen peroxide as an oxidant is much more promising. In the last years in publications there is high interest for this problem. This in general happens due to next advantages. Hydrogen peroxide is much cheaper than hydroperoxides and not as corrosive as peracids. The only byproduct of epoxidation with hydrogen peroxide is water. Using aqua solutions of hydrogen peroxide with concentration less than 50 % does not endanger to the risk of explosion as in case of organic hydroperoxides. Hydrogen peroxide epoxidation proceeds in the presence of transition metals and complexes of their derivatives as catalysts. The most often used catalysts are based on oxides of titanium, tungsten, rhenium and

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manganese. There is large number of catalytic system of these oxides- homogeneous and heterogeneous, different solutions of hydrogen peroxides, different additives, etc.

For epoxidation of vegetable oils by hydrogen peroxide we used a tungsten oxide based catalytic system. Epoxidation was done by 35 % aqua solution of hydrogen peroxide in immiscible mediums (oil and water phases) in the presence of tungsten oxide derivatives and phase transfer catalysts.

The optimal conditions of rapeseed oil epoxidation were chosen. The study shows that at right proportion of the components epoxidation of rapeseed oil by hydrogen peroxide on tungsten catalyst can be quite effective. Unlike the other catalytic systems of epoxidation with tungsten catalysts our system is efficiently working without using of organic solvents.

Depending on the goal, the variation of technological parameters of reaction allows to obtain high value of epoxide number, high value of selectivity peroxide consumption, faster reaction and low catalyst load. The best results for mentioned indexes are shown in Table 1.

Table 1. Results of rapeseed oil epoxidation by hydrogen peroxide in presence of tungsten catalyst and interphase agent.

T, °C	Time, min	Molar ratio, double bond: hydrogen peroxide	Catalyst concentration, % mass	Degree of epoxidated double bonds, %	Hydrogen peroxide selectivity, %
50	480	1:1,15	0,56	82,9	72,1
80	60	1:1,13	0,59	77,2	68,1
65	90	1:0,96	0,56	75,8	79,3
65	240	1:1,29	0,56	88,9	68,7
65	240	1:1,37	0,39	78,3	57,0

Also was developed catalytic system able to effective rape seed oil epoxidation which can be used repeatedly, at least two times without loss of product quality. Degree of epoxidation in last cases came nearer 90% when hydrogen peroxide selectivity was near 65%. However time of recycled reaction increased to over 10 hours.

THE PECULIARITIES OF CATALYSIS AT DIRECT HYDROLIQUEFACTION OF SULPHUROUS COALS OF UKRAINE

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Some peculiarities of hydroliquefaction of sulphurous coals with high pyrite content have been examined. The role of “internal” and “external” liquid substances – solvents which are the hydrogen donors for fragments of coal organic matter is discussed. The possible distinctions in the mechanism of influence of native “internal” catalyst – iron sulphide and additional iron-containing wastes have been shown. The assumption concerning the possibility and availability of using nanocatalysis principles in the process of direct coal liquefaction has been suggested.

From the point of view of catalysis at the primary direct hydroliquefaction of coals the stubborn problem is the catalyst regeneration in its initial form. At this process catalyst is inevitably mixed with the mineral part of coal which is presented by various compounds and unreacted residual coal organic matter (COM).. The optimal direction is considered to be the using inexpensive, available and sufficiently catalytically active compounds which may not regenerate.. Among these compounds are first of all the iron compounds (pyrite and oxidized ores, oxides, wastes of different metallurgical plants and so on) which are the active ones at 380-470 °C and the pressure equal 10-20 MPa.

During the investigation of sulphurous coals the high correlation (coefficients up to 0,9-0,95) of conversion degree and yield of liquid products (“coal oil”) with the sulphur content in initial coals, especially pyrite and organic sulphur, as well as with iron content has been found. The most active was the finely dispersed pyrite. Thus for the sample of subbituminous coal of Northern Donbass (total sulphur content is 4,2 % by mass) the high conversion degree (more than 82 % of COM) without using of additional (“external”) catalyst was obtained.

In the case of using heterogeneous catalysts the possibility of initial COM activation by such catalysts is practically impossible. However at the absence of solvents – hydrogen donors, for example, with molybdenum catalysts of oil-processing the high conversion degrees of bituminous and subbituminous coals have been observed. It should be supposed that in these cases during hydrogenation without “external” solvent the role of hydrogen transfers evidently plays the extracted part of initial coal which is not strongly connected with

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coal matrix. This extracted part becomes the mobile one at relatively low temperatures and may be adsorbed and hydrogenated on solid catalysts. According to literary data the hydrogenated coal liquid products are the better donors – hydrogen transfers compared with tetralin and other hydroaromatic compounds. At the case of sulphurous coals H₂S also takes part in the hydrogen transferring to coal fragments.

According to experimental data the mechanism of coal liquefaction in the presence of native finely distributed pyrite and additional iron compounds is apparently different. During coal hydrogenation without additional catalysts the role of “internal” catalyst (pyrite) most probably consists in rehydrogenation of intermediate liquid coal products which are the solvents for COM – donors and hydrogen transfers. The hydrogenation of naphthalene which is formed preliminary or simultaneously from tetralin almost does not take place (naphthalene is accumulated). The plausible reason is the better adsorbability of liquid coal products compared with naphthalene as well as their location nearer to the “internal” catalyst. In the presence of additional “external” catalysts their role consists mainly in the rehydrogenation of naphthalene again into tetralin; in this case the total conversion of COM is higher one.

It is the authors' opinion that the spreading of nanocatalysis principles in the process of direct coal liquefaction has certain prospects. It has been shown that nanoscale particles of iron- containing wastes can be obtained by mechanoactivation in fluidized or vibrated fluidized bed of inert material. The use of such nanoscale particles allows to shorten the process duration as well as to increase “coal oil” yields at the same time using the decreasing catalyst quantity.. Undoubtedly that in this line of investigations it is necessary to overcome the serious technological and technical difficulties.

CATALYTIC MEMBRANE CONTACTOR/REACTOR FOR DEEP REMOVAL OF DISSOLVED OXYGEN FROM WATER

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This work describes the development of a catalytic Pd-loaded polypropylene porous hollow fiber membrane contactor for removal of dissolved oxygen from water.

The lab-scale catalytic membrane module was prepared and coated with Pd catalyst by ex-situ and in-situ methods. The commercially available membrane contactor was coated integrally as delivered, without disassembly. The concentration of dissolved oxygen in water was reduced to the sub-ppb level by catalytic reaction with Pd-loaded commercially Celgard membrane contactor/reactor.

Dissolved oxygen is one of the major contaminants to be removed for the production of ultra-pure water, e.g., for the semiconductor industry or for boiler feed water preparation in electricity production. Also, in the brewing of beer (heavy brewing) and in the oil & gas industry (injection water) oxygen removal is important.

For the removal of oxygen to very low levels, catalytic reduction with hydrogen is an attractive method. This work describes the development of a catalytic Pd-loaded polypropylene porous hollow fiber membrane contactor for this purpose. The commercially available Membrana Liquicel contactor module was impregnated with a palladium catalyst by an in-situ method.

The method of chemical deposition of Palladium was used for the reduction of palladium salts by an aliphatic alcohol [1]. The method for the coating of single hollow fiber membrane and principle of removal of dissolved oxygen from water by Pd-loaded polypropylene porous hollow fiber membranes have been described in earlier work [2].

Subsequently, after development of the method for the coating of single membrane fibres, the method was adapted for the in-situ coating of a complete commercially available membrane module (1.4 m² of membrane surface area). As an intermediate step, custom made modules with a glass outer tube were coated.

The removal of dissolved oxygen from water by catalytic membrane contactor/reactor was studied in a flow-through system in both once-through and recirculation mode. The

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concentration of dissolved oxygen in water was reduced to the sub-ppb level by catalytic reaction.

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CATALYTIC ACTIVE LAYERS ON VALVE METALS

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The surface structures containing copper and nickel compounds in addition to Al₂O₃ or TiO₂ have been obtained on aluminium and titanium supports by plasma electrolytic oxidation (PEO) technique. The data on the composition and a catalytic activity of structures formed in the reaction of CO oxidation into CO₂ are given in the report.

Two approaches have been used for obtaining surface structures on metals.

First approach. The films on titanium were formed in aqueous electrolytes containing polyphosphate complexes of Ni(II) and Cu(II). Fig.1 shows the dependence of films composition (the thickness averaged data of XPA) on a relation of copper and nickel concentrations $m=[\text{Cu(II)}]/[\text{Ni(II)}]$ in solution.

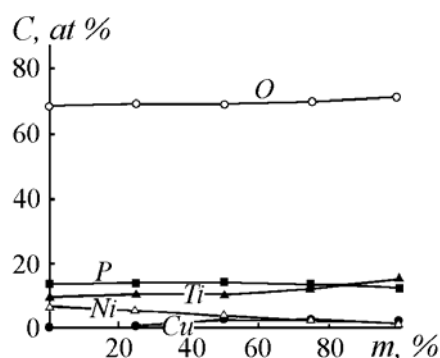


Fig. 1. The elemental composition of films on titanium.

Formed compositions show the certain catalytic activity in reaction of CO oxidation into CO₂, Fig. 2a, that decreases under the influence of high temperatures during a catalytic testing.

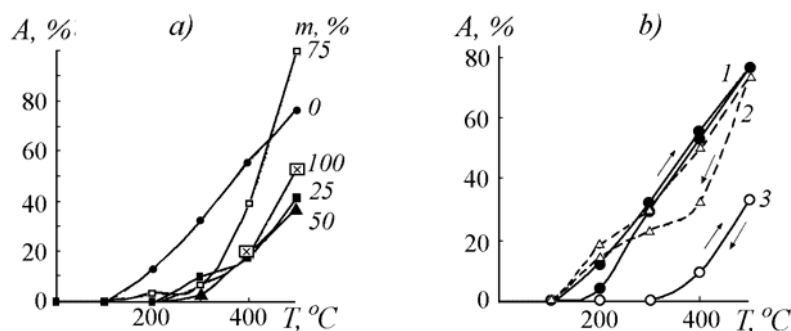


Fig. 2. CO conversion (A) vs. reaction temperature of the catalysts: (a) the effect of coatings composition; (b) the temperature dependences for first, second and third cycles of heating-cooling catalytic tests for Ni-containing film on Ti.

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According to the XPS data the films composition is essentially inhomogeneous on the thickness. Titanium is absent on the surface, there is carbidous carbon. After catalytic test nickel and copper concentrations increase on the surface, the portion of Cu^{2+} in respect of Cu^+ increases. It is possible that changes in the catalytic activity are related with the surface composition changes.

The second approach. The films on aluminium have been formed in electrolytes suspensions, for example, in electrolyte containing $\text{Na}_3\text{PO}_4 + \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{WO}_4$ (PBW), in which acetates of nickel(II) and copper(II) have been added. The temperature dependences of CO conversion into CO_2 for compositions Al/Ni- and Cu-containing films (a), and results of the cycling catalytic test of the system PBW/NiCu (b) are given in Fig. 3. According to the XPS data the surface composition of the system PBW/NiCu is practically invariable under catalytic test, Fig.3c.

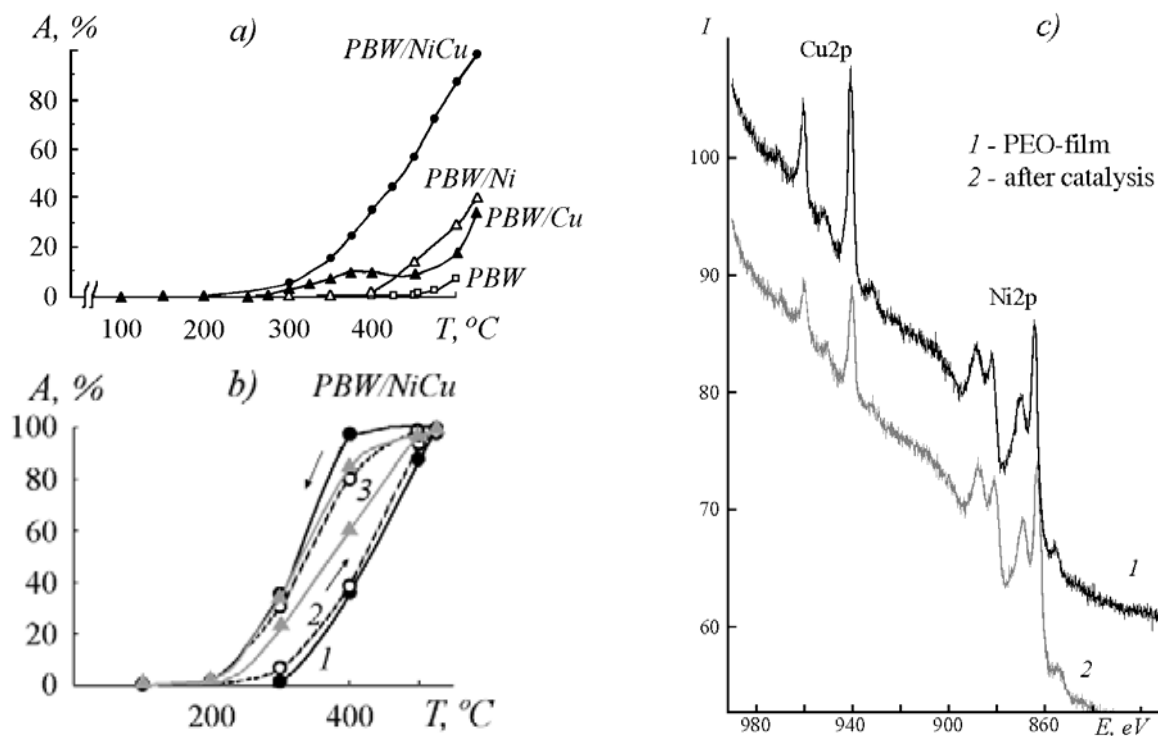


Рис. 3. CO oxidation under the catalysts (a, b) and the surface composition (c) of systems Al/NiCu-containing film.

Thus the compositions Ti/NiCu-film and Al/NiCu-film reveal the certain catalytic activity in CO oxidation into CO_2 . CO conversion correlates with the surface chemical composition. Present compositions may be recommended both as support and catalyst system for redox reactions.

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MODIFICATION OF COMPOUNDED RUBBERS WITH LIQUID POLYKETONE

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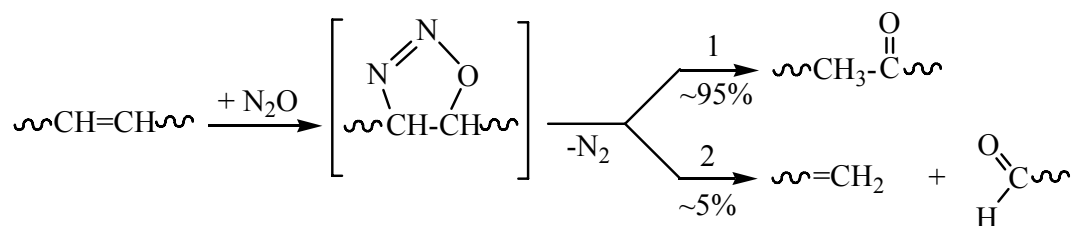
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Effect of a low-molecular polyketone ($M_n = 2200$, oxygen content 9.9 wt %) addition on the properties of compounded rubbers obtained with polybutadiene (SKD) or nitrile-butadiene polymer (BNKS) was studied. Polyketone was prepared via carboxidation of polybutadiene by N_2O . The addition of polyketone into SKD-rubber decreases abrasability and mechanical losses. When polyketone is introduced into BNKS-rubber, this increases tear strength and frost resistance, and decreases the rate of rubber ageing. Other physico-mechanical properties of vulcanized rubbers remain virtually unchanged. Polyketone addition is considered to be a promising method for improving the performance of these type rubbers.

Recently, a method of synthesizing new functional oligomers containing carbonyl groups has been developed at the Boreskov Institute of Catalysis SB RAS. The method consists in treatment of unsaturated polymers containing double $C=C$ bonds with nitrous oxide (N_2O) at temperature 180–230°C and pressure 30–80 atm (the so-called carboxidation). The reaction proceeds via non-catalytic 1,3-dipolar cycloaddition of N_2O to $C=C$ bonds accompanied by the formation of $C=O$ groups in the polymer backbone. The carboxidation of *cis*-1,4-polybutadiene SKD ($M_n = 128000$) can be presented by the following scheme [1]:



Main route (95%) of the reaction proceeds without cleavage of $C=C$ bonds and leads to the formation of ketone groups in the polymer backbone. A minor route (5%) of the reaction proceeds with the cleavage, yielding smaller fragments containing aldehyde and vinyl end groups. This may lead to a dramatic decrease in the molecular weight, which, depending on the carboxidation degree, may be 1–2 orders of magnitude less than that of the parent polymer. The carboxidation of more than 15% of the polybutadiene $C=C$ bonds transforms it into a $C=O$ functionalized liquid oligomer having quite a narrow molecular-weight distribution ($M_w/M_n \approx 2$). The materials obtained are unsaturated polyketones containing double $C=C$ bonds, ($>C=O$) groups, and aldehyde and vinyl end groups.

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The present work considers a possibility to use liquid polyketones as a modifying additive to compounded rubbers for the improvement of their technological and operating characteristics. For this purpose, we studied the effect exerted by addition of liquid polyketone on physico-mechanical and technological properties of standard industrial compounded rubbers produced with polybutadiene (SKD) or nitrile-butadiene polymer (BNKS). Rubber samples were obtained by vulcanization of appropriate raw rubber compounds. The liquid low-molecular polyketone (oxygen content 9.9 wt %, $M_n = 2200$, $M_w/M_n = 2.5$) was synthesized via carboxidation of *cis*-1,4-polybutadiene SKD by nitrous oxide at 230 °C for 18 hours.

It was shown that addition of 5 parts by weight of the liquid polyketone into raw rubber compounds containing SKD or BNKS has no detectable effect on their main physico-mechanical properties, but decreases the rate of their vulcanization.

After vulcanizing rubber compounds, characteristics of the resulting rubbers were tested. The polyketone addition decreases abrasability and mechanical losses of SKD-rubber. The drawback is a small increase in the rate of rubber ageing. When polyketone is introduced into BNKS-rubber, this increases tear strength and frost resistance, and decreases the rate of rubber ageing. Other physico-mechanical properties of the rubbers studied (strength, hardness, and elasticity) remain virtually unchanged.

Therefore, the rubbers modified with liquid polyketone have some advantages over stock-produced samples, with main physico-mechanical properties being retained. The study performed demonstrates that addition of liquid polyketones is a promising method for improving the performance of various type rubbers.

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EFFECT OF LIQUID POLYKETONE ON THE PROPERTIES OF CUSHION RUBBER

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Effect of a low-molecular polyketone ($M_n = 2200$, oxygen content 9.9 wt %) addition on physico-mechanical and technologic properties of cushion rubber obtained with polyisoprene SKI-3 was studied. Polyketone addition was shown to increase the strength of rubber coupling with metal cord, which will improve the performance of rubber-cord systems.

Recently, a method of synthesizing new functional oligomers with a specified concentration of carbonyl groups and a controllable molecular weight, has been developed at the Boreskov Institute of Catalysis SB RAS. The method consists in treatment of unsaturated polymers containing double C=C bonds with nitrous oxide, N_2O (the so-called carboxidation). Carboxidation proceeds via non-catalytic 1,3-dipolar cycloaddition of N_2O to C=C bonds accompanied by selective formation of C=O groups in the backbone.

A small fraction of C=C bonds reacting with N_2O is cleaved in the reaction, which decreases the molecular weight of the parent polymer. Thus, carboxidation of *cis*-1,4-polybutadiene ($M_n = 128000$) at temperature 180–230 °C and pressure 30-80 atm yields liquid unsaturated polyketones, the oligomers containing double C=C bonds, (>C=O) groups, and aldehyde and vinyl end groups [1].

Having a relatively low viscosity, the resulting liquid polyketones can be mixed with various ingredients and fillers. Due to the presence of carbonyl groups in the polymer backbone, these polyketones have high polarity and good adhesion to metals and other materials.

In this connection, these materials possibly could be used as modifying additives to cushion rubbers to improve the strength of their coupling with tire metal cord. For this purpose, we studied the effect exerted by addition of liquid polyketone on physico-mechanical and technologic properties of the cushion rubber prepared with *cis*-1,4-polyisoprene SKI-3. The liquid low-molecular polyketone (oxygen content 9.9 wt %, $M_n = 2200$, $M_w/M_n = 2.5$) obtained by carboxidation of *cis*-1,4-polybutadiene SKD with nitrous oxide at 230°C for 18 hours was used as a modifying additive.

PP-III-23

The introduction of 5 parts by weight of the liquid polyketone into initial raw rubber compound does not virtually change its vulcanization-kinetic and physico-mechanical characteristics. After vulcanization of the rubber compound, characteristics of the resulting rubber were tested. Addition of polyketone was shown to increase the strength of rubber coupling with metal cord. Presumably, this is due to efficient interaction of polar carbonyl groups of polyketone, which is present in the rubber compound, with brass coating of the cord. Such physico-mechanical properties of rubber as hardness, elasticity, and frost resistance remain unchanged. The study performed indicates good prospects of using the liquid polyketones for the improvement of operating characteristics of the rubber-cord systems.

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CATALYSTS SEARCH FOR α -METYLBENZYLPHENOLS

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Alkylation reactions of phenol and its derivatives by styrene in the presence of different catalysts as well as inhibitors of styrene polymerization were examined in our work.

The influence of catalysts sort, initial reagents ratio, reaction time and temperature on final products structure was studied.

Nowadays arylalkylphenols are widely used as antioxidants for synthetic rubbers and latexes. One way of their synthesis is alkylation of phenol by unsaturated compounds (olefines, cycloolefines).

Alkylation reactions of phenol and its derivatives by styrene in the presence of different catalysts as well as inhibitors of styrene polymerization were examined in our work.

The influence of catalysts sort, initial reagents ratio, reaction time and temperature on final products structure was studied.

Aryl-sulfonic acids and synthetic cation-exchange resins (SCER) were used as catalysts of the process. The phenol alkylation using aryl-sulfonic acids was accompanied with intensive side-reactions, which led to increase of viscosity of reaction mixture. Liquid chromatography was used for identification of the structure of alkylation products.

It was found that the mixture of 2- α -methylbenzylphenol, 4- α -methylbenzylphenol, 2,4-di-(α -methylbenzyl)phenol, and 2,6-di-(α -methylbenzyl)phenol is generated during the reaction, and di- and oligomerization processes were occurred. The oligomerization process is not desirable due to difficulties for final product isolation and catalysts separation from it.

That is why it is necessary to carry out the synthesis of arylalkylphenols in the presence of inhibitors of polymerization. Agidol-1, Agidol-2, 2,6-di-*tert*-butylphenol, diphenoquinone were used as inhibitors of styrene polymerization. If we used Agidol-1, we found out, that the viscosity of reaction mixture was not increase.

If we use SCER as catalyst, we find out that side-reactions are much less intensive. The significant advantage of SCER over homogeneous catalysts is that in their presence monoalkyl derivatives are produced in less quantities; the styrene polymerization process is not proceeded. If we use as catalysts SCER, for instance, KU-23, we will get mainly para-substitution process and 2,6-di-(α -methylbenzyl)phenol formation in considerable amounts.

PP-III-24

The optimal conditions of the stabilizer synthesis were found: it was determined that maximal yield of the alkylation products was reached at the molar ratio of phenol: styrene =1: 1,71; reaction time 2 hours and with the use as catalysts SCER in the quantity 20% of phenol weight.

PARTIAL OXIDATION OF PROPANE-BUTANE MIXTURE IN MINI REACTORS

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Partial oxidation of propane-butane mixture with oxygen has been studied in quartz mini-reactors over heated Ni-Cr-Fe wire. Within short contact times conversion of hydrocarbons is up to 89 %, however, concentration of CO₂ in the products does not exceed 3 %. Among the main products are hydrocarbons with shorter C-C chain, hydrogen, CO and liquid oxygen containing hydrocarbons.

Partial oxidation of propane-butane mixture with oxygen has been studied at volume flow rate of 500000 h⁻¹ over Ni-Cr-Fe wire.

The wire was heated up to 1000 °C with electric current; in steady state its temperature could be maintained without electricity due to exothermic reactions on its surface if the ratio O₂:C_xH_{2x+2} is more than one.

Experiments in the reactors with different volumes showed that conversion of hydrocarbons is growing from 15 to 89 % together with increase of surface : volume ratio of the reactor. Conversion of hydrocarbons is always more than conversion of oxygen. When conversion of butane is 74 % conversion of oxygen is approximately 45 %.

Stoichiometry of the reaction is as follows:

$C_3H_8 + 3i-C_4H_{10} + 8C_4H_{10} + 8O_2 = 4H_2 + 5CO + CO_2 + 3CH_4 + 3C_2H_6 + C_2H_4 +$ liquid oxygen containing hydrocarbons and water.

Study of the effect of volume and shape of the reactors on the rate of conversion lead to establish that most part of processes (up to 75 %) proceed over the hot wire and neighboring hot surfaces. However, part of chemical reactions proceeds also in the volume and over cold surfaces. Therefore, the zone in proximity to the wire (less than 0.06 cm³) could be considered a micro-reactor where conversion of the gas mixture proceeds within millisecond time span.

Even at high conversion of initial gas mixture only small percent of CO₂ was registered in the products (less than 3 %) i.e. partial oxidation is the prevailing process.

Electron microscopy showed that surface of the wire is covered with complex mixture of nickel, chromium and iron oxides.

Introduction of water vapor to the initial gas mixture leads to increase percentage of hydrogen in the products.

Scheme of the mechanism of radical and surface reactions is proposed.

ENHANCEMENT OF PHOTOCATALYTIC ACTIVITY OF NANOSTRUCTURED TiO₂ FILMS BY DEPOSITION OF Ag NANOPARTICLES

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It has been shown that a deposition of 3-nm silver particles radically improves the performance of TiO₂ thin-film photocatalyst operating in air conditions. The observed effect is discussed in terms of a modification of surface states distribution resulting in lower level of recombination losses and higher hydrophilicity of metal-modified surface of the photocatalyst.

The intrinsic hydrophilicity in oxide photocatalysts (*e.g.*, TiO₂) enables an effective UV light-driven to photodegradation of organic and bacterial contaminants in the contact with air via mechanisms typical of aqueous suspensions of the photocatalyst that opens a variety of practical applications (air purification, odor control, disinfection, *etc.*). In the present work we demonstrate the possibility of a radical enhancement of photoactivity of nanostructured TiO₂ in air conditions by the modification of their surface with silver particles.

The photocatalytic coatings were obtained by spraying the aqueous colloid of TiO₂ (with the particles' size of 4 nm) onto the glazed ceramic tile followed with a calcination at 450°C. The amount of photocatalytically-deposited silver was determined by Rutherford backscattering spectroscopy. To evaluate the photocatalytic activity, the photodegradation of Rhodamine 6G adsorbed on the photocatalyst surface was used as the probing reaction.

The modification of TiO₂ films with Ag nanoparticles results in the *ca.* three-fold enhancement of the photocatalytic activity, this effect being observed in a rather narrow region of Ag concentrations ($1-2.5 \times 10^{15}$ Ag at./cm²) that corresponds to the particles with medium size of *ca.* 3 nm according to TEM). The chemiluminescent measurements with luminol solution evidenced higher yield of superoxide generation under UV illumination as compared to bare TiO₂, whereas the photoelectrochemical measurements showed that Ag-modified TiO₂ films exhibit the *ca.* two-fold increase in the photocurrent generation efficiency that points to lower recombination level. It has been shown previously [1] that the deposition of fine Ag particles (2-4 nm in size) results in "splitting" of electronic states in the forbidden zone of TiO₂ that destroys the recombination channel, this effect being almost negligible for larger particles due to the recrystallization of the metal deposit. Another factor responsible for the enhanced photocatalytic activity of TiO₂-Ag films is higher inherent hydrophilicity in the metal-modified surface (the water contact angle decreases from 72 to 45° when coming from TiO₂ to TiO₂-Ag films).

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BIODIESEL SYNTHESIS BY CATALYTIC AND SUPERCRITICAL METHODS

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Ecologically benign methods of biodiesel preparation are described. The methods include the use of solid superacids as catalysts for vegetable oil transesterification by methanol and the use of sub- and supercritical methanol without any catalyst for this reaction.

Biodiesel is an alternative fuel, which is produced from vegetable and animal oils [1, 2]. Its main advantages are: ecological purity, relatively low price and production from renewable sources. Unlike petrochemical products biodiesel is completely degraded in soil and water and the level of CO emission when biodiesel is burnt is much lower than that of conventional diesel fuel. The biodiesel production is permanently increasing and it is estimated that in 2020 up to 8 % of engines in Europe will use biodiesel.

Usually biodiesel is a mixture of methyl and ethyl esters of long- chain fatty acids. It is produced from vegetable and animal oils by catalytic transesterification by methanol or ethanol.

Nowadays mainly alkaline catalysts are used for biodiesel production because they are much more active than acidic ones. Nevertheless, the technological process of alkaline-catalyzed transesterification is rather complicated due to high demands to starting materials (low water and free acids content must be provided because both deactivate the catalyst). Besides, soap is always produced during the alkaline-catalyzed reaction and soap is difficultly separated from the product.

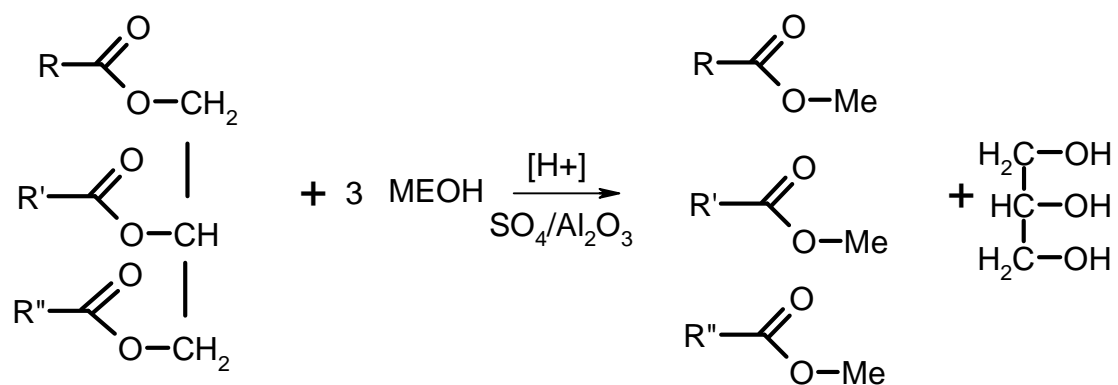
We have elaborated two novel non-alkaline procedures for biodiesel preparation.

The first procedure employs transesterification of vegetable oil by methanol using solid superacids as catalysts. These superacids are based on sulfate modified metal oxides – Al_2O_3 , TiO_2 .

Heterogeneous catalyst is easily removed from the reaction mixture and can be further regenerated. No soap is formed.

The second procedure is a sub- and supercritical transesterification without a catalyst. The procedure needs elevated temperature (220 – 260 °C), but no catalyst is used and there are no separation problems while using this procedure.

PP-III-27



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**PRODUCTION OF BIO-SYNGAS VIA AUTOTHERMAL GASIFICATION OF
CARBONIZED BIOMASS AND AUTOTHERMAL REFORMING OF TAR**

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Biomass is the most perspective energy source to substitute for mineral energy resources and a precursor of valuable chemicals. However many of chemical technologies for biomass processing are not competitive in efficiency with the currently employed oil refining and petrochemical processes; they need large-sized equipment and high power consumption.

Implementation of the profitable processes of biomass processing is mainly constrained due to specific composition of the renewable feedstock, its relatively low calorific value, substandard fraction compositions, as well as due to undesirable by-products. At present the biomass gasification is the most advanced process for biomass treatment aimed at the energy generation. The most elaborated are processes of air- and air-steam gasification of carbonized biomass. In the processes, the formation of undesirable products (tar and coke) along with the target product (synthesis gas) makes it impossible to feed the synthesis gas directly to power generating units. Minimizing the tar formation needs pre-carbonization of the biomass to remove volatile oxygen-containing products resulting from decomposition of the organic constituents. On the other hand, a biomass carbonization may cause a loss of carbonaceous feedstock, while the tar may be an additional source of synthesis gas. We propose a method for the gasification of differently carbonized biomass by combining two stages – autothermal air-steam gasification of carbonized biomass and catalytic reforming of tar – in one reactor. The following advantages are thus provided:

1. The gasified tar is fed to the reaction zone with the reforming catalyst, the stages of condensation and separation being omitted to provide energy saving.
2. The tar is not an undesirable product but involved in the reforming to provide, eventually, an increase in the calorific value of the power gas.
3. The minor pre-carbonization degree provides an improved yield of the target product (synthesis gas) with respect to the initial feed (biomass) and a decrease in the required

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quantity of steam while the residual water of the partially carbonized biomass is used in the process.

It is expected that the application of reforming catalysis will allow the biomass pre-carbonization to be avoided in order to make the power gas synthesis simpler and cheaper.

The application of steam reforming catalysts results in a decrease in the tar content in the power gas from 10-150 g/m³ to 0.1 g/m³ to meet requirements for gaseous fuels of internal combustion engines.

The gas mixture produced by steam-air gasification of the carbonized biomass in autothermal mode consists of 27% H₂, 12% CO, 18% CO₂, 15% H₂O, 28% N₂ at 600 °C and 20% H₂, 38% CO, ~1% CO₂, ~1% H₂O, 40% N₂ at 900 °C. Inspection of the data obtained that O₂/C and H₂O/C ratios are the most important process parameters; they are chosen to minimize the formation of coke and methane.

Catalysts for autothermal conversion of model mixtures of C₅ – C₁₆ hydrocarbon constituents of tar were developed at the Boreskov Institute of Catalysis. These are:

- Porous metal monolithic Co-Mn catalysts on stainless steel or fechral reinforcing net covered by Al₂O₃, SiO₂, BaO;
- Porous metal monolithic Ni- catalysts on stainless steel reinforcing net covered by Al₂O₃, and lanthanum, magnesium and barium oxides;
- Porous metal monolithic Rh-catalysts on stainless steel reinforcing net covered by Al₂O₃.

The prepared catalysts were tested to choose most promising systems. Criteria for the catalyst selection were the resistance to coke formation, catalytic activity and the H₂/CO ratio in the products. The coke resistance was determined from changing in the catalyst weight after testing. The results of 80-hour experiments at O₂/C=0.5 и H₂O/C=1.5 showed close to equilibrium composition of the products which did not change in time (Fig.1), neither coke formation nor changes in the catalyst weight being observed.

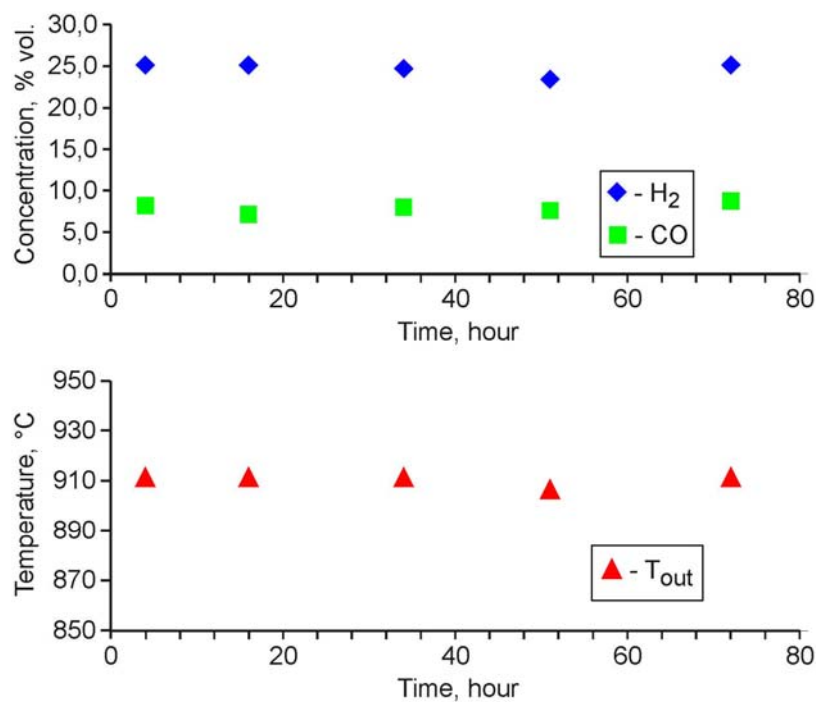


Fig. 1. Changes in H₂ and CO concentrations and temperature during life test of porous metal monolithic Co-Mn catalyst supported on stainless steel reinforcing net covered by Al₂O₃, SiO₂, BaO. Flow rates: 0.045 g/s of C₁₀H₂₂, 0.1 g/s of H₂O, 12 l/min of air; catalyst monolith of 55 mm diameter and 55 mm length.

The data obtained lead to conclude that these monolithic catalysts are appropriate for autothermal conversion of tar and for effective autothermal biomass gasification to decrease the tar content down to 0.1 g/m³ in the target product.

**PREPARATION AND INVESTIGATION OF MICROPOROUS CARBONIC
ADSORBENTS WITH LIMITED SPECIFIC SURFACE AREA FROM HIGH-ASH
BIOMASS**

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Microporous carbons with A_{BET} up to $3500 \text{ m}^2\text{g}^{-1}$, V_{pore} up to 3.0 ml g^{-1} and $V_{\text{micropore}}$ up to 1.9 ml g^{-1} are prepared by chemical activation of carbonized biomass. The influence of various activation parameters is investigated and the optimal ones are chosen.

The main aspects of the mechanism of the interaction of activating agent and carbonaceous precursor are determined.

The obtained samples of the carbons have shown a significant adsorptive capacity: they were to absorb up to 41 wt % of methane (at 273 K and 60 atm) and more than 6 wt % of hydrogen (at 77 K and 50 atm).

Now biomass is attractive for scientists of many countries as a resource of various valuable products to substitute for fossil resources (oil, coal etc.). One of the most widespread products of biomass processing is activated carbons, which have high adsorption capacity and are used as adsorbents in purification systems for fluids and gases cleaning, in chemical industry, medicine and so on. Microporous carbons (MCs) are the activated carbons which have limited specific surface area (A_{BET} is about $3000 \text{ m}^2\text{g}^{-1}$), and take on special place among carbonic adsorbents. The MCs can be prepared by the chemical activation method that is the interaction various carbonaceous precursors with such activating agents as ZnCl_2 , H_3PO_4 , hydroxides and carbonates of potassium and sodium. The best MCs among the currently produced are Maxsorb (Kansai Coke and Chemical Co Ltd., Japan). They are being prepared via the preliminary oxidation treatment of the carbonaceous precursor by aquafortis with following fusion with KOH at $700 - 800 \text{ }^\circ\text{C}$ [1, 2]. Such MCs have A_{BET} about $2700 \text{ m}^2\text{g}^{-1}$ on average and micropore volume (V_{μ}) about $1,2 \text{ ml g}^{-1}$. However, toxic gaseous and liquid wastes (nitrogen oxides and mineral acids) are produced in considerable quantities in this case.

In the Boreskov Institute of Catalysis the samples of MCs are prepared from high ash biomass by the example of rice husk (RH). RH was first carbonized in the fluidized bed of catalyst, then the prepared precursor was activated by KOH at $700 - 900 \text{ }^\circ\text{C}$ (Table 1). The obtained samples were to absorb up to 41 wt % of methane (at 273 K and 60 atm) and more than 6 wt % of hydrogen (at 77 K and 50 atm).

Table 1: Texture and adsorptive characteristics of the MCs samples obtained at different temperatures

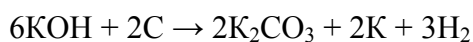
Activation temperature, °C	A_{BET} , m^2g^{-1}	V_{Σ}/V_{μ} , ml g^{-1}	Micropore proportion, %	Hydrogen adsorption capacity, % weight	Methane adsorption capacity, % weight
700	3170	1.77/1.45	81.9	4.7	28
750	3450	2.01/1.68	83.6	5.7	27
800	3360	2.18/1.87	92.3	6.3	33
850	3170	2.26/1.74	77.0	5.8	34
900	3210	2.97/1.48	49.8	6.2	41

Furthermore, the MCs were also prepared from oat husk and wheat straw having lower ash content (Table 2).

Table 2: Texture characteristics of the MCs samples obtained from rice and oat husk and wheat straw at 800 °C

Precursor	A_{BET} , m^2g^{-1}	V_{Σ}/V_{μ} , ml g^{-1}	Micropore proportion, %
Rice husk	3360	2.2/1.9	92.3
Oat husk	2930	1.8/1.6	94.6
Wheat straw	3270	1.6/1.5	99.5

The thermodynamic computations of possible reactions with comparing to results of analysis of the products of activation have shown that the main chemical process happening under interaction of KOH with carbonaceous precursor is the next reaction:



Thus the above data demonstrate that microporous carbons with the very large specific surface area can be synthesized from the high-ash biomass. The MCs obtained are superior in their textural characteristics to the known best analogues synthesized by treating petroleum pitch with nitric acid and can be used in membrane systems and accumulators of fuel gases.

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MRI STUDY OF ADVECTION-CONVECTION INFLUENCE ON CHEMICAL WAVES PROPAGATION

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The present work deals with MRI investigation of reagents transport as well as convective flows influence on chemical waves in different media, such as packed bed and thin capillary. Three autocatalytic chemical systems were studied: cobalt(II)-hydrogen peroxide system, iron(II)-nitric acid system and chlorite-thiosulfate system. For the cobalt(II)-hydrogen peroxide system qualitative data are gained. For the iron(II)-nitric acid system chemical wave velocity *vs* average fluid flow linear dependence is obtained. According to it, wave velocity is not the additive sum of flow velocity and front velocity without any reagents transport. For the first time NMR-thermometry is employed in order to visualize wave propagation in chlorite-thiosulfate system.

Traveling waves in liquid-phase attract great interest because of their thermodynamical importance. The reaction-diffusion model, which is the theoretical base of wave activity origin in autocatalytic reactions, is used for the description of many biological, medical and geophysical phenomena. On the other hand, investigation of wave dynamics in open systems gives information about mutual influences of chemical reaction and reagents transport, which is important for chemical engineering.

The main goal of the present work is to gain general experimental data about interactions between chemical waves and flows of different nature in various media. Experiments were performed by means of magnetic resonance imaging (MRI), apparently the only technique suitable for the purpose. Three wave active chemical systems were examined: oxidation of Co^{2+} ethylenediamine complex by H_2O_2 (cobalt(II)-hydrogen peroxide system), oxidation of Fe^{2+} by nitric acid (iron(II)-nitric acid system) and oxidation of $\text{S}_2\text{O}_3^{2-}$ by NaClO_2 (chlorite-thiosulfate system).

In the MRI experiment with iron(II)-nitric acid system acquiring of contrasted images was based on the difference in paramagnetic properties of Fe^{2+} and Fe^{3+} ions. Experiments were performed in a packed-bed reactor and a thin capillary. In both cases it was found that wave velocity dependence on average flow velocity has a linear character. Experimental data for the packed-bed reactor are presented in the Figure 1 along with two extreme cases. It is obvious from the graph, that front velocity is not a sum of flow velocity and wave velocity without any reagent transport, so it looks like wave velocity is adjusting to the alternation of

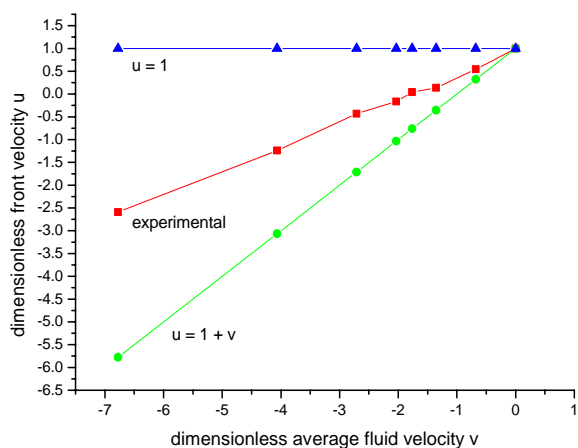


Figure 1. Wave velocity dependence vs flow velocity in packed-bed for iron(II)-nitric acid system.

flow rates. Also, in no case arising of stationary concentration patterns resembling the Belousov-Zhabotinsky reaction system was observed¹. It is interesting, that in a certain range of flow velocities concentration front propagates with variable velocity, which switches back and forth between two constant values. This fact can be explained by a presence of double-diffusive convection at the border of

two phase states of iron(II)-nitric acid system and may be considered as a first instance of stable oscillating convection².

In order to visualize propagation of chemical waves in chlorite-thiosulfate system by means of MRI, an extreme exothermicity of this oxidation process was used. By employing methodologies of NMR-thermometry a mapping of temperature distribution was performed, that was never done before for investigation of a chemical reaction. It has been found, that first two theoretical convection modes for vertical tube are present during the evolution of chemical wave in chlorite-thiosulfate system.

For the cobalt(II)-hydrogen peroxide system only qualitative data were acquired, because of oxygen gassing during the reaction.

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ISOMERIZATION OF HIGH-MOLECULAR N-PARAFFINIC HYDROCARBONS IN FUEL AND LUBRICATING OIL PROCESSES. CATALYSTS

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New catalysts based on crystalline molecular sieves of definite structure and composition have been synthesized for the diesel and lube oil isodewaxing and isomerization processes. Using these isomerization catalysts diesel fuel samples meeting the GOST R 52368-2005 (EN 590:20040) requirements for cold climate and arctic fuel had been obtained by means of isomerization of a hydrotreated diesel fraction with the cloud point of minus 6 °C

By means of isomerization of the C₁₄ - C₁₇ paraffinic fraction (T_{melting} = plus 7 °C) a diesel fuel component with the cloud point ranging from minus 12 to minus 15 °C have been obtained.

From hydrotreated slack waxes isoparaffinic oils of group III exhibiting a VI about 130 have been obtained. The experiments have been performed using laboratory units of dawn-flow type with a catalyst charge of 15-30 cm³, hydrogen pressure of 4,0 MPa, hydrogen :feedstock ratio in the rang of 1000 -1500 nm³/ m³, different temperatures and space velocities.

In the commercial production of fuel and lubricating oil such processes as isodewaxing (selective hydrocracking and partial isomerization of n-paraffins while retaining their initial boiling range) and isomerization without their removal from the feedstock resulting in n-paraffin conversion to isomers, being desirable components of all kinds of fuels and lubricants are used on an ever growing scale along with the removal of liner (n-) paraffins by means of selective dewaxing using solvents, dewaxing - selective hydrocracking on catalysts exhibiting molecular-sieve properties. For this purpose new zeolites and crystalline elementoalumophosphates and on their basis active and selective catalysts have been synthesized.

Such zeolites and catalysts have been produced and commercially used abroad for many years.

Currently winter grades of diesel fuel are being produced in Russia by the final boiling point reduction resulting in the fuel yield decrease, by blending of summer fuel with kerosine or gasoline, as well as by catalytic dewaxing. However, in the latter case the resulting fuel yield is not high and the cetane number is reduced. These problems can be resolved by means of n- paraffin isomerization.

In this connection we have investigated in the possibility of obtaining a winter diesel fraction by means of isomerization of a hydrotreated diesel fraction (sulfur content < 30 ppm) with the cloud point of minus 6 °C). For this purpose modern catalysts containing various crystalline molecular sieves of certain structure types and compositions have been

synthesized. Experiments had been conducted in laboratory units of dawn-flow type with a catalyst charge of 15-30 cm³ at temperatures in the range of 320-360 °C, space velocity 0,75-1,0 h⁻¹, hydrogen pressure 4,0 MPa, hydrogen:feedstock ratio = 1500 nm³/ m³.

The experiment resulted in a diesel fuel fraction with the cloud point ranging from minus 34 °C to minus 44 °C, flash point in closed cup above 55 °C, cetane number minimum 47, yield – more then 90 %. These fractions are in compliance with GOST R 52368–2005 (EN 590: 20040) requirements for fuels to be used in cold and arctic climatic zones. The results of comparative testing of zeolite-containing and amorphous catalysts are also presented in the report.

In order to obtain a diesel fuel component research was performed aimed at isomerization of the C₁₄ – C₁₇ paraffinic fraction from the Parex process (T_{melting} = plus 7 °C). It has been found that at P = 4,0 MPa, T = 270 – 370 °C, V_{sp} = 0,5 – 0,75 hr⁻¹, H₂: feed = 1500 nm³ / m³ it is possible to obtain a diesel fuel component exhibiting the following properties: cloud point from minus 12 °C to minus 15 °C ; pour point from minus 14 °C to minus 18 °C , flash point 60 °C and 80 % yield, based on initial feedstock.

The task of producing high-VI isoparaffinic base oils (VI > 130) complying with the group III quality requirement by API, capable of competing with synthetic oils of PAO (polyalphaolefins) type is very actual. Isoparaffinic oils are produced from a byproduct of lube oil solvent dewaxing – paraffinic fraction (slack wax) by means of combining the following processes: hydrotreating, isomerization, isodewaxing and dehydrogenation.

The experiments on isomerizing preliminarily hydrotreated slack wax to sulfur content below 30 ppm and nitrogen content below 2 ppm with melting point in the range of + 51 ÷ + 59 °C and lube oil fraction content ranging from 6,0 to 7,0 % have been performed on a specially developed catalyst. The tests have been conducted in a dawn-flow-type reactor in the 320 – 370 °C temperature range, space velocity of 0,5 hr⁻¹, hydrogen pressure 4,0 MPa, hydrogen: feed ratio = 1500 nm³ / m³.

The catalysate yield amounted to 80 – 90 %, the melting point was in the range from + 30 °C to minus 5 °C depending on the experimental conditions.

To obtain oils with a pour point of minus 15 °C a second stage of the process is required to remove the residual linear paraffines from the slack wax.

The report presents the results of testing using the method of solvent dewaxing, as well as dewaxing on new special purpose catalyst on the second stage. The use of this catalyst has permitted to obtain an oil with a viscosity index exceeding 135, pour point minus 15 °C and yield of 55 %, based on feedstock, while producing primarily a diesel fraction as byproduct.

Ru-CeO₂/CARBON CATALYSTS IN WET AIR OXIDATION OF ORGANIC POLLUTANTS**Dobrynkin N., Batygina M., Noskov A.***Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia**E-mail: dbn@catalysis.ru*

The present work is focused on the development of the methodology of design of heterogeneous catalysts for processes of catalytic wet air oxidation (CWAO) of organic substances in a water phase. The presentation is widely covered specific aspects of the selection of catalysts for practical application, problems of preparation, catalytic activity, selectivity, deactivation and durability of catalysts, as well as the peculiarities of the oxidation mechanisms of variety organic molecules in water solutions. The practical recommendations are formulated and considered.

The development and study of Ce-promoted carbon-supported Ru catalysts in wet air oxidation of organic pollutants (starting with phenol, aniline, alcohols, acids, ethers and ending with chloroorganics) of a various structure are the objectives of the consideration in this work. The main principles of design of catalysts are based on specific requirements for the selection of catalysts of practical application stated in work and as well on the peculiarities of the oxidation mechanisms of variety molecules in water solutions. There are two aims to be intensively pursued in developing CWAO catalysts: to boost catalytic activity by creation of new chemical compositions and to increase the catalyst stability by application of new synthetic materials. In the Boreskov Institute of Catalysis, intensive studies are focused on metal catalysts supported on modifications of porous graphite-like materials of the Sibunit family. Sibunit is superior to conventional active carbons in the stability in aggressive and oxidative media; it behaves as adsorbent and catalyst in liquid-phase oxidation of various compounds with oxygen. Pure Sibunit samples were shown to be active catalysts for organic pollutants oxidation, including hard-to-oxidize phenol and aniline. So it was used in the present study as universal support, both as a catalyst and an adsorbent simultaneously. The choice of a catalytic system Ru-CeO₂/Carbon is justified by results of studies of variety catalytic systems (oxides and supported noble metals Ru-, Pt-, Pd-/C), shown the highest efficiency of Ru-CeO₂/Carbon (the combination of activity in deep oxidation of a carbon chain and selectivity of formation of molecular nitrogen or sulfates) for oxidation of various nitrogen -, sulfur-, and chlorine-containing compounds at T = 160 – 200 °C, P_{O₂} = 0.3 - 1.0 MPa.

It is established, that created low-percentage ruthenium-carbon catalysts Ru-CeO₂/Sibunit are surpassed in activity the catalysts-analogues with the high content of an active component, are steady in oxidation of organics (200 °C, 50 bar O₂), practically are not subject to washout of an active component, and their activity is kept by a constant during long period of tests in a trickle bed reactor (Fig. 1).

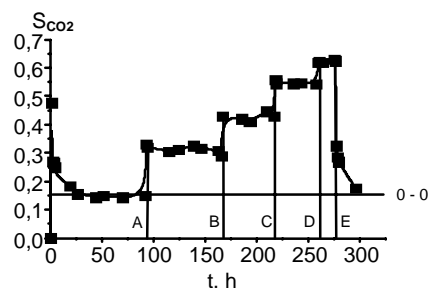


Fig. 1. Selectivity of CO₂ formation in long term test of Ru-CeO₂/C catalyst in phenol oxidation. ($m=1.0$ g, $C_{\text{PhOH}}=1.00$ g l⁻¹, 180 °C, $P=5.0$ MPa, $V_{\text{air}}=5$ l h⁻¹, $V_{\text{liq}}=1.0$ ml min⁻¹). Recycling after 92 (A), 165 (B), 216 (C), 257 (D) hours; fresh solution after 276h (E). Line 0-0 - initial level of activity.

The systematical researches are currently pursuing in Boreskov Institute of Catalysis have allowed to solve problems of creation of the catalyst for industrial application and to develop on its basis highly effective catalytic technologies of wastewater treatment from various toxic components.

Acknowledgment: The financial support of this study by INTAS (grant Nr. 05-1000007-420) and the Russian Foundation for Basic Research (grant 05-03-22004-CNRS_a) is gratefully acknowledged.

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SYNTHESIS AND INVESTIGATION OF CARBON SUPPORTED ADSORPTIVE CATALYSTS FOR PROCESSING OF TOXIC CHLORORGANIC COMPOUNDS

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Polychlorinated aromatic compounds (PCAC) are very toxic substances. Processing and recycling of these compounds are complicated not only by their thermal and chemical stability, but also by formation of very hazardous pollutants - dioxines. The adsorption technologies developed for waste treatment of the industry do not solve a problem of the further recycling highly toxic PCAC. To solving this problem the two step technology - adsorption of chlorocontaining pollutants on adsorptive catalysts from water and hydrogenolysis in multiphase system is proposed.

In 80-s' years of 20 century it has been established, that polychlorinated aromatic compounds (PCAC) are very toxic substances. Processing and recycling of these compounds are complicated not only by their thermal and chemical stability, but also by formation of very hazardous pollutants - dioxines. The adsorption technologies developed for waste treatment of the industry do not solve a problem of the further recycling highly toxic PCAC. The analysis of various methods of processing PCAC has shown that the most perspective is the catalytic hydrogenolysis process. The combination of adsorption step and catalytic hydrogenolysis allows to considerably simplify the scheme of processing PCAC, preventing dioxines formation and increasing the durability of the equipment.

The goal of the research work is synthesis of the active and stable adsorptive catalysts, capable to adsorb highly toxic polychlorinated aromatic compounds from objects of an environment for the further processing.

During this research work the adsorption step of chlorobenzene (CB) from water solutions was studied and it was shown, that the quantity of adsorbed CB and a kind of adsorption isotherms are in a good accord with porous structure of carbon adsorbents. The most effective CB adsorbents are microporous carbons with the high surface area MeKS, FAS, AG-2000. On the basis of the given carbons, palladium catalysts were synthesized and their activity in liquid-phase hydrodechlorination of CB by molecular hydrogen was studied. Conditions of the process were optimized. As a result of the investigation of the prepared

adsorptive catalysts in adsorption catalytic cycle, it was shown, that 1 % Pd/AG-2000 specimen possesses high adsorption capacity in relation to CB and has the highest catalytic activity in multiphase reaction medium under mild conditions (pressure 1 atm and temperature 50 °C). Two steps adsorption-catalytic cycle is very promising method for processing of toxic chlororganic compounds from different mediums.

The authors gratefully acknowledge the Ministry of Education and Science of Russian Federation (state contract 02.442.11.7313) and the Russian Foundation for Basic Research (№ 04-03-32869-a) for their financial support.

**DESIGN OF THE CATALYST' FOR THE CLEANING OF THE EXHAUST GASES
OF THE MOTOR TRANSPORT WORKING WITH METHANE**

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The Ag-Mn catalysts promoted by 0,1% Pt at the block metal carriers with the honeycomb channels structure were elaborated and they were tested at the “poor” mixtures. For the efficient wastes lowering at the “poor” mixtures ordinary two catalysts (with the sizes 45x50 mm every sample) were used in front of the turbocompressor and two catalysts (with the sizes 110x90 mm) on the spot of the regular silencer were placed. The cleaning efficacy was by NO_x -59%, CH_x-76%, CO-99%. Thus as its followed from the tests results the Ag-Mn catalysts using in both complete set led to the improvement was equal to European standards by the wastes.

Every year the transport development and increase of its using in the different load transportation is growing. This in its turn lead to a marked atmosphere pollution by the toxic gases which fatal influence on flora and fauna. The engine current characteristics improvement and transition to another alternative fuels reduce the total volume of the wastes but even the transport transfer to the “blue” fuel doesn't solve the ecological problem. At the same time with the toxic gases also the hydrocarbons, nitric oxides, carbon oxide are present and their concentrations lowering is possible to reach by only catalytic method.

We carried out the comparative researchings by using catalytic neutralizers of the waste gases at KamAZ (model 820.52-260) with the turbo-inflatable gas engine which was working at methane with the foil injection distribution and the electronic management. It was revealed that the catalyst led to considerable lowering of the CO wastes, insignificant decrease of CH₄ and it didn't influence to NO_x wastes. The catalytic neutralizers had the low efficacy by methane neutralization at the rotations of the idle motions and also at the work with the small loading at the waste gases temperature at the entrance of neutralizer didn't exceed to 250⁰C. At the engine work with the stoichiometric mixture composite the effect of neutralization of NO_x, CO, CH_x to standard Euro III as a result of the oxidation-reduction was observed. But the engine economical characteristics got worse. By this reason we carried out the tests of the elaborating Ag-Mn catalysts promoted by 0,1% Pt at the block metal carriers with the honeycomb channels structure at the “poor” mixtures. For the efficient wastes lowering at the “poor” mixtures work two catalysts (with the sizes 45x50 mm every sample) in front of the

turbocompressor and two catalysts (with the sizes 110x90 mm) on the spot of the regular silencer were placed. As a result of the KamAz (model 820.520-260) gas engine tests at the minimum idle motion regime with the complete set primary and secondary neutralizers of the wastes the cleaning efficacy was by NO_x -59%, CH_x -76%, CO-99%.

Thus as it follows from the tests results the Ag-Mn catalysts using in both complete set led to the improvement was equal to European standards by the wastes.

CATALYTICAL PURIFICATION OF CAR EXHAUST FROM NITROGEN OXIDES AND CARBON (II) OXIDE

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The exhaust of industrial enterprises and motor transport contains carbon oxide (CO), hydrocarbons (C_xH_y), and nitrogen oxides (NO_x). Reduction of their concentration by means of combustion improvement and novel technologies of exhausting gas purification is now a topical problem. Catalytical techniques are most promising of all the available ones. Among various heterogeneous-catalytical reactions, of special environmental interest is complex redox neutralization of nitrogen oxides with carbon monoxide or hydrocarbons.

Motor transport exhaust containing nitrogen and carbon oxides, benz(α)pyrene, formaldehyde, hydrocarbons etc. contributes much to air pollution in big cities of Russia.

To reduce the harmful effect of this exhaust on the public health is an important task in the framework of atmosphere-protection measures for a city. Aluminum-nickel-copper catalysts prepared in different conditions of ultrasonic treatment of the heterogeneous system carrier + aqueous solutions of active metal salts were studied. The system was treated in a commercial plant (Fig. 1) at a working voltage of 260 V, the temperature was $-25\text{ }^\circ\text{C}$, frequency 22 and 35 kHz, duration 2 min, a resonance mode of operation with developed cavitation in water.

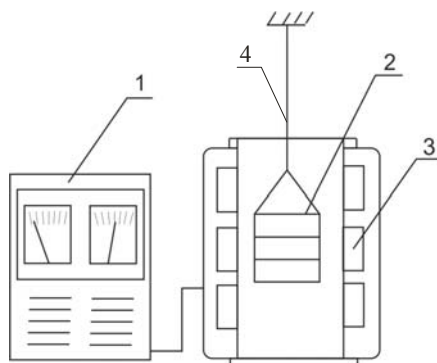


Figure 1. A scheme of the commercial plant for ultrasonic treatment of catalysts.
1 - an ultrasonic generator UZGZ-4, 2 - an ultrasonic reactor RAP-1 (acoustically transparent), 3 - a support, 4 - a suspension with the material to treat

The reaction of complex exhaust neutralization was performed on a laboratory flowing-type set at a volume rate of the neutralized gas 1000 h^{-1} within $100\text{--}500\text{ }^\circ\text{C}$. Ultrasonic treatment was employed for targeted influence on the catalytic system.

The Cu, Ni/ γ -Al₂O₃ catalyst obtained under the action of 22 kHz ultrasound possesses activity in complex exhaust neutralization but the conversion degree by CO and NO_x reaches 100% at 300 °C only. We have a sample of the Cu, Ni/ γ -Al₂O₃ catalyst (prepared under 35 kHz ultrasound) with a 100 % activity at 200 °C

Our new methods of catalyst preparation enable the properties to be improved substantially in comparison with the impregnation technique. The catalytic characteristics may vary widely depending on the technique and conditions of preparation due to changes in the nature of interaction between the catalyst's components, dispersity, porosity, crystal chemistry changes, and other factors affecting the course of catalytic reactions.

Optimal synthesis conditions of polymetallic catalytic systems under ultrasonic treatment with a frequency 35 kHz and a duration 2 min at 25 °C have been established.

The experimental data obtained demonstrate that ultrasonic treatment can be used to design a novel environment-safe technology for the synthesis of various catalysts with their properties comparing favorably with those of similar commercial ones made by means of the traditional impregnation techniques.

**FRAME STRUCTURED CORDIERITE-LIKE HONEYCOMB CATALYSTS
IN AMMONIA OXIDATION PROCESS**

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Frame structured cordierite-like honeycomb catalysts doped with Fe, Co, Mn, Bi and V cations were prepared by extrusion. All prepared catalysts had high activity in ammonia oxidation reaction: the conversion degree at 850-900 °C was about 95-100 %. NO yield strongly depended on catalysts chemical composition and cell density. Frame structured catalysts has high durability and thermoshock resistance. Stability of the prepared catalyst was checked by the 3-months life test in the UKL-7 high pressure nitric acid plant.

Bulk honeycomb monolith iron oxide catalyst for ammonia oxidation process (BIC-42-1) developed by the Boreskov Institute of Catalysis is now commercially used in nitric acid plants working under high pressure [1]. However, its application for medium pressure plants is questionable due to its geometry. Monoliths with high cell density and high thermoshock resistance are required [2].

The frame structured cordierite ($2\text{MgO} * 2\text{Al}_2\text{O}_3 * 5\text{SiO}_2$) honeycombs are characterized by the low TEC ($2*10^{-6}$ 1/K) and often used as a refractory carrier for high temperature catalyst applications [3]. A frame structure allows to obtain modified materials with 3d active cations instead of Mg, that may be active in ammonia oxidation.

In this study, we investigated performances and behaviors of frame structured cordierite-like honeycomb catalysts doping with Fe, Co, Mn, Bi and V cations in the high-temperature processes of ammonia oxidation into NO in nitric acid production.

The honeycomb cordierite-like catalysts were obtained by extrusion of plastic paste prepared by mixing of raw materials and 3d oxides (Fe_2O_3 , Co_3O_4 , Bi_2O_3 , V_2O_5) taken in a stoichiometric ratio with water solution of methylcellulose. Prepared monoliths were air-cured at room temperature for 5-14 days, dried at 350°C for 4 h, and than calcined at 1000-1250 °C for 4 h. The resulted monoliths had triangular and square channels with 45, 56 and 180 number of channels per square inch (CPSI).

Catalytic properties of micromonolithic samples (diameter 22 mm and length 50 mm) were tested in NH_3 oxidation process with and without one Pt sheet under atmospheric

pressure at 800-900 °C. The reaction gases (5-10 % ammonia in the air preheated at 450 °C in a quartz mixer) were flowed through the catalyst with 7.6 l/min flow rate (0.33 m/s at STP). An on-line UV spectroscopic method has been used for quantitative analysis of reaction gases (NH₃, NO and NO₂).

The structural and textural properties of frame structured cordierite-like catalysts were studied by XRD, SEM, and adsorption measurements.

According to X-ray data, cordierite phase was revealed in catalysts after their calcinations at 1000-1200 °C for 4 h. However, catalysts with calcinations temperature below 1100 °C do not have fully formed frame structure and contain a portion of free 3d oxides. It was found that Bi adding facilitates cordierite structure formation.

All prepared catalysts had high activity in ammonia oxidation reaction: the conversion degree was about 95-100 % for all samples. NO yield strongly depended on catalysts chemical composition and cell density. The highest NO yield was measured to be about 80 % and it was observed for the samples with high content of active component and 180 CPSI.

It was shown that increase of calcination temperature did not significantly affect on catalytic activity, whereas, it increased durability and thermoshock resistance of the monoliths.

Catalysts testing in a two-stage catalytic system at normal pressure were carried out. The two-stage system (one Pt gauze + monoliths with 180 CPSI) provides 100 % conversion of ammonia and NO yield about 94 %.

The stability of Fe- and Mn-doped frame structured catalyst was checked by the 3-months life test in the UKL-7 high pressure nitric acid plant. The catalyst has retained its mechanical and catalytic properties.

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CATALYSIS OF SOOT OXIDATION FROM DIESEL EXHAUST GAS

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Introduction:

Diesel engine with direct fuel injection (DI) exhibit the highest efficiency for the automotive applications. As consequence the low fuel consumption of diesel vehicles leads to reduced emissions of the greenhouse gas carbon dioxide (CO₂). However the serious constraint of the diesel engines is the emission of the pollutants hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x) and particulate matter (PM). The latter is defined as the material that is separated from the exhaust at 5 °C by the use of a filter paper. Principally, diesel particulates are constituted by a carbonaceous matrix (soot) that contains trace metallic inclusions (e.g. iron and calcium), adsorbed sulfuric acid, water and hydrocarbons [1].

Result and discussion:

In this work, the reaction of soot with O₂ on Fe₂O₃ catalyst was studied as a part of the simultaneous conversion of soot and NO_x in oxygen rich diesel exhaust. The mechanism was examined by using both FTIR Spectroscopy and temperature programmed techniques (TPD and TPO). In the presence of Fe₂O₃ catalyst soot ignition temperature decreases drastically, while soot is mainly oxidized into CO₂ [Figure 2]. Without catalyst CO is the major product [Figure 1]. Thermal desorption of these groups results in the formation of CO and CO₂ [Figure 3], whereby molar CO/CO₂ ratio is found to be 4. Pure soot exhibits carbonyl, ether, hydroxyl and carboxylic surface groups. Hence we deduce that carbonyl and ether groups are the dominating surface components being in accordance with our FTIR data [Figure 4].

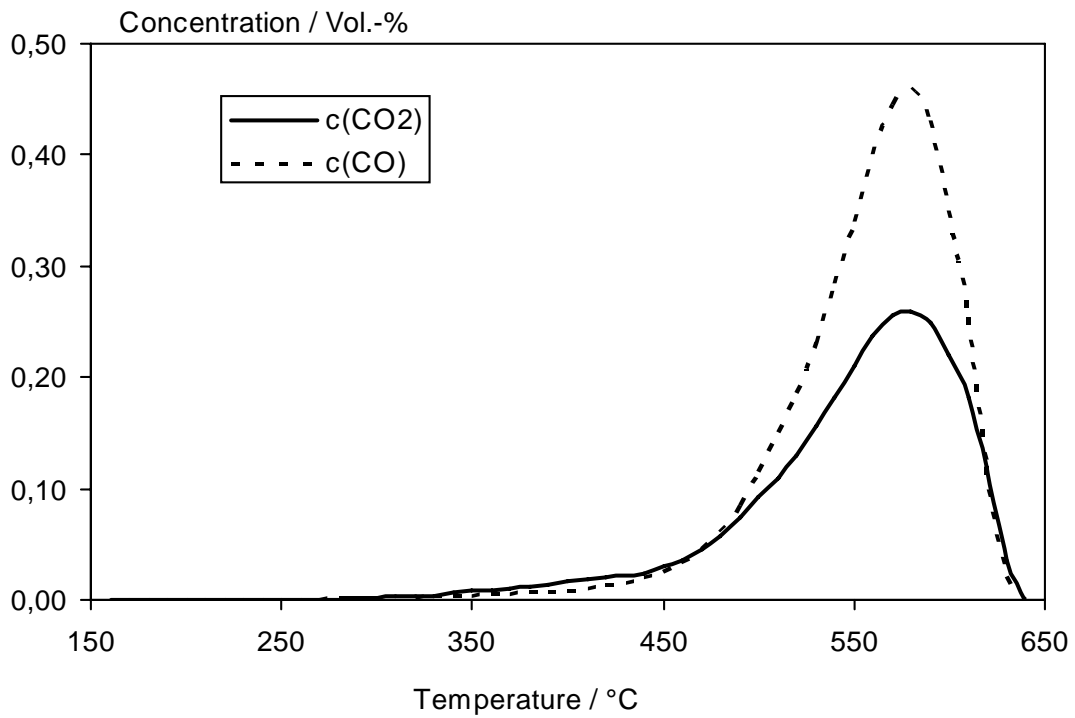


Figure 1: Concentration of CO and CO₂ in the TPO of pure soot

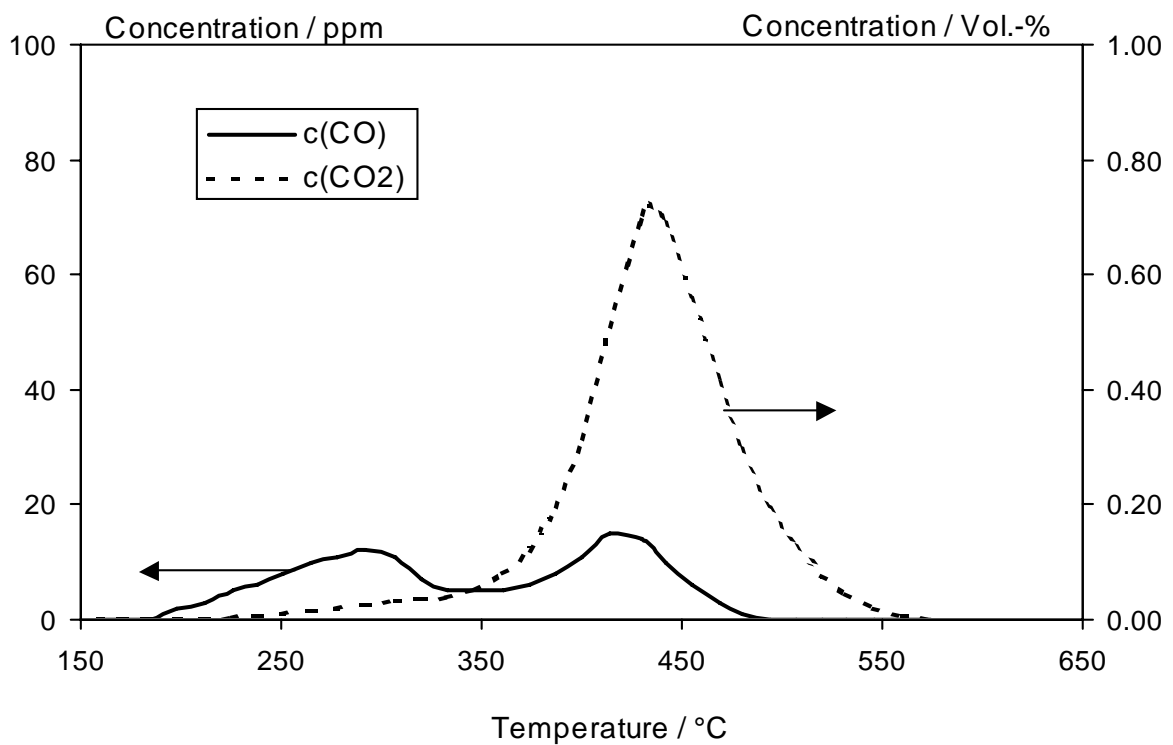


Figure 2: Concentration of CO and CO₂ in TPO an soot/ α -Fe₂O₃ Mixture

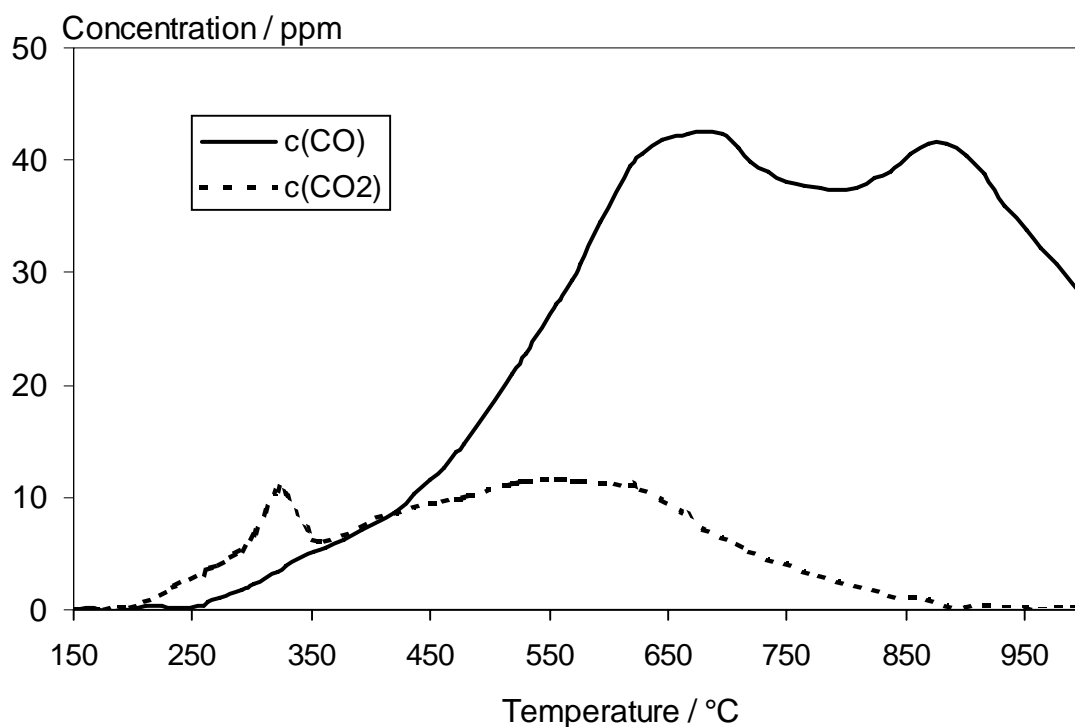


Figure 3: Formation of CO(—) and CO₂(--) in TPD of soot. Reaction conditions:
 $m(\text{soot})=120 \text{ mg}$, $N_2 \text{ flow}= 500 \text{ ml/min}$, $\Delta T/\Delta t = 10 \text{ K/min}$

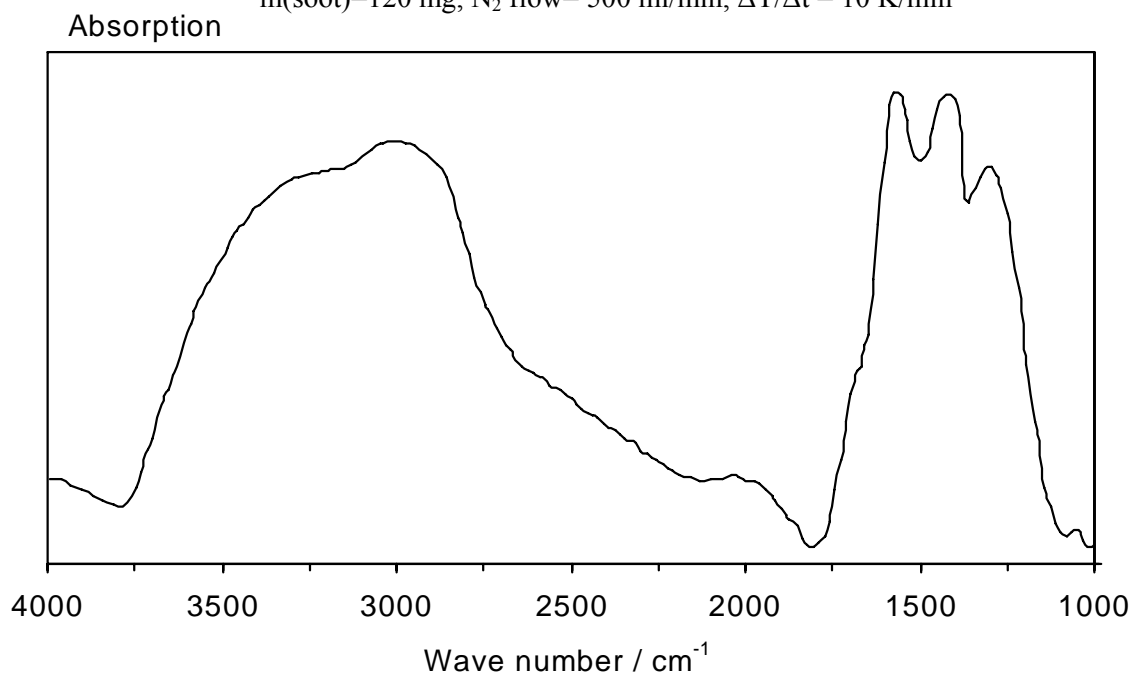


Figure 4: FTIR-Spectra of soot (0,125 Mass% soot in KBr, 2000 Scans)

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HETEROGENEOUS-CATALYTIC DECOMPOSITION OF EDTA ON CARBONIC MATERIALS IN NITRATE MEDIUM

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The research of degradation of EDTA on carbonic materials - Sibunite and carbon activated fibres ANM is carried out. The influence on degradation of temperature and acidity of medium is studied. The rate constants and activation energy of reactions are determined.

The problems of processing liquid radioactive wastes often require preliminary removal of a number of organic and inorganic compounds - activated complexons, oxalic acid, hydrazine, hydronitric and nitric acids. Use of catalytic oxidation - reduction processes is more preferable to their removal, as they do not increase volumes of radioactive waste. In the review [1] the example of use of activated charcoals and Pt/Si as catalysts of decomposition complexons is given.

Work is directed on definition of ANM catalytic properties for process of EDTA oxidation in cube residue with the purpose of extraction of radioactive nuclides, and also comparison ANM with known catalysts (BAC, Sibunite).

As a result of research it is stated, that for temperatures 50, 60 and 72 °C rate constants on ANM are 0,0653, 0,1469, 0,283 min⁻¹, respectively. Upon the comparison of these rate constants with constants for the activated carbon of mark - BAC [2], it is obvious, that they are similar: so for BAC at 60 °C the rate constant is equal 0,138 min⁻¹, and for ANM this value is equal to 0,147 min⁻¹.

For Sibunite rate constants of reaction for the same temperatures have values much lower: 0,0131, 0,0264, 0,0774 min⁻¹. Thus mass ratio solid/liquid (S/L) for ANM and for Sibunite is two orders lower, than for BAC. For Sibunite the presence of a latent site is marked, when degradation of EDTA is not fixed. The size of a latent site depends from acidity of medium.

Dependences of the rate constants of reaction for ANM and Sibunite from temperature are given in figures 1, 2.

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The activation energy found out from these dependences for ANM makes 61,6 kJ/mole, that practically coincides with the data published in work [2] for catalytic decomposition EDTA at activated charcoal (BAC) and platinized silica gel.

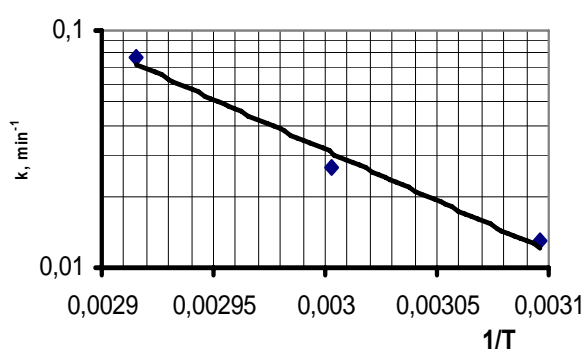


Fig. 1. For Sibunite: S/L = 1/100;
N (HNO₃) = 2,19

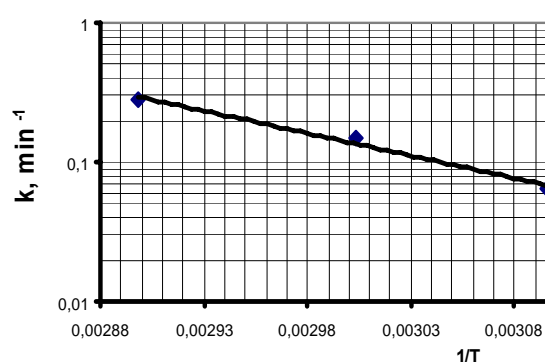


Fig. 2. For ANM: S/L = 1/100;
N (HNO₃) = 2,19

For Sibunite activation energy is $E_a = 81,6$ kJ/mole.

Stability of carbon materials is checked up at long influence of nitric acid in a researched interval of temperatures. The possible mechanism of heterogeneous - catalytic decomposition of EDTA is discussed.

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HYDROISOMERIZATION OF CATALYTIC REFORMING GASOLINE FOR PRODUCING CLEAN MOTOR FUELS

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The influence of conditions of hydroisomerization of industrial alkane-arene mixture (reformate) on platinum promoted sulfated zirconia has been studied. Hydroisomerization products, containing high-octane isoalkanes and alkylcyclopentanes, can be used as intermediate or finishing component for producing environmentally clean motor fuels.

Present-day requirements to gasoline are mostly regulated by environmental restrictions. In this respect, some present and perspective specifications, particularly European specifications, focus on the reduction of the content of aromatics, especially benzene in gasoline. Therefore hydroisomerization of products of catalytic reforming which is the main process for the refining of straight-run naphtha is an important part of novel technologies for producing clean motor fuels with low aromatics content.

In this work the influence of conditions of hydroisomerization of reformate, containing saturated and aromatic hydrocarbons C₆-C₁₂, is studied for the first time.

Under studied conditions (150-200 °C, 15-30 atm, mole ratio H₂/hydrocarbon feed = 8, WHSV = 1h⁻¹) platinum promoted sulfated zirconia provides more than 99 % hydration degree of aromatic hydrocarbons containing in reformate. Cyclohexanes, which are formed as primary products, isomerize to alkylcyclopentanes. Content of alkylcyclopentanes in the products reaches 35-37 wt% (Fig. 1).

Total alkanes in hydroisomerization products differ insignificantly from their percentage in original reformate. Principal difference is in the ratio between branched and linear alkanes. In comparison with original reformate branched to linear alkanes ratio in hydroisomerization products 3 times higher and is equal to 5.5-6.3. Because of high isoalkane and alkylcyclopentane concentration research octane number (RON) of liquid products reaches 71-73 points.

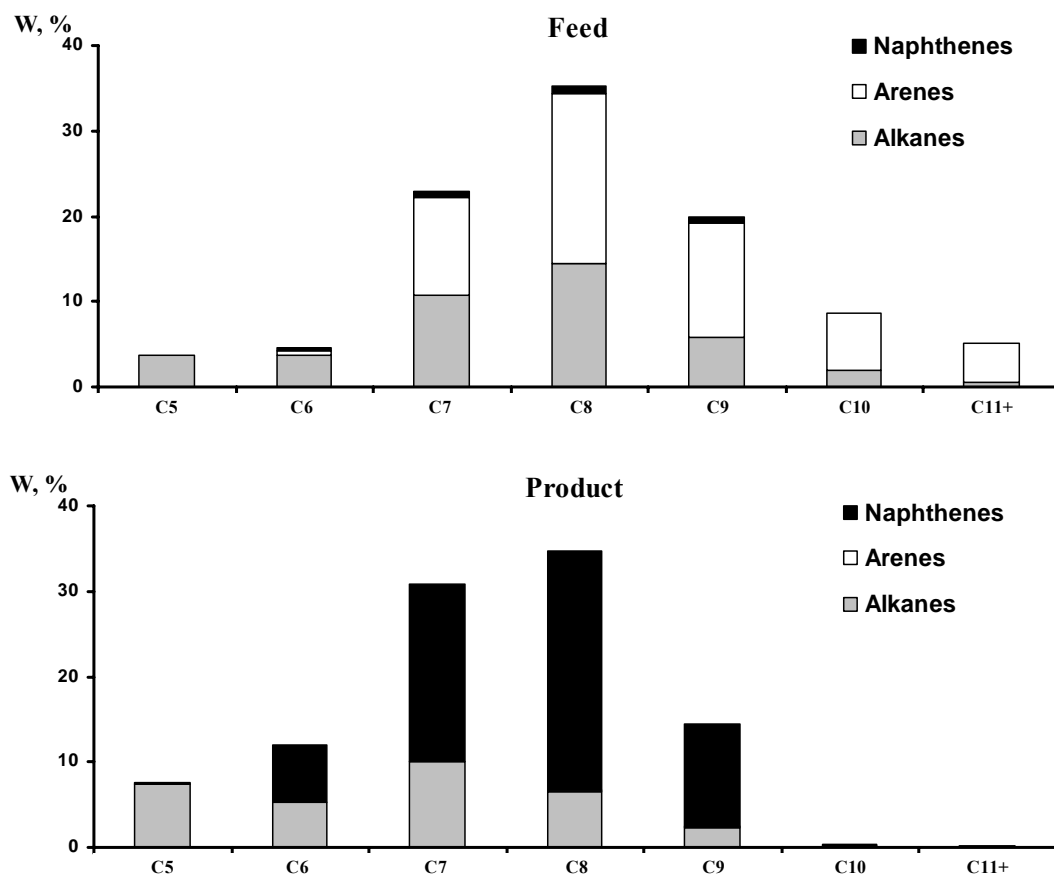


Fig. 1. Hydrocarbon type content of feed (reformate) and liquid products of hydroisomerization (W – mass concentration)

Hydroisomerization process is considered to be a step of novel reforming technologies aimed at production high-octane (95 points) gasoline components with lower aromatics content (less than 50 wt%). Schemes for further implication of hydroisomerization liquid products by compounding or catalytic refining for producing Euro-3, Euro-4 and Euro-5 gasolines without catalytic cracking and alkylation products are offered.

METHOD OF CATALYTIC UTILIZATION OF AK TYPE MELANGES

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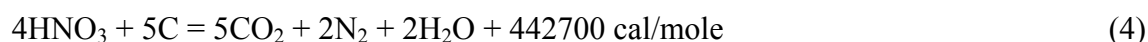
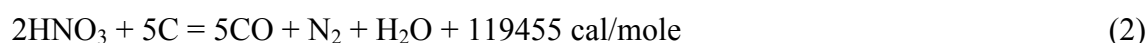
Under consideration is an ingenious method of utilization of melanges using catalytic decomposition over various coals.

The new approach to oxidizer utilization process will allow significantly reduce capital and energy costs in case of carrying out utilization in abandoned mines.

In the course of research work performed a number of distinctive features and potentials have been identified with regard to process structure of AK type oxidizers (melanges) utilization by interaction with coal proceeding with temperature decrease which results in technology simplification and cost reduction. The new approach to the oxidizer utilization process will allow, along with great reduction in capital and operating costs, to develop a new unique competitive technology implementation of which will significantly decrease energy and metal intensity of the process.

In interaction between coal and melanges there is observed gas generation and decrease of the process temperature from 22 to 12–14 °C. In the initial period when melange is added to coal insignificant emission of nitrogen oxides takes place caused by acid formation reaction which later stops. The process proceeds for 10 hours.

Based on the experimental data it has been established that in interaction between coal and melanges the following reactions occur:



Although reactions (1–4) are exothermic, energy required to break bonds between carbon atoms in coal which is equal to 124000–171700 cal/mole significantly exceeds overall heat of reactions (1–4). It has been demonstrated that carbon atom formation from its molecules reaches 60–70 % and reacted coal rate is 30–60 %.

**Fe- AND Fe/Al-PILLARED CLAYS IN THE CATALYTIC WET PEROXIDE
OXIDATION OF AZODYES**

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Catalytic wet peroxide oxidation of azodyes was carried out using Fe- and Fe/Al-pillared clays as catalysts. Pillared clays were prepared from naturally occurring montmorillonites by intercalating with polyoxocations containing iron, iron and aluminium with Fe/Al = 1:1, 1:10. The PILC materials were characterized by IR spectroscopy, XRD, BET surface area measurements. Fe/Al (1:10)-PILCs allows almost total colour removal of the dyes and 90% removal of COD without the significant leaching of Fe ions. Fe-, Fe/Al (1:1)-PILCs have high activity, but they are less stable.

Layer-pillar structured materials synthesized by intercalating metallic polyoxocomplexes between silicate layers of swelling clays, such as montmorillonites attract the interest as heterogeneous catalysts. Fe-containing pillared clays (PILCs) might be promising catalysts for the successful wet oxidation of organic pollutants. Dyehouse effluents from the textile industry impose serious environmental problems because of their colour and their high chemical oxygen demand (COD).

In this study catalytic wet peroxide oxidation of azodyes (Straight Clean-Blue, Acid Chrome Blue-Black) was carried out using Fe- and Fe/Al-pillared clays as catalysts, and the catalytic performance of the clays was investigated.

Pillared clays (PILC) were prepared from naturally occurring montmorillonites by exchanging interlayer cations (Mg^{2+} , Na^+ , K^+) with polyoxocations containing a) iron (Fe-PILC), b) iron and aluminium within the complex with Fe/Al = 1:1, 1:10 (Fe/Al-PILCs). The obtained PILC materials were calcined at 500 °C and characterized by chemical analysis, IR spectroscopy, XRD, BET surface area measurements.

Table

Characteristics of PILCs

Catalyst	Content, wt. %		S_{BET} , m^2/g	D_{pore} , Å	V_{pore} , cm^3/g	d_{001} , Å
	Al_2O_3	Fe_2O_3				
Fe-PILCs	11.8	6.6	136	76.4	0.271	12.4
Fe/Al (1:1)-PILCs	12.5	4.8	118	63.0	0.212	14.0
Fe/Al (1:10)-PILCs	16.7	2.1	219	78.0	0.268	18.3

S_{BET} – surface area, V_{pore} – pore volume, D_{pore} – average pore diameter, d_{001} – interlayer distance.

Catalytic properties of Fe-PILCs and Fe/Al-PILCs were studied in the wet peroxide oxidation of azodyes. It was found that catalytic activities of PILCs correlated with the iron contained in the catalyst, BET surface area and the total amount of dissolved iron. The effects of different reaction parameters such as initial pH, catalyst and hydrogen peroxide concentrations, temperature on the oxidation of the dye aqueous solutions were studied. It was established that Fe/Al (1:10)-PILCs allows almost total colour removal of the dyes (99 %) and a significant removal of COD (82-91 %) without the significant leaching of Fe ions. Leaching tests indicate that the activity of the catalyst Fe/Al (1:10)-PILCs is not due to leached iron ions.

Fe-PILCs and Fe/Al (1:1)-PILCs also have high catalytic activity, but they are less stable. It was also observed that by using these catalysts it is possible to extend the range of pH value (pH 3-6) for which Fenton-type oxidation can occur. At reuse of catalyst Fe/Al (1:10)-PILCs the decreasing of a rate of the dye oxidation and iron leaching were insignificant. The results on oxidation of organic dyes demonstrate prospects of practical use of Fe/Al-PILCs during the oxidation of organic pollutants of wastewaters.

Acknowledgements

The authors gratefully acknowledge the Russian Foundation for Basic Research for the financial support (Grant 06-08-01064).

**CATALYTIC METHODS FOR CLEANUP OF GASES FROM COAL THERMAL
CONVERSION PROCESSES FOR SUBSEQUENT APPLICATION IN POWER AND
CHEMICAL INDUSTRIES**

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The problem of exhausting deposits of oil and natural gas is leading to increased interest in coal as a source of heat, electricity and feedstock for chemical processes. Gaseous products of coal coking and gasification are readily transportable, promising for chemical synthesis and provide highly efficient heat conversion to electricity. However, the gases contain high-boiling unstable admixtures and corrosive compounds, such as hydrogen sulfide and hydrogen cyanide. To make the gases acceptable for use in compressors and to meet strict ecological standards, the content of H₂S and HCN in the gases must be reduced to ~20 ppmV. The method of aqueous alkaline oxidative absorption at ambient temperature is quite acceptable for this purpose. The solution absorbs heavy compounds and resins, while H₂S, HCN and NH₃ are bound chemically into nonvolatile safe compounds. The key process of this method is the oxidation of the absorbed H₂S to sulfur and ammonium thiosulphate by air. The reaction of hydrogen cyanide with polysulphides – an intermediate product of H₂S oxidation – yields ammonium thiocyanate, excessive H₂S gives sulfur and ammonium thiosulphate. These compounds are commercially valuable and can be utilized.

Based on the screening of catalysts for H₂S oxidation in solutions, a catalyst was selected containing cobalt phthalocyanine derivatives. The catalyst performance exceeds by several orders of magnitude that characteristic of other catalysts (salts and complexes of transition metals and quinones). Specific feature of cobalt phthalocyanine derivative determining its unique catalytic behavior consists in the formation during catalytic reaction of the redox species containing Co with oxidation degrees 2, 3 and 1, as well as CoPc complexes with molecular oxygen. The reactions of H₂S and HCN binding are accompanied by alteration of Co oxidation degree. Experimental tests proved high efficiency of H₂S and HCN removal from the coke gases.

Realization of this gas purification scheme will allow more efficient conversion of gas combustion heat in a gas-turbine power plant with down-stream utilization of the spent gas

heat in a steam-power unit. The scheme will provide a 15-20% increase of a heat-to-work conversion efficiency.

After H₂S and HCN removal, the gas can be compressed to ≥ 15 -20 atm prior to feeding to combustors of gas-turbine power units or use in chemical industry for syntheses of methanol, dimethyl ether, motor fuels. Technological schemes combining gas cleanup processes with the synthesis of chemical compounds and power generation processes are discussed.

**LIQUID PHASE OXIDATION OF BENZOTHIOPHENE AND
DIBENZOTHIOPHENE WITH CUMYL HYDROPEROXIDE IN THE PRESENCE
OF METAL-OXIDE CATALYSTS**

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The regularities of liquid phase oxidation of benzothiophene and dibenzothiophene in the presence of metal-oxide catalysts have been studied. In catalytic system containing octane and MoO₃/SiO₂ catalyst, at 50°C, the content of BT and DBT was reduced from 1000 ppm S to 40 and 10 ppm S, correspondingly. The reaction proceeds via formation of intermediate complex of substrate with hydroperoxide and catalyst, through parallel hetero- and homolytic routes.

The fuel oils contain considerable amounts of benzothiophene (BT) and its alkylsubstituted derivatives or dibenzothiophene (DBT) and its alkylsubstituted derivatives. These compounds possess low reactivity toward hydrogenolysis of C-S bond and, therefore, can not be removed by traditional technology of hydrorefining. New technologies of deep and ultra-deep refining of fuel oils are related to development of the processes of BT and DBT oxidation to sulphones and subsequent separation of the products by means of extraction or sorption.

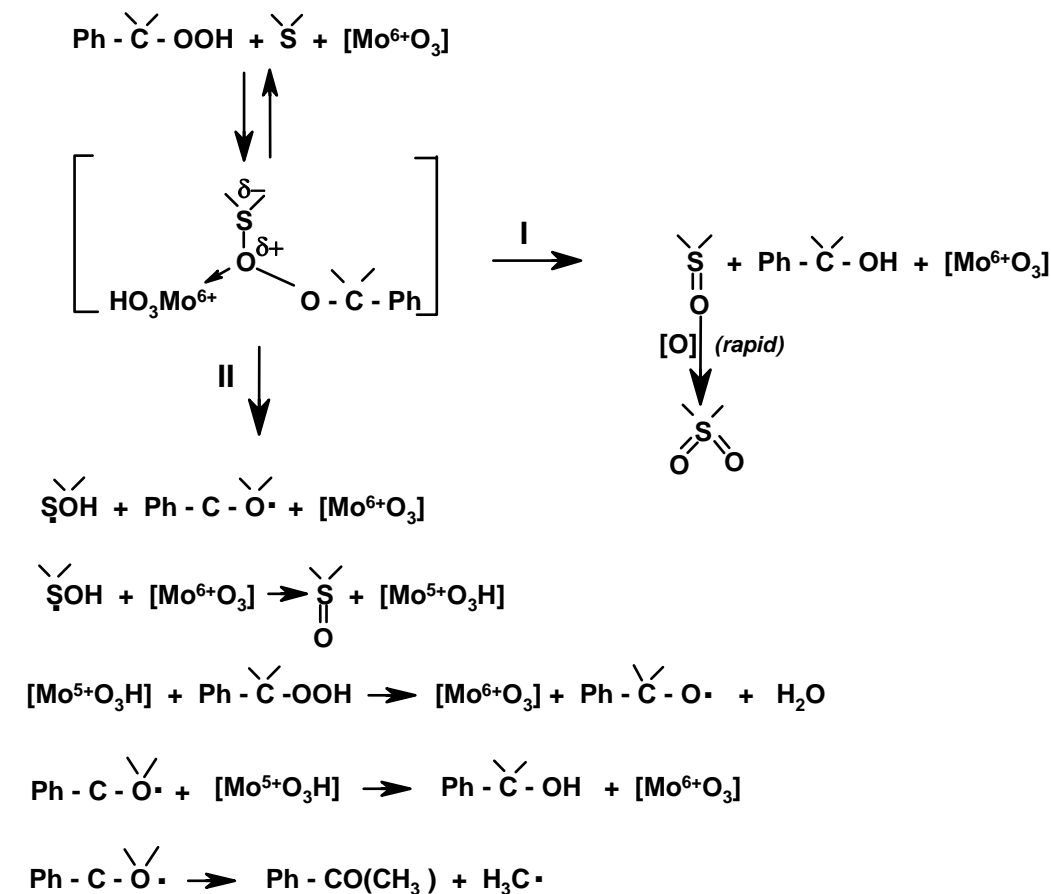
Searching of catalytic system for complete and selective oxidation of BT and DBT was the point of present work. Characteristics of oxidation of benzothiophene and dibenzothiophene with cumyl hydroperoxide (CHP) to corresponding sulphones were studied at 50 °C in octane medium. Concentration of BT or DBT was $4,3 \cdot 10^{-2} - 2,1 \cdot 10^{-3}$ mol/l, and concentration of CHP was close to stoichiometric one required for complete oxidation of benzothiophenes.

Oxidation of the least reactive substrate BT was tested in the presence of solid catalysts of different composition: 1) redox active metal (Fe, Co, Cu, V) oxides; 2) d⁰ metal oxides (MoO₃, WO₃, TiO₂, ZrO₂) capable of formation of peroxide complexes; 3) Lewis acids (Al₂O₃, AlCl₃, ZnCl₂). The second type catalysts were revealed to be the most effective.

In the presence of 15%MoO₃/SiO₂ conversion of DBT reached 100 %. Conversion of BT did not exceed 60 % at the same conditions. Unreacted with benzothiophenes CHP completely decomposed. When CHP was introduced by several portions, final conversion of BT was higher.

In this way, the content of BT and DBT was reduced from 1000 ppm S to 40 and 10 ppm, respectively. The possibility of the catalyst recycling was proved in oxidation of DBT.

Study of BT and CHP conversion and sulphone yield depending on reagents concentrations, measurements in time of sulphone formation and CHP consumption, comparison of the products of CHP transformation during BT or DBT oxidation with the products of CHP decomposition in the absence of substrate, allowed us to draw conclusions about mechanism of the processes occurring with the assistance of $\text{MoO}_3/\text{SiO}_2$ catalyst. In the absence of substrate, CHP decomposes to phenol and acetone on acidic centers, and to acetophenone and 2-phenyl-2-propanol via radical route participated by molybdenum ions. Benzothiophenes oxidation is supposed to proceed via formation of intermediate complex of molybdenum oxide with CHP and substrate molecule (Scheme), that prevents CHP decomposition. Conversion of the intermediate complex proceeds in two routes I and II to form oxide of BT or DBT, which than rapidly oxidizes to sulphone. The route I is electrophilic oxygen transfer to sulphur resulting in CHP conversion to 2-phenyl-2-propanol. The route II represents radical conversion of benzothiophene and CHP to form 2-phenyl-2-propanol and acetophenone. The route I predominates in the case of dibenzothiophene, whereas contribution of radical way II is remarkable during oxidation of the less reactive benzothiophene.



Scheme. Proposed mechanism of benzothiophene and dibenzothiophene oxidation

**METAL-CARBON NANOCOMPOSITE SYSTEMS AS HIGHLY SELECTIVE
CATALYSTS FOR CHLOROBENZENE TRANSFORMATIONS**

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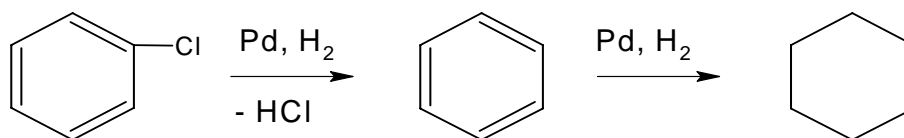
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Gas phase reductive transformations of chlorobenzene in H₂ were investigated in the presence of nanosized Pd and Ni particles encapsulated in carbon matrix. Palladium-based composite was very selective in cyclohexane formation. On Ni-based composite only benzene was formed in the temperature range of 50 – 300 °C.

Nanocomposites on the base of Pd and Ni encapsulated (@) in carbon matrix were tested in chlorobenzene conversion to benzene and cyclohexane. These composites were prepared by novel method, which promotes their outstanding properties: from TEM, XPS and Raman spectroscopy studies it is evident that systems have high metal dispersion, the mean diameter of metal particles is in range of 5 and 20 nm, and the metal concentration varies from 10 to 50%. Also they possess high stability to oxidation because they have metal particles which are covered with carbon.



Hydrodechlorination was carried out in a fixed-bed flow reactor under the excess of hydrogen at 50 – 300 °C and atmospheric pressure using 0.05 g of catalyst. The products were analyzed by gas chromatography. The selectivity of catalysts based on different 3d-metal changes dramatically. For example in presence of Pd@C total chlorobenzene conversion was observed in temperature range of 150 – 200 °C, the only product was cyclohexane. When the temperature was decreased to 50 °C, chlorobenzene conversion decreased from the value of 100 % to 90 %, the main product was benzene with 75 % yield. When Ni@C was used the process turns toward 100 % benzene formation with no signs of further hydrogenation to cyclohexane in the temperature range of 50-300 °C.

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THE ECOLOGIC AND ECONOMIC ASPECTS OF CATALYSIS APPLICATION IN GAS CONDENSATE PROCESSING UNDER THE CONDITIONS OF SIBERIA

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The abstract shows the importance of solving a complex of ecologic and economic problems in gas-condensate and oil-refining regions located at a distance from industrial centers such as Siberia and the North of Russian Federation.

A short description of achievements in the field of condensate processing, as well as a list of fuels recovered on the developed mini Condensate Processing Plant (CPP) of the Mastakh gas-condensate field of Yakutiya.

A possibility to recover commercial motor gasoline as well as diesel oil quality improvement is shown. This can be achieved due to application of newly developed high-silica zeolite, manufactured with the use of available nitrogen-containing organic compounds, after their modification by aromatizing and isomerized metal-containing components.

The solution of ecologic and economic problems of regions rich in oil, gas and gas condensate located at distance from industrial centers has both important environmental and enormous national economic significance. Canada, USA and Russian Federation faced these problems in the last quarter of the XX century.

The processing of low-sulfur gas-condensate raw material, recovered simultaneously during natural gas production and preparation to transportation at distant fields of Eastern Siberia and the North turned out to be the most promising.

As a result of creative collaboration of the AZNIPIgas and the Yakutgasprom Production Association the joint efforts of their specialists (Aliyeva R.B., Mekhtiyev J.S., Semenov P.N. and others) put an end to the contamination of environment, in other words, a very vulnerable ecology of huge gas production region and eliminated the possibility of recurrence of such incidents in future. On the other hand significant amount of the following fuel was recovered out of pollutants (that is out of gas condensate) by means of their most efficient processing: motor gasoline A-76 brand, completely meeting all the requirements, diesel oil of wide fractional composition and fuel oil. All of them met the developed technical specifications in force, in other words quality requirements (TU 51-116-82; TU 51-856-79; TU 51-815-78).

It is significant that gasoline, recovered on the above equipment, was defined by octane level 76 based on the motor method, boiling start 36 °C – boiling end 156 °C and also the

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following hydrocarbon type content: aromatics – 2.45, naphthenes – 51.2, paraffin – 46.35% of mass.

The experience of the Mastakh gas-condensate field of Yakutiya was later used creating more improved processing equipment in other regions of Siberia and the North with active participation of VNII gas in this project, which resulted in the creation of more perfect condensate processing plants.

The analysis of physicochemical characteristics of low-sulfur gas condensate gasoline fractions and their correlation with the appropriate octane numbers on many fields of Siberia showed that high content of isometric structure paraffin and naphthene hydrocarbon play significant role here.

By the example of gas condensates of a number of fields (Mastakh, Ust-Viluy, Sredniy-Viluy and others) we have shown the possibility of compounding appropriate gasoline fractions recovered on condensate processing equipment by products of catalytic processing of unbalanced part of these fractions based on modified high-silica zeolite, manufactured to inventor's certificate USSR # 1721013.

It is indicated that the use of unbalanced, that is low-octane gasoline fraction, recovered, for example, on a mini Condensate Processing Plant (CPP) of Mastakh gas condensate field, can be used as raw material for catalytic processing.

At the same time the unbalanced part of the reaction products is presented as a separate stream recycle into the reactor, where it is processed together with the above initial gasoline fraction. Part of it can be used for other purposes as well.

Gasoline fraction compounded by the extracted catalysate provides the possibility to obtain required quantities of mix gasoline with octane numbers 76 and 85.3 based on motor method and containing benzene hydrocarbon ≤ 10 % of mass depending on used initial gasoline fraction of a gas condensate field.

Thus, the possibility of highly efficient recovery of gasoline A-76 as well as AI-93 (research method) on a mini CPP is shown under the conditions of gas condensate field of Siberia and the North, improving at the same time qualitative characteristics of diesel oil of wide fractional composition (increasing temperature of its boiling start up to $\geq 80^{\circ}\text{C}$, and also its viscosity characteristics).

**INFLUENCE OF SUPPORT NATURE AND PREPARATION METHOD OF
INDIUM-CONTAINING CATALYSTS ON THEIR ACTIVITY IN NO SCR BY
LIGHT HYDROCARBONS**

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It was shown that activity of the In-containing catalysts in SCR of NO_x - C_1 - C_4 hydrocarbons depends on the amount of indium, nature of the support and preparation method. The $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts exhibited the high H_2O -tolerance.

The problem of NO_x reduction in lean conditions (SCR-process) in the presence of water steam and SO_2 , is still under conversation. The attractive feature of the indium containing catalysts is their tolerance to SO_2 and H_2O [1].

In this study we have investigated the influence of support nature (Al_2O_3 and ZrO_2) and the method of indium loading in support's matrix (wet-impregnation and coprecipitation) on catalytic performance in SCR of NO by light hydrocarbons (methane, propane-butane mixture, propene) also in the presence of SO_2 and H_2O .

The results of electron microscopy investigations (TEM-125K) testify to polydisperse frame of support: the conglomerates of the carrier of the different size (up to 100-120 nm) consist of 10 nm size Al_2O_3 particles and also separate single crystals. According to the data of XRD powder diffraction the main Al_2O_3 phase is γ - Al_2O_3 , and ZrO_2 the monocline modification.

The activity of indium-doped alumina catalysts on SCR of NO by propene was strongly dependent on the In_2O_3 loading. The maximum NO conversion was obtained for the 2.5wt. % and 5wt. % In_2O_3 -contained catalysts (conversion of NO was 67-69% at 350-400°C). Activity decreasing of coprecipitated sample (5% In_2O_3 -95% Al_2O_3) in SCR of NO by C_3H_8 in comparing with analogous one, obtained by impregnation of In_2O_3 from the solution, can be explained by the lower value of the In_2O_3 surface concentration in it. 5% $\text{In}_2\text{O}_3/\text{ZrO}_2$ sample showed the low activity for NO reduction by propene (maximum of NO conversion is 11% at 400 °C).

Fig.1 (curves 1, 3, 4) presents the temperature dependences of NO conversion for 5% $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst with different hydrocarbons: methane, propane-butane mixture and propene. They indicate a higher activity of olefins in comparison with alkanes in SCR process

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[2]. Note that the activity of impregnated catalysts did not change in the presence of H₂O. For coprecipitated sample (5%In₂O₃-95%Al₂O₃) the catalytic activity slightly decreases. This is probably caused by competitive adsorption of H₂O with NO and C₃H₆ at the catalyst active sites.

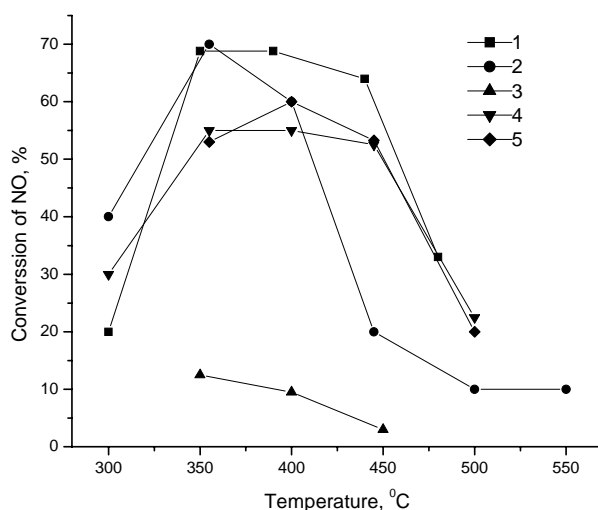


Fig.1. Temperature dependences of NO conversion for 5%In₂O₃/Al₂O₃ catalyst in SCR by HC in reaction mixtures /0.05% NO + 0.09% C_nH_m + 5%O₂/:
1 - C₃H₆; 2 - C₃H₆ + 9%H₂O; 3 - CH₄ ;
4 - C₃H₈- C₄H₁₀; 5 -C₃H₆ +0.01% SO₂.

The observed decreasing of the activity of 5%In₂O₃/Al₂O₃ in the presence of SO₂ in reaction feed (fig. 1. curves 1, 5) can be the result of aluminum and indium sulfates formation with following decreasing of concentration of active sites on the surface [3].

Thus, the activity of indium containing catalysts in SCR of NO by light hydrocarbons depends on the amount of indium, nature of the support and preparation method. No activity decreasing due to the presence of H₂O was observed for In₂O₃/Al₂O₃ samples, while to SO₂ the samples are less tolerant.

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MIGRATION OF SUPPORTED PLATINUM METALS IN CATALYSTS FOR AUTOMOTIVE EXHAUST PURIFICATION

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Ageing of a Pt-Rh catalyst for automotive exhaust purification causes migration of Pt and Rh for a distance of several microns. The migration results in the formation of Pt-Rh alloy from Pt and Rh particles separated from each other in the initial catalyst. Moreover, raising the temperature and time of the catalyst ageing leads to the transport of platinum metals from Al₂O₃ to CeO₂ that is accompanied by significant increase in dispersion of supported alloy particles.

More than one platinum metal (typically, platinum and rhodium) are often introduced into automotive exhaust purification catalysts in order to improve their performance. To avoid alloying of platinum and rhodium that might affect negatively on the performance of the automotive catalysts, metals are deposited on a substrate in separate layers.

Such a two-layer Pt-Rh catalyst (B08/40) designed and produced by Ural Electrochemical Integrated Plant, was studied by TEM, XPS, XRD and BET methods after ageing at different conditions. The inner layer of the catalyst in its initial state attached directly to a cordierite substrate consists of a mixture of CeO₂ and Pt supported on γ -Al₂O₃. The outer layer contains Rh supported on γ -Al₂O₃. Such distribution of the components given by a preparation procedure guarantees the separation of Rh particles from Pt and CeO₂ by distance of about several tens of microns. Before physical-chemical characterization, samples of the B08/40 catalyst were aged:

- in a motor testing bench for 4, 10 or 20 hours at reaction gas temperature of 1000 ± 50°C;
- in a motor vehicle during the run of 120000 km;
- in hydrothermal conditions (HTC) at 980 °C.

A washcoat layer containing active components of the catalyst was detached from the substrate after ageing procedures and was then studied with physical-chemical methods mentioned above.

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In spite of significant spatial separation of Pt and Rh in the initial catalyst, only Pt-Rh alloy particles are detected by TEM-EDX method in all aged samples. XRD data confirms the formation of Pt-Rh alloy. Two types of Pt-Rh particles are observed by TEM. Bimetallic particles of the first type are located on Al₂O₃ and have the mean size of ~ 10 nm or above (Table 1). Particles of the second type belong to the surface of CeO₂ and are characterized by the mean size of several nanometers. Statistical analysis of the TEM images indicates that relative population of the Pt-Rh alloy particles supported on alumina and ceria depends on the ageing conditions. The main portion of Pt-Rh particles in the sample aged in the motor vehicle or at the HTC conditions is supported on the surface of Al₂O₃. After the ageing in the motor testing bench during 4 or 10 hours, Pt-Rh particles are detected both on Al₂O₃ and CeO₂. Raising the ageing time till 20 hours makes it impossible to find Pt-Rh particles on the Al₂O₃. Thus, the ageing in the motor testing bench results in gradual transport of platinum metals from Al₂O₃ to CeO₂.

Table 1. The mean size (in nm) of Pt-Rh particles supported on the surface of Al₂O₃ and CeO₂ in B08/40 catalyst depending on the ageing conditions

Ageing condition	Motor vehicle, 120000 km	Motor testing bench			HTC 980°C
		4 hours	10 hours	20 hours	
Pt-Rh/Al ₂ O ₃	~ 50	~ 10	8.5	-	5-10
Pt-Rh/CeO ₂	-	1-2	3.5	3.5	-

According to XPS data, platinum is in metallic state in all samples studied. Rhodium is undetectable due to a small Rh loading and overlapping of Rh photoemission lines with lines of other elements. The [Pt]/[Al] atomic ratios calculated from XPS data for the aged samples are shown in Table 2. The largest [Pt]/[Al] ratios are obtained for the samples aged in the motor testing bench. This observation is in accordance with relatively high contribution of small Pt-Rh particles located on ceria in these samples compared with the samples aged in motor vehicle and at the HTC conditions where relatively large alumina-supported alloy particles are present solely (Table 1). In this connection, the monotonic increase in the [Pt]/[Al] atomic ratio with the ageing duration in the motor testing bench can be explained by increase in the contribution of small alloy particles due to migration of platinum metals from alumina to ceria.

Table 2. The [Pt]/[Al] atomic ratios calculated for samples of B08/40 catalyst aged in various conditions

Ageing condition	Motor vehicle, 120000 km	Motor testing bench			HTC 980°C
		4 hours	10 hours	20 hours	
[Pt]/[Al]	0.0053	0.013	0.016	0.023	0.0056

Thus, this work shows that ageing of catalysts for automotive exhaust purification, including a prolonged operation on board of a motor vehicle, causes migration of supported platinum metals for a distance of several microns. For the catalyst studied in this work, the migration results in the formation of Pt-Rh alloy particles. Raising the temperature and time of the catalyst ageing leads to the transport of platinum and rhodium from Al₂O₃ to CeO₂ that is accompanied by significant increase in dispersion of supported alloy particles.

**THE STUDY OF CATALYTIC ACTIVITY OF TRANSITION METAL OXIDES IN
THE PROCESS OF HETEROGENOUS CATALYTIC OXIDATION OF
HALOGENATED ORGANIC COMPOUNDS**

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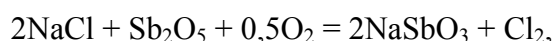
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The chloride-ions oxidation in patterns of NaCl-Me_xO_y-O₂(N₂) was investigated with the methods of DT-TG, XRD and chemical analyses. Thermal destructon of antimony oxide (V) was studied in temperature range 350-600 °C, reaction order and apparent activation energy of thermal destruction were determined.

During deep oxidation of halogenated hydrocarbons, chloride-ions accumulating occurs. This causes the increasing of melting point and viscosity of the melt and as a result the catalytic activity reducing. Chlorine emission occurs if transition metal oxide is added to the catalytic blend [1].

To correlate rates of halogenated organic substances destruction and chloride-ions oxidation and to study the mechanisms of those reactions blends of NaCl-Me_xO_y were investigated under air or nitrogen. Reaction constant of Cl⁻ oxidation in the pattern of NaCl-Sb₂O₅ (20 wt. %) in air described with equation



are calculated according pseudo first reaction order is $(0.39 \pm 0.06) \cdot 10^{-5} \text{ s}^{-1}$. For comparison, reaction rate of Cl⁻ oxidation in the melt NaCl-V₂O₅ is $(0.69 \pm 0.04) \cdot 10^{-4} \text{ s}^{-1}$. The presence of NaSbO₃ in reaction products has been shown with XRD analysis. In addition, Sb₆O₁₃ и Sb₂O₄ formed during the reaction. These results agree with literature data [2]. The amount of chlorine evolving from NaCl-Sb₂O₅ depends on flowrate and type of feeding gas (fig.).

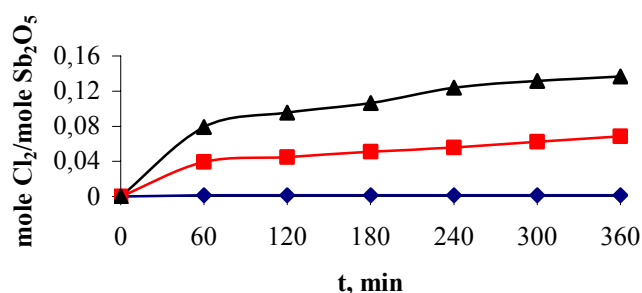


Fig. The amount of chlorine evolved from NaCl-Sb₂O₅ (20 wt. %) with the heating from 20 to 820 °C an then at 820 °C under flow of air
 ● – 2.5 l/h;
 ■ – 1.7 l/h;
 nitrogen
 ◆ – 2.5 l/h.

Under nitrogen atmosphere chlorine formation lapses in about 60 minutes – in this case reaction runs with only participation of oxygen contained in Sb_2O_5 .

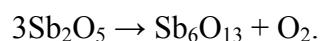
Antimony oxide (V) in temperature range 350-950 °C transforms to Sb_2O_3 through several stages which are accompanied by oxygen emissions [3]. The influence of copper and vanadium oxides additions are shown in the table.

Table

The amount of chlorine (g/g of melt) evolved from $\text{NaCl-Me}_x\text{O}_y$ under air flow over the blend surface (2.5 l/h) and heating from 20 to 820 °C and then at 820 °C

$\text{NaCl-V}_2\text{O}_5$ (20 wt. %)	0.0227
$\text{NaCl-(Sb}_2\text{O}_5 + \text{V}_2\text{O}_5)$ 20 wt. %, $\text{V}_2\text{O}_5 : \text{Sb}_2\text{O}_5 = 1:1$ mol.	0.0107
$\text{NaCl-Sb}_2\text{O}_5$ (20 wt. %)	0.0058
$\text{NaCl-(Sb}_2\text{O}_5 + \text{V}_2\text{O}_5 + \text{CuO})$ 20 wt. %, $\text{V}_2\text{O}_5 : \text{Sb}_2\text{O}_5 : \text{CuO} = 1:1:1$ mol.	0.0011

Destruction of the Sb_2O_5 in temperature range 350-600 °C in air (nitrogen) atmosphere was studied by the differential thermal analysis. It was shown that DTA patterns and weight losses (O_2 emissions) are the same regardless of type of feeding gas (air or N_2). According to calculations destruction reaction can be described with following equation



The presence of Sb_6O_{13} is determined by XRD analysis. This reaction has the zeroth order, apparent activation energy is 23 kJ/mole. Such low magnitude of activation energy indicates the reaction is limited by oxygen diffusion.

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IMPROVEMENT OF ECOLOGICAL PROPERTIES OF REFORMING GASOLINE

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The new standards applied in USA and several countries of Europe (Eurosuper -3, 4, 5) for engine fuels in relation with strengthening of ecological requirements consider an abrupt alteration of component content, as well as restrictions of content of aromatic hydrocarbons (especially benzene), olefins, sulfur, absence of tetraethyl of lead. By these requirements the content of sulfur in the gasoline will be decreased to 10-30 ppm, the benzene content to 0-1 % ob.

The influence of reforming gasoline (which is the main component in general gasoline fund) on the quality of commercial gasoline is not unambiguous: the octane number increases, but the deterioration of ecological indicators due to higher content of benzene and aromatic hydrocarbons take place.

Analysis of individual hydrocarbon content of the raw material of reforming process (fr. 85-180 °C) separated by rectification on lab installation indicates that the content of benzene in it is 0 %, the content of benzene forming hydrocarbons is up to 0.669 % mass.

The gasoline fraction 85-180 °C was subjected to catalytic reforming at temperatures of 475, 490, 520 °C, at pressure 8 atm., the volume inlet of raw material 1.0 h⁻¹ and quantity of hydric gas 1000 l per liter of raw material, in presence of industrial catalyst R-132 at model plant with loading of catalyst 150 cm³.

The obtained results indicate that with increasing of temperature from 475 up to 520 °C at the constancy of the other parameters of the process the output of aromatic hydrocarbons and benzene increases from 68.5 up to 87 % and from 0.6 up to 2.6 %, respectively, while the octane number increases from 86.5 up to 96 by engine method in pure form.

The content of benzene at mild regime (t = 475 °C) is 0.6 % mass. against 6.7 % obtained for analogical industrial fraction.

In reformates the aromatic hydrocarbons are concentrated in higher-boiling fractions. The fraction boiling up to 100 °C in reforming gasoline has an octane number 71-73 in spite of required 77-78 p. by m.m.

With aim to achieve the homogenous distribution of octane number by fractions, to decrease content of aromatic hydrocarbons in reforming gasoline the separated light gasoline fraction with s.b. $-85\text{ }^{\circ}\text{C}$, is suggested to be used as a component into reformat after adding the octane increasing less toxic additives. The octane number of fraction with s.b. $-85\text{ }^{\circ}\text{C}$, thus, increases from 69.5 up to 79 p. by engine method.

So, on the basis of reformat and light gasoline fraction with s.b. $-85\text{ }^{\circ}\text{C}$ for decrease of the content of general aromatics, benzene, as well as for increase of distribution uniformity of octane number by fractions in commercial gasoline A-92 we suggest:

- clear fractioning of raw material reforming with output of light fraction (fr. with s.b. $-85\text{ }^{\circ}\text{C}$) containing benzene-forming hydrocarbons;
- the conduction of reforming at a lower temperature (mild regime) in order to prevent cyclodehydrogenation of paraffin and demethylation of high-molecular aromatic hydrocarbons leading to formation of benzene;
- usage of light gasoline fraction (fr. s.b. $-85\text{ }^{\circ}\text{C}$) after adding the octane increasing additive as a component into the reformat.

The obtained gasoline meets the international standards.

**THE CATALYTIC UTILIZATION PROCESS OF SULFUR DIOXIDE OF EXIT
GASES OF THE ENTERPRISES OF NONFERROUS METALLURGY WITH
OBTAINING OF ELEMENTARY SULFUR**

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Researches on revealing an opportunity of practical application of modified clinoptilolite were carried out as the catalyst for restoration process of sulfur dioxide by gaseous reducers. Optimum conditions of carrying out restoration process of sulfur dioxide by hydrogen (on cobaltclinoptilolite) and hydrogen sulfide (on ironcontaining clinoptilolite) were determined. Kinetic studies were carried out and kinetic parameters of both processes were determined.

The restoration process of sulfur dioxide of exit gases of the enterprises of nonferrous metallurgy by gaseous reducers (natural gas and products of its conversion, carbon monoxide, hydrogen sulfide) is possible to carry out by thermal and catalytic way. Introduction of high-temperature (homogeneous) technology of obtaining of sulfur from gases of furnaces suspended melting and Vanyukov melting on Norilsk Mountain - metallurgical combine /Russia/ has allowed revealing the same essential lacks which are inherent also by other thermal methods.

Introduction of low-temperature (catalytic) process of obtaining of sulfur from exit gases autogenous melting will allow to reduce temperature of process up to 700 °C (instead of 1250-1300 °C at a high-temperature way), to reduce the consumption of natural gas on 25-30 %, to provide increase of a degree of extraction of sulfur from gases from 75-80 % up to 90-95 %, to get sulfur of the first-rate quality, to increase reliability of work of a reactor.

The basic group of the catalysts, used for restoration of sulfur dioxide by all gaseous reducers, represents the catalysts, containing aluminum oxide, as in pure state, so as in various compounds, natural and synthetic. Modified by cobalt and nickel alumooxide catalysts, suggested by us, have passed successful tests on the Ryazan testing - experimental metallurgical plant (in 1989) and the initial data for designing pilot installations were given.

Presently we carry out researches on revealing an opportunity of practical application of zeolites, as more available and cheap for restoration of sulfur dioxide by gaseous reducers.

The active catalyst for restoration process of sulfur dioxide with hydrogen (as a conversion product of natural gas) was developed on the basis of natural zeolite -

clinoptilolite (Aydag deposit, Azerbaijan), containing 10 mas.% of cobalt. Optimum conditions of carrying out process were determined: an interval of temperature 350-400 °C, volumetric speed 1000-2000 hrs.⁻¹; ratio H₂/SO₂=2,1-2,2; the output of sulfur makes 79-96 % (at restoration of 20 and 100 % SO₂, accordingly). The adequate mathematical model of process as the linear equation of regress was made. Using statistical processing of the obtained data on PC by means of a package of statistical programs Excel in Windows 98, there was calculated the degree of correlation between an output of sulfur and a degree of crystallinity of samples of clinoptilolite, inciderated at various temperatures: it is positive and equal to $k=+0,79$. On the basis of experimental results the probable scheme of conversion of sulfur dioxide was suggested and the kinetic model, describing the restoration process of sulfur dioxide by hydrogen on cobaltclinoptilolite was developed. For the first time it was experimentally established, that catalytic activity of clinoptilolite containing catalyst in this process was connected with concentration of exchange cations and the modified transition metals structure. Dependence of catalytic activity of the catalyst on its acidity was established. In the presence of e strong Brensted acid centers in zeolite the activity decreases.

For the restoration process of sulfur dioxide by hydrogen sulfide (of Claus process) there was suggested ironcontaining (10 mas.%) clinoptilolite, optimum conditions were determined and the five- stage mechanism of process was suggested. Kinetic parameters were determined.

Thus, application of the modified zeolites as catalysts is perspective and carrying out researches on the integrated laboratory installation will determine success of transition from the theory to practice.

CATALYTIC PYROLYSIS OF 1,2-DICHLOROETHANE

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Pyrolysis of 1,2-dichloroethane in the presence of heterogeneous catalyst has been studied. The catalyst contains platinum as active component and glass-fiber carrier.

Due to the addition of the catalyst mentioned the conversion is increased at the same cleavage temperature, or the cleavage temperature is reduced at the same conversion.

It is well known that vinyl chloride monomer (VCM) can be produced from 1,2-dichloroethane (commercial name ethylene dichloride (EDC)) by splitting off a molecule of hydrogen chloride. The process is typically accomplished by heating EDC, in the absence of catalyst at high temperature (500-550 °C) and pressure (20-40 kg/cm²). A serious disadvantage of the standard process is need of large amount of costly heat energy and rapid deposition of solid by-products (coke) on the reactor tubes that limits running time before cleaning.

To reduce the problems observed in the standard pyrolytic process, various catalysts were proposed [1-5]. We studied pyrolysis of EDC in the presence of fiber glass catalyst with platinum as an active component. All experiments were carried out in laboratory continuous-flow system at elevated temperatures and atmospheric pressure in the presence (or absence) of catalyst. EDC with purity over 99.9 % was used. The catalyst fibers were located in a pyrolytic zone of reactor in three beds with two-centimeter intervals. The reaction mixtures were analyzed by GLC.

It was found that EDC conversion in the presence of catalyst is 10% higher at the same temperature of the process. Thus, the selectivity of process did not vary essentially. The application of the catalyst made it possible to reduce the cleavage temperature to 450 °C. EDC conversion increased from 48 % to 69 % at reaction temperature 480 °C. Selectivity of the process was reduced slightly, though. Thus, the concentration of undesired chloroprene increased two-fold. New by-products of reaction in the presence of the catalyst were not found.

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**PHOTOCATALYTIC REMOVAL OF NITROGEN OXIDE FROM AIR ON BULK
AND ALUMINA-SUPPORTED TiO₂**

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Alumina-supported TiO₂ samples with Ti loadings 3-96 wt % of were prepared by sol-gel and incipient wetness impregnation methods. The samples were characterized by XAFS and UV-Vis techniques. An anatase-like phase was present at higher Ti content (>50 %), whereas for Ti-loadings <23%, the Ti coordination number decreased indicating the formation of isolated or clustered Ti ions. Bulk TiO₂ Degussa P-25 and TiO₂/Al₂O₃ (10-50 % Ti) were tested on photocatalytic oxidation of NO to NO₂ by oxygen in flow experiments. It is concluded that the presence of surface TiO₂-like phase is a prerequisite for the occurrence of photo-deNO_x reactions. The photoadsorption capacity of TiO₂/Al₂O₃ to NO_x is considerably higher than that of bulk TiO₂.

A series of titanium-containing materials with different Ti contents (3-96 %) and host matrices were synthesized. The introduction of Ti-containing species into alumina was performed by incipient wetness impregnation and sol-gel methods. For the sake of comparison, a series of zeolite samples (ZSM-5 and AlSiPenta) with TiO₂ contents < 4 wt% was obtained by CVD. The samples synthesized were characterized by UV-VIS spectroscopy and XAFS to estimate the size of encapsulated nanoparticles, coordination number (CN) of titanium ions and, in some cases, when an EXAFS analysis was possible, the lengths of Ti-O bonds.

It is found that local environment and coordination number of Ti⁴⁺ ions incorporated into alumina and ZSM-5 are governed both by the titanium content and the nature of the support. At higher Ti content (> 50 wt%) in TiO₂/Al₂O₃, an anatase-like phase with CN = 6 is formed which is stable up to 500 °C. As the Ti content diminishes from 23 to 3 wt%, the CN gradually decreases and a blue shift of the UV-light absorption edge increases. Most likely, Ti ions in such samples have different coordination numbers. In Ti-ZSM-5 obtained by CVD, the CN of Ti ions is close to 4, and the degree of their dispersion is highest. Isolated Ti ions or small clusters are predominant in these samples.

Bulk titania Degussa P-25 and TiO₂/Al₂O₃ with Ti content 10, 20 and 50 wt % of Ti were tested in flow experiments on photocatalytic NO elimination from a gas mixture of NO (50 ppm), O₂ (8 vol. %) and N₂ (balance) at atmospheric pressure under irradiation of two

Black light UV lamps. The only reaction product is NO_2 . Time dependencies of NO and $\text{NO}_x = \text{NO} + \text{NO}_2$ concentrations in absence and presence of UV-irradiation were measured. Typically, just after the start of irradiation, the outlet NO_x concentration rapidly drops to its minimum value ($\text{NO}_x(\text{min})$), remains at this minimum level for a certain time (retention time, $t(\text{ret})$), and then slowly grows approaching a steady state in which $\text{NO}_x(\text{ss})$ is nearly equal to the inlet NO concentration.

For bulk TiO_2 , it is found that an increase of the pretreatment temperature in a flow of dry air from 623 to 773 K has no effect on NO conversion and on the NO/NO_2 ratio at the steady state, but extends $t(\text{ret})$ by a factor of 3 and decreases $\text{NO}_x(\text{min})$. Saturation of the gas flow with water vapor further significantly improves characteristics of the photo-de NO_x process: Thermodesorption experiments show that mostly NO_2 and some NO desorb from TiO_2 (maximum desorption rate at 650-680 K) after photoreaction indicating the formation of surface nitrate and nitrite species. Heating TiO_2 in an air flow at 600-773 K completely restores its initial activity.

A comparison of the photoadsorption capacity to NO_x for TiO_2 -based catalysts is given in the table. NO oxidation does not occur under UV-irradiation of $\text{TiO}_2/\text{Al}_2\text{O}_3$ at TiO_2 loadings below approximately 10 wt%. It appears that the presence of a TiO_2 -like phase is a prerequisite for the occurrence of the photo-de NO_x reactions. On the other hand, the photoadsorption capacity is considerably higher for 20 % and 50 % $\text{TiO}_2/\text{Al}_2\text{O}_3$ samples compared to bulk TiO_2 . TPD experiments show the presence of two NO_x desorption peaks at ~ 200 °C and above 250 °C. The low-temperature peak can be attributed to weakly bounded NO_x species on the alumina surface, whereas at higher temperatures NO_x species are desorbed from TiO_2 surface. It should be emphasized that the amount of the NO_x desorbing above 250°C increases with TiO_2 content.

Table. Photoadsorption capacity of TiO₂-based catalysts

Sample	NO _x storage capacity, μmole/g _{cat}	Specific NO _x storage capacity, mole NO _x /mole TiO ₂
Bulk TiO ₂	59.6	0.00476
50% TiO ₂ /Al ₂ O ₃	320.5	0.05122
20% TiO ₂ /Al ₂ O ₃	179.7	0.07177
10% TiO ₂ /Al ₂ O ₃	0	0

Acknowledgement. This work was supported by INTAS under grant 03-51-6088 and by the Russian Foundation for Basic Research under grant 05-03-32490.

USE OF THE NITROGEN-CONTAINING CARBON MATERIALS IN THE ENVIROMENTAL CATALYSIS

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The aim of the work is studying of the properties of nitrogen-containing carbon materials as the carrier in red-ox reactions of the enviromental catalysis. The active carbons (AC-N) SKN, KAU and the active carbon similar in content of nitrogen 1-6 % on mass was study. The introduction of nitrogen in matrix of AC-N results in essential increase of activity of catalysts. Dependence of catalytic activity on the content of nitrogen on the carrier has extreme character. The carbon matrix with 3 mas. % of nitrogen in structure of sample is most active.

Now carbon materials are widely applied in heterogeneous catalysis, basically, as the carrier of catalytically active phase. It is caused, first of all, by donor-acceptor properties of a carbon matrix, and, in the second, by suitable structure of the carrier - the high specific surface, advanced porous structure and an opportunity to vary rather easy these properties. Donor-acceptor properties of a carbon matrix depends on chemistry of a surface of carbon materials - structure and amount of surface groups and on presence of heteroatoms in structure of a carbon matrix.

Oxidized carbons are manufactured by carbon materials processing by various oxidizers (nitric acid, peroxide of hydrogen, oxygen of air) at high temperatures, or by removal of surface oxygen groups at calcination of the samples at high temperatures in the inert gases. Such variation of the structure of surface groups of carbon materials results in change of donor-acceptor properties of carbon matrix that should have effect on catalytic properties of samples in oxidation-reduction reactions.

One more successful way to change donor-acceptor properties of carbon materials is introduction of heteroatoms (for example, nitrogen) in the structure of a carbon matrix. Thus also there is a change of donor-acceptor properties of carbon materials which may be used in some reactions of ecological catalysis, such as oxidation of CO and clearing of gases from hydrogen sulphide with formation of elemental sulfur.

Carbon materials in these processes may be used as carriers of active elements or directly as catalysts.

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The aim of this work is to study the catalytic properties of the nitrogen-containing carbon materials in the model and red-ox reactions of the environmental catalysis.

The active carbons (AC) SKN, KAU and the active carbon cloth (ACC) were studied. Nitrogen-containing activated carbon SKN was produced by step pyrolysis of a vinylpyridine-divinylbenzene copolymer at 350-900 °C in an inert atmosphere, and further steam activation at 850 °C. For preparation of AC-N it was used AC KAU prepared from peach and apricot stones. Initial carbon KAU and ACC were obtained by a procedure, specially designed by the authors: impregnation with water solution of melamine in various relations melamine:carbon, then subjected to heat treatment at 800°C in a stream of argon. As a result the KAU-N and ACC-N with content of nitrogen 1 - 6 % on mass were obtained.

The introduction of nitrogen in a matrix of AC-N results in essential increase of activity of catalysts. Dependence of catalytic activity on the contents of nitrogen on the carrier has extreme character. The carbon samples with the 3 mas. % of nitrogen in structure are most active.

CATALYTIC BEHAVIOUR OF VARIOUS Fe/ZSM-5 ZEOLITES TOWARDS WET H₂O₂ OXIDATION (CWPO) OF RHODAMINE G DYE IN AQUEOUS PHASE

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It was demonstrated that catalytic activity of Fe/ZSM-5 zeolites in wet H₂O₂ oxidation (CWPO) of Rhodamine G dye in aqueous medium depends on nature, location, dispersion of iron species, as well as redox ability of iron forming those species. The impact of preparative aspects on the catalytic properties of catalysts is discussed in details along with their characterizations by ICP, H₂ TPR, X-ray diffraction, in-situ FT-IR and electron microscopy.

Fenton's reagent (Fe²⁺/Fe³⁺/H₂O₂) is one of the most common homogeneous oxidative catalytic systems utilized for degradation of dyes. However, the need for removing the precipitated catalyst significantly increases the overall costs. This drawback can be overcome by application of heterogeneous catalysts such as iron-containing zeolites. It is generally known that the preparation method and further treatment has a profound influence on the iron speciation and therefore may affect the final catalytic properties to a great extent. Here, we report on our efforts to study the influence of such parameters on the performance towards CWPO of *Rhodamine G* dye in water over Fe/ZSM-5 catalysts.

Catalysts with different iron loading were prepared via conventional ion exchange (CE), improved aqueous ion exchange (IE) methods and by direct incorporation of Fe in the silicalite framework during synthesis. For Fe/ZSM-5(IE), iron is predominantly present in the form of well-dispersed Fe²⁺ ions, while Fe/ZSM-5(CE) and Fe-isomorphously substituted materials contain mainly ferric ions as small oligonuclear (FeO)_n clusters. The difference in catalytic behaviour in CWPO of the various catalysts is related to the different nature of the iron species. The catalyst activity strongly depends on the zeolite surface properties and composition, the dispersion of iron, the reaction temperature and parameters as pH and H₂O₂ addition rate. At 323 K, quasi-neutral pH (4.9), short contact time, a catalyst concentration of 1.0 g.l⁻¹ and a peroxide addition rate of 41.2 mmol h⁻¹, Fe/ZSM-5 prepared *via* the improved procedure and isomorphous substitution allow total degradation of the dye accompanied by removal of 80% of TOC without notable leaching of Fe ions.

HDS DEGREE AND HYDROGENATION ACTIVITY OF NiMoV/ γ -Al₂O₃ HYDROTREATING CATALYSTS

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In this work influence of additives of vanadium compounds on the activity of NiMo/ γ -Al₂O₃ catalysts was studied. A series of NiMoV/ γ -Al₂O₃ catalysts has been prepared by means of different chemical methods for determination of optimal content of vanadium. The extremely high activity was achieved with the catalyst with the mole ratio Mo : V = 12. Totality of the experimental data suggests that in hydrothermal stage of preparation of NiMoV/ γ -Al₂O₃ catalysts precede the formation of heteropolycompound (HPC) VMo₁₂ type. Influence of additive of Sn on the catalytic activity of the supported NiMo/ γ -Al₂O₃ catalysts was investigation also. The results suggest that during the preparation of NiMoSn/ γ -Al₂O₃ catalysts precede the formation and that this compound increase the catalytic activity NiMo/ γ -Al₂O₃ catalysts.

Addition into NiMo/ γ -Al₂O₃ catalysts various inorganic compounds is the possibility of the increasing their hydrodesulfurization (HDS) and hydrogenation activity. This P, As, B, Ti, Si and others compounds. Character of change of catalytic activity in case of each element can be various; the reasons of this change can be various, but once can have a uniform explanation.

In this work influence of additives vanadium compounds on the activity of NiMo/ γ -Al₂O₃ catalysts was studied [1]. A series of NiMoV/ γ -Al₂O₃ catalysts has been prepared by means of different chemical methods for determination optimal content of vanadium. In each series of NiMoV/ γ -Al₂O₃ catalysts has been prepared the sample of comparison (NiMo/ γ -Al₂O₃). The catalytic properties of these catalysts were determined in the reactions hydrogenation of polycyclic aromatic compounds (PCAC) and HDS in following conditions: hydrogen pressure 3.5 MPa, hydrogen : feedstock ratio 450 Nl/l, volume velocity feedstock 2.5 h⁻¹, temperatures 340, 360, 390 and 410 °C. Before screening, the catalyst was sulfided at 350 °C for 2 h with 2 % H₂S/H₂ mixture gas and packed to the reactor ($V = 8 \text{ cm}^3$). The feedstock was the straight-run diesel fraction containing 2.29 wt % sulfur, and 6.47 wt % PCAC. The extremely high activity was achieved with the catalyst with the mole ratio Mo : V = 12. The extraction of MoO₃ of catalysts by means of solution of NH₃, and extraction NiO solution of HCl [2] was carried out. The quantity of extracted metals is at the most for the most active catalyst. The differential thermal analysis of the samples of the catalysts after test, which consists coke

and sulfur, was spent (figure). The quantity of coke is a minimum for the most active catalyst. Totality of the experimental data suggests that in hydrothermal stage of preparation of NiMoV/ γ -Al₂O₃ catalysts precede the formation of heteropolycompound (HPC) VMo₁₂ type. By analogy to others HPC be take the synthesis (NH₄)_x[V(MoO₃)₁₂]·nH₂O assumed formula. In this compound FTIR-spectra was found the HPC characteristic bands. (NH₄)_x[V(MoO₃)₁₂]·nH₂O was use for preparation of the NiMoV/ γ -Al₂O₃ catalyst (sample 1). The catalyst with the same contents metals has been prepared from (NH₄)₆Mo₇O₂₄•4H₂O and NH₄VO₃ (sample 2). The sample of comparison was NiMo/ γ -Al₂O₃ (sample 3). The maximal activities in HDS and in hydrogenation of PCAC have the sample 1, the minimal activity have the sample 3.

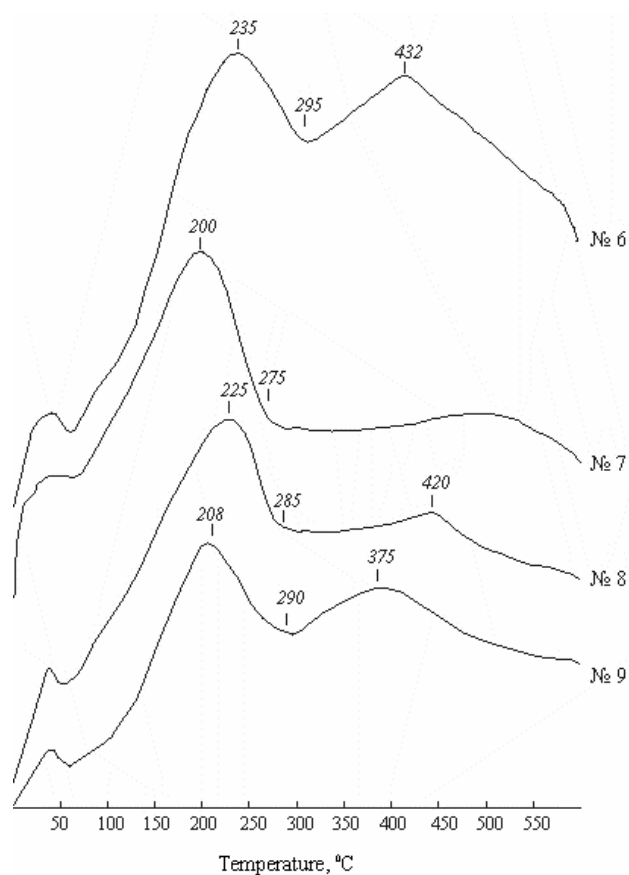


Fig. DTA spectra of the catalysts after test

Influence additive of Sn on the catalytic activity of the supported NiMo/ γ -Al₂O₃ catalysts were investigation. The results suggest that during of the preparation of NiMoSn/ γ -Al₂O₃ catalysts precede the formation and that this compound increase the catalytic activity NiMo/ γ -Al₂O₃ catalysts. Earlier was shown that modification the Ni(Co)Mo/ γ -Al₂O₃ catalysts with additions P and Si lead to formation corresponding HPC. Probably, formation of HPC occurs at introduction of the majority of other additives offered for catalysts of hydrotreating, i.e. the reason of increase of catalytic activity is universal; however it demands experimental check.

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**DESTRUCTIVE OXIDATION OF HALOGENATED ORGANIC SUBSTANCES ON
EARTH ALKALI OXIDES AND HYDROXIDES**

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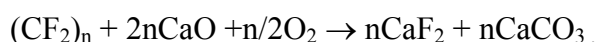
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Interactions of fluorinated liquid M-1 and polyvinylchloride (PVC) with CaO, MgO and Ca(OH)₂ were studied. The composition of reactions products and kinetic parameters were determined. The influence of various factors on bonding degree of halogen evolved from organic compound to ecologically nonhazardous compounds was established. It was shown, that interaction between mentioned halogenated organic compounds and alkali earth oxides (hydroxides) runs according to “solid – gas” reaction type with participation of gaseous oxidation products

Utilization of residues of solid and liquid halogenated organic compounds production is complicated problem which is not completely solved nowadays. It was shown, that fluorinated liquid M-1 is destructed with high efficiency in molten catalyst (LiCl-NaCl-KCl) eut.+15 wt.% V₂O₅ [1]. However, during the reaction emissions of F₂, HF and CO₂ to the gas phase occur. At the same time, these emissions can be avoided in reaction between polytetrafluoroethylene and earth alkali oxides (hydroxides) in the presence of oxygen [2].

With the help of DT-TG analysis behavior of M-1 at nonisothermal conditions was studied. Weight losses occurred at 90-240 °C are connected with evaporating of this liquid. Reaction between M-1 vapor and calcium oxide in the presence of atmospheric oxygen in flow reactor at 450-550 °C produces nontoxic compounds – calcium fluoride and carbonate according to the equation



bonding degree of the fluorine in this reaction depending on process conditions is 98-99 %, bonding degree of the carbon – 92-95 %.

Thermal-oxidative destruction of PVC and its reactions with MgO and Ca(OH)₂ runs through several stages in temperature rage 190-450 °C and includes stage of dehydrochlorination and consequent interaction of evolved HCl with alkali earth metal oxide (or hydroxide).

Kinetics of interaction of PVC with MgO and Ca(OH)₂ was studied in temperature range 290-320 °C and mass ratio (M) MgO (Ca(OH)₂) : polymer of 2 and 3. Dependence of polymer Cl₂ bonding degree with time is S-shaped, this indicates the acceleration of metal chlorides forming at the initial period caused by autoacceleration of PVC dehydrochlorination process [3].

Specific reaction rates of Ca and Mg chlorides formation to the period of reaction rate decline (table 1, 2). Effective activation energy of CaCl_2 formation process was calculated with various Cl_2 bonding degree, it was 70 ± 7 kJ/mole ($M=2$, $\alpha=20\%$) and 52 ± 6 kJ/mole ($M=3$, $\alpha=30\%$), and MgCl_2 , равная 60 ± 5 kJ/mole ($M=2$, $\alpha=20\%$) and 39 ± 6 kJ/mole ($M=3$, $\alpha=30\%$)

Table 1

Dependence of specific reaction rate of CaCl_2 formation (W) with Cl_2 bonding degree (α) at various temperatures and relation of $\text{Ca}(\text{OH})_2/\text{ПВХ}$ (M)

		$W \cdot 10^2$, mmole $\text{CaCl}_2/(\text{g Ca}(\text{OH})_2 \cdot \text{min})$							
		$M = 2$				$M = 3$			
α , %	t , °C	290	300	310	320	290	300	310	320
	10		13,9	17,0	19,5	24,9	9,2	11,6	14,5
20		18,0	21,1	25,5	34,7	12,3	14,3	17,2	24,3
30		19,5	24,6	31,2	44,2	15,1	17,2	19,8	28,4
40		-	27,0	37,5	52,8	17,1	20,0	22,6	32,9

Table 2

Dependence of specific reaction rate of MgCl_2 formation (W) with Cl_2 bonding degree (α) at various temperatures and relation of $\text{MgO}/\text{ПВХ}$ (M)

		$W \cdot 10^2$, mmole $\text{MgCl}_2/(\text{g MgO} \cdot \text{min})$							
		$M = 2$				$M = 3$			
α , %	t , °C	290	300	310	320	290	300	310	320
	10		6,7	7,8	8,5	11,6	5,8	6,0	6,9
20		9,8	11,6	13,2	18,3	8,5	9,5	10,8	12,0
30		-	15,9	18,0	25,3	11,2	13,0	14,1	15,3

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IMPROVING THE PROCESS OF HYDROREFINING WITH ECOLOGICALLY CLEAN DIESEL FUEL OUTCOME

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The work concerns the development of the improved hydrofining system of diesel cuts for the purpose of production of low-sulfur content fuel. There are described the results of the AGKD-205A catalyst used for production of diesel fuel with sulfur content less than 0,1 %, and at the same time the catalyst service cycle was increased.

Operation characteristics for decreasing fuel sulfur content to 50 and 10 ppm were revealed. The dependence of the quality of the outcome products on the feed quality and the process conditions were also revealed. The production techniques of ecologically clean diesel fuel with the new catalysts AGKD-400BN and AGKD-400AN were developed.

The JSC «Angarsk Petrochemical Company» active hydrofining unit L-24/6 is operated under pressure of 40 Bar (g) and feed volumetric flow rate of 5,0 h⁻¹ with the use of diesel cuts including 30 % of secondary gas oils as the feed. At 330-350 °C catalyst AGKD-205A has been working for 45 months without regeneration providing residual sulfur content less than 0.1 %. Decreasing feed volumetric flow rate down to 3,0 h⁻¹ enables to decrease hydrogenate sulfur content down to 0.03-0.04 %. In recent years in connection with toughening of environmental requirements it became necessary to convert operational units to making diesel fuels that meet Euro-3 and Euro-4 quality specifications and at the same time the sulfur content should not exceed 50 and 100 ppm respectively, as for multiring aromatic hydrocarbons their content should be less than 11.0%. The mentioned problems were a challenge in creating a brand new catalyst composition. In accordance with the research results the brand new catalysts AGKD-400BN and AGKD-400AN were developed. The preparation technique used consisted in supporting on medium granule impregnating modified with boron and phosphorus compounds.

The pilot tests of catalyst AGKD-400BN upon various processing characteristics are shown in Table 1. It is clear that it is necessary to decrease volumetric flow rate down to 1,5-2,0 h⁻¹ to have the end product with sulfur content less than 50 ppm under pressure of 40-50 Bar (g). In order to keep diesel fuel sulfur content less than 10 ppm it is necessary to increase the pressure in the reactor up to 70 Bar (g). It should be mentioned that using a

special catalyst system with protective layer FOIR-1 enabled to decrease the content of multiring aromatic hydrocarbons from 14,5 to 5-7 % depending on the process conditions.

Table 1

Process characteristics effect on the depth of extraction of sulfur compounds during various processing modes.

Virgin diesel fraction, S=0,62%				Mix feed			
P, Bar (g)	V _C , h ⁻¹	T, °C	S, ppm	P, Bar (g)	V _C , h ⁻¹	T, °C	S, ppm
40	1,5	330	62	40	1,5	340	92
40	4,0	330	365	40	1,5	350	48
50	2,0	340	40	40	1,5	350	34
50	4,0	340	91	50	1,5	340	38
70	2,0	330	23	50	1,5	350	46
70	2,0	330	9	70	1,5	340	9
70	2,0	340	5	70	1,5	350	6

Catalysts of grade AGKD are also recommended to be used for hydrofining of gasoline fractions and vacuum gas oil.

Hydrofining of vacuum gas oil at the pressure of 5,0 MPa and feed volumetric flow rate of 1,0 h⁻¹ enable to decrease the amount of sulfur compounds to less than 0.1 % at the same time decreases the amount of nitrogen and coke compounds by 35-40 %. The above mentioned method is favorable for the behavior of the catalyst cracking process. Use of such feed enables to increase the gasoline output by 1,5-2 % at the same time decreasing the amount of such waste product as sulfur and nitrogen compounds and carbons disposed into the atmosphere.

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VANADIA/GLASS-FIBER CATALYST FOR HYDROGEN SULFIDE SELECTIVE
OXIDATION TO SULFUR BY OXYGEN

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Novel catalysts, comprising vanadia pentoxide supported on micro-fibrous glass fibers, were prepared and tested in hydrogen sulfide selective oxidation reaction. The observed performance was found to be compatible with existing commercial catalysts. The proposed catalyst looks practically attractive due to its unusual geometrical and physical properties.

Hydrogen sulfide selective oxidation into elemental sulfur is currently applied in commercial practice for cleanup of Claus units tail gases and desulfurization of natural gas. The efficiency of such processes is in a major extent defined by efficiency (selectivity, activity, catalytic and mechanical stability etc.) of the applied catalysts. Though significant progress in this area is achieved [1], further developments and investigation of new catalytic system are still actual.

The current study was devoted to development of new catalyst for H₂S oxidation, prepared on the base of micro-fibrous glass-fiber (GF) support [2]. Vanadia was chosen as an active material due to its highest activity in hydrogen sulfide oxidation reaction among all other oxides [3]. The research included preparation of V₂O₅/GF catalyst samples with vanadia loading of 0.34 and 0.77 % mass.

The lab experimental tests performed in temperature region from 200 to 250 °C with mixture containing 1% H₂S and 0.9% O₂ (balance – helium) showed good performance of the catalyst – the observed conversion was as high as 90-95 % with selectivity into sulfur not lower than 95 %.

Though the achieved level of catalyst efficiency does not exceed the level of existing commercial catalysts, the proposed catalyst looks practically attractive due to its unusual geometrical and physical properties (mechanical flexibility giving the way for construction of novel compact reactors, low pressure drop and decreased mass transfer limitations).

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UTILIZATION OF WASTE BIOMASS AND OBTAINING ZrO_2 WITH LARGE SURFACE AREA

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Sawdust impregnated by $ZrO(NO_3)_2$ in the ratios of 1/1, 1/10 (ZrO_2 /sawdust,w/w) were used as starting materials for preparation of ZrO_2 . Optimum parameters of the treatment were selected (carbonization: 500 °C, 1 hour; calcinations: 600 °C, 4 hours). The following values for surface area were obtained: 13 and 38 m²/g for the ratios ZrO_2 /sawdust=1/1 and 1/10 correspondingly. ZrO_2 was also prepared by direct calcination of precursor (sawdust/ $ZrO(NO_3)_2$) in the ratio 1/10. Its surface area was 33 m²/g.

The surface of ZrO_2 exhibits acid-base and reductive-oxidative properties at the same time, that's why zirconia finds application in numerous catalytic processes (isomerization, polymerization, polycondensation of organic compounds, etc.) [1]. There are plenty of methods for ZrO_2 obtaining, which require the use of chemical agents and besides produce wastewater while washing off residual matter. Searching for processes that use fewer toxic chemicals and produce less waste while using less energy is of great importance nowadays. That is one of the basic concepts of green chemistry. Besides utilization of biomass has a certain environmental contribution as well. So obtaining of metal oxides via pyrolysis of sawdust impregnated by salts of metals has two advantages. The first one is utilization of biomass and obtaining carbon black, which is widely applied. And the second is obtaining metal oxides, which are expected to be promising catalysts due to unique properties that appear as a result of nontraditional method of synthesis [2]. The aim of the present work is to study physicochemical properties of zirconia, obtained in the result of catalytical pyrolysis of pinewood sawdust. Sawdust (particle size varying from 0.63 to 1.25 mm) impregnated by $ZrO(NO_3)_2$ were used as a precursor. Samples were prepared in the ratios of 1/1, 1/10 (ZrO_2 /sawdust, w/w). In the end of pyrolysis product contained carbon black and zirconia (partially reduced). To obtain pure ZrO_2 calcination of these products was performed. Conditions for the pyrolysis and calcinations were chosen according to the data, achieved by Differential Thermal Analysis (DTA) and Thermogravimetry (TG). The process of pyrolysis was carried out under a nitrogen atmosphere and was characterized by the following parameters: dynamic segment - heating rate 15 °/min up to 500 °C, isothermal segment – temperature 500 °C, isothermal time 1 hour. For calcinations, samples were held at 600 °C for

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4 hours in an air atmosphere. Under the chosen treatment conditions all processes were completely finished, i.e. weight of the samples stayed constant with increasing temperature and time of treatment. After calcination samples looked like white fibres. Scanning Electron Microscopy (SEM) data show that obtained zirconium oxide reproduces the structure of sawdust. The less amount of zirconia is contained in the initial sample – the more porous and bulk is the structure of the final oxide. Data on the surface area of obtained zirconia depending on the composition of the initial mixture are presented in Table 1.

Table1

ZrO ₂ /sawdust, w/w	BET SA, m ² /g
1/1	13
1/10	38

Thus, decreasing the amount of zirconia in initial samples leads to obtaining larger surface area of ZrO₂. To find out if two-stage process (pyrolysis and calcinations) is important, ZrO₂ was prepared by calcination of precursor (ZrO₂/sawdust=1/10, 600 °C 4 hours) avoiding carbonization stage. The surface area of this oxide appeared to be a few less than that of the one of the same ratio (1/10) obtained in the two-stage process and amounted to 33 m²/g. It can be explained in the following way: during carbonization ZrO₂ is fixed on the surface of carbon and thus carbon support prevents from oxide agglomeration. The fiber structure of zirconia and possible presence of mineral matter in the sawdust [3], that contribute to the composition of final ZrO₂, can influence its catalytic properties.

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**MECHANOCHEMISTRY AND MECHANO-CATALYTIC PROCESSES IN
ENVIRONMENTAL PROTECTION**

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Mechanochemical activation of solids and catalysts in particular is well known. In our works were shown that mechanochemical treatment VPO catalysts and introduction of promoters permitted to increase catalytic activity and selectivity of these compositions in n-butane partial oxidation to maleic anhydride and decrease the pollution of CO, CO₂, CH₃COOH, C₂H₃COOH, etc. Mechanochemical synthesis of V-Ti-O composition from vanadia and titania allows to prepare the catalyst, which oxidizes o-xylene at 280-300 °C with selectivity up to 90 %, that decreases the formation of pollutants.

In this study the mechanochemical treatment (Fritsch-6) was used for modification of Cu-Ce-O catalyst properties prepared by citrate method. It was shown that treatment medium (air, Ar, H₂O, C₂H₅OH) influences on surface morphology and valence state of the elements. The Cu-Ce-O catalyst treated in ethanol was very active in CO, C₆H₆ and C₃H₈ total oxidation. As a result of treatment the total CO conversion is reached at 85 °C and retains on this level more than 100 h. This catalyst is active and selective in CO oxidation in excess of hydrogen (1 % CO, 1 % O₂, 98 % H₂) at low temperature.

The established [1] at mechanochemical treatment of metal oxides effect of water decomposition with formation of hydrogen peroxide was used for mechano-catalytic oxidation of aromatic hydrocarbons traces in the water. The data of chromato-mass-spectrometry show that after treatment in the presence of catalyst of water containing 1 vol. % of hydrocarbon (benzene, toluene, o-xylene, phenol) its concentration decreases up to 40 ppm. The formation of CO₂ which was one product of reaction after treatment was established. The nature of catalyst determines the rate of oxidation reaction.

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**PROGRAMMING OF SIMULATION PACKAGE HYSYS FOR CALCULATION OF
FISHER-TROPSCH SYNTHESIS**

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New imitating methods of FT synthesis simulation are introduced. The basis of this method is the high-level simulation package «HYSYS» affording to possibility of intuitive and interactive programming with programming of reactor and catalysts properties.

The simulation model of FT synthesis for two types of catalysts and three types of reactors is built. Comparisons by means of model Fe and Co-catalysts in various reactors and under various conditions are realized. It was demonstrated that initial conditions for synthesis gas production and the selective production of target compounds demand determine the catalyst and reactor combination.

The simulation model of Fisher-Tropsch (FT) synthesis, based on «HYSYS» simulation package is introduced. It includes systems of compression and heating of synthesis gas and primary separation of products, the organization of recycling blocks from the standard set, and the reactor block realized by means of the built in programming language possibilities. Kinetic models were made for Fe and Co catalysts and for three types of reactors: ARGE with fixed bed of the catalysts, Syntrol with a fluidized bed of the catalysts and slurry. The model affords opportunities to set arbitrary value of the majority of process parameters. It is possible to set broadly the most efficient combinations by initial conditions variations. Also it is possible to modify the incorporated mathematical model of flow and the catalyst-reactor combination with the purpose of model generation for other reactors and catalysts or to increase the model accuracy. The influence of activity, selectivity and catalyst type on economic efficiency of stage FT is discussed. Calculations were made for three types of reactors and a number of initial conditions. Results obtained for selectivity and product yield are in good correlation with the industrial production parameters. Selectivity for C₅₊ in a tubular reactor with the Co catalyst (and other typical conditions for FT synthesis) was found 74 % (in commercial plants of 70-83 %). The calculated synthesis gas consumption is about 175 (syngas vol.,m³/reactor vol.,m³) for 210°C, this number is in good agreement with the consumption for commercial FT processes.

CATALYTIC INTENSIFICATION OF NATURAL GAS HYDRATES FORMATION

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Chemical-technology approaches allowing catalytic intensification of the prevention processes of gas hydrates formation at motion of gas-liquid stream of natural gas in system natural gas well – gas wire have been worked up. Technological regimes of treatment of gas stream have been determined.

The features of continuous influence of inhibitory factors on process of gas flow at low temperatures and relatively high pressure differences ΔP have been studied by using of technological installation modulating the system natural gas well – gas wire.

The dependences of gas quantity flowing from installation on ΔP at low temperatures have been studied with consideration of real states of process of gas – liquid phase flowing. Obtained experimental data for non-inhibitory and inhibitory processes have been compared under the same conditions.

It was established that when intensification of prevention process of gas hydrates formation is high, at the same thermodynamic conditions due to continuous treatment of gas by methanol and polyvinyl alcohol, which are absorbed into the bentonite, by glycol, absorbed into the silica gel, and by calcium chloride.

Vibration conjugate process of gas hydrates formation and break-up taking place in gas-liquid system with using of membrane electrode of electrochemical cell has been found.

Periodic vibrations of membrane potential have been found at treatment of natural gas by methanol at low temperatures. Periodic character of vibration effect is determined by conjugate variations of equilibrium concentrations of components gas hydrates formation and break – up.

Dependence of potential value on time of gas stream current across gas pipeline is given in temperature interval 262 –293 K and at pressures from 0.15 to 0.5 MPa.

**DEVELOPMENT OF MODELS OF CATALYTIC PROCESSES OF SEWAGE
TREATMENT**

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Technological modes of carrying out of deep cleaning catalytic processes of real sewage from toxic impurities, in particular from heavy metals ions by use of applied mathematics methods are proved.

Intensive development of power, chemical, oil, machine-building and other industries results in increase of industrial toxic emissions. Local pollutions as a result of emissions of the industrial enterprises in many cases surpass the maximum permissible sanitary norms. E.g. works connected to an oil recovery, have led to pollution of huge territories of the Azerbaijan Republic, including Caspian Sea.

Development of scientific bases of optimization of operating practices of industrial sewage treatment will allow to liquidate the harmful impurities. It is necessary for preservation of the environment to increase the clearing and sewage quality degree.

During modeling a real process of sewage treatment from polluting impurities we need to build more and more complex models. It demands in return the application of applied mathematics methods for process of clearing of liquids. General theory and technology of sewage treatment, in particular, from heavy metals now are absent.

Achievement of an object provides for solution of the following problems: a) Research of laws of influence of various technological and physical and chemical parameters on efficiency of waste treatment from heavy metals; b) Development of the effective reagents, allowing to remove from sewage cations of toxic heavy metals; c) Construction of statistical models of an experimental material on clearing concrete sewage.

The basic results consist in the following. Modern ways of intensified sewage treatment from heavy metals ions are developed. Optimum compositions of reagents besieging harmful impurities are determined. Quantitative dependences between parameters of process of sewage treatment in real conditions are established. The models, allowing to carry out mode modeling of sewage treatment processes from heavy metals toxic ions are developed.

ABOUT WHAT MANUFACTURE OF CATALYSTS IS SILENT?**Bakaev A.Ya.***LLC Schelkovsky Catalyst Plant, Schelkovo, Russia**E-mail: scat2006@yandex.ru*

By the example of the Schelkovsky catalyst plant the renewal of the catalyst manufacture after recession in 90th years has been shown. It is stated that in 2006 the production capacity has reached approximately 40 % related to 1990. The aspects of problems arising in capacity increasing due to severe competition on the catalyst market, insufficient technical maintenance and economic complexities concerning a science and manufacture has been head lighted. The decision on creation of the Russian Catalyst Association due combining numerous catalyst manufacturers has been made.

Scientific bases of catalysis, catalytic processes and contact devices, ways of preparation of catalysts - mainstreams of scientific activity of Georgy Konstantinovich Borekov.

Besides, he could unite a science and manufacture, having created a special designing-technological bureau of catalysts and a number of catalysts manufactures. Therefore, due to academician Borekov G.K. in the middle of 80th years it has been created in Voskresensk large-tonnage manufacture sulfur acid vanadium pent oxide catalysts which capacity approximately on 70 % provided needs of all country for the given catalysts. Catalysts IC-1-4 and IC-1-6 till now are successfully maintained in industry, but, unfortunately, already almost for 10 years are not produced.

Recession of industrial production in the country in 90th years has touched also manufacture of catalysts because of which the significant approximately 80 % reduction of delivery amounts of domestic catalysts has been taken place.

To return the lost positions it is very difficult in a competition to such international firms, as Engelhard, Shell, BASF, etc.

Becoming of manufacture of catalysts in the Russian Federation is complicated with the following reasons:

- dissociation numerous catalysts manufacture;
- economic complexities concerning a science and manufactures;
- difficulties in technical maintenance and selection of personnel.

However, it is possible to note growth of volume of manufacture of domestic catalysts last years.

By the example of work of LLC Schelkovsky catalyst plant the increase in volume of release of catalysts (fig. 1) is visible. After 2000 the factory has increased more than twice manufacture spherical aluminum oxide and on his basis manufacture of sorbents, desiccants, catalysts of gas purification. Manufacture of sulfur acid vanadium pent oxide catalysts,

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including high-temperature catalyst SVD on a basis of diatomite from Inza factory of filtering materials is renewed. Manufactures of micro spherical aluminum oxide and on its basis the catalyst for dehydrogenation of hydrocarbons C3 –C5 were created. Manufacture cadmium - calcium phosphate catalyst for acetaldehyde synthesis due to vapor-phase hydrating of acetylene was mastered.

Additionally to the above-stated technological developments a number of technical developments had been applied in the production. So, original dryer CB-O5 for drying powder-like products by capacity up to 30 kg /h on evaporated moisture and thermal efficiencies about 80 % has been created. The equipment for saturation of aggressive substances and the filter for a filtration of low dispersed suspensions are made.

A number of new devices and the equipment, including the tempering furnaces PKG, flexible feed-screw for transportation of raw material and semi products, devices for mixing loose components and batchers were put in to the production.

The production enterprises are not able to solve many questions of the scientific plan which are necessary for successful development of manufacture. Therefore, it is difficult to provide the analysis of catalytic properties of some produced catalysts and development of techniques of the analysis. For example, it is expedient to have a technique of definition of abrasive properties of the catalysts working in fluidized bed, including catalysts for dehydrogenation, oxichlorination, oxidations, etc.

The big successes in development of manufacture of domestic catalysts can be reached, if the Russian catalyst association will be created under entering the interested scientific and industrial branches.

Probably, the decision on creation Russian catalyst association would be welcomed also by Georgy Konstantinovich Boreskov.

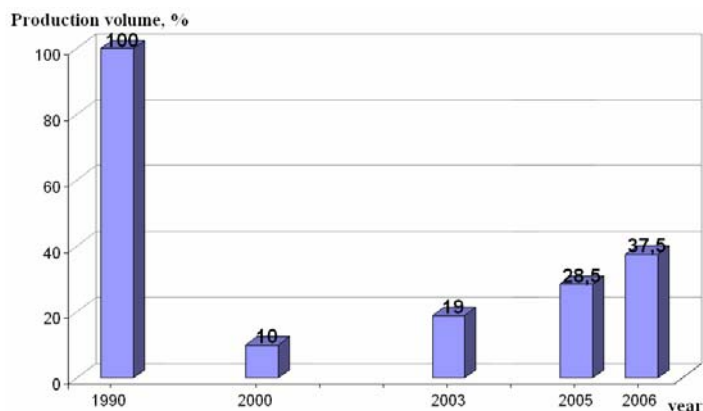


Fig. 1. Production volume on price 2005

OXDATIVE CONVERSION OF HYDROCARBON FUELS TO SYNGAS IN A MONOLITH REACTOR

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Presented is a study of syngas generation from hydrocarbon fuels in a monolith reactor. The processes of methane, isooctane and gasoline partial oxidation over monoliths developed in the Boreskov Institute of Catalysis are considered on the base of theoretical and experimental data. Also discussed are problems emerged from the short contact time reactor operating at a pilot scale.

Hydrogen's unchallenged potential to reduce greenhouse gases and atmospheric pollutants will always make hydrogen a major candidate to fulfil the world energy demand. To avoid a hydrogen supply infrastructure, hydrogen generation in a small scale by processing the conventional fuels near the point of usage may be a good solution. Typically, in the first step of the fuel-processing technologies the hydrocarbon is transferred into a gas containing large quantities of hydrogen and carbon monoxide (syngas). Two leading liquid fuel reforming techniques considered to be the candidates for the small-scale application: direct partial oxidation with air and so called indirect partial oxidation, i.e. combination of partial oxidation and steam reforming in stand-alone catalytic system, viewed as autothermal reforming [1,2] have been studied in the paper. Generally, the partial oxidation of organics to syngas may be expressed as following:



The oxidation processes in a monolith reactors exhibit features not observed in conventional packed bed reactors. Indeed, monoliths operate at 800-1200 ° C with the gas flow velocities of -1 m/s with open channel catalyst structures for effective contact times of a few milliseconds. The composite ceramics and metallic monoliths were employed in the experiments. Platinum and LaNiO₃ along with the Ce-Zr-La-O mixed oxide layer (~10 wt. %) were applied in the washcoat [3]. The experiments on the oxidative conversion of hydrocarbon fuels with air to syngas were conducted in a nearly adiabatic monolith reactor using methane, isooctane and the real gasoline containing 191 hydrocarbon species. The experimental data were compared with the results of accompanying thermodynamic modelling. It was shown that for monoliths under the study, the composition of the product gas is mainly ruled by thermodynamic equilibrium at the exit temperature which is determined by the feed composition and reaction heat evolved (the adiabatic temperature rise) [4]. The thermodynamic equilibrium restrictions on the operational parameters have been outlined on the base of the numerical simulations.

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In spite of the fact that the hydrocarbon reforming reactions proceed quickly and equilibrate rapidly, both radial and axial temperature gradients may arise in monolith reactors. The metallic monolith catalysts employed in the experiments secured an extremely efficient dissipation of the reaction heat through a proper choice of support material and monolith geometry. Nevertheless, in the range of the experimental parameters applied, the longitudinal temperature gradients of about 100 degrees for the partial oxidation reforming and of 60-80 degrees for the gasoline-air-steam (autothermal reforming) feed mixture were experimentally detected in the metallic monoliths. The temperature profiles are results of interplay among kinetics, hydrodynamics, and heat transfer.

Fundamental understanding of the processes occurring in the multiscale levels, their interrelation and interaction is essential to control such intensive, fast reaction in a specific monolith reactor. Information about dynamics of the local temperature and concentrations may have a considerable influence on rational design of both reactor and catalyst as well as the choice of design materials. A dynamic mathematical model with detailed molecular, unsteady-state kinetics for surface reactions was used to simulate the methane partial oxidation process in the monolith reactor.

Also discussed are problems encountered with a short contact time reactor operating at a pilot scale, issues that are largely independent of the catalysts employed. Radiant heat transfer affects the behaviour of the monolith reactor due to transmission of heat against the direction of the feed stream, which otherwise takes place principally by the solid thermal conduction in the wall of reactor and monolith. Moreover, it was found that this particular reactor design is prone to pre-reformation of the fuel prior to catalytic reaction and breakthrough of the feed mixture in the monolith reactor. Feed composition, superficial velocity, and design factors affect these phenomena in monolith reactors [5].

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COMPLEX QUALITY CONTROL SYSTEM FOR AUTOMOTIVE CATALYTIC CONVERTERS

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In this report, we described the results of using, in the factory laboratory environment, the equipment system for testing the quality of catalytic converters produced in the Institute of Catalysis of the Russian Academy of Science. We studied parametric dependences between the catalysts activity, their textured features and physical and chemical conditions of the experiment. We examined the possibility of the kinetics extrapolation of gas conversion in the experimental conditions onto the real operating conditions of catalytic converters. Positive result of the equipment usage was noted.

For our company ROS ECO (catalytic converters), the Boreskov Institute of Catalysis SB RAS, developed a complex system for automotive catalytic converters quality control to accomplish the following tasks:

- prompt in-process control;
- development of new catalysts;
- analysis of consequences of the catalysts accelerated aging to control their operational resource.

This equipment complex includes:

- Flow- circulation system Bi-CATr (CH₄, CO, NO_x) to define the catalytic activity, developed in two operational versions;
- Equipment Bi-CAT flow to define hydrothermal ageing of catalysts;
- Equipment Sorbtometer-M to measure the catalyst specific surface area by single-point (BET) and multipoint methods, with the possibility to study pores distribution by their size;
- Bi-Sorbchemo instrument to define the surface area and dispersity of coated metals by a gas impulsive chemisorbtion method;
- Purification gas system Bi-GAScleaner.

This work is dedicated to the results of using these instruments in the factory lab environment. During the initial stages, the focus was on the solution of methodical tasks.

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With regard to the Bi-CATr instrument, the procedure of carrying out the typical kinetic experiments is still an open issue, as well as is a related issue of the results reproducibility by using standard samples. It is especially important in conditions of bringing model experiments closer to the real ones when the gas composition by its components (CH_4 , O_2 , CO , NO_x) is close to the composition of exhaust gases corresponding to lean and rich fuel mixtures. In such cases, it is probably necessary to take into account the change of order of reactions and kinetic design equations. In our opinion, it is necessary to develop additional software to create and process the experimental data base with a view to detect one- or multiparametric dependences of the catalytic activity on the composition, technological parameters of catalytic synthesis, etc.

In order to use the procedures of measuring the specific surface areas of catalysts and coated metals, there will required standard samples with the known specific surface area and characteristics of porosity. The Bi-Sorbchemo instrument, if slightly modified, will allow to make experiments on thermoprogrammed oxidation and revivification.

As a conclusion, we would like to point out that this equipment complex is operating continuously, and the received results enabled our company to fulfil a number of production task. The joint cooperation has proved to be positive.

INFLUENCE OF DIFFUSION, SIZE AND SHAPE OF CATALYST SURFACE ON REACTION RATE

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Dependence of mean reaction rate and amplitude of oscillations on solid catalyst surface upon its size and shape (plate, cylinder, sphere, torus) was investigated.

Simple schemes of heterogeneous catalytic reactions traditionally act as an objects for investigation of critical phenomena in chemical kinetics. In particular, oscillations of reaction rate, wave propagation processes and pattern formation were revealed for the first time on simple models.

We considered kinetic model corresponding to the «catalytic oscillator + diffusion» system:

$$\begin{aligned}\dot{x}_1 &= 2k_1 z^2 - 2k_{-1} x_1^2 - k_3 x_1 x_2, \\ \dot{x}_2 &= k_2 z - k_{-2} x_2 - k_3 x_1 x_2 + D(z \nabla^2 x_2 - x_2 \nabla^2 z), \\ \dot{x}_3 &= k_4 z - k_{-4} x_3.\end{aligned}\tag{1}$$

where x_1, x_2, x_3 are the surface coverages of interim substances, $z = 1 - x_1 - x_2 - x_3$, k_s and k_{-s} are adsorption and desorption rate constants of stage s , D – diffusion factor.

Differential equations system (1) was solved numerically with the next parameter values: $k_1 = 2,5$; $k_{-1} = 1$; $k_2 = 1$; $k_{-2} = 0,1$; $k_3 = 10$; $k_4 = 0,0675$; $k_{-4} = 0,022$. If $D = 0$ then this model corresponds to the «catalytic oscillator» in oscillating mode. Boundary conditions were added to equations system (1) depending on catalyst shape. Peculiarities of numerical integration algorithms for different catalyst shapes (plate, cylinder, sphere, torus) were described in our previous papers. Stability of these algorithms is conditioned by $\Delta t \leq q(\Delta h)^2 / D$, where Δt is a step of integration by time scale, Δh is a step of integration by spacial scale, q is a multiplier of order 10^{-1} . Two different kinds of initial conditions were considered: zero-filled and random-filled surfaces. It turned out that obtained results for sufficiently long process time are not depend on choice of these conditions.

Results of system (1) integration depend on typical time of diffusion $\tau = L^2/D$, where L is a typical linear size of catalyst (width of plate, radius of sphere, cylinder and torus). In our calculations values of τ were changed from 1 sec to 10^8 sec. Mean reaction rates for certain catalyst surface were calculated on every time step with use of formulae:

$$\bar{w}(t) = \frac{k_3}{N} \sum_{i=1}^N [x_1(t)]_i [x_2(t)]_i \quad (N \text{ is a count of integration cells}).$$

The length of time integration interval t_0 as usual was limited in range of 4000–6000 sec. Main period of system (1) oscillations T was changed from 120 sec to 160 sec depending on catalyst shape and value of τ . Maximum entropy spectral analysis was hold on all obtained time series. Mean

reaction rates were calculated in the end of considered time intervals as $W = \frac{1}{T} \int_{t_0-T}^{t_0} \bar{w}(t) dt$ and

mean amplitudes of rate oscillations A_w were estimated. Dependencies of W and A_w from τ were built and analysed for different catalyst shapes.

Main results of our investigations.

1. When $\tau \rightarrow 10^8$, mean amplitudes of oscillations A_w and mean reaction rates W completely coincide for all considered catalyst shapes. Amplitude of oscillations A_w does not change during process. Spectrum of oscillations contains two harmonics with periods varying near 150 sec and 80 sec in depend on catalyst shape.

2. When $\tau \rightarrow 1$, oscillations do not decay on plate, more than that A_w and W increase (for 23% and 14% respectively). Spectrum form does not change essentially, excepting some decreasing of oscillation periods (period of main harmonic decreases from 153 sec to 118 sec).

3. When $\tau \rightarrow 1$, oscillations quickly decay on spherical catalyst surface. Already for $\tau = 10^4$ sec and $t = 2000$ sec oscillations of reaction rate are almost absent ($A_w = 0$). Spectrum of oscillations become complex when τ is decreased, also spectral lines are widen and period of the main harmonic is slightly increased. The main peculiarity of considered catalytic reaction on sphere surface is that when $\tau \rightarrow 1$, mean reaction rate is increased almost twice. This means that when diffusion factor is fixed, catalytic reaction would progress twice faster on smaller particles than on bigger.

4. Investigation results for torus surface require special discussion, because new variable parameter is introduced. It is the mean curvature of torus. Common regularities for torus and sphere are the same: with decreasing of parameter τ oscillations are decayed and reaction rate is increased.

ONE STEP PROCESS FOR HYDROGEN PURIFICATION IN A CYCLIC WATER GAS SHIFT REACTOR

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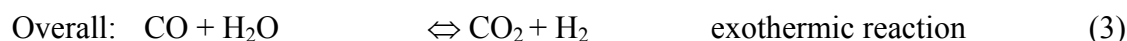
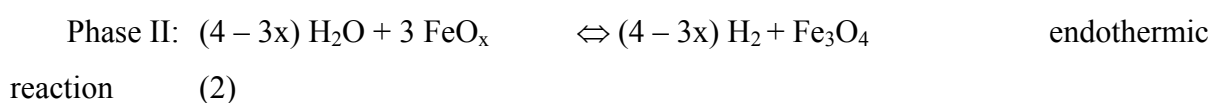
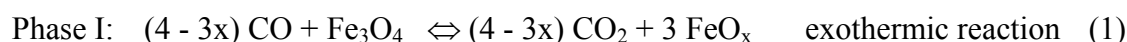
There is much current interest from scientists, engineers, industry and policy makers in the role that hydrogen may play as a synthetic fuel and energy carrier in the future. Hydrogen is seen as having a particularly important future role in the transport sector. Basically, there are two ways to make a vehicle run on hydrogen: by using the hydrogen in an internal combustion engine or by using the hydrogen in a fuel cell.

Fuel cell technology allows the highly efficient conversion of chemical energy into electrical energy without emissions of environmental pollutants, thereby making fuel cells one of the most promising sources for future power generation.

Hydrogen is fuel for all type fuel cells. Steam reforming, partial oxidation and auto-thermal reforming of hydrocarbons, alcohols are the major routes for hydrogen generation. Hydrogen also can be produced by gasification of solid fuels. But all these methods produce a large amount of carbon oxide as a byproduct along with hydrogen. Hydrogen is the fuel for low-temperature fuel cells such as PEMFC and PAFC, which can be obtained by fuel reformulation on-site for stationary applications or on-board for automotive applications. When natural gas or another hydrocarbon fuel is used in a PAFC system, the reformat must be processed by water–gas-shift (WGS) reaction. A PAFC can tolerate about 1–2% CO. When used in a PEMFC, the product gas from water–gas-shift must be further processed to reduce CO to <10 ppm. Typically high and low temperature water gas shift reactors are used in series to minimize the amount of water to be fed to the WGS reactor. Finally, the CO content is reduced to a few ppm in a preferential oxidation reactor, a methanation reactor or a hydrogen membrane separation unit. Hydrogen can be introduced in the PEMFC only after this circuitous procedure of removing CO. Removal of CO to ppm levels from hydrogen stream not only makes the process extremely complex and bulky, but also leads to a decrease of system efficiency.

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As an alternative to the described conventional technology, hydrogen purification from CO can be achieved by a novel cyclic water gas shift reactor which is based on the iron redox cycle. This process can be carried out in one single reactor without any additional post-processing steps for the gas. The process is based on repeated reduction/re-oxidation cycles of iron oxides. During the reduction phase of each cycle, CO reduces the iron oxide Fe_3O_4 to iron in lower oxidation state, FeO_x , according to Eq.(1). During the re-oxidation phase, steam oxidizes FeO_x and simultaneously hydrogen is being produced according to Eq.(2). The product gas contains also steam and can be supplied directly to a PEMFC. The overall reaction of the process is the water gas shift reaction according to Eq.(3).



Overall, this scheme can be seen as a mediated WGS reaction where the CO reducing phase and H_2 production phase are decoupled in time, using catalytically active iron oxide material as a mediator which can store oxygen. This enables the simple and complete removal of carbon monoxide from any syngas feed.

The proposed one step hydrogen purification process has two major advantages:

- i in-situ separation of the two WGS reaction products CO_2 , H_2 and N_2 whereby high-purity hydrogen gas is produced which will give a high Nernstian voltage of the PEM fuel cell.
- ii saving of investment costs by cyclic operation of one single process instead of a sequential train of purification units.

The objective of the present work is to report and discuss experimental performance data for this cyclic hydrogen production process being based on the iron redox cycle. In particular, it will be shown that this process is able to decrease the CO content of syngas down to a level of 10 - 20 ppm which is an acceptable level for PEM fuel cell operation. In order to identify suitable operating conditions for the process cycle, first the reduction phase and the oxidation phase were investigated separately, and then the behavior of several subsequent cycles was elucidated.

FEATURES OF DRAG FACTOR FOR COMPLEX SHAPE CATALYSTS

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The gas-dynamic drag of granular bed in the narrow tube filled with various complex shape catalysts for hydrocarbons reforming now widely used commercially was measured for several values of Reynolds number within the range of 2000÷9000. Data thus obtained are ready for use in tube furnaces design. It is shown that they do not fit conventional correlations presumably due to much more profound effects of granule shape and bed structure than is commonly accepted.

The common present-day tendency when revamping ammonia or methanol plants is to use the existing equipment to the utmost extent. Nowadays the bottleneck stage of such a plant is the tube furnace. Of course, replacement of tubes by those with greater inner diameter can solve this problem partially. Nevertheless, renovating a plant from 1360 mtons per day to, say, 1700 mtons per day may rise pressure drop across a tube furnace to the unallowable level.

According to common approach [1], pressure drop across a granular bed can be calculated using the following expression:

$$\frac{\Delta P}{L} = \frac{\rho w^2}{2} \cdot \frac{a}{\varepsilon^3} f_e$$

где $\Delta P/L$ – pressure drop per unit length, Pa/m; w – superficial linear gas flow velocity (per full bed cross-section), m/c; ρ – gas density, kg/m³; a – specific geometrical surface of the bed, m²/m³; ε – bed porosity; f_e – drag factor.

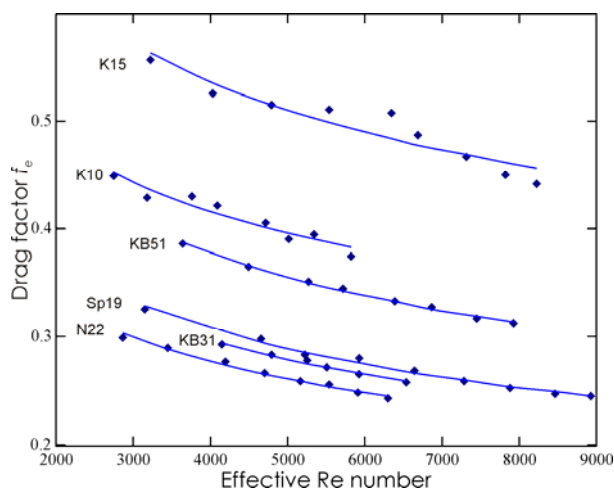


Fig. 1. Drag factor f_e vs. effective Re number.

It is usually accepted that f_e is a universal function of the Re number, the discrepancy for various granule shapes being limited to 30% [1]. Taking into account that the performance of a catalyst bed in hydrocarbons reforming is mainly proportional to a [2], the only way to raise it without simultaneous increase in pressure drop is to enlarge ε which is not the best way out. On the other hand, some commercially running catalysts show too low pressure drops.

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In order to get data on gas-dynamic drag involving only catalyst bed itself, pressure drops vs. flow rates were measured for the granular beds in the steel tube 95 mm in inner diameter and 1.635 m long with the air flow at ambient temperature in it. Flow rates were chosen in such a way that Re number and ρw^2 complex values would be in the same range as in the tube furnace of typical Kellogg ammonia plant. Granules were of various dimensions and shapes, namely, rings, perforated cylinders and spheres. Results are shown in the fig. 1.

Blue diamonds there show values, calculated from experimental data, and solid lines – their fitting using power law. It can be seen that data for rings (K15&K10) differ distinctly from those for perforated cylinders (KB31, KB51, N22) and spheres (Sp19), as well as power law parameters fitting them (exponent values are 0.22 and 0.28, respectively. The difference between rings may be due to effect of their dimensions (outer diameters are 15 mm for K15



Fig. 2. N22 granules

and 10 mm for K10) on the bed structure. The same can be said about KB31 and KB51 (outer diameters are 19 mm and 16 mm, respectively). KB31 has slightly bigger central hole than N22 (shown on fig. 2), but that is enough for the latter to demonstrate the best gas-dynamic properties. Having the sufficient value of a ($427 \text{ m}^2/\text{m}^3$) it is now widely used commercially mainly in Russian ammonia plants.

Power law parameters fitting these data differ essentially from commonly accepted ones[1]. Drag factor values for N22 are surprisingly low. On the whole, the discrepancies in gas-dynamic properties in question are greater than one can expect.

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FIXED BED REACTORS WITH GRADIENT CATALYST**Khanaev V.M., Borisova E.S., Noskov A.S.***Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia**E-mail: khan@catalysis.ru*

In the present paper, we suggest general approach for finding the optimal distribution of the active component along the catalyst bed for various optimization purposes: economy of the total active component amount; improvement of the reactant conversion; optimization of the temperature profile; changes in the reaction selectivity and focus special attention on the theoretical aspect of the problem.

The reactor optimization problem assuming longitudinal non-uniform active component distribution was studied before by several authors (see, for example, [1, 2]), but only particular cases were taking into consideration. The mathematical model describing the effect of non-uniform distribution of active component along the monolith at catalytic oxidation of methane has been suggested in [2], although the authors did not purpose to find the optimal distribution of the active component. As usual, there were considered some supplementary tasks, such as reaching the uniform temperature profile along the catalyst monolith [1], and facilitated ignition of the monolith [3]. The uniform catalyst activity distribution was proved optimal for the first order heterogeneous reaction under isothermal conditions [4]. However, the general problem for process optimization by means of optimal distribution of the active component along the catalyst bed was not formulated; and no analytical studies of it were performed. In the present paper, we suggest general approach for finding the optimal distribution of the active component along the catalyst bed for various optimization purposes and focus special attention on the theoretical aspect of the problem.

High-energy catalytic processes operated in fixed bed reactors are widely used in many fields of Chemical Engineering, so the improvement of specific intensities of such processes to minimize the equipment size and related capital cost, to enhance the reliability is of great importance. The specific features of such processes are reactant concentration gradients through the bed length which may cause considerable temperature gradients in exo-endermic reactions; therefore, the catalysts used for the existing and innovative high-energy catalytic processes must meet severe requirements. The catalytic processes in fixed bed reactors are rather complicated and usually include the chemical reactions, the processes of mass and heat transfer and reactant adsorption/desorption. As a result, a specially organized catalytic fixed bed with non-uniform

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properties (gradient catalysts) may appear more appropriate in some cases than the uniform one.

In the theoretical investigation the attention is being increasingly focused on the complex approach based on the optimization of heat- and mass transfer and of the activity of the whole catalyst bed through the optimal bed packing, granule shape, distribution of the active component, heat conductivity etc., i.e. through creation of some optimal gradient medium for conducting the catalytic process.

Fundamentals for optimization of the spatial bed structure, in particular for optimization of the active component distribution through the bed length, are developed intensively with regard to synthesis of new materials and creation of new methods for arranging reaction beds (for example, in microchannel reactors). The authors of the present paper are the first who proposed to use the variational approach for solving these problems, so they theoretically formulated the problem of a catalytic process optimization by means of non-uniform spatial active sites distribution and obtained the analytic solutions for several cases.

In the present paper, the following points will be discussed:

1. Setting the optimization problem for a catalytic fixed bed reactor, development of theoretical methods for analysis of the obtained mathematical problem with different reaction rate equations under conditions of intensive heat and mass transfer. Theoretical analysis of the influence of gradient catalysts on:

- Economy of the total active component amount;
- Improvement of the reactant conversion;
- Optimization of the temperature profile;
- Changes in the reaction selectivity.

2. Evaluation of influences of optimal active component distribution on the conversion and selectivity in real processes, in particular in the selective oxidation of methane.

Mathematical formulation of each optimization problem under consideration has been developed and the analytical and numerical methods suggested for obtaining the optimal active component distribution through the catalyst bed length. Decreasing the active component loading due to the optimal longitudinal distribution at a given outlet reactant concentration is reduced to solving variational problem for finding the functional minimum. The problem for reaching the maximal outlet reactant conversion at the given active component loading is reduced to solving an analogous variational problem with specific boundary conditions. The question of selectivity improvement also has been considered as

respective variational problem. Mass transfer limitations or non-isothermal temperature profile is a necessary condition for potential optimization of the catalyst distribution along the bed length. Beyond the region of mass-transfer resistance and at a constant catalyst temperature, the reactant conversion is independent of the active component distribution along the bed. Under isothermal conditions with linear dependence of the reaction rate on reactant concentration at a constant mass-transfer coefficient, the uniform distribution is optimal. In the case of non-linear dependence of the reaction rate on reactant concentration the optimal distribution allows the total active component loading to be minimized, the economy being dependent on the mass transfer intensity and increasing with an increase in the total active component amount. The most efficient optimization in adiabatic reactor with exothermic reaction can be achieved if reaction ignition occurs in some point inside the bed. In this case, the use of the optimal activity distribution can facilitate ignition in the inlet part of the catalyst bed that allows considerable decrease of the active component loading in other regions. It has been shown, that some other theoretical problems are to be solved in this case, for example, the problem of multiple solutions that can appear at activity redistribution.

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**DEVELOPMENT OF NEW CATALYSTS AND TECHNOLOGY OF PROPYLENE
PRODUCTION BY PROPANE DEHYDROGENATION IN FLUIDIZED BED**

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The results of development of new high-effective catalysts and technology of propylene production by propane dehydrogenation in fluidized bed are listed below. New catalysts developed by OAO NII “Yarsintez” are characterized by high strength and improved dehydrogenation properties. Reactor system of propylene production is optimized.

Propylene consumption growth in Russia in recent years is 5-7 % per year. That is firstly explained by trend of polypropylene quota increasing and substitution of other polymer materials by polypropylene, which is characteristic feature of Russia like of other countries. Besides that producing of chemical products on the base of propylene such as isopropanol, propylene oxide, acrylonitrile, butyl alcohols and others is stably increased.

Propylene production in Russia like in majority of other countries is based on ethylene (base product) production by pyrolysis of different hydrocarbon feedstock and on oil-refining processes. Capacities of pyrolysis plants and oil refineries are limited and completely used, that's why there are no reserves of propylene production in the country. Propane dehydrogenation is one of the variants of propylene production. This process is especially attractive when cheap propane is available. Propane resources in Russia are great. In this connection construction of complexes of propylene production by propane dehydrogenation is expedient.

The existing commercial processes of propylene production by propane dehydrogenation provide conversion of 30-40 % wt. at selectivity of 80-85 % wt.

In the recent time at OAO NII “Yarsintez” there are obtained such catalysts samples that provide selectivity not below 85 % at conversion of 40-45 % in propane dehydrogenation process. These catalysts possess unique thermal stability. They keep catalytic properties after calcination at 1000⁰C for many hours, what guarantees long operation of new catalysts. The catalysts are characterized by high mechanical strength. In propylene production process the catalyst consumption will not exceed 2,0 kg/t of olefin.

New reactor design is proposed. Reactors optimization and new catalysts allow to reach propane conversion up to 45 % at it volumetric feed rate of 300-400 h⁻¹ and high selectivity.

Operation at high volumetric rates leads to decrease of reactor overall dimensions and to investments lowering.

For optimization of reactors of propane catalytic dehydrogenation with fluidized catalyst bed mathematical model of reactor was developed. It takes into account features of hydrodynamics and thermophysics of fluidized bed sectioned with horizontal grids and with directed catalyst circulation. Process scheme provides for maximum using of heat streams. Process meets the strictest environmental requirements. Comparing with world known commercial processes the new one requires less construction investments. The technology allows using high-power units (more than 400 000 MTPY of propylene).

At OAO NII “Yarsintez” there is catalyst production for fluidized bed dehydrogenation processes with capacity of 1000 MTPY.

**DEVELOPMENT OF COMMERCIAL CATALYST AND REACTOR FOR STYRENE
PRODUCTION PROCESS**

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The researches and industry implementation results on effective catalyst and reactor system for styrene production process are given. The work was done at JSC RI «Yarsintez» and implemented at commercial plants of Russia in 2003-2005. The catalyst is characterized by a new effective chemical composition and new patented geometry of granules. The newest achievements of process simulation, the kinetic data on ethylbenzene thermal decomposition and experience of commercial plants operation have been used at reactor design development. The volume of the commercial production with the application of new catalyst is ~ 30 %, and with the application of new reactor design ~ 48 % against the total styrene production in Russia.

Styrene is one of the major large-capacity products of petroleum chemistry, widely used monomer for polystyrene, plastics and rubbers production. In the period since 2003 the significant changes in the progress of commercial styrene production took place in Russia: according to the technology of JSC RI «Yarsintez» there was started up a new large styrene production by ethylbenzene dehydrogenation under vacuum at JSC «Salavatnefteorgsyntez» with the capacity of 200 000 MTPY in 2003 and the styrene production unit of 100 000 MTPY capacity was modified and started up in 2005 at CSC «Sibur--Khimprom» with further prospect of capacity increase up to 120 000 MTPY with process transfer to the vacuum alternative also.

The great work on the development and improvement of new catalysts and apparatuses design for styrene production process is performed at JSC RI «Yarsintez». As a result the effective alternative of the catalyst KDE-1 for ethylbenzene dehydrogenation was developed. The new combination of all KDE-1 catalyst components allows significantly increase catalyst activity, selectivity and thermal stability. In industry the catalyst provides the selectivity on styrene more than 95 % wt. at pressure below atmospheric one; the catalyst has been patented and is produced at JSC RI «Yarsintez». New granules geometry of KDE-1 catalyst in comparison with catalyst of cylinder shape allows to reduce the hydraulic resistance by ~ 15 % and at the same time to increase the ratio of the external surface to weight unit which additionally increase the catalyst efficiency.

It was performed the optimization of the geometry of styrene reactor system which includes the minimization of apparatus pressure drop, minimization of residence time of vapor-feedstock and reaction mixture in high temperature zones of the system in accordance with requirements of the process thermodynamics and kinetics, and also maximum decrease of reactor system metal consumption and achievement of minimum irregularity level of gas stream flows on catalyst bed. Deflector of the patented shape is installed in the internal perforated cylinder of the catalyst holder (distributing receiver) in order to increase the uniformity of gas stream distribution on catalyst bed and reduce the volume of high temperature sub catalyst zone. As a result it was succeeded to exclude non-catalytic decomposition of ethylbenzene essentially in full and decrease the stream distribution irregularity level at the catalyst bed inlet from ~ 12 %, available earlier, up to less than 4.0 % at CSC «Sibur-Khimprom» at present.

The results of the researches have been used at the development of new units at JSC «Salavatnefteorgsyntez», Salavat, and at CSC «Sibur-Khimprom», Perm.

**PHYSICO-CHEMICAL AND TECHNOLOGICAL BASIS FOR COMPUTER
FORECASTING AND OPTIMIZATION OF PETROCHEMICAL PROCESSES
ON Pt-CATALYSTS**

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Proposed approach to the development of kinetic models of reforming processes represents the sequence of stages of formation of the adequate scheme of mechanism of chemical-technological process with its further kinetic description, on the basis of which non-stationary generalized model of catalytic reactors and of the whole chemical technological system is formed. This model allows not only to efficiently assess the optimal regimes of processes for this raw material but also to forecast the catalyst activity during the intergeneration period and during its entire life time and to solve the problem of complex processing of crude oil at oil-processing plants and of modernization of active commercial plants

Methodological aspects of intellectual systems (IS) formation and their usage for forecasting of petrochemical processes and for training of university students and plant engineering staff on questions connected with physical-chemical and technological laws of industrial processes are considered. The objective necessity of IS using while preparation of engineers according to discontinuous and encyclopaedic principle is shown. The principles of IS creation and realization on the base of generalization of industrial units operation experience for special data processing in computer dialogue regime for users are expounded. Methods of forming of physical-chemical models of heterogenous catalytic processes counting catalyst deactivation are generalized (Fig. 1).

The work sets new approach to the efficiency rising and optimization of commercial benzene production by use of computer modelling based on physical-technical and technological peculiarities combined with the data obtained from the existing production lines. Physical-chemical analyses with computer processing of experimental data from refineries offer solutions for the problems of catalyst tests varied due to peculiarities of raw material and technological process, optimal level for Pt-contact of acid and metallic activity, technological parameters stabilisation and catalyst regeneration period forecasting. A model for commercial benzenes compounding based on calculation of molecular links intensity between the mixture components and efficiency of joint optimization on technological and

production stages of refinery process have been set. A description of training system for both operational and emergency mode for refinery process has also been included.

The approach offered to development intellectual systems represents consecutive set of stages of formation of the adequate circuit of the mechanism of chemical-technological process with subsequent its kinetic description, on the basis of which non-stationary generalised model of contact apparatus and all chemical-technological system as a whole are formed. This model allows not only operative estimation of optimum modes of processes for the given raw material, but also to predict activity of the catalyst during period between regeneration and general service life, to decide a problem of complex processing of petroleum raw material on ORF and modernisation of working plants.

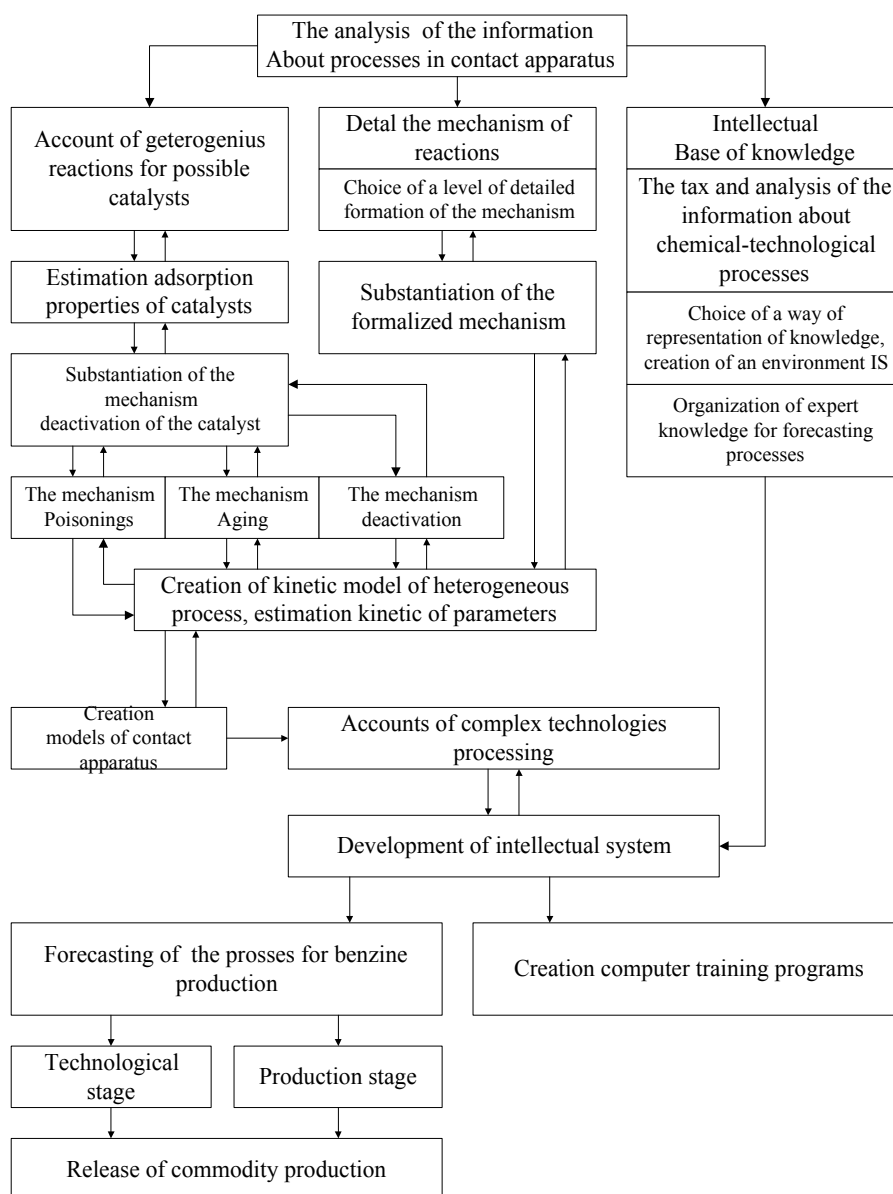


Fig. 1 Basic development cycles and applications IS at chemical-technological processes

**MODELLING OF TEMPERATURE DEPENDENCES OF YIELDS OF PRODUCTS
OF CATALYTIC PROCESSES WITH PARTICIPATION OF HYDROCARBONS**

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In [1] based on the concept «the molecular topological form (MTF)», suggested in [2], has been proposed the term «the skeletal molecular form (SMF)» - set of $3n$ space coordinates

$$F = \{x_i, y_i, z_i\} \quad (i=1, \dots, n) \quad (1)$$

for conformers of compounds with n atoms different from H, including hydrocarbons which will be considered further. As well as in the case of MTF, the set (1) is broken into three classes: (1) atoms at tops of the convex figure, applicable to SMF - "external"; (2) atoms on sides of this figure - "boundary" and (3) "internal atoms" of SMF.

The geometrical figure formed by external atoms in [1] is named visualization of SMF. By analogy to atoms, we shall name external those C-C bounds which are edges of visualization SMF. The working hypothesis is put forward: it is necessary, that given atom of carbon or C-C bounds have to be external for participation of this atom of carbon or C-C bound in catalytic process on an even surface of the catalyst.

The measure of availability of i -th atom ("external") in j -th conformer (with nonplanar SMF) is determined as $p_{ij}=1-(\Omega_{ij}/2\pi)$ (Ω_{ij} – a solid angle in top of visualization of SMF, applicable to this atom), and C-C bounds ("external") between i -th and k -th atoms in this conformer (bounds (i, k)) - as $p_{ik,j}=1-(\alpha_{ik,j}/\pi)$ ($\alpha_{ik,j}$ – two-sided angle at a applicable edge of visualization). If SMF is flat, than $p_{ij}=1-(\alpha_{ij}/\pi)$ (α_{ij} – angle at applicable top of visualization), than availability of all bounds are equal 1. In the case of linear SMF all of bounds are equal and trailer atoms. Availability of atoms and bounds, not being external, are considered to be equal 0.

Then in n -ALKANE, in view of equivalence of i -th and $n-i+1$ -th atoms and bounds $(i, i+1)$ and $(n-i, n-i+1)$, the probability of attack of atom C (C-C bounds) is calculated under formulas

$$p_i = f_i(n) \left(\sum_{j=1}^N \omega_j p_{ij} + \sum_{j=1}^N \omega_j p_{(n-i+1)j} \right) / n, \quad (2)$$

$$p_{ik} = f_i(n-1) \left(\sum_{j=1}^N \omega_j p_{ik,j} + \sum_{j=1}^N \omega_j p_{(n-k+1)(n-i+1),j} \right) / (n-1), \quad (3)$$

where ω_j – a molecular ratio of a conformer j , calculated with the use of distribution Bolcmans, and $f_i(x)=1$, if $x \neq 2i$, and $f_i(x)=0,5$, if $x=2i$. Energy of a conformer relied to be linearly dependent on the number of trans-and 1,3-parallel fragments in them. For a conformer with steric difficulties in a skeleton $\omega_j=0$.

Modelling of temperature dependences of yields of products of catalytic processes with participation of hydrocarbons was maid with use of these probabilities, and also tabulated data (for example, potentials of ionization of radicals). The obtained results correlate with experimental data (a cracking of butane on Pt-Ga/MFI). Modelling of yields of products of hypothetical reaction on the basis of homolytic decomposition of C-C bounds on a surface of the flat catalyst with the subsequent recombination of alkyl radicals for some n-ALKANE as initial substances is carried out

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**OPTIMIZATION OF THE TEMPERATURE DISTRIBUTION IN THE METHANOL
STEAM REFORMER**

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The present work is aimed at studying the effect of microreactor design on the methanol steam reforming (MSR) efficiency. Heat conduction coefficient of the corrugated brass and foam nickel microchannel plates (MCP) depending on the MCP compression ratio was measured. Two microreactors with different schemes of MCP heat supply were studied. Microreactor with copper plates is two times more effective than microreactor without them. Microreactor with internal flat microelectroheaters can produce up to 140 l/h of hydrogen.

Microchannel microreactors have many advantages compared to traditional fixed-bed reactors, including high heat and mass transfer rates and large surface-to-volume ratio. Thus, endothermic reaction of the MSR can be carried out more effectively in the microreactor. The goal of this work is to investigate the effect of microreactor design on the temperature distribution in the microreactor and the catalyst efficiency.

The MCP heat conduction coefficient was measured at different temperatures by means of special self-made setup using comparative approach [1]. As a result we received the heat conduction coefficient value of the corrugated brass and foam nickel MCP at 270 °C versus MCP compression ratio. Heat conduction coefficient of the foam nickel MCP depends on MCP compression ratio, but the MCP compression ratio does not affect the heat conduction coefficient of the corrugated brass MCP. The heat conduction coefficient of the corrugated brass MCP is equal to 4.7 W/(m·K), that is twenty five times smaller than the heat conduction coefficient of bulk brass.

Our investigations of the MSR in the microreactors with hydrogen production more than 50 l/h reveal that heat transfer limitations between MCP's affect the MSR and reduce the hydrogen production. We studied two microreactors with different scheme of MCP heat supply. Both microreactors were made of stainless steel. The Cu/Ce/Al catalyst [2] was deposited on MCP by the method described in [3].

In the first microreactor we insert 2x3 mm corrugated brass MCP's (cross-section of channels is 0.8x0.2 mm). To improve the heating 2 mm copper plates was placed after each

three MCP's. In the second microreactor we used special 0.5 mm flat microelectroheaters instead of copper plates. We found that in both microreactors MSR is carried out more effectively. In the first microreactor the hydrogen production is two times more than that for the microreactor without copper plates. Microreactor with internal flat microelectroheaters reaches hydrogen production equal to 140 l/h at the reaction volume 22 cm³.

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**NON - LINEAR ABSOLUTE FUNCTIONAL MODEL OF SELF-SUSTAINED
DYNAMIC PHENOMENON AND ITS IMPLEMENTATION FOR DESCRIPTION
OF CATALYSIS AND NON-EQUILIBRIUM KINETICS**

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In this paper is presented a new non-linear non-equilibrium dynamic model for explanation of catalytic phenomenon in exothermic reactions. The non –linear absolute functional model of self-sustained dynamic phenomenon describes the change of reaction direction (macroscopic branching) and the stability of the steady state condition of the catalyst. The non-linear absolute functional model of entropy production allows to give alternative description of catalytic phenomenon, selectivity and phase transformations on the basis of macroscopic branching of non-linear processes to the thermodynamic state having maximum value of entropy production.

Introduction

The aim of our present paper is to bring some lights on connection of catalysis and non-equilibrium thermodynamics by non- linear absolute functional model of self-sustained dynamics based on inter- reaction energy distribution regularities which describes a entirely new concept of dynamics connecting the intensivity of change with personal properties of the system.

Non - linear absolute functional model for description of non-equilibrium processes

The change of entropy production rate is described by non-linear absolute functional model. With the increase of entropy the kinetic consistent of the model decreases and the non-equilibrium process selects the way where activation energy is less and recourses of exothermic reactions is more. The change of direction (selectivity) of the reaction is realized through in-situ formation of new active centers which compensate the decrease of entropy production rate in original direction.

During branching of the reaction the irreversible process modifies the intermediate active complex according to the new route through changing of structure of the active complex and the nature of active sties.

The change of kinetic parameters during evaluation of the non equilibrium process to the equilibrium

Close to equilibrium the role of kinetic principles decreases and thermodynamics plays an essential role. By non-linear approach, formation of steady state active sites takes place only

during the reaction. The irreversible process organizes the effective active center to realize maximum entropy production rate. Close to equilibrium the system tries to connect more steps and in this case a process mostly is regulated by associative mechanism. On the way to equilibrium the limitation step changes from the initial step to the down part stages, mostly to desorption step.

Stability phenomenon on the basis of non linear dynamic model and steady state condition of catalysts

By our approach in dynamic equilibrium always there is instability and the stability of the system has no kinetic nature. At high conversion the non-equilibrium nature of the reaction is replaced by the dynamic equilibrium performance and active site to continue the reaction with initial rate involves more reagent molecules to the intermediate complex and the structure of intermediate complex changes. This leads to the lost of available energy fraction of catalyst centers for desorption of components.

Catalyst is not stable if its entropy is less than entropy of reagents. In this case in accordance with the non-linear model the driving force of interaction will be directed to increase of entropy of the catalyst /1-4/.

Conclusion

The non -linear absolute functional model of self-sustained dynamics presented in our study is very useful for practice of catalysis. It has been shown that the phase reconstruction of catalyst at in situ conditions is due to the requirement of irreversible phenomenon which tries to realize entropy production with initial rate. The driving force of the process is the heat translation between “heat reservoirs of the reaction” which plays main role as a internal parameter of the dynamics. Close to equilibrium the role of this parameter decreases. These principles show that at high conversion the reaction always has a trend to change the reaction way for production of more entropy .On the basis of theses principles it is possible to select the optimal condition of reactions and catalysts.

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**DISTINCTION OF DIFFUSION IN CALIBRATED AND CHAOTIC PORES.
COMPUTER SIMULATION AND EXPERIMENT**

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Diffusion of molecules through ordered calibrated mesopores of MCM-41 type materials appears to be accompanied with narrower distribution of molecule retention time comparing to disordered porous space of traditionally prepared materials. This phenomenon was examined both with computer modeling and chromatographic studies of adsorption-diffusion of gas mixtures. Simulation of Knudsen diffusion in pores of different geometry was performed, and average value of retention time and its dispersion were calculated. Obtained diffusion characteristics are used for interpretation of the experimental data.

Computer and analytical modeling of molecular diffusion through porous spaces was elaborated during the last century. As a result, powerful methods for simulation of various mass-transfer processes were developed. Since the named task is mathematically very difficult, analytical approaches are restricted to the models of pores of simple forms, e.g. cylinders. To deal with pores of complex forms computer simulation is necessary. In reality a molecule can leave a pore after only a few contacts with the surface, or can be “lost” in the labyrinth of pores for ambiguous time. It means that the distribution of molecules retention time in various systems of pores can be very different. This has a significant meaning for mass-transfer processes, such as adsorption and catalysis. In the latter case the number of molecule (reagent or product) contacts with a catalyst surface is one of the key factors for selectivity. Since the former case appears to be easier to consider we have started investigation of this field from chromatographic separations as an example of adsorption mass-transfer process.

Diffusion of molecules in calibrated (cylindrical) and disordered (inside random packing of spheres) pores has been performed using molecular dynamic computer simulation in the frame of Knudsen approximation. Ensemble of cylindrical pores is a model of MCM-41 type materials, and a disordered packing of spheres represents porous space for silica gel. Adsorption interaction was modeled by accounting time of adsorption as $\tau = \tau_0 \exp(\Delta H/RT)$, where $\tau_0 = 10^{-13}$ s is the characteristic time for molecular vibration, and ΔH is the adsorption

enthalpy calculated for various molecules from the chromatographic experiment. Retention time t and standard deviation of the retention time Dt were calculated for cylindrical pores with various aspect ratios and for porous space in layers of packings of spheres with different depth and porosity. The criteria for comparison of different porous systems were chosen by analogy to chromatography parameter $\alpha = (Dt)^2$. The results of computer simulation confirm an intuitive explanation of the narrowing distribution of retention time, which reduces time of separation of gas mixtures in MCM-41 column.

We prepared a capillary column with thin MCM-41 film and tested it in chromatographic separation of a mixture of $C_1 - C_4$ hydrocarbons. This column was compared to commercial Varian column under the same conditions.

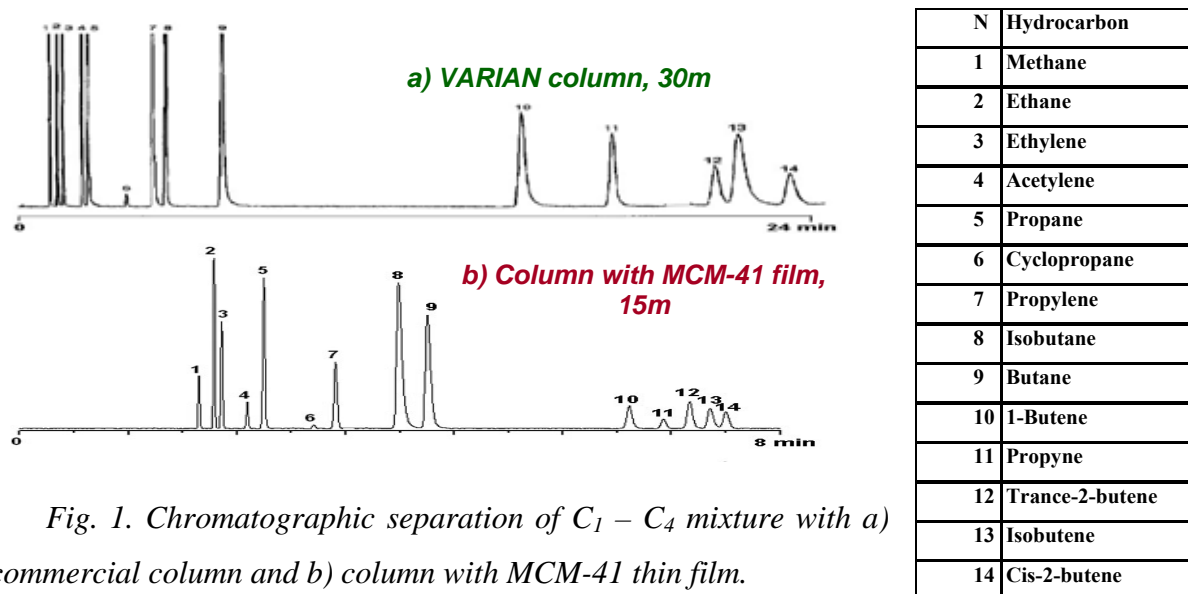


Fig. 1. Chromatographic separation of $C_1 - C_4$ mixture with a) commercial column and b) column with MCM-41 thin film.

Separation by both columns has similar effectiveness and selectivity, however time of full separation is smaller for MCM-41 column, and overloading of this column occurs at tenfold larger amounts of hydrocarbon mixture comparing to commercial column.

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STUDY OF CATALYTIC OXIDATION PROCESSES OF CARBONIC COMPOUNDS

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Theoretical modeling of catalytic oxidation of carbon particles is carried out. Processes of soot and CO oxidation on $Cs_xLa_{1-x}VO_4$ and $M_xLa_{1-x}MnO_3$ are experimentally investigated. It is shown promoter action of phases Al_2O_3 and $MnAl_2O_4$ in oxidizing reaction CO on perovskites $M_xLa_{1-x}MnO_3$.

Complex oxides have high catalytic activity in oxidizing reactions of organic compounds, CO, soot. For protection of atmosphere against toxic exhausts it is necessary to oxidize solids and light-end products.

One of important conclusions, obtained during the study of kinetic peculiarities of carbonaceous materials oxidation on complex oxide catalysts, is the possibility of two kinds of catalytic effect on a heterogeneous reaction: contact and remote. On the one hand, catalyst can accelerate the process of oxidation of carbon up to CO, on the other hand – oxidation CO up to CO_2 . The first process is accelerated immediately in contact area of catalyst and a carbon particle. Due to an essential exothermicity of the second process the temperature combustion front appears, which propagates on considerable distance from a contact surface. It results in a raise of a total velocity of oxidation process and a change of a particle form.

The theoretical model describing the process of carbon particles oxidation on a surface of catalyst is built. The model takes into account a velocity of level-by-level burning of a particle, remote action of catalyst and a modification of particle geometry during burning. We selected two basic alternatives as models, when the form of carbonaceous particles is close to cylindrical or spherical. For example, we supposed that the part of a cylindrical particle contacting with catalyst during oxidation takes a shape of a truncated cone. Eventually the area of surface, subject to non-contact oxidation is increased. Various interrelations of efficient kinetic constants of level-by-level burning (H) and non-contact oxidation (C) were accepted for model calculations. In fact, the modification of the interrelations mentioned above can actually occur as a result of temperature change and in dependence on nature of catalyst also. One can expect that at rather low temperatures, the velocity of process of contact oxidation is higher, and at relatively high temperatures, the second process dominates. When the kinetic constant of remote oxidation is much less, than constant of contact burning and there are no difficulties in transfer of an oxidant and reaction products, the process of linear oxidation of carbon particles (a mass loss) can be realized. The designed program allows

calculating kinetics of particles oxidation in the case when process of particles oxidation due to a contact and remote operation does not submit to the linear law. Thus the aspect of dependences of kinetic constants from time, obtained, for example, experimentally can be included for calculations.

The data received as a result of modeling show time dependence of a mass loss of carbon particles for particles with the given initial dimensions. The solution of the received equations in program package Maple 9, allows determining the time of a full combustion of particles (fig.). The comparison of calculated and experimental data on oxidation of carbon on catalyst based on lanthanum - cesium vanadate showed their good correlation. During experiments, the gravimetric method and microscopic observations of a change of carbonaceous subject form were also used.

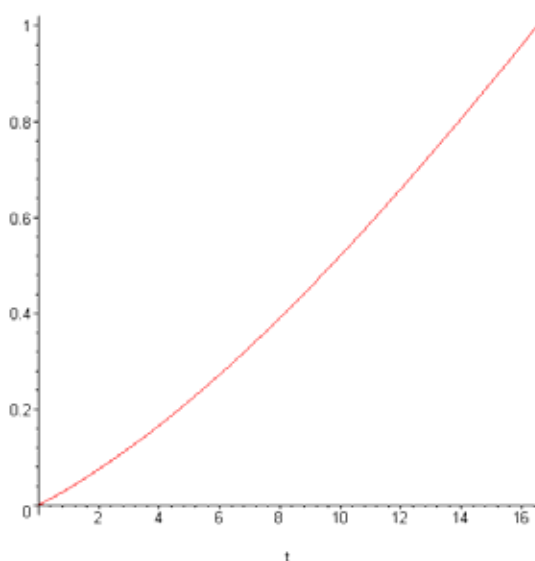


Fig. Calculation curves of a mass loss ($\Delta m/m_0$) at catalytic oxidation of quasi-cylindrical particles of carbon on a surface of the catalyst (t - time in second). The radius and height of particles are 1 micron; kinetic constants H and C are equal to 0.033 microns/second.

It is shown; that $Cs_xLa_{1-x}VO_4$ promoted Cs_2SO_4 has high activity at oxidation of soot. However, this activity for CO oxidation at low temperatures is concerning low in comparison with perovskites $M_xLa_{1-x}MnO_3$. The hypothesis that vanadate at low temperatures accelerates mainly the first stage of oxidation of carbon up to CO is confirmed. The kinetics of oxidation on air at presence $Cs_xLa_{1-x}VO_4$ of soot samples is investigated. It is established, that process of oxidation at small degrees of fractional conversion proceeds in a kinetic mode. The kinetics is described by the equation of the compressed cylinder. Then there are diffusive difficulties, burning of soot is well described mathematically by Yander equation. It is concerned with accumulation on a catalyst surface of the unburnt inorganic compounds.

Besides it is immediately shown promoter action on covering catalysts $M_xLa_{1-x}MnO_3$ of underlying phases Al_2O_3 and $MnAl_2O_4$ at catalytic CO oxidation. Phase $MnAl_2O_4$ arises at interaction of perovskit with Al_2O_3 . Measurements carried out by means of a reactor of flowing-circulating type Katakon 1.1 and electronic gas analyzer Testo-350 XL.

**CATALYTIC TREATMENT OF OFF GASES WITH VARIABLE
CONCENTRATION OF ETHYLENE OXIDE**

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An absorption-oxidation catalytic method (ABSOX) for efficient treatment of off gas from sterilization cameras with variable concentration of ethylene oxide as an alternative to the conventional thermal treatment method has been developed. Based on the research results, a pilot plant at the enterprise “UniOnex” (Berds, Novosibirsk Region) has been designed and constructed, providing abatement of ethylene oxide emissions below sanitary standards.

The degassing of the sterilization camera after processing medical instruments with ethylene oxide proceeds in several cycles of evacuation and filling the camera with air, thus at each step the concentration of ethylene oxide in the outlet gases decreases.

The outlet gases of the sterilization camera containing up to 300 g/m³ of ethylene oxide and up to 1000 g/m³ of carbon dioxide are usually subjected to thermal treatment which is accompanied by the emission of toxic products of incomplete combustion due to changes in calorific value of the gas and the flame instability.

Effective oxidation of ethylene oxide in the outlet gases of the sterilization camera can be carried out by catalytic methods which provide a high degree of oxidation of organic compounds ($\geq 99.5\%$) and the absence of secondary pollutants. At the same time, the efficient application of catalytic methods requires certain limitations on the deviations of the concentrations of the gas components from the average values.

For complete and efficient oxidation of ethylene oxide in the outlet gases of sterilization cameras at the enterprise “UniOnex”, an absorption-oxidation method (ABSOX) was developed. The method is based on the absorption of ethylene oxide from the outlet gas by water during the cycles of degasification, desorption of the captured ethylene oxide and its catalytic oxidation on the catalyst ICT-12-8 to carbon dioxide and water.

Based on the obtained results a pilot plant was designed at NGPII “VNIPIET” and built at the enterprise “UniOnex”. The schematic diagram of the plant (Fig. 1) comprises: sterilization camera 1, water vacuum pump 2, heat exchanger 3, tank 4, jet scrubber 5, water pump 6,

ventilators 7 and 10, flame arrester 8 and catalytic reactor 9. The technical characteristics of the units of the plant are given in Table 1.

The catalytic reactor is a single-piece apparatus containing a two-channel spiral heat exchanger, a catalytic section and an electric heater. By contrast to conventional catalytic reactors it has a rather high degree of heat recovery (80-85 %). The photograph of the reactor with a capacity of 1000 m³/h is shown in Fig. 2.

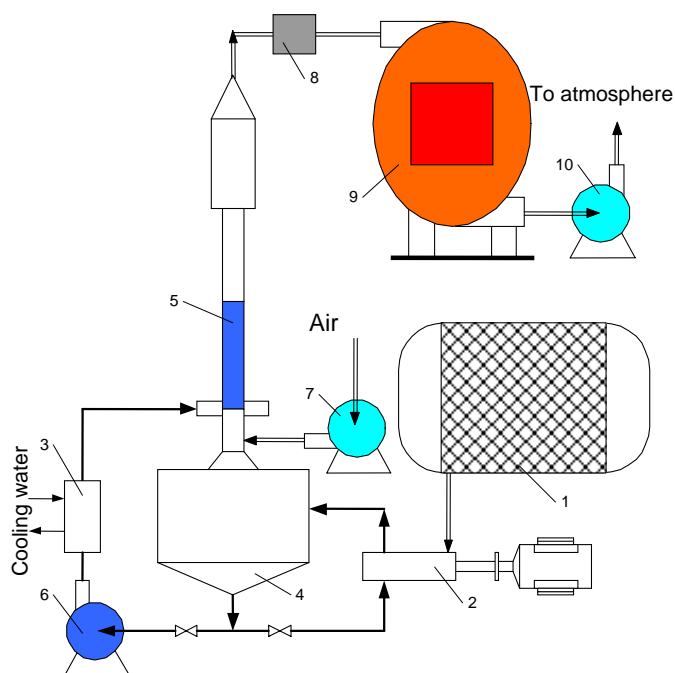


Fig. 1 – Schematic diagram

Table 1. Technical characteristics of the units of the pilot plant at “UniOnex”

Apparatus	Characteristic	Value
Water vacuum pump	Maximum gas flow rate	660 Nm ³ /hr
	Maximum inlet concentration of ethylene oxide	300 g/m ³
Jet scrubber	Gas flow rate	1000 Nm ³ /hr
	Water flow rate	10-15 m ³ /hr
Catalytic reactor	Gas flow rate o	1000 Nm ³ /hr
	Temperature of the catalyst	430-450°C
	Installed electric power	30 kW
	Degree of ethylene oxide oxidation	99.8-99.9 %

MATHEMATICAL MODELING OF TOLUENE INTERACTION WITH V/Ti-OXIDES IN ANAEROBIC CONDITIONS

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One of the ways to perform the process of hydrocarbon catalytic oxidation is to divide the reaction space in a few separate zones, for instance, a zone of the catalyst reduction by hydrocarbon and a zone of its oxidation by oxygen and catalyst circulation between zones (see, for example [1, 2]). This operation was industrially used in the DuPont process of butane oxidation to maleic anhydride over vanadium-phosphorous catalysts [3].

Second way is regulation (or periodic operations) when the reagents concentrations, gas flow rates are changed periodically in the fixed bed catalytic reactor input - cyclic reduction and re-oxidation of a catalyst [4, 5]. The possible objectives of the use of periodic operation of catalytic reactors are to provide an increased conversion, improved selectivity, and reduced deactivation. Additionally, an important information could be extracted from the transient behavior of the reaction after the fast change of the composition of reaction mixture over the catalyst. Modeling of the transient phenomena allows obtaining valuable kinetic constants, which often could not be determined from the steady state experiments.

The aim of this work is modeling of toluene interaction with a pre-oxidized vanadia/titania catalyst under periodic operation.

The catalyst was prepared via a well-known grafting technique by the vapor deposition of VOCl_3 on the surface of TiO_2 (Aldrich). The BET specific surface area was equal to $9 \text{ m}^2/\text{g}$, the amount of vanadium was found to be 0.57 wt. % that corresponds to 0.75 of a monolayer (ML) [7]. It is important that this catalyst contained only about a monolayer of the surface vanadia species and did not contain any bulk crystalline V_2O_5 .

A typical transient behavior of the toluene, benzaldehyde and CO_2 concentrations as a result of interaction of toluene with the 0.75 ML V/Ti-oxide catalyst is demonstrated in Fig. 1 [8]. The main products of the interaction of toluene with the pre-oxidized vanadia/titania catalyst in the temperature range 523-633 K are benzaldehyde (BA), CO_2 , CO and H_2O . The transient behavior of CO is similar to CO_2 , but the CO concentration is 5–6 times lower. Hence, it was not taken into account. It is seen that the dynamics of the CO_2 and benzaldehyde formation are different. CO_2 is formed during the initial time of the reaction, declining quickly with time, while BA is formed for a prolonged time.

A kinetic scheme with the minimal amount of steps that appropriately describes the response curves of toluene and reaction products was chosen. It includes 5 steps [8]:

- 1) $C_6H_5CH_3 + 2 [YO] \rightarrow 2 [Y] + C_6H_5CHO + H_2O,$
- 2) $2 C_6H_5CHO + 3 [YO] \rightarrow 2 [YC_6H_5COO] + [Y] + H_2O,$
- 3) $C_6H_5CH_3 + 18 [ZO] \rightarrow 18 [Z] + 7 CO_2 + 4 H_2O,$
- 4) $C_6H_5CH_3 + [ZO] \rightarrow [ZOC_7H_8],$
- 5) $[ZOC_7H_8] + 17 [ZO] \rightarrow 18 [Z] + 7 CO_2 + 4 H_2O.$

The kinetic equations corresponding to steps 1–5 are as follows:

$$r_1 = k_1 C_T \theta_{YO}^m, \quad r_2 = k_2 C_{BA} \theta_{YO}, \quad r_3 = k_3 C_T \theta_{ZO}^n, \quad r_4 = k_4 C_T \theta_{ZO}, \quad r_5 = k_5 \theta_T \theta_{ZO},$$

where C_T and C_{BA} are the concentrations of toluene and benzaldehyde in the gas phase (mole fractions); θ_{YO} , θ_{ZO} , θ_{YB} , θ_{ZT} are the fractions of adsorbed species, benzoate and toluene on the catalyst surface, correspondingly; θ_Y , θ_Z are the fractions of not occupied sites of the monolayer; k_j are the rate constants of the corresponding steps (s^{-1}); m , n are the reaction

On the base kinetic model the modeling of the interaction of toluene with the pre-oxidized vanadia/titania catalyst has been performed. It was shown, that under periodic operation it is possible to increase selectivity towards to BA essentially with comparison steady state ones. This was due to presence a different surface oxygen species: nucleophilic lattice species and electrophilic surface species participating in the parallel routes of the toluene oxidation. The latter species could be formed easier in the presence of gaseous oxygen providing the decrease of BA selectivity.

The benzaldehyde formation is probably determined by nucleophilic-lattice oxygen, involved in the monolayer vanadia species. Electrophilic oxygen, formed at a higher concentration of vanadia, is responsible for the formation of carbon oxides and main part of surface carbon containing species. The proposed kinetic model was used to estimate the rate constants, reaction orders, activation energies and relative amount of active oxygen sites. It satisfactorily describes the transient behaviour of benzaldehyde, CO_2 and toluene for the sub-monolayer catalysts in the temperature range 523-633 K. The model demands a modification to simulate kinetics of the toluene interaction with the 3.7 ML V/TiO₂ catalyst explained by the presence of V₂O₅ in excess. This V₂O₅ provides oxygen participating in the interaction with toluene.

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NEW TECHNIQUE FOR DEPOSITION OF METAL OXIDE CATALYSTS ON METAL SUPPORTS

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Metal supported catalysts are very promising to use in high temperature catalytic processes where high heat transfer is required or in car converters. Recently, the application of metal supported catalysts as a part of integrated separator for methane reforming in high temperature fuel cells was proposed. In this case, catalytic coatings and the separator itself are exposed to severe conditions, i.e. aggressive media composed of wet hydrogen, carbon dioxide and electrolyte vapor. The deposition of catalytic coatings exhibiting high protective and adhesive properties requires the use of new or modification of known techniques. The spraying techniques may give unique possibility to solve these problems [1]. In this paper the advantages of the use of cold gas dynamic spraying are demonstrated for the synthesis of metal oxide catalysts supported on metal foils.

A gun with supersonic jet working at ambient temperature [2, 3] was applied for deposition of catalytic coatings on flat and corrugated thin (0.1-0.2 mm) metal foils. Alumina coatings having different microstructure were sprayed on metal foils. Different active components were introduced into the coatings via wetness impregnation. The procedure of the deposition of Al_xO_y coatings with BET area in the range of 10-40 m^2/g and pore volume 0.05-0.2 cm^3/g on metal foils was worked out. The optimum composition of Al_xO_y layer was defined depending on adhesive properties of the coatings examined by SEM and thermal cycling experiments (Fig. 1). The activity of Pd, Pd-Mn, Cu-Cr, Mn catalysts introduced into optimum coatings on metal foils was tested in methane oxidation reaction. The Pd and Pd-Mn catalysts demonstrated the highest activity, Fig. 2, as well as stable operation at 900 °C.

The prospects of cold gas dynamic technique was demonstrated for fabrication of pilot scale Pd-containing sample on corrugated foil of 500 mm length, Fig. 3. It was found that the preparation method developed allows deposition of a uniform coating along the full length and introduction of up to 10 g of Pd per square meter of the foil. The pilot sample of the catalyst demonstrated high activity in methane combustion process and adhesive properties.

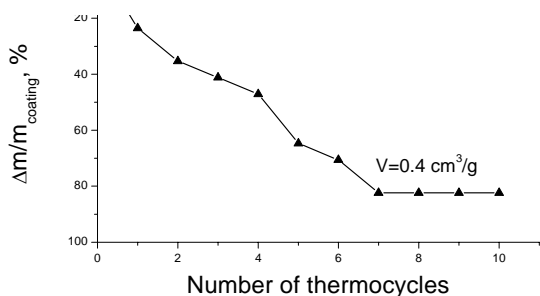


Fig. 1. Loss of the mass of the coating (%) during thermal cycling of samples $\text{Al}_x\text{O}_y/\text{foil}$ of different pore volume.

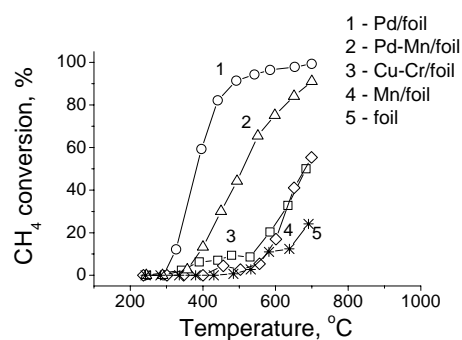


Fig. 2. Temperature dependencies of methane conversion ($1\% \text{CH}_4$ in air, 1000h^{-1}) on different catalysts deposited on metal foil.

It was concluded that the technology developed has no limitation in scaling and therefore it can be widely applied in future for the preparation of catalysts on metal surfaces. In particular, this technique is planned to be applied for deposition of catalytic coatings on the integrated metal separator for methane reforming in high temperature fuel cells.

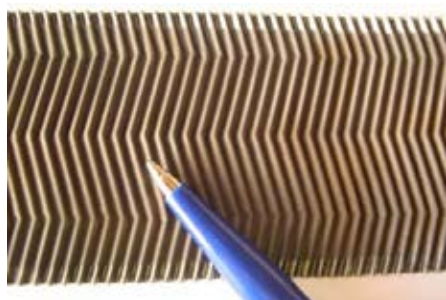


Fig. 3. The photos of the Pd-containing catalyst (50 mm x 500 mm) supported on corrugated metal foil.

Acknowledgements

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**MATHEMATICAL MODELING OF MASS-EXCHANGE, CHEMICAL AND
HYDRODYNAMIC PROCESSES IN HIGH-POROUS HONEYCOMBED
CATALYSTS**

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On the basis of equations of Navier-Stokes using the method of final elements, the hydrodynamic stream structure in a cell and in a layer of a highly porous cellular material is considered. Hydrodynamic resistance of highly porous cellular materials is determined during the transfer of liquid and gaseous environments. Experimental data are compared.

Support and development of up-to-date level of industrial catalytic processes requires radical solutions in the field of producing new-generation catalysts possessing unique physicochemical and mechanical properties along with high operation characteristics. As such promising modern catalysts the block catalysts based on high-porous honeycombed materials (HPHM) can be considered, which are prepared by the polymer matrix replication and are characterized by high permeability, reliable work in the external diffusion zone etc. HPHM were developed for filtration of gases, liquids, metal melts and are virtually unknown as catalyst supports. In industrial processes HPHM-based block catalysts had not been used at all since there are no existing preparation technologies for high-porous honeycombed supports and deposited high-porous honeycombed catalysts. Thus it appears reasonable to investigate HPHM-employing mass-exchange, chemical and hydrodynamic processes in the new apparatus arrangement. Structure of high-permeable high-porous honeycombed materials represents a 3D-skeleton formed by crosspieces conjoined in the nodes in four and having in cross-section the form of a curvilinear triangle. Spatial dislocation of the nodes is not random but possesses certain regularity. Due to such organization HPHM structure can be considered as a group of elementary cells in form rather close to regular dodecahedron whose vertices correspond to the nodes while the edges are formed by strips connecting the nodes. However, the angles between faces in a regular dodecahedron are such that can't allow full volume filling with regularly aligned dodecahedra.

In terms of the work on thesis the HPHM elementary cell geometry was developed that provide the volume filling with the regular packing. Such HPHM cell is characterized by:

- diameter of its generating sphere;
- interception degree (further called overlapping degree) – the distance from the center of the cell generating sphere to the plane intercepting a spherical segment referred to the cell diameter.

The overlapping degree affects the window diameter – diameter of a circle resulting from spherical surface intersection with the secant plane, as well as on the obtained foamed material porosity. To exclude overlapping of the neighbor windows, overlapping degree is limited by some minimum value.

For comparing the modeled HPHM structure with the real structure, the correlation of one of the model geometry parameters (overlapping degree) with the real structure parameters (porosity, specific surface) was found.

The stationary flow driven by the applied constant pressure drop was considered.

Along with the laminar flow for the gas also the turbulent flow was considered using the k- ϵ turbulence model

In terms of work on the thesis the HPHM hydrodynamic properties was compared with those for materials with regular structure and also with filled materials characterized by random structure.

Mathematical modeling of the flow was based on Navier-Stokes equations and was realized using the finite-element modeling packages (ANSYS and Fluent)

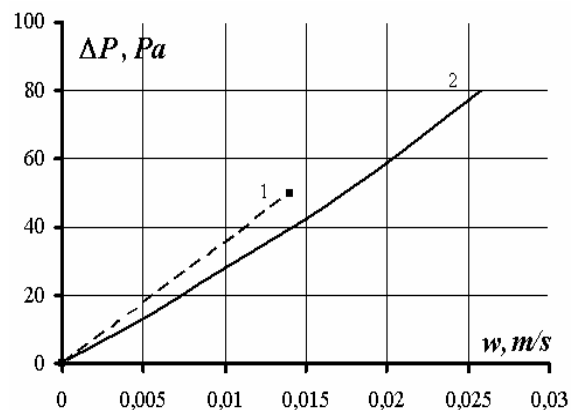


Fig. 1. Dependence of pressure drop on velocity of a water for HPHM with $d_c=0.9$ mm with porosity $\Pi=0.9$, height of layer $L=15$ mm. 1 – experiment; 2 – simulation

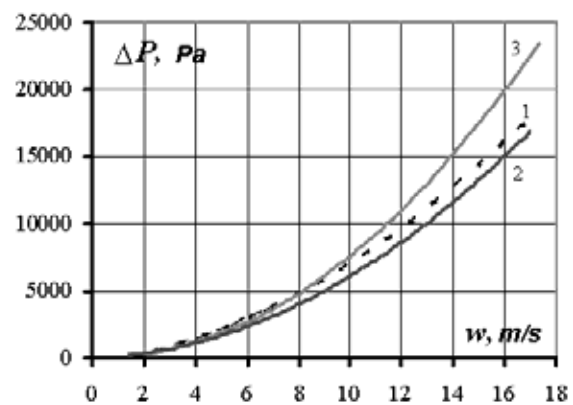


Fig. 2. Dependence of pressure drop on velocity of air for HPHM with $d_c=2.1$ mm with porosity $\Pi=0.9$, height of layer $L=70$ mm. 1 – experiment; 2 – turbulent; 3 – a laminar condition.

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THE RING CATALYST WITH LOW HYDRAULIC RESISTANCE

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Comparative experiments by definition of size of hydraulic resistance of granular bed of ring-shaped thick-walled pellets of various diameter are executed. It is shown, that the results of calculation of hydraulic resistance have satisfactory convergence with experiment in the case when factors of resistance of granular bed for the particles of the cylindrical or irregular form were used.

For fixed-bed catalytic reactors the major characteristic is the hydraulic resistance which is determined by the form of pellets and its sizes. The industrial samples of gamma-aluminum oxide produced hitherto in Russia (as the most commonly used catalyst carrier) were granulated in the form of spheres or cylinders, however the bed of such pellets is characterized by high hydraulic resistance. Recently the industrial company "Catalyst" (Novosibirsk) started the production of the ring-shaped thick-walled extrudates based on gamma-aluminum oxide with the size less than 10 mm (technical specifications 6-68-146-02).

We have measured the hydraulic resistance of series of industrial samples of ring extrudates with external diameter from 6.6 up to 8.4 mm (the basic characteristics are presented in table 1). Hydraulic tests were performed on a wind tunnel with the diameter of 45 mm (mobile phase - air, ambient temperature, volume of loading of pellets 1 dm³).

Table 1 - Characteristics of the tested samples

Index	Dimension	The Sample		
		1	2	3
External diameter	mm	8.4	7.4	6.6
Internal diameter	mm	3.2	2.8	2.5
Height	mm	7.7	7.7	7.2
Splitting strength	kg/pellet	16.1 ± 0.8		
Specific surface	m ² /g	160 ± 10		

In figure 1 experimental data on hydraulic resistance of ring extrudates, cylindrical extrudates of gamma-aluminum oxide AOA-type with the diameter (4.35 ± 0.05) mm (GOST 8136-85), spherical pellets an alpha-aluminum oxide with the diameter (5 ± 0.5) mm are presented.

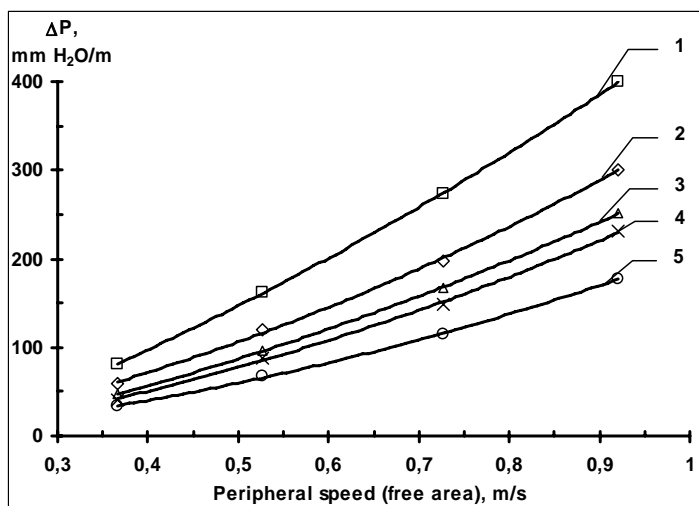


Fig. 1. Hydraulic resistance of granular bed:

- 1 - cylinder-shaped;
- 2 - sphere-shaped;
- 3 - ring-shaped $\varnothing = 6.6$;
- 4 - ring-shaped $\varnothing = 7.4$;
- 5 - ring-shaped $\varnothing = 8.4$.

The calculated value of hydraulic resistance of bed of the ring-shaped extrudates found by the known equation II.49, p.45 [Aerov, M.E. Device with stationary granular bed / M.E. Aerov, O.M. Todes, D.A. Narinsky - StP.: Chemistry, 1979, 175 p.], is mainly defined by the factor of resistance of bed. Satisfactory convergence between experiment and calculations for the ring-shaped extrudates of all diameters is obtained using the factors of resistance of granular bed from particles of the cylindrical or irregular shape (the error of calculation does not exceed $\pm 30\%$). It is important to notice, that use of factor of resistance for the bed made of rings results in the significant underestimation of hydraulic resistance (from “—“ 70 up to “—“ 300 %). Possibly, it is connected with the fact that the dependence of factor of resistance recommended for ring pellets on Reynold’s criterion is based on experiments with Raschig Rings for which internal diameter is close to external. Unlike the Raschig Rings, the pellets studied in the present work are thick-walled and their internal diameter essentially less than external.

In cooperation with the laboratory of industrial company "Alvigo-M" (Elektrogorsk, the Moscow district) the laboratory samples of shell-type palladium catalysts with the content of palladium 0,1 - 0,2 mass% based on ring-shape extrudates were produced and tested. The catalytic activity of all samples in hydrogenation of unsaturated hydrocarbons from the liquid phase obtained after pyrolysis of gaseous raw material does not concede to the industrial catalysts with palladium content of 0.25 mass% (PK-25 and analogues).

SELECTIVE PROCESS OF HYDROGEN PRODUCTION BY CATALYTIC PYROLYSIS OF PROPANE

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Catalytic propane pyrolysis in temperature range of 400-700 °C was studied. Monometallic 90 wt.% Ni/Al₂O₃ and bimetallic 70 wt.% Ni–20 wt.% Cu/SiO₂ and 50 wt.% Ni–40 wt.% Cu/SiO₂ catalysts were used. Catalytic decomposition of propane with using of all three catalysts yielded hydrogen, methane and unreacted propane, and carbon nanofibers. It was found that bimetallic Ni-Cu catalysts exhibited significantly lower propane decomposition temperatures and longer time-on-stream performances than monometallic Ni catalyst. Furthermore, at the temperature of 600 °C high hydrogen content with only few vol.% of methane admixture can be achieved by using 50 wt.% Ni–40 wt.% Cu/SiO₂ catalyst.

A number of methods of hydrogen production are known. Nevertheless hydrocarbon steam conversion today finds the widest adaptation. The main process disadvantage is the formation of by-products such as CO and CO₂. And even if the hydrogen is used in fuel cells, the serious problem is to purify the hydrogen from CO, because the carbon oxide is a poison for catalysts which are used in fuel cells.

To prevent CO and CO₂ formation during the hydrogen production it is suggested to use a process of high-temperature (1200-1800 °C) pyrolysis of hydrocarbons. But the pyrolysis also has several shortcomings related to high temperature (such as the need for special materials and high energy losses).

Several years ago a new way of CO-free hydrogen and valuable nanofibrous carbonaceous material production based on catalytic decomposition of hydrocarbons (mostly methane) over Ni and Ni-Cu-containing (up to 90 %) catalysts in temperatures of 500-800 °C was suggested. The works followed this direction are mostly devoted to the studying the catalytic decomposition of methane.

As it appeared from thermodynamics, the only products of hydrocarbons decomposition in relatively low temperatures are C, H₂ and CH₄. And the lower temperature is the lower concentration of hydrogen is obtained. In the temperature of 550 °C the concentration of hydrogen is less than 30 %. To obtain the higher concentration of hydrogen the methane-hydrogen mixture need to be partitioned and the temperature of the process must be increased.

The effective partition of methane and hydrogen is a large problem. Implementation of methane decomposition in increased temperature is another challenge because of the fast deactivation of catalyst.

In this paper the opportunity of selective hydrogen production by catalytic propane pyrolysis is shown.

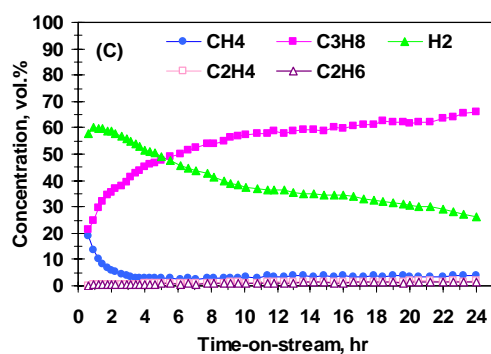
Experiments were carried out in quartz flow reactor with propane flow of $100 \text{ L}\cdot\text{h}^{-1}$ per 1 gram of catalyst in temperature range of $400\text{-}700 \text{ }^\circ\text{C}$, under atmospheric pressure.

It was found that lifetime of catalyst and composition of gaseous products are significantly depend on the process temperature and catalyst composition. Experimental data obtained allow to suppose that there are two different types of active centers in Ni-containing catalysts which participate in the process of propane decomposition:

- first type centers, which brake the C-C bond in propane molecules and subsequent separation of hydrogen atoms from chemisorbed fragments of propane molecules ($k_1\text{-C}_n\text{H}_m$);
- second type centers make possible the braking and restoration of C-H bond in methane molecules (as propane decomposition product), i.e. interaction of chemisorbed hydrogen atom and methyl complex ($k_2\text{-CH}_3$).

Therefore increasing of selectivity of propane converting into hydrogen is related to rapid blocking of second type active centers.

The highest characteristics of process (selectivity, conversion, yield and catalyst life-time) can be achieved by using of 50 wt.% Ni–40 wt.% Cu/SiO₂ catalyst. At the temperature of $600 \text{ }^\circ\text{C}$ this catalyst is providing production of mixture with 30 vol.% of hydrogen content (as it can be seen on the figure). Thus, the hydrogen/methane ratio in the reaction products is more than 8/1 during 22 hours proceeds. After removal of propane from reaction products one can receive CO-free mixture of hydrogen and methane containing more than 90 vol.% of hydrogen. This mixture is suitable for low-temperature fuel cells as a fuel.



Products distribution during pyrolysis of propane on 50 wt.% Ni–40 wt.% Cu/SiO₂.
T=600 °C, G=100 L·h⁻¹·g⁻¹.

**MODELING OF EVOLUTION OF CARBONIC SUBSTANCES IN
AUTOCATALYTIC THERMAL PROCESSES****Tsyganova S.I., Tsyganov A.D.¹***Institute of Chemistry and Chemical Technology SB RAS, Krasnoyarsk, Russia*¹*Krasnoyarsk State University, Krasnoyarsk, Russia**E-mail light@icct.ru*

Ideas and methodology of modeling of carbonic substance evolution are presented to reveal dialects of the composition-structure-property interdependence for transformation of complex hydrocarbon composition (pitch) influenced by temperature. Thermochemical conversion of the pitch is presented as a cyclic autocatalytic conjugate process requiring insignificant total energy consumption. Phenyl was taken as an autocatalyst, inducing these processes. The schematic model of pitch thermoconversion sketched out in form hexagon enabled to see carbonic substance evolution as development of the system on a whole.

In the network of the environmental risk conception, laid by V.A. Koptug and A.G. Anshits at the close of the last century, an assessment of carcinogen risk of aluminum manufacturing has been given and main source of emission of carcinogenic substances, such as carbonization processes of pitch, has been found [1, 2].

Complex analysis of thermochemical conversion of pitch [3] has been carried out. As a result, dynamics and routes of products formation, including carcinogenic substances, during pitch carbonization have been shown.

A progress in the study of carbonic substance thermoconversion has been made using the interdisciplinary approach. Thermochemical conversion of carbonic substance has been presented as evolution of complex system, where continuous conjugate transition from fusion to decomposition reactions in gaseous, liquid and solid phases has been observed [4].

The aim of this paper is modeling of the complex system evolution, which is the next stage of studying of the carbonic substance thermoconversion.

The modeling is based on the principle of energetic and structural conjugation of all system, where the high-energy intermediate is a driving force, causing the initiation of the reactions, accompanied by the migration of electrons and structural pattern recognition.

The schematic model of evolution of pitch thermoconversion is shown in the hexagon form as benzene molecule, in which carbon atoms are associatively substituted by specific products (pitch – mesophase – semicoke – semiconductor – coke – tar), sequentially formed during pitch carbonization. We suggest that the elementary aryl intermediate – phenyl is

autocatalyst of thermoconversion processes of carbonic substance, i.e. there is an autocatalytic thermal process in the system.

Diagnostics of experimental data concerning thermoconversion of hydrocarbon materials confirms the suggested mechanism of the process. It was shown that mathematical accounts of kinetics of autocatalytic conjugate processes passing in the open system are significantly simplified.

This modeling of evolution of this system allows displaying elements of self-organization and self-reproduction, as the living matter has. Similarity of living carbonic matter conversion and “carbonic lifeless matter” thermoconversion consist in mechanism of these processes, i.e. hypercyclic autocatalytic processes [5]. So, common features for living and lifeless carbonic matters can be found by modeling of complex carbonic system.

Thus, the analysis and modeling of evolution of pitch thermoconversion gives an opportunity to calculate and to forecast the dynamics of complex processes as well as to explore a new ways of carbonic material production.

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PARTIAL OXIDATION OF METHANE IN MONOLITH REACTOR: EFFECTS OF THE INTERNAL CONFIGURATION AND MATERIALS

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The work concerns mathematical modeling of methane partial oxidation dynamics, especially during the reaction ignition in monolith reactor. Dissipation of reaction energy internally through the different mechanisms, such as radiation, convection, conduction and thermodiffusion is considered in dependence on configuration and material of both monoliths-catalyst and heat shield. In addition to the detail surface kinetics the gas phase reactions are taken into account in the mathematical model developed.

Partial oxidation of hydrocarbons to synthesis gas in monolith reactor at short contact times is characterized by the high temperature in the frontal part of catalyst [1-2]. To avoid the heat losses by radiation a heat shield are usually placed before the catalytic monolith. The temperature between the heat shield(s) placed upstream of the catalyst and catalyst may gradually go up with the run time. The high temperature initiates pre-reforming reactions upstream of the catalyst with releasing of some chemical energy in the noncatalytic reactions. This phenomenon may be favored in syngas production because of a milder catalyst temperature profile is created. Furthermore, hydrogen formed in the catalytic partial oxidation reaction may pass into the gas phase upstream the flow due to thermodiffusion. Thus, the two-phase 1D numerical model of methane partial oxidation takes into account a specific configuration of the monolith reactor with the heat shield and catalytic monoliths inside.

The reactor model is developed on the base of differential equations of mass and energy changes [3]. The detail surface and gas phase reactions are taken into account in the mathematical model developed. Accumulation terms are considered in all equations. The following assumptions are considered in the model: isolation of sidewalls of the monolith reactor; non steady-state heat- and mass transfer; heterogeneously of the system; both the axial and thermo diffusions in the gas phase; thermal conduction of solid phase by means of effective axial thermal conductivity; heat loss due to radiation at the reactor inlet and outlet.

Dissipation of reaction energy in the reactor internally is considered in dependence on both geometry and material of the monoliths.

The influence of such parameters as feed composition, superficial velocity, reactor configuration (distance between shields or between shield and catalyst, the length of shields and catalyst), materials of shields and catalyst monolith (foam and extruded monoliths, metal, ceramics) on the reactor dynamics has been studied.

Acknowledgement

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CONVERSION OF NATURAL GAS INTO LIQUID PRODUCTS OVER BIMETALLIC ZEOLITE CATALYSTS

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Joint promoting action of molybdenum and gallium on catalytic zeolite properties with Si/Al ratio of 40 in the process of natural gas conversion into liquid products is studied. It is shown that the introduction of gallium cations into a Mo-containing zeolite results in increased catalyst activity in the process of natural gas conversion. It is established that maximal amount of aromatic compounds is formed over a bimetallic zeolite system containing 4.0 % of Mo nanopowder and 1.0% of gallium oxide.

The development of chemical processes of natural gas conversion belongs to the priority tasks of fuel-energy complex. At the same time direct conversion of natural gas into higher hydrocarbons is limited due a high stability and low reactivity of methane fraction. It is impossible to carry out chemical conversion of natural gas components into liquid organic compounds without applying highly active polyfunctional catalysts. A zeolite of pentasil family containing a certain amount of promoters that posses, as a rule, an increased dehydrating ability is the main component of such catalysts. That is why this work aims to study a joint promoting action of molybdenum and gallium on catalytic properties of a zeolite with Si/Al ratio of 40 in the natural gas conversion.

The zeolite was modified via dry mechanical mixing of a zeolite powder with a nanosized Mo powder (4.0 wt%) produced by wire electroexplosion in argon medium. Mixing was carried out in the KM-1 vibration mill on air for 2 h. Then the mixture obtained was impregnated by aqueous solution of gallium nitrate (the weight fraction of gallium was changed from 0.5 to 5.0%), dried at 100-110 °C and calcined on air at 550 °C for 5 h. Conversion of natural gas of the composition (wt%): methane 81.6, ethane 6.46, propane 7.40, butanes 4.04, pentanes 0.47 was carried out in a flow type installation equipped with a quartz reactor under atmospheric pressure, at the reaction temperature of 500-750 °C and gas hourly space velocity (GHSV) 1000 h⁻¹.

Fig. 1 shows the effect of the process temperature on the composition of natural gas conversion products over a sample 4.0% Mo/ZSM-5 containing 1.0% Ga₂O₃ at the gas hourly space velocity 1000 h⁻¹. The conversion degree of initial feedstock and yield of aromatic

hydrocarbons increases with increasing reaction temperature and reach 35.6 and 29.5%, respectively, at 750 °C.

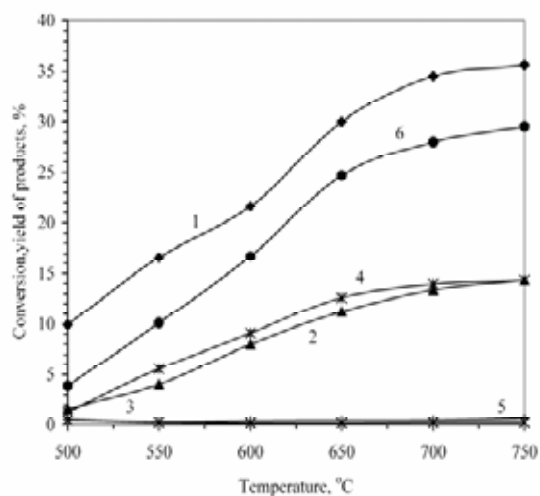


Fig. 1. Conversion (1) and yield of benzene (2), toluene (3), naphthalene (4), C₁₁-C₁₂ ArH (5) and C₆₊ ArH (6) v.s. temperature of natural gas conversion process over 1.0% Ga-4.0% Mo/ZSM-5 (GHSV = 1000 h⁻¹).

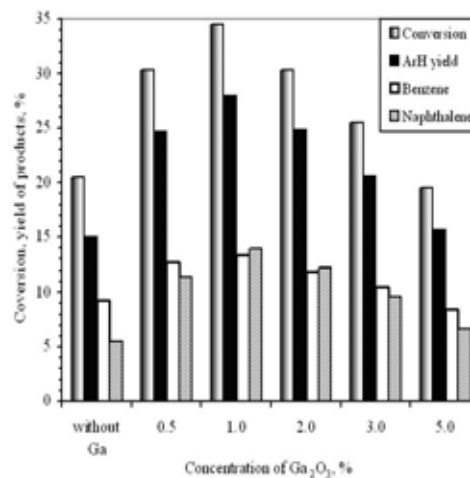


Fig. 2. The effect of the gallium oxide concentration in the 4.0% Mo/ZSM-5 catalyst on the natural gas conversion and composition of its products at T = 700 °C and GHSV = 1000 h⁻¹.

Liquids products contain more benzene, naphthalene and less toluene and C₈-C₉ alkylbenzene. When the temperature rises to 550 °C, alkylnaphthalene concentration drastically decreases in the beginning, then its increase is observed. Gaseous products have higher hydrogen concentration and lower concentrations of alkanes and alkenes with increasing reaction temperature. The selectivity of aromatic hydrocarbon formation over the catalytic system 1.0% Ga-4.0% Mo/ZSM-5 within the temperature range 600-750 °C changes from 80.3 to 82.9 %. Similar relationships between conversion and yield of natural gas conversion products are observed over zeolites containing 0.5, 2.0, 3.0 and 5.0% Ga₂O₃.

As is seen from the data of Fig. 2, the introduction of 0.5% Ga₂O₃ into the 4.0% Mo/ZSM-5 catalyst results in a significant increase both of natural gas conversion and yield of aromatic hydrocarbons. The yield of aromatic hydrocarbons increases mainly due to the rise in the formation of naphthalene hydrocarbons. The increase in the gallium oxide content in the zeolite to 1.0 wt% leads to further rise in total and aromatizing catalyst activity in natural gas conversion. The increase in gallium concentration in the zeolite to 2.0% and higher in the sample 4.0% Mo/ZSM-5 reduces the catalyst activity in the process of natural gas aromatisation, the conversion and yield of aromatic hydrocarbons being 19.5 and 15.7%, respectively.

Thus, over a zeolite with Si/Al of 40 modified by molybdenum and gallium the natural gas is converted into a mixture of aromatic hydrocarbons at a sufficiently high degree. The maximal amount of aromatic compounds is formed over a zeolite system 1.0% Ga-4.0% Mo/ZSM-5 and reaches 29.5% at 750 °C and 1000 h⁻¹, the selectivity of their formation being 82.9%.

**KINETIC MODEL FOR THE FCC GASOLINE SECONDARY REACTION BASED
ON INDEPENDENT DEACTIVATION**

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In contrast to situation in other countries, over eighty percent of gasoline comes from fluid catalytically cracked (FCC) reaction in China. The notable character of FCC gasoline is the olefin seriously exceed the required concentration, therefore, reducing the olefin's percent is an important task.

For the FCC gasoline, the secondary reaction is an effect method to produce clean gasoline. Though it has been applied in the oil refining, the kinetics of FCC gasoline secondary reaction is still in short of deep investigation because it involves hundreds of hydrocarbon molecules and thousands of chemical reactions, among which there are complicated mutual influences.

The lump method is a useful way to describe the process of FCC gasoline secondary reaction, however, to our best knowledge, there is no one to consider the deactivation of the catalyst in this process among the reported results up to now. In fact, the catalyst in the riser reactor is deactivated easily because of the high temperature and the coke problem. For this reason, it is necessary to improve the traditional lump theory to predict and describe the FCC secondary reaction more correctly; this work will be an important theoretical foundation to produce cleanliness gasoline in large scale.

In this paper, a novel eight lumps kinetics model is presented based on the analyzing of all reactions. The mechanism of the independent deactivation is adopted and a nonselective deactivation kinetic model is established to research the kinetics behavior and the variation of the product distribution. The model is solved by hybrid genetic algorithm method and the simulation results agreed well with the experiments results.

AUTOWAVE PROCESSES IN A STATIC CATALYST BED**Gerasev A.P.***Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia**E-mail: a.gerasev@ngs.ru*

The purpose of this is modern description of nature of autowave processes in static catalyst bed. The thermodynamic description of physicochemical processes in a catalytic bed is considered. The entropy balance equation was constructed and analyzed. The total entropy production in a distributed open nonlinear system was shown to be a functional of the autowave solution to the mathematical model. The analysis was done with three kinds of autowave processes in catalyst bed: fast autowaves, slow autowaves and hybrid autowaves.

The theory of propagation of nonlinear waves in active distributed kinetic systems was originated by Kolmogorov, Petrovskii, and Piskunov; Fisher; and Zel'dovich and Frank-Kamenetskii. The problem of the formation of structures stable in time and space in complex open systems as a result of the loss of homogeneous state stability is very general, and the accompanying processes are called autowave. The term autowave process (AWP) usually means a self-sustained nonlinear wave process (including stationary structures) whose characteristics (propagation velocity, period, wave (impulse) length, amplitude, and shape) remain unaltered due to an energy source distributed in the medium. In an established regime, these characteristics depend on the local properties of the medium alone and are independent of the initial conditions. Physical media with an energy source at each spatial point are referred to as active media. The principal goals of the AWP theory are elucidation of the general ideas, methodology, and rules pertinent to self-organization processes in a various systems and the establishment of the physical magnitude and criteria for the relative degree of regularity and organization of various nonequilibrium states in open system. The modern qualitative AWP theory is wholly based on the qualitative theory of dynamic systems. Successful investigations into nonlinear wave phenomena have greatly promoted the understanding of many of these phenomena based on a common approach and developing a number of universal methods for their survey.

Prigogine et al. were the first to consider the thermodynamic aspect of the problem, namely, energy dissipation (entropy production) processes. The purpose if this work was to analyze the thermodynamic properties and construct the nonequilibrium entropy of a distributed open nonlinear system under the conditions of stationary propagation of autowave processes. Qualitative and numerical studies of the rules governing local and total production

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of entropy in a system provide deeper insight in the physical nature of these complex nonlinear phenomena. The variational principles of the thermodynamics of irreversible processes were extended to slow heat autowaves, which arose in a bed of a preliminary heated catalyst when a cold reaction mixture was supplied [1]. When a reversible reaction occurred, fast heat autowaves could propagate alongside well-known slow heat autowaves. The existence of such autowaves became known only after theoretical studies. The existence of a spatial-temporal dissipative structure (a fast heat autowave) near the thermodynamically equilibrium state was established.

The development of new technological processes on basis of autowave phenomena supposes research of influence of every essential factor that characterizes a static catalyst bed [2, 3]. Some of these factors are processes of particle-to-fluid heat and mass transfer in static catalyst bed. The mathematical model of autowave processes has been built. This model includes the heat and mass transfer coefficients that are determined by given parameter values. Qualitative and numerical analysis of behavior integral curves of the dynamic system with three-dimensional phase space was performed. The peculiarities of topological structure of the dynamic system have been shown, including the draw into singular point two-dimensional invariant multiplicity mathematically equal autowave solutions. New effective method of searching physically meaningful autowave solution is developed basing on qualitative peculiarities. This method consists of solution of variation problem, every step of which unknown parameter value is calculated – propagation velocity of autowave – and Cauchy problem with initial conditions is solved. The cycle of numerical researches is completed for some typical collection of parameter values of dynamic system. A number of regularities are discovered. Discovered regularities show theoretical possibility and various ways of autowave processes stabilization.

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KINETIC AND THERMODYNAMIC STUDIES OF CATALASE-LIKE ACTIVITY OF THE ONE DIMENSIONAL MANGANESE COORDINATION POLYMER FOR HYDROGEN PEROXIDE DISPROPORTIONATION

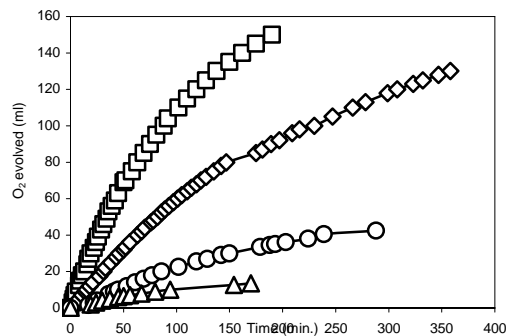
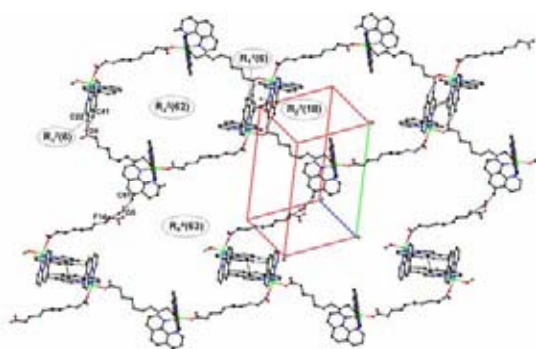
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Polymeric complex $[\text{Mn}(\text{O}_2\text{C}(\text{CF}_2)_8\text{CO}_2)(\text{phen})_2]_n\text{H}_2\text{O}$ synthesis and full characterization has been done with physical methods. Crystallographic data show that each Mn(II) ion is octahedrally coordinated by two bidentate phenanthroline ligands and the carboxylate oxygen atoms from two symmetry related perfluorosebacate ligands which are coordinated in a *cisoid* position. The structure consists of polymeric chains, with the perfluorosebacate ligands bridging the Mn(II) ions in a monodentate fashion. The complex catalyzes the disproportionation of hydrogen peroxide into water and dioxygen and it does not exhibit saturation kinetics with substrate. No induction period was needed before vigorous evolution of dioxygen occurred in methanol. The initial reaction rates and their temperature and base dependencies were investigated by monitoring the dioxygen evolution. These kinetic studies support the experimental rate law as $\text{rate} = k [\text{catalyst}] [\text{H}_2\text{O}_2]$ in the range of concentration studied: $-\ln v_0 = 1.41 \ln[\text{catalyst}] - 1.231$; $-\ln v_0 = 0.839 \ln[\text{H}_2\text{O}_2] - 7.544$. Activation parameters have been calculated at 301 K: $E_a = 50.0 \text{ kJ mol}^{-1}$; $\Delta H^\ddagger = 47.5 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -153.8 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta G^\ddagger = 96.3 \text{ J K}^{-1} \text{ mol}^{-1}$. UV-*vis* spectroscopy was used to monitor the reaction catalyzed by manganese complex.



methanol (□), acetonitrile (◇), DMF (O), water (Δ)
Conditions; [catalyst] = 0.886 M [H₂O₂] = 4.850 M at 295 K.

DISCRETE CATALYST REACTORS AND PRINCIPLES OF THEIR MODELLING

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The theoretical substantiation and principles of mathematical modelling of catalytic reactors uniting the phenomenon catalysis is offered and adsorptions is direct during transformation of an initial mix, that at pulse input of a reactionary mix (chromatographic mode) allows to divide an initial mix from products of reaction and to eliminate their braking influence. Recommendations on designs of discrete reactors and their mathematical description including two interconnected blocks are given: adsorptive-dividing and kinetic. In conditions of easily separated gas - carrier pulse input of an initial mix will allow to remove braking influence of products and to create reactors with the greater productivity of unit of volume.

Reaction rate and selectivity of process essentially depend on depth of transformation of initial substance that is typical for catalytic reactions in which adsorption of products blocks their active surface. Integrated productivity of such reactors in the field of deep degrees of transformation of initial substances is essentially reduced.

To avoid the influence of products it is possible, probably, to carry out the process discretely on catalysts - adsorbents which in the certain conditions can play a role of motionless chromatographic phases.

The portion of a reaction mix at the expense of different adsorptive abilities of its components can be divided, eliminating thus braking influence of formed products. Hence, at pulse input of a reactionary mix in process upon its passage through long enough layer of the catalyst, it is possible chromatographic division of initial substances and products of reaction. The front part of the entered pulse can constantly contact without a competition to products for an active surface of the catalyst. There is an effect of automatic realization of principle Le Chatelier with displacement of balance aside educations of products and elimination of their braking influence. The described phenomenon opens prospects of creation catalytic reactors with pulse input of a reactionary mix in which 100 % transformation of initial substance with high speed and selectivity are possible. Such reactors can be named discrete, or chromatographic.

The developed mathematical model of a similar sort of reactors includes two blocks:

1 - the adsorptive block of calculation of dividing ability of a layer of the catalyst of different length, times of keeping and retaining volumes for components of a reactionary mix

which mathematical description is based on the theory of calculation chromatography columns [1-2].

2 - the kinetic block including the differential equations of calculation of fields of temperatures, pressure, concentration and rates of streams of a reaction mix on a layer of the catalyst [3].

The design of such reactors should take into account, impact jobs, necessity of presence of long layers of the catalyst, heating systems of a reactor, easy liberation of gas of the carrier and other features.

Creation of the reliable theory of synthesis of catalysts - adsorbents and models of calculation chromatography reactors will allow to develop their designs in which realization of reactions with a deep degree of transformation for one pass is possible, with elimination recycling contours that will allow to create more harmless energy -and resource-saving technologies of the future.

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**APPLICATION OF ZIRCONIUM-CONTAINING CATALYSTS FOR OBTAINING
OF NEW FUELS**

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Copper-zinc-zirconium catalytic systems were synthesized. Their formation has been investigated by XRD, DTA and IR-spectroscopy. It has been shown that the introduction of zirconium compounds results in increase of copper-zinc catalysts efficiency in methanol conversion.

Application of methanol in industry obtains more and more wide application. Now perspective direction is use of methanol and gaseous products of its catalytic decomposition as alternate motor fuel oil. In this connection there is a need for creation of high-performance catalysts and definition of optimum conditions of their activity.

Existing data shows that the introduction of zirconium compounds in copper catalytic systems promotes increase of activity and selectivity in a number of processes. The proposed catalysts are copper-zinc-zirconium cement-containing systems. The conducted researches have shown availability of active Cu-Zn-Zr-O phase components interaction that causes decreasing the average size of coherently scattering domains (CSD) of CuO (up to 12 nm), increasing of the amorphous ZnO part and stabilization of zirconia in the amorphous condition. Also the introducing zirconium compounds has promoted increasing the specific surface and porosity of the obtained catalysts.

By results of activity tests in the methanol decomposition and methanol-water mixture conversion it has been determined that the zirconium-containing contacts show higher activity and selectivity as contrasted to Cu-Zn-catalysts. The achievement of the maximum degree of methanol conversion in the presence of zirconium-containing catalysts has occurred at lower temperatures. Thus during the methanol decomposition process the methane formation as by-product were reduced by 6 – 7 times, and CO content in products of methanol – water mixture conversion was 2 times as less as one was in the presence of copper-zinc catalysts without zirconium-containing agent.

The researches have shown that the introduction of zirconia provides essential increase of copper – zinc catalysts efficiency in the process of methanol conversion with the purpose of obtaining the hydrogenous fuel.

UTILIZATION OF LARGE-SCALE COMPOSITE SOLID ROCKET PROPELLANT CHARGES WITH APPLICATION OF CATALYTIC TECHNOLOGIES

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A novel technology of utilization of composite solid propellant charges with recovery of main components was developed. The method provides full environment safety due to application of effective catalytic technologies for purification of toxic and harmful products.

The objective of this work is to develop a new, efficient, and environmentally safe technology for processing large-scale composite solid rocket propellant (SRP) charges (up to 50 tons) in order to dispose of the strategic missiles discarded due to technical reasons in the course of production, storage and service, and also subject to dismantlement according to the START-2 treaty.

The technology is based on chemical disruption of SRP polymer binder. The technological stages (Fig. 1) include preliminary fragmentation of the charge by jet cutting with an organic solvent, treatment of the obtained SRP lumps by special disruptive compositions, followed by separation of the propellant solid components and their recycling into commercial products: octogen, ammonium perchlorate and aluminum compounds. The process of SRP charge fragmentation by high-pressure toluene jets was worked out and adjusted (Fig. 2). Kinetic studies of chemical destruction of propellants of 2 types were conducted. The composition of the reaction products was studied by NMR, IR spectroscopy, UV-VIS spectroscopy, GC/MS, etc. Basing on these studies a general tentative mechanism of the process was proposed. The stages of charge fragmentation, SRP chemical destruction, separation of SRP components, regeneration of the disruptive mixtures, catalytic treatment of off-gases and catalytic combustion of organic waste residues were tested and optimized in bench-scale installations.

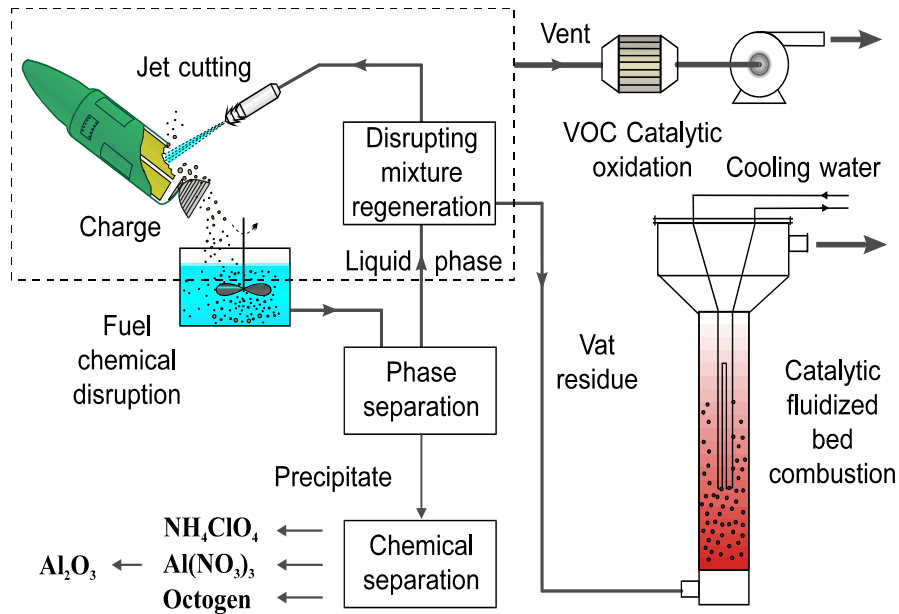


Fig. 1. Scheme of processing large-scale composite solid rocket propellant charges



Fig. 2. SRP charge fragmentation by high-pressure toluene jets

Based on the conducted studies the input data set for the detailed design of an experimental-industrial plant for processing of the full-scale third stage SRP charges with masses up to 3.5 tons, and the block diagram for scaling the process to charges with masses up to 50 tons were developed.

This work was supported by International Science and Technology Center, Project No. 1632

CATALYTIC TECHNOLOGY OF UTILIZATION OF UNSYMMETRICAL DIMETHYLHYDRAZINE

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The aim of this work is to develop environmentally safe technology for utilization of toxic liquid rocket fuel 'heptyl' - unsymmetrical dimethylhydrazine (UDMH). A pilot installation for UDMH combustion in catalytic fluidized catalyst bed with an off gas treatment system has been designed and fabricated. The testing of the installation proved high efficiency and environmental safety of the technology developed

Reduction and conversion of weapons productions in Russia have made extremely urgent the problems of development and implementation of environmentally safe and efficient processes for disposal of rocket fuels. One of the most pressing problems is the development of the disposal process for extremely toxic rocket fuel 'heptyl' - unsymmetrical dimethylhydrazine (UDMH) and industrial wastes containing UDMH.

Boreskov Institute of Catalysis and State Rocket Center "Makeyev Design Bureau" have developed a technology of fluidized bed catalytic combustion of liquid rocket fuels.

Initially, a study of oxidation of UDMH vapor over a number of solid catalysts has been carried out and an optimum catalyst providing efficient UDMH oxidation and minimum NO_x formation was chosen.

A pilot plant for UDMH combustion in a fluidized catalyst bed with an off gas treatment system was designed and fabricated at the State Rocket Center (Fig. 1). The process is carried out in a fluidized bed of alumina supported Cu-Mg-Cr oxide catalyst at a temperature of 600-700 °C. Experiments on UDMH catalytic combustion were performed. The main products of UDMH catalytic combustion are CO₂, water and nitrogen. Admixture of nitrogen oxides in the exhaust gas is removed over monolithic honeycomb catalysts by selective catalytic reduction with ammonia. Additionally, the gas is scrubbed with a water suspension of a special catalyst for UDMH oxidation in aqueous solutions.

The plant was tested under the following conditions: UDMH feed rate 1.8-2.4 l/h, air feed rate 28 m³/h, temperature of the catalyst in the main fluidized bed reactor 600-725 °C.

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The concentrations of UDMH at the outlet of the main reactor were $0.1\text{-}2\text{ mg/m}^3$ and NO_x concentrations were $2000\text{-}6000\text{ mg/m}^3$. The SCR catalyst provided removal of nitrogen oxides with the efficiency of $\geq 90\%$ at a temperature $405\text{-}450\text{ }^\circ\text{C}$.

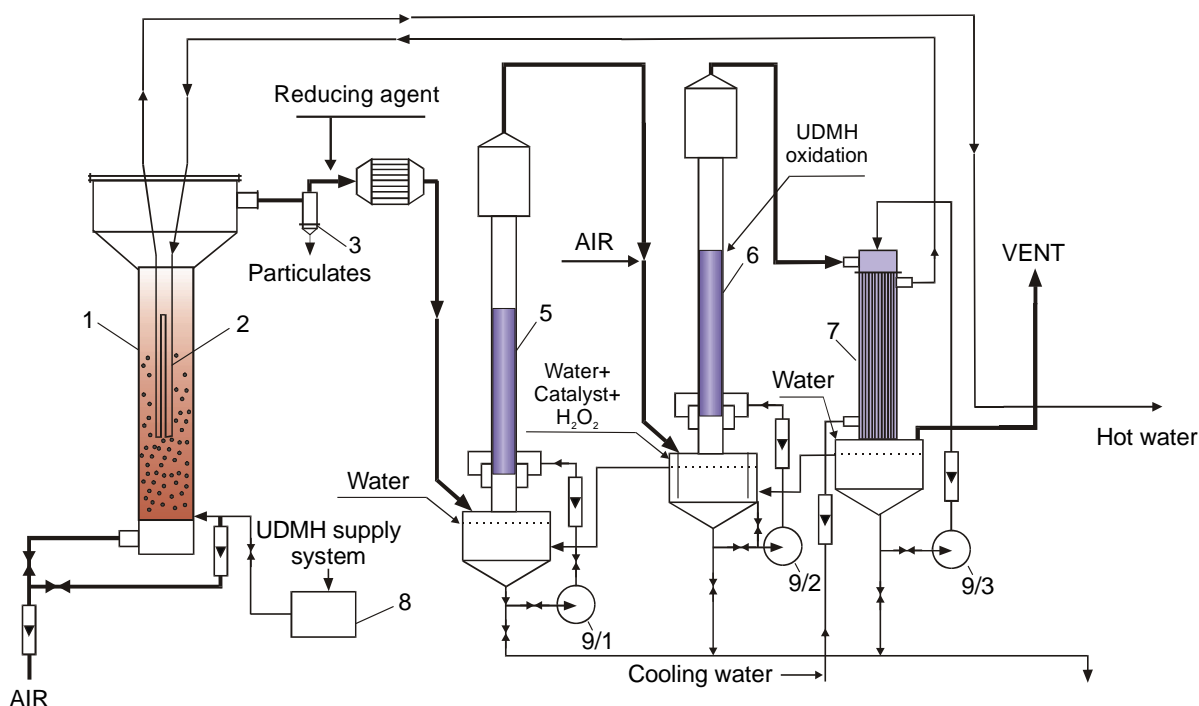


Fig. 1. Flow diagram of the pilot plant for catalytic utilization of UDMH: 1 - catalytic fluidized bed reactor; 2 - water heat exchanger; 3 - cyclone; 4 - SCR reactor; 5, 6 - jet scrubber; 7 - absorber-condenser; 8 - tank for UDMH; 9/1-9/3 – pumps

The monolithic oxidation catalyst placed in the reactor after the SCR catalyst provided the oxidation of excess ammonia with the efficiency over 99.9% and oxidation of UDMH with the efficiency about 80% .

The study of operation of off gas treatment units showed high performance in gas purification from UDMH trace amounts in the scrubber containing the catalyst $2\%\text{Fe}/\alpha\text{-Al}_2\text{O}_3$ for liquid phase UDMH oxidation. Outlet UDMH concentration was below 0.1 mg/m^3 . The testing proceeded under stable operation of all units of the plant and proved efficient destruction of UDMH with suppression of emission of toxic substances to the atmosphere.

This plant designed as a mobile unit will allow UDMH treatment at distant locations (submarine bases and arsenals), and thus exclude hazardous and sometimes-impossible transportation of UDMH to treatment facilities located in densely populated areas.

This work was supported by International Science and Technology Center, Project No. 959

**PROPERTIES AND ACTIVITY OF Ti-Si AEROGELS IN PHOTODEGRADATION
OF ORGANIC COMPOUNDS**

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High temperature supercritical dried (HTSCD) titania-silica aerogels from tetraethoxysilane (TEOS) and titanium butoxide (TB) were prepared by using two methods: precursors co-hydrolysis and silica gel impregnation method. Titania content in aerogels was varied in the range 10 - 30 wt %. The photocatalytic activity studies were carried out in a photoreactor containing 20 and 50 ppm water solutions of model organic compound – methylene blue (MB). Prepared aerogels were meso-, macroporous materials with surface areas up to 1150 m²/g and pore volumes up to 6.7 cm³/g. Up to 96 and 76 % (respectively for 20 and 50 ppm systems) decolorization of solutions was stated after irradiation, as measured by UV spectroscopy.

It was found that highly porous titania-silica aerogels can be prepared by two described methods, namely co-hydrolysis and silica gel impregnation, with use of TB as a titania precursor. Good performance of prepared aerogels in photodegradation of methylene blue from aqueous solutions is a result of accessibility of well developed, photocatalytically active titania species. Influence of alcohol used during the synthesis of sol-gel photocatalysts is more evident in case of co-hydrolysis method than in case of impregnation. Application of simple, co-hydrolysis method leads to materials containing isolated titania on titania-silica matrix. Titania is better utilized in case of aerogels with its relatively small content, what confirms our previous studies concerning salicylic acid photodegradation.

INTERACTION OF N₂O WITH ZSM-5 TYPE ZEOLITES – A TRANSIENT TAP STUDY

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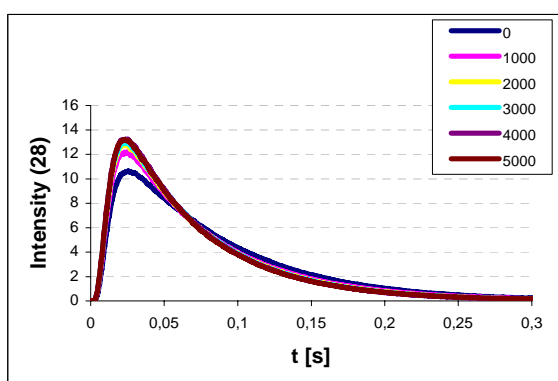
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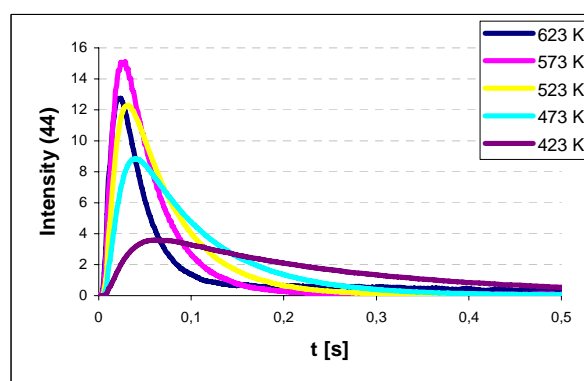
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Iron-containing zeolites of the ZSM-5 type are an important catalyst class for the removal of nitrous oxides from waste gases and in partial oxidations [1]. The catalytic performance is strongly dependent on the formation of surface oxygen species. There is an ongoing discussion in the literature about the influence of different iron species on the formation of those surface oxygen species. However, only few studies addressed the problem of surface oxygen concentration. Generally, these studies are limited by the experimental setup. Therefore it was started to employ transient methods to investigate zeolites [1]; these multipulse experiments were done by injection of 0.31 μmol of N₂O into a continuous flow of inert gas.

In this study, we applied another transient technique, the temporal analysis of products (TAP) method [2], in which we decreased the pulse size by two orders of magnitude compared to [1]. Thereby, we tried to enable a more detailed elucidation of active surface centres and their change in the course of the reaction. Additionally, we investigated the influence of the catalysts' pre-treatment with different gases (He, O₂, N₂) during the activation procedure. The TAP method was also suitable for studies of kinetics, diffusion and sorption processes occurring on the catalyst.



N₂ response curves with growing amount of pulsed N₂O



N₂O response curves at different temperatures

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PREPARATION AND CHARACTERIZATION OF NANOSTRUCTURED SULFATED ZIRCONIAS

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Sulfated zirconia is considered to be a promising catalyst for the isomerization of alkanes. There are several factors which contribute to the activity of the catalyst including the nature and the amount of sulfate groups, acidity as well as structural properties like crystallinity and morphology.

As most of the metal oxides, sulfated zirconia exhibits a sponge-like disordered mesostructure. In order to better understand the influence of structural properties on the catalytic activity, a preparation of catalysts with well-defined and predictable structures is necessary. One possible strategy is the use of surfactants as structure directing agents.

In this study, sulfated zirconia samples were prepared with the help of templates varying in molecular weight (Pluronic P123, Brij-56, CTAB) and characterized with the techniques mostly suitable for the investigation of structures on micro- and nano-scale (SEM, TEM, XRD, nitrogen adsorption). Small angle reflection (Fig. 1) as well as TEM images (Fig. 2) confirmed the ordered mesostructure of sulfated zirconias. Additionally, the influence of the calcination temperature on the stability of materials is discussed. Subsequently, samples were tested for the catalytic activity in the *n*-butane isomerization reaction.

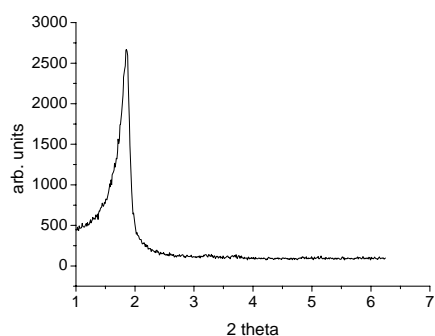


Fig.1 Small angle XRD of the sample templated with CTAB

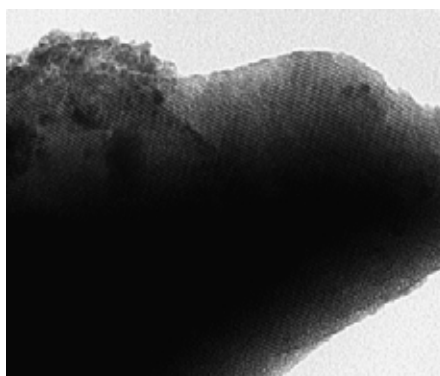


Fig.2 TEM image of the sample templated with CTAB

**EFFECT OF PREPARATION METHOD AND TiO₂ CONTENT ON THE NATURE
OF NICKEL OXIDE SPECIES IN Ni/SiO₂TiO₂ CATALYSTS**

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Recent environmental legislation on diesel fuels focuses on sulphur content, polynuclear aromatics (PNA), and cetane number (CN). CN improvement needs deep hydrogenation of aromatics. Aromatic hydrogenation is necessary for selective ring opening as an additional step in diesel fuel upgrading. Intensive research efforts have been conducted in recent years in order to develop catalysts and process for aromatic hydrogenation [1, 2]. The TiO₂ containing mixed oxides were regarded as very promising supports of catalysts [3]. A number of studies have been devoted to NiMo/Al₂O₃TiO₂ HDS catalysts [4].

The present work tries to understand the effect of TiO₂ (10, 25 and 50 wt. %) content on the nature of oxide nickel phases supported on Si-Ti binary oxides prepared by deposition of TiO₂ on the silica surface via hydrolysis of titanium precursors (Method A and D) and by sol-gel one step hydrolysis (Method E). Catalysts containing 5 wt.% of the nickel were characterized using ICP, TPR, TPO, XRD and SEM methods. Properties of the supports are given in Table 1.

Table 1. Results of N₂ adsorption and NH₃ chemisorption of supports (extruded and calcined at 450 °C).

TiO ₂ content, wt.%/ preparation method	Composition	S, m ² /g	V, cm ³ /g	r, nm	a, mmol NH ₃ /g
10/A		434.3	0.15	1.22	0.149
25/A		464.5	0.21	1.90	0.322
50/A		501.0	0.29	1.61	0.397
10/D		64.8	0.14	0.48	0.079
25/D	SiO ₂ -TiO ₂	338.3	0.55	3.30	0.103
50/D		275.2	0.62	4.54	0.091
10/E		85.5	0.09	2.03	0.297
25/E		338.3	0.56	5.40	0.634
50/E		245.4	0.10	1.32	0.665

The comparison of TPR runs proved that reducibility of supported nickel oxide species might be modified by TiO₂ introduction method. The reduction courses of catalysts supported on SiO₂-TiO₂ containing 10 wt.% of TiO₂ show that nickel is considerably more weakly bound with the surface of support prepared by one step hydrolysis of chelated titanium isopropoxide (TiPOT) and tetraethoxysilane (TEOS). Catalyst obtained by this method is completely reduced in the temperature range 290-580 °C ($T_{max.}$, 420 °C). The TPR result of catalyst prepared by deposition of TiO₂ on the silica surface via hydrolysis of TiCl₄ (Method D) demonstrated that reduction occurs in two, partly overlapping stages. The obtained profile shows maxims at temperature 415 °C and 550 °C. On the TPR profile of catalyst prepared by deposition of TiO₂ on the silica surface via hydrolysis of TiPOT (Method A) one can observe maximum hydrogen uptake at 470 °C. The results show that increase of TiO₂ content in the supports obtained by deposition of TiO₂ on silica surface leads to T_{max} shift towards higher temperature. In the case of one step hydrolysis method reduction of oxide nickel species supported on SiO₂-TiO₂ containing 50 wt.% of TiO₂ occurs in lower temperature range than on SiO₂-TiO₂ containing 25 wt.% of TiO₂. After the first TPR run (TPR up to 900 °C), the catalysts were subjected to re-oxidation at temperature 400 °C followed by the second TPR run (TPR up to 900 °C). The obtained profiles show maxims in the temperature range 300 – 350 °C. Reducibility of the catalysts was related to the TiO₂ phase composition: anatase > rutile > amorphous TiO₂. SEM results show an affinity of nickel to titania rather than to silica (Fig. 1).

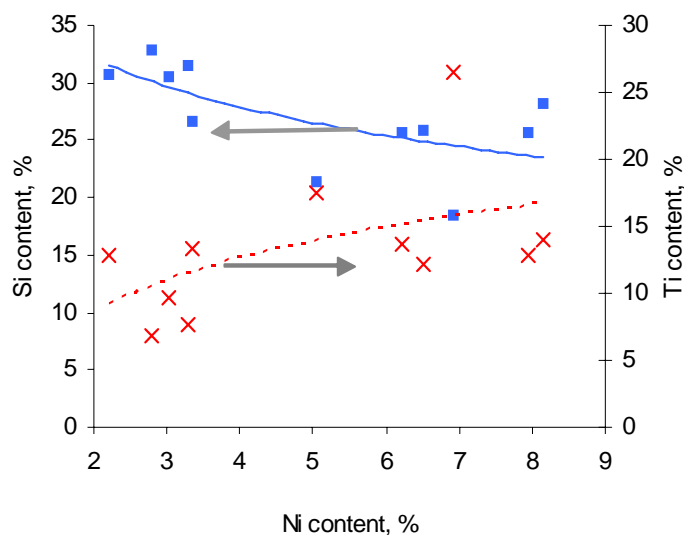


Fig. 1. Correlation between TiO₂ content and Ni content.

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**PRODUCTION OF CATALYTIC COATINGS FOR VEHICLE EXHAUST GAS
CONVERSION**

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In this report we have studied main development and formation stages of catalytic coatings production on the bases of company ROS ECO. We have thoroughly covered questions concerning cooperation with customers, studied prospects of the application of catalytic coatings for neutralization of exhaust of vehicles.

In April 2005, in Togliatti, at the promises of ROS ECO, there started serial production of catalytic coatings for underfloor catalysts of VAZ cars. The first deliveries were preceded by a long-run job including tests, production set-ups, and start-up processes. The catalytic coating for underfloor applications, to meet EU-2 requirements, got the name RE-100c and became basic for further developments. At the end of 2005, upon completing the tests on serial close coupled catalysts of VAZ 2110 family cars, the RE-300c coating was launched featuring better characteristics of the “cold” start, thermo stability and reliability.

Throughout the three years since ROS ECO foundation, the scientific and production personnel have been systematically working to improve the product quality and to reduce its prime cost.

Today, the company is making coatings which meet EU-2, -3, and -4 requirements for benzene and diesel IC engines, with various PGM loadings, series RE-100c, RE-200c, RE-800c, RE-D and others. The company sustains stable business relations with its partners among which are such major OEMS as AVTOVAZ, GAZ, UAZ, KAMAZ, MAZ, IzhMash. For its principal customer, AVTOVAZ, the company is producing a coating which, by its characteristics, ultimately covers the entire range of AVTOVAZ cars, including future perspective projects. In 2006, ROS ECO company has developed a catalytic coating and the method of applying it to use in diesel engine vehicle exhaust systems. This work was done for OAO “GAZ” which will start producing GAZEL vehicle with “Steier” engines in 2007. The knowledge of the diesel engines operation, has enabled, in the shortest time, to get prepared for this production, too.

The company is continuously searching for ways to reduce the prime cost and to satisfy its customers, as well as to enlarge the range of products; this enables ROS ECO to survive in the severe market competition.

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О нас

Мировой лидер в химической отрасли, компания BASF приобрела компанию Engelhard («Энгельхард»), являющуюся ведущим в мире поставщиком технологий для охраны окружающей среды, совершенствования производственных процессов, внешнего вида и характеристик. Объединение ресурсов компании BASF с более чем тридцатилетним опытом лидерства компании Engelhard в области разработки экономически эффективных решений по борьбе с загрязнением атмосферы газообразными отходами позволит предоставить потребителю еще более ценную продукцию. Наша технология контроля за составом выбросов включает в себя решения для маломощных бензиновых и дизельных двигателей, дизельных двигателей повышенной мощности, мотоциклов, двигателей малого объема и многого другого.

Ассортиментный портфель компании BASF включает в себя разнообразную продукцию от химикатов, пластмасс, сельскохозяйственной продукции, химических продуктов тонкого органического синтеза и продукции с высокими техническими характеристиками до сырой нефти и природного газа. Работая в качестве партнера практически во всех отраслях промышленности, компания BASF, благодаря своим решениям в области интеллектуальных систем и продукции с высокой потребительной ценностью, помогает своим клиентам добиваться еще больших успехов.

Компания BASF разрабатывает новые технологии, используя их для раскрытия дополнительных возможностей. Мы совмещаем экономический успех с ответственным отношением к обществу и окружающей среде, внося, таким образом, свой вклад в построение лучшего будущего.

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Применение инновационных технологий для уменьшения загрязнения атмосферы газообразными отходами

Как ведущий в мире поставщик катализаторов компания BASF не имеет равных в разработке технологий по сокращению вредных выбросов для различных областей применения технологических систем, предотвращающих загрязнение воздуха, которым мы дышим. Накопленный опыт дал компании BASF возможность стать пионером в разработке первого каталитического дожигателя выхлопных газов для автомобилей.

Сильной стороной компании BASF является не только технология катализаторов, но также область прикладного инжиниринга и технологии производства. Уникальная способность компании BASF эффективно использовать все три сферы своей компетентности дает отличные результаты сейчас и перспективу на будущее.

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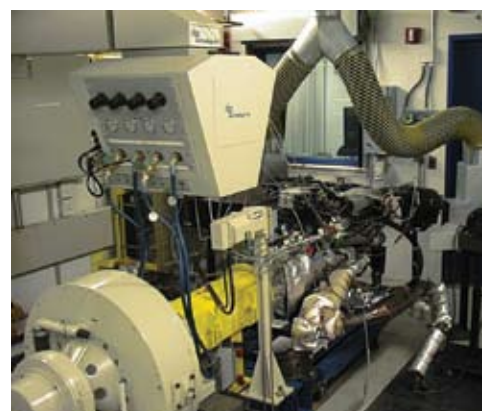
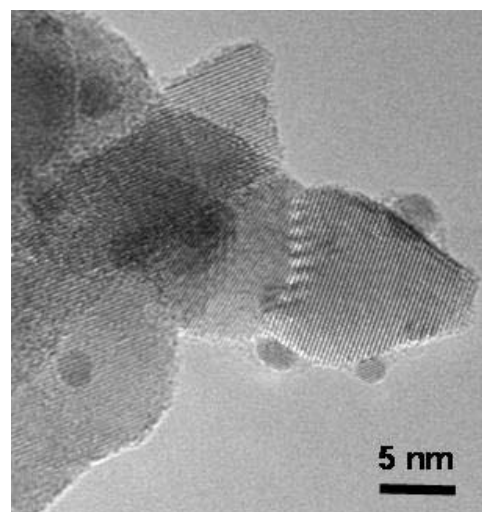
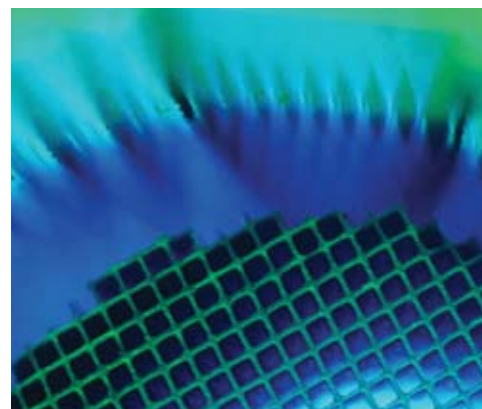
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Прикладной инжиниринг

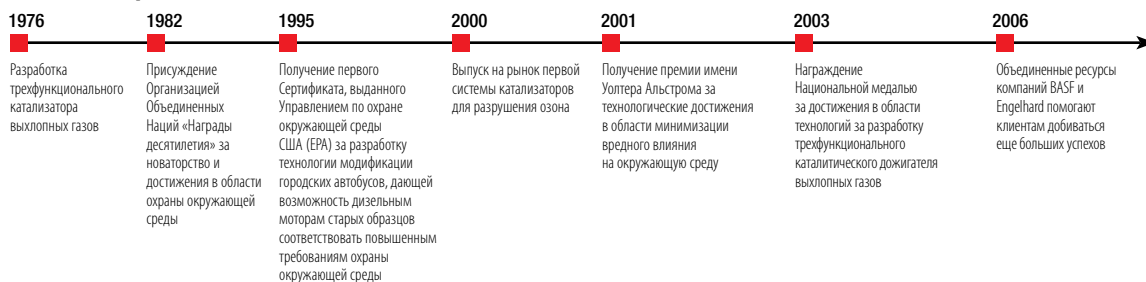
Компания BASF вложила значительные средства в предприятия и персонал прикладного инжиниринга для построения более тесного сотрудничества с клиентами и разработки оптимальных решений в борьбе с загрязнением атмосферы газообразными отходами.

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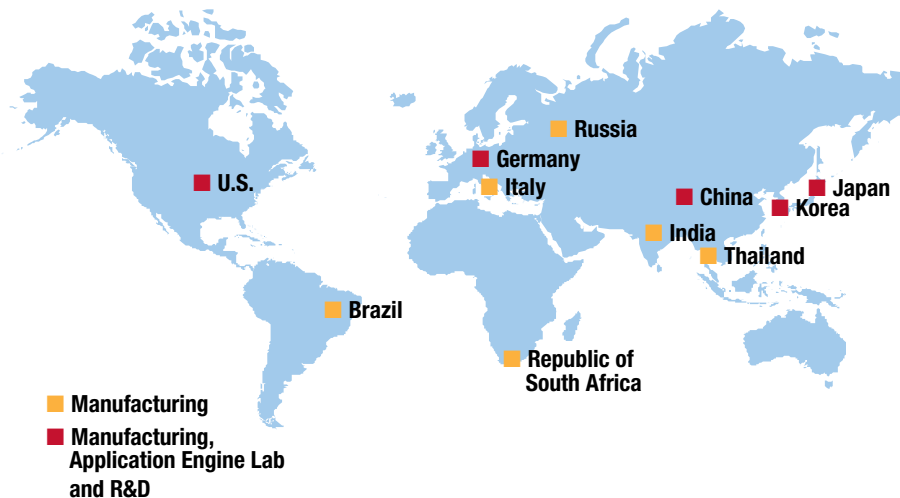
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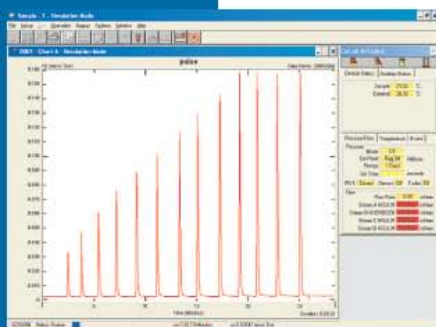
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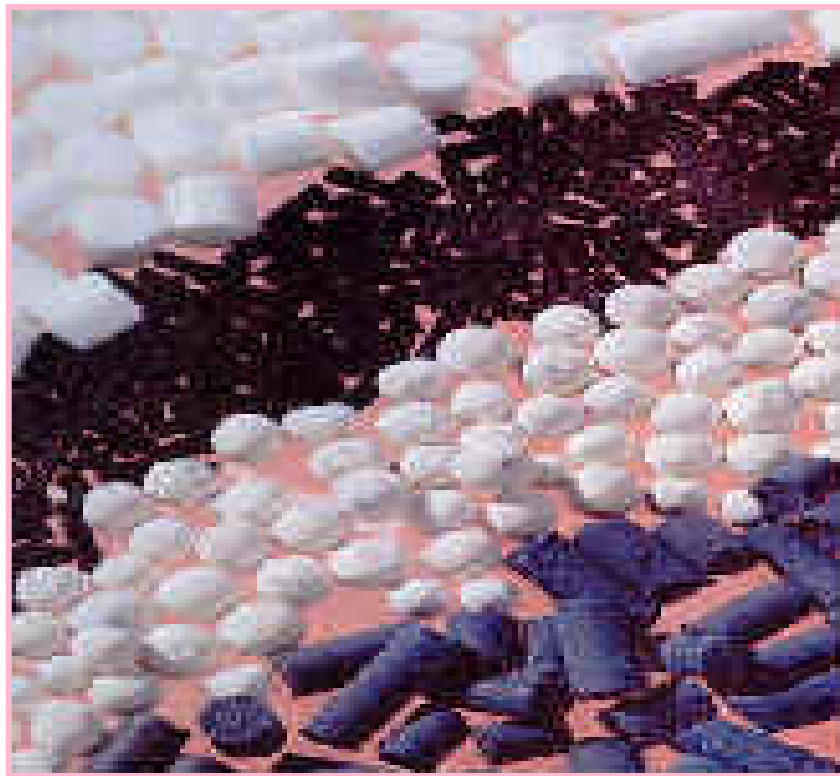
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Catachem Company Ltd and its affiliated branches are working since 1991 in the Russian market of catalysts and oil processing and petrochemical industries.

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- hydrofining of oil raffinats for obtaining base oils with viscosity index of 112-115;
- hydropreparation of vacuum gas oil as a feed of cracking on microspherical catalyst (FCC) and on formed catalyst (TCC);
- mild hydrocracking of vacuum gas oil with the yield of diesel fraction up to 25% mass.

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- development of the optimal running conditions of catalytic set for execution of concrete task;
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Catachem Company Ltd is opened for Russian and overseas consumers for the delivery of catalysts and technologies of the hydroprocesses and the cracking on moving bed, and also is opened in a partner capacity when developing new catalysts and technologies.

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