

***"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**  
**“Catalysis: Fundamentals and**  
**Application”**

**dedicated to the 100<sup>th</sup> anniversary**  
**of Academician Georgii K. Boreskov**

**July 4-8, 2007**  
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**ABSTRACTS**

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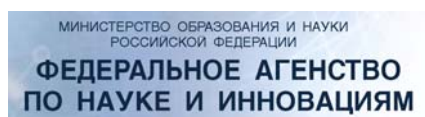
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# PLENARY LECTURES







**THE SCIENCE OF CATALYSIS****Bell A.T.***Department of Chemical Engineering, University of California**Berkeley, CA 94720-1462, USA**E-mail: alexbell@uclink.berkeley.edu*

The availability of active and selective catalysts continues to be essential for the fuels and chemical industries. In fact, it is hard to imagine the successful operation of these industries without ongoing discovery of new catalysts and the improvement of existing ones. While commercial catalysts continue to be developed on the basis of past experience, good chemical intuition, and guided empiricism, knowledge drawn from the science of catalysis is steadily reducing the level of empiricism involved in catalyst discovery and development. The advancement of catalyst science has come as a consequence of the steady development of analytical tools capable of providing structural and compositional information at the atomic and molecular levels in many cases under actual reaction conditions. The past decade has also seen the rapid growth in the application of theoretical methods as a result of advances in computational methods and computer speed. As a consequence, it is possible to observe changes in catalyst composition and structure in situ and to study by means of various spectroscopic methods the relationships between catalyst structure and performance. The use of theoretical methods has enabled the helped in the interpretation of experimental findings and, in some instances, has provided answers to questions not addressable by experimental means. This talk will illustrate how the applications of experimental methods and theoretical methods have contributed to gaining new insights into the factors defining the activity and selectivity of catalysts. Examples will be presented of the application of modern analytical techniques for the characterization of zeolites, metal oxides, and supported metal catalysts. The use of theory in combination with theoretical methods to elucidate reaction mechanisms and kinetics will also be discussed.

**DESIGN OF SELECTIVE HETEROGENEOUS OXIDATION CATALYSTS BASED  
ON THE “SEVEN PILLARS OF OXIDATION CATALYSIS”**

**Grasselli R.K.**

*Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716, USA  
and Department of Chemistry, Technische Universität München, Lichtenbergstrasse 4, D-85748  
Garching, Germany*

*E-mail: Grasselli@cup.uni-muenchen.de*

Twenty five percent of the most important industrial organic chemicals and intermediates are produced by selective heterogeneous oxidation catalysis: they comprise acrolein, acrylic acid, acrylonitrile, methacrylic acid, maleic anhydride, phthalic anhydride, ethylene oxide and propylene oxide.

Over the past fifty years great efforts have been expanded, particularly by industrial researchers, to make selective oxidation processes and their catalysts ever more efficient and environmentally friendlier. The very term “selective oxidation catalysis” implies efficiency, preservation of matter and environmental responsibility. The recently coined term “green chemistry” has already been practiced for the past fifty years by researchers active in the area of selective oxidation catalysis, and that with ever-greater prowess, particularly as the fundamental understanding of catalyst behavior on an atomic and molecular level is continuously improved and refined.

It is the objective of this presentation to give a brief account of some of the most important fundamental principles governing selective oxidation catalysis and how these can be applied to the design of new catalysts. At least seven fundamental principles (“seven pillars”) [1] vital for achieving selective heterogeneous oxidation catalysis can be defined and comprise the selection of the key catalytic element(s) with the respective roles played by lattice oxygen, metal-oxygen bond strength, host structure, redox, multifunctionality, site isolation, and phase cooperation. An illustration of each of these principles applied to actual oxidation catalysts will be presented. The discussion will culminate in demonstrating their applicability to the currently most advanced light paraffin oxidation and ammoxidation catalysts and how they aid in explaining the high efficiencies of these catalytic systems.

In general, the principles are useful in understanding the behavior of metal oxide catalysts and comprise broad guidelines for the design, synthesis and ultimate commercialization of new and more efficient catalytic systems.

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## GREEN CATALYTIC TECHNOLOGY: RECENT DEVELOPMENTS OF HETEROPOLYACID AND PEROVSKITE CATALYSTS

**Misono M.**

*National Institute of Technology and Evaluation (NITE, Shibuya-ku, Tokyo 151-0066, Japan*

*E-mail: misono-makoto@nite.go.jp*

After Green Chemistry (GC) and the roles of catalytic technology in GC are briefly described, recent developments of heteropolyacid and perovskite catalysts (both heterogeneous) are introduced with examples of practical applications. Among the examples are the syntheses of acetic acid and ethyl acetate using heteropolyacid catalysts and automobile catalysts based on the combination of noble metal and perovskite.

Green Chemistry (GC) is defined as innovative chemical technology to minimize the consumption of depletive resources and the discharge of wastes as well as the risks caused by chemical technology, through the life cycle assessment of chemical products and processes at the stage of design, and to secure the health, soundness and safety for the humankind and the environment. Precaution rather than after-treatment is stressed in GC. GC is, in a word, environmentally friendly chemical technology and an essential technological element of the sustainable society. Two reasons why GC is necessary are (i) the limit of massive growth of the activities of humankind and (ii) the anxiety in the society concerning the chemical risks. The aims of GC are (i) significant reduction of environmental impacts and chemical risks (see Eq. 1), (ii) harmonization of economy and environment, and (iii) establishment of sound relationship between chemical community and the society.

$$\begin{aligned} & \text{Environmental Impacts (EI) and Chemical Risks (CR)} \\ & = \{(\text{EI, CR})/\text{GDP}\} \times (\text{GDP}/\text{Population}) \times \text{Population} \end{aligned} \quad (1)$$

In this lecture, the importance of Green Catalytic Technology is described with some successful examples; (1) processes of the syntheses of acetic acid and ethyl acetate using heteropolyacid (HPA) catalysts and (2) automobile catalysts based on the combination of noble metal and perovskite. In the case of ethyl acetate, the control of thin layer structure of HPA on silica support as well as its pore structure and purity are essential for promoting the main reaction and suppressing undesirable side reactions (e.g., oligomerization) that bring about deactivation of catalyst. With these ideas Showa Denko Co. successfully improved their industrial processes. Catalyst life has become more than three times longer. In the latter example, Daihatsu Motor Co. successfully developed Pd or Pt/perovskite catalysts in which

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Pd or Pt ion is atomically incorporated in the perovskite lattice in the oxidizing atmosphere and forms nanoparticles of Pd or Pt metal in the reducing atmosphere. The structure and processes are confirmed by several physicochemical measurements. The catalysts are very much durable when applied to automobile emission that alternatively changes between reducing and oxidizing atmosphere. The invention enabled to reduce the amount of noble metal usage by 70% in the case of Pd/perovskite.

**OXIDATION CATALYSIS: ACTIVE OXYGEN IN SELECTIVE OXIDATION****Panov G.I.***Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia**E-mail: Panov@catalysis.ru*

Oxidation catalysis was a central part of Boreskov's scientific interest. Most of his general ideas moved forward in catalysis (approximate constancy of specific catalytic activity, role of bond strength, influence of reaction mixture on the catalyst, energy compensation, relationship between concerted and stepwise mechanisms) were mainly based on results obtained with catalytic oxidation.

There are two approaches used for understanding the mechanisms and regularities of oxidation catalysis. The first one assumes a key role of activation of organic molecules (with the importance of C–H bond energy) and is mainly used to rationalize the results on selective oxidation. The second approach, developed mainly by Boreskov and his school, assumes a key role of oxygen activation in terms of its bond energy to the surface, and is mainly used to rationalize the results on complete oxidation.

The lecture reviews literature data related to various oxygen species identified on metal oxide surfaces and their possible role in selective oxidation catalysis. A present-day concept, which has been basically formulated by Boreskov in the 60s, in a somewhat simplified form can be presented as follows:

1. Selective oxidation is provided by strongly bonded and low reactive lattice oxygen in the form of terminal (M=O) or bridging (M–O–M) species;
2. Complete oxidation is provided by weakly bonded and high reactive adsorbed oxygen species.

This concept, supported by many experimental results, serves as a useful guideline in the field of heterogeneous catalysis. However, some important mechanistic questions remain unanswered. In particular, does the lattice oxygen interact directly with the molecules to be oxidized, or via its preliminary transformation into a more reactive intermediate species?

Recent studies on the oxidation with N<sub>2</sub>O over FeZSM-5 zeolites showed that formation of selective oxidation products in this system proceeds with participation of O<sup>-</sup> radicals, which are weakly bonded and very reactive surface species. This result seems to be of principal importance for further development of the present-day concept. It assumes a possible integration of a once suggested (but not recognized) radical oxygen idea supposing O<sup>-</sup> radicals to be intermediate species in selective oxidation. This species can be considered as a universal tool for the activation of organic molecules via the hydrogen abstraction step, which may have relevance not only for heterogeneous but also for homogeneous and biological oxidation.

**CO HYDROGENATION ON COBALT CATALYSTS****Holmen A.***Department of Chemical Engineering, Norwegian University of Science and Technology,**NO-7491 Trondheim, Norway**E-mail: holmen@chemeng.ntnu.no*

In Fischer-Tropsch synthesis CO and H<sub>2</sub> are converted to hydrocarbons. Modern Fischer-Tropsch synthesis focuses on maximizing the yield of long chain paraffins (waxes) which are hydrocracked to high quality diesel and other products. The synthesis is usually described by a chain growth mechanism where a C<sub>1</sub> unit is added to a growing chain. A key element in improved Fischer-Tropsch technology is the development of active catalysts with high selectivity to waxes. The synthesis gas may be produced from natural gas, oil fractions, coal or biomass.

The purpose of the present contribution is to review the state of the art of the development of modern FT catalysis.

It has generally been assumed that the Fischer-Tropsch synthesis is a structure insensitive reaction. However, it has recently been shown that for catalysts with cobalt particle sizes smaller than 6-8 nm the turnover frequency decreases with decreasing particle size. It has also been claimed that support modifications may influence the turnover frequency. Steady-state isotopic transient kinetics is an efficient method for determination of intrinsic activity. The particle size of cobalt and the type and structure of the support have a large influence on the selectivity to a long chain paraffins. Water is a main product from the Fischer-Tropsch synthesis on Co catalysts and water may influence the reaction in different ways. The dependence of the selectivity as well as the activity to long chain paraffins on catalyst properties will be addressed. The development of theoretical models for description of the reaction is important for the understanding of the reaction mechanisms.

Cobalt catalysts usually deactivates with time on stream. It has been proposed that the deactivation is partly due to surface oxidation of small Co particles. However, detailed characterization of used Co catalysts indicates no oxidation of the Co particles. Possible deactivation mechanisms will be discussed.



**FORCED UNSTEADY-STATE CATALYTIC PROCESSES.  
POSITIVE AND NEGATIVE EXPERIENCE**

**Matros Yu., Bunimovich G.**

*Matros Technologies, Inc., 14963 Green Circle Dr., Chesterfield, MO 63017, USA*

*E-mail: yurii@matrostech.com*

Forced unsteady-state operations in catalytic reactors have been discussed intensively in several thousands publications during last 30 years. The area of research covers composition and temperature modulations and periodic flow reversal in fixed bed reactors, catalyst recirculation in fluidized and transport bed reactors, flow modulations in trickle bed reactors, various techniques applied for periodic control of separating reactors. Many academic studies have demonstrated potentially attractive practical solutions. It was established that allowing cycles for continuous operations creates unusual and often more efficient catalyst states, temperature and compositions distributions in catalytic reactors.

The development of commercial unsteady-state processes is a multi-level and multi-stage task involving pilot and commercial-scale tests coupled with extensive mathematical modeling. New and competition technologies are compared and economic analysis is carried out repeatedly along the project development. Many unexpected hurdles may obstruct commercialization.

This lecture discusses the experience in such unsteady-state technologies as DuPont circulating fluid bed reactor for maleic anhydride production, Goal Line SCONOX<sup>TM</sup> catalytic adsorption system for NO<sub>x</sub> reduction after gas turbines, sulfuric acid, coal mine methane utilization, and VOC control reverse-flow reactors that reached the commercialization stage. Based on the open literature we consider the processes origins and history of the development, results obtained in pilot and commercial units, comparison to the competition technologies.

In application to a mature VOC control reverse-flow reactor technology we discuss such practically important factors as catalyst stability and poison resistance, packed bed non-uniformities, outlet composition spikes, and reactor and valve mechanical designs.

**ASSISTED HETEROGENEOUS CATALYSIS, A LOOK TO THE FUTURE**

**Ledoux M.J.**

*Laboratoire des Matériaux, Surfaces et Procédé pour la Catalyse (UMR7515), CNRS-Univ.*

*Louis Pasteur-ECPM-ELCASS, 25 rue Becquerel, 67000 Strasbourg, France*

*E-mail: marc.ledoux@cnrs-dir.fr*

Like many other disciplines, catalysis have grown by accumulation of concepts, often accompanied by progress in available experimental and analytical techniques. The first generation of catalytic studies mainly focused on the macroscopic parameters ruling the reaction : composition of in and out reactants, temperature, pressure, the natural parameters involved in kinetics. The second generation started to involve surface chemistry, using surface techniques to bind the surface structure of the catalyst to its selectivity, this was followed by the birth of *ab initio* theoretical calculations. The third generation saw the massive intervention of material science in the catalysis world which opened the « black box » in which the catalyst was confined. All along this history, some pioneers were looking at exotic approaches of catalysis like mechano-catalysis, electro-catalysis, photo-catalysis, magneto-catalysis, etc, with disputable success, mainly because they were considered as outsiders by the heart of the catalysis community.

Because of the progress in the mastering of the nanodimension in material science and with the help of computer technology, it is possible to go toward a new generation of scientific investigations in catalysis : the assisted heterogeneous catalysis. This does not exclude what the past generations have built by using mainly the effect of temperature and pressure, but opens new horizons where the catalytic act will be assisted by electrons, by photons or by shaped nanostructures or even better by their cumulative addition.

Examples of the role of the nanoshape, of new photocatalytic systems and conjunction of nanoshaped catalysts with electrocatalysis and photocatalysis on reactions dealing with sustainable chemistry and environment problems, will illustrate the lecture.

## COLLOIDAL METAL PARTICLES FOR THE SYNTHESIS OF CATALYTIC MATERIALS

**Schüth F.**

*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim, Germany*

*E-mail: schueth@mpi-muelheim.mpg.de*

Metal nanoparticles are in use in catalysis for many decades, even if it was not totally clear in the early days of catalysis research that, for instance, in supported noble metal catalysts the active metal was present in the form of nanometer sized particles. However, with the advent of novel analytical techniques and novel synthetic methods it has become possible to synthesize and manipulate colloidal particles in a very controlled manner in order to produce catalytic materials “by design”. Numerous methods have been developed for the synthesis of colloidal nanoparticles with different compositions. Such nanoparticles can be used for many different tasks in heterogeneous catalysis. The presentation will focus on four examples where such designed catalysts have been produced and used.

Simultaneous reduction and stabilization of many different transition metal colloids has been achieved with main group metal alkyls, such as trialkylaluminum or dialkylzinc species, in organic solvents. This method produces metallic colloids of transition metals which are stabilized by a surface layer of partly oxidized Al- or Zn-alkyl species. With copper as the transition metal, interesting models for technical methanol synthesis catalysts can be produced. Aluminum-stabilized copper colloids synthesized by this method were found to have a surprisingly high activity in quasi-homogeneous methanol synthesis at temperatures of 170 °C [1].

Gold-based nanoparticles have been found as active in many catalytic reactions since the discovery of room temperature CO-oxidation activity by the Haruta-group. The synthesis of gold based catalysts proceeds mostly via deposition-precipitation or coprecipitation. However, in such processes, the gold particle size can not be controlled independently of the support material. Deposition of preformed gold-colloids on different supports allows to separate the influence of the support properties from all other factors. Using such strategies one can clearly show that the support does have an influence on catalytic activity, which, however, does not correlate with the reducibility of the support material [2].

Gold-based colloids, as well as platinum based materials, have also been used for the construction of sinter-stable catalysts by encapsulating individual, single metal nanoparticles

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in hollow spheres of zirconia or titania with a permeable shell. Since only one particle is present in each hollow sphere, sintering is effectively prevented until the sphere structure collapses at temperatures of around 800 °C [3].

Finally, nanoparticles can also be used to impart properties to a catalytic material which it does not have intrinsically. Thus, superparamagnetic Co-nanoparticles were anchored to the surface of high surface area silica or carbon and subsequently protected against corrosion. These materials can be loaded with catalytically active species and are fully magnetically separable from solution, thus avoiding cross-flow filtration in slurry reactions where finely divided catalyst particles are needed [4].

Details on these systems, together with recent developments and perspectives will be discussed in the presentation and put in perspective to related work in the field.

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# **KEYNOTE LECTURES**

**KL1 ÷ KL-18**

# **SECTION KEYNOTE LECTURES**

**KLS-I, KLS-II, KLS-YS**







## DEVELOPMENT OF CATALYSTS BASED ON HIERARCHICALLY-ORGANIZED 1D NANOSTRUCTURE

**Centi G., Perathoner S.**

*Dip. di Chimica Ind. ed Ing. dei Materiali (INSTM – UdR Univ. Messina and ELCASS), Salita  
Sperone 31, 98166 Messina, Italy  
E-mail: centi@unime.it*

A heterogeneous catalyst should be optimized on a multiscale level, e.g. from the molecular level to the nano, micro- and meso-scale level [1]. However, often in catalysts a well defined 3D structure (both on short and long-range) is absent, being composed of irregularly shaped nano-crystals. There is thus the need to develop new catalytic materials having a well defined local nano-architecture, which extend in an ordered way over the long-range [2]. In going to this direction, we discuss here two cases: (i) the development of electrodes based on carbon nanotubes (CNT) and carbon nanofibers (CNF) for uses in PEM fuel cells [3] and in the electrocatalytic conversion of CO<sub>2</sub> to long C-chain hydrocarbons [4] and (ii) the preparation of photoactive ordered arrays of 1D nanostructures of titania obtained by anodic oxidation of titanium foils [5, 6].

The first topic will show how the improvement of the efficiency in the chemical to energy conversion will depend from the development and understanding of the organized structure of the electrode, based on metal nanoparticles supported or included in carbon 1D nanostructures which were grown over carbon micro-fibers. This allows improving both fuels cells efficiency and stability with respect to deactivation by CO. The second topic will show how it is possible to prepare different Titania thin films having well defined 1D-array nanoarchitecture. These materials are both interesting for photocatalytic uses and to develop novel type of catalysts based on organized 1D nanostructures.

Work realized in the frame of the collaboration within ELCASS and the EU Network of Excellence IDECAT.

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**STRUCTURAL DESIGN OF Mo-V-O BASED COMPLEX METAL OXIDE  
CATALYSTS ACTIVE FOR ALKANE SELECTIVE OXIDATION**

**Ueda W.**

*Catalysis Research Center, Hokkaido University, Sapporo, Japan*

*E-mail: ueda@cat.hokudai.ac.jp*

New crystalline  $\text{Mo}_3\text{VO}_x$  solids were synthesized by hydrothermal method for the first time and characterized structurally to orthorhombic and trigonal phases. Both of them have a layer-type structure with the particular arrangement of  $\text{MO}_6$  (M=Mo, V) octahedra forming slabs with pentagonal, hexagonal, and heptagonal rings in (100) plane with depending on the crystal phases. These materials are considered to be formed via condensation of discrete octahedron ensemble units. The crystalline solid materials showed extremely high catalytic performance in alkane selective oxidation as well as acrolein oxidation

High dimensional organization of catalytic components is highly important for catalyst preparation, particularly for a multi-functional one which is often necessary for alkane selective oxidation. Preparation of Mo-V-based oxide catalysts is not exceptional; it appeared that careful controls should be made in a whole preparation procedure for making active catalysts. Therefore, inorganic soft syntheses like sol-gel method, hydrothermal method, solvothermal method, and so on, thought to be significantly important for preparation of complex metal oxide catalysts instead of conventional dry up method.

In fact we found that new crystalline solid materials of  $\text{Mo}_3\text{VO}_x$  could be synthesized in a single crystalline form using a hydrothermal method for the first time. We obtained two types of solids in orthorhombic and trigonal structures, both of which have a layer-type structure with the particular arrangement of  $\text{MO}_6$  (M=Mo, V) octahedra into pentagonal bipyramids, hexagonal, and heptagonal rings in (100) plane of slabs, and in the direction of *c*-axis the slabs connect each other through M-O-M bonds in the layer distance of 4.0 Å.

The Mo-V mixed solution before the hydrothermal synthesis exhibited the Raman peaks at the 800–1000  $\text{cm}^{-1}$  with almost the same as observed in the Mo (and V) cluster anions ( $\text{Mo}_{57}\text{V}_6$ ,  $\text{Mo}_{72}\text{V}_{30}$ , and  $\text{Mo}_{132}$ ), all of which possess the pentagonal unit with a central  $\text{MoO}_7$  and five  $\text{MoO}_6$  octahedra with edge sharing,  $[\text{Mo}_6\text{O}_{21}]^{6-}$ . These results allowed us to speculate that the essential structural unit in the orthorhombic structure already presents in the preparative solution before the hydrothermal synthesis and that the fundamental structure of the  $\text{Mo}_3\text{VO}_x$  is formed as a result of the self-organization between the negatively charged pentagonal units and  $\text{VO}^{2+}$  cations.

More details on the preparation of the  $\text{Mo}_3\text{VO}_x$  catalyst, structural information, and results of alkane selective oxidation will be presented.

**CATALYSIS BY NANOXIDES: A LOOK AHEAD****Cortés Corberán V.***Institute of Catalysis and Petroleumchemistry, CSIC, Madrid, Spain, 28049 Madrid, Spain**E-mail: vcortes@icp.csic.es*

The application of nanotechnology to mastering the properties of oxide catalysts at the nano scale brings along new research and development challenges to fully understand their behaviour, as well as new opportunities for their application to current and non traditional catalytic uses. The main needs of research and the potential applications in which nanotechnology can have a higher impact will be presented.

Metal oxide catalysts play a key role in the production of petrochemicals, intermediate and fine chemicals, in energy applications and in environmental protection. The control over their nano structure brings new possible applications through new physico-chemical properties, fully different from those of the bulk. Properties of nanoparticles are known in Catalysis since long ago with metal catalysts, but oxide catalysts have specific issues, as a part of their atoms (oxianions) takes part in the reactions they catalyze, and they are in dynamic equilibrium with the reaction medium. This brings additional complexity to their understanding and makes their performance to depend strongly not only on their nature and structure, but also on reactor and process design.

As a consequence, the mastering of the properties and structure at the nano scale in oxide catalysts by application of nanotechnology brings both new challenges and opportunities.

On one hand, it causes new specific research and development (R&D) needs to fully understand them, their preparation and their integration in reaction systems. These needs require co-ordination and integration of R&D activities on oxide catalysts and their related catalytic technology in various dimensions: a broad multidisciplinary approach (chemistry, physics, materials and surface sciences, engineering), “vertical” integration (from concept to process design and final uses) and “horizontal”, by bridging the gaps and lack of communication between the different research communities involved in different areas of applications (electronics, materials, catalysis).

On the other, it opens new ways to both, improving current industrial processes (VOC and NO<sub>x</sub> abatement, selective oxidation and hydrogenation processes, etc.), as well as creating new ways to non-traditional applications of catalysis (detection systems, multi-functional pigments, etc.). A European consortium (CONCORDE) has recently prepared a technology roadmap on nanostructured oxide catalysts for redox applications [1], that has analysed the

present gaps and needs and has identified and ranked 25 application lines where nanotechnology can have a high impact, also analysing their technical risks and potential market growth. Their main finding and conclusions are presented and discussed.

All these issues reveal that the preconceived view of catalysis by oxides as a mature technology is false and should be avoided.

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**MODERN TRENDS IN UPGRADING OF HYDROCARBONS PROCESSING  
TECHNOLOGY**

**Likholobov V.A.**

*Institute of Hydrocarbons Processing SB RAS, Omsk, Russia*

*E-mail: val@incat.okno.ru*

World upgrading trends for processes of oil and gas origin hydrocarbons treatment are mainly directed to increasing of valuable products fund (raw materials for petrochemistry, motor fuels, carbon black, etc.). Development of new more perfect catalysts acts the important part in these trends providing. But it is impossible without holding of thorough fundamental researches of active centers nature of these catalysts as the basis for appropriate technological improvements. In the report the analysis of these items for the set of basis processes for hydrocarbons treatment: reforming, cracking, isomerization, alkylation; organic synthesis processes; carbon black synthesis is carried out. New processes combining the treatment of oil fractions and nature gas components in the same reactor (biforming, bicracking) are examined.

Some new data about the factors influencing on catalytic properties of catalysts active components in basic process and appropriate new generation catalyst waiting practice application are presented.

The development trends of oil and gas treatment basic processes and the appropriate fundamental researches directions are analyzed.



## SURFACE PHASE TRANSFORMATION OF TiO<sub>2</sub> AND ITS PHOTOCATALYTIC SIGNIFICANCE STUDIED BY UV RAMAN SPECTROSCOPY

Can Li

*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

*E-mail: canli@dicp.ac.cn Homepage: www.canli.dicp.ac.cn*

### Introduction

Titania (TiO<sub>2</sub>) has drawn much research attention in recent years due to its possible applications to environmental purification and solar energy conversion<sup>1</sup>. Anatase and rutile phase are the two major phases of TiO<sub>2</sub>. Many studies suggested that the photoactivity of TiO<sub>2</sub> was governed by its crystalline phase<sup>2</sup>. The surface phase of TiO<sub>2</sub> should be responsible for its photoactivity because the photocatalytic reaction takes place on the surface. However, the surface phase of TiO<sub>2</sub>, particularly during the phase transformation has not been well investigated. Additionally, the correlation between the surface phases of TiO<sub>2</sub> and its photocatalytic performance is of great significance, but has remained unclear. The difficulty in answering the above questions was mainly due to lacking suitable techniques that can sensitively detect the surface phase of TiO<sub>2</sub>.

UV Raman spectroscopy is found to be more sensitive to the surface phase of a solid sample when the sample absorbs UV light<sup>3</sup>. This finding leads us to study the crystalline phase in the surface region of TiO<sub>2</sub> by UV Raman spectroscopy as TiO<sub>2</sub> strongly absorbs UV light and further try to correlate the surface phase of TiO<sub>2</sub> and its photoactivity.

### Results and Discussion

Figure 1 shows XRD patterns (Figure 1a) and UV Raman spectra (Figure 1b) of TiO<sub>2</sub> calcined at different temperatures. Pure anatase phase is formed at 500 °C. The anatase phase starts to transform into the rutile phase at 550 °C and the rutile content in the bulk is 5.7 % based on the results from XRD. As the calcination temperature is increased from 600 to 680 °C, the percentage of rutile phase in the bulk is changed from 32.9 to 90.7 %. However, the anatase is the only crystal phase when the temperature below 680 °C from UV Raman spectrum (Figure 1b). After calcination at 700 °C, the rutile content in the bulk is increased to 97.0 % while rutile content in the surface region is 56.1%. The bulk region is in pure rutile phase after calcination at 750 °C. But the surface region is still in the mixed phases of anatase and rutile, and the rutile content is 84.3 %.

As presented above, the anatase phase is detected by UV Raman spectroscopy for the sample calcined at higher temperatures than when it is detected by XRD. TEM results show

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that the TiO<sub>2</sub> samples are composed of aggregated particles after the calcination. Based on the experimental observations and combined with the results from the literature<sup>4</sup>, we suggest that the phase transformation of TiO<sub>2</sub> starts from the interfaces among the anatase particles of the agglomerated TiO<sub>2</sub> particles<sup>5</sup>.

A direct correlation has been proposed between the surface phase of TiO<sub>2</sub> and the rate of H<sub>2</sub> production from the photocatalytic reaction of water and methanol over TiO<sub>2</sub> (deposited with Pt as co-catalyst) (Figure 2a) and photodegradation methylene blue (MB) (Figure 2c). It is found that the presence of the surface anatase is important for keeping the high photocatalytic activity of TiO<sub>2</sub> and the photoactivity is sensitive to the surface phase of TiO<sub>2</sub>. Although the bulk region is gradually transformed into the rutile phase with elevated calcination temperature, the samples with surface anatase phase still exhibit the similar photoactivities (Figure 2a, 2c). The photoactivity decreases dramatically when the anatase phase in the surface region is transformed into the rutile phase. The synergistic effect between the surface anatase phase and bulk rutile phase is significantly responsible for the high photocatalytic activity of sample. The synergistic effect could be interpreted in terms of a semiconductor heterojunction between anatase and rutile, which essentially enhances the charge separation efficiency between excited holes and electrons.

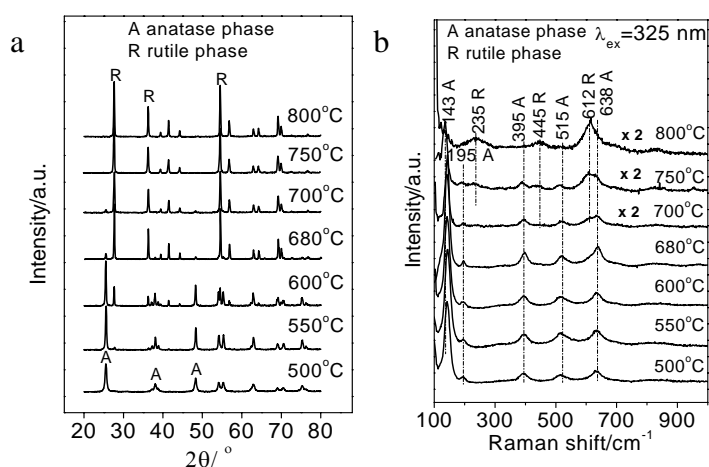


Fig. 1. XRD patterns (a) and UV Raman spectra (b) of the sample calcined at different temperatures.

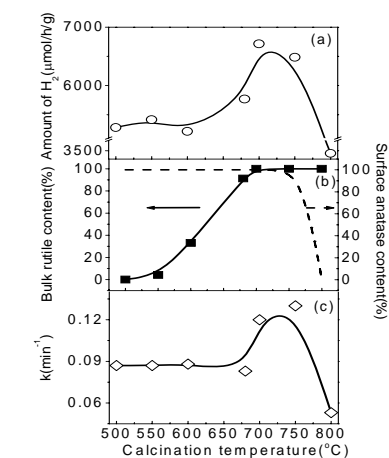


Fig. 2. The overall amount of H<sub>2</sub> production for the photocatalytic water splitting (a) and the apparent rate constants (min<sup>-1</sup>) of the photocatalytic degradation of MB (c) on TiO<sub>2</sub> sample calcined at different temperatures.

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## NEW ASPECTS IN THE PROMOTION OF SULFIDE CATALYSTS

**Lacroix M., Geantet C., Thanh Son Nguyen, Glasson C.**

*Institut de Recherches sur la Catalyse et l'Environnement, UMR 5256 CNRS-Université  
Claude Bernard Lyon 1 ; 2 avenue Albert Einstein 69626 Villeurbanne cedex France, France  
E-mail: michel.lacroix@ircelyon.univ-lyon1.fr*

This work presents a quick overview on the sulfidation processes of an alumina supported Co promoted molybdenum sulfide catalyst. A detailed mechanism will be presented and the role of an hydrocarbon or other additives on this industrial key step will be discussed. A comparison between laboratory gas phase and industrial activations will be done.

Molybdenum and tungsten sulfides promoted by Ni or Co are still the best formulations in oil hydrotreating namely for the removal of S, O and N impurities attached to organic molecules. In the next future the application of these catalysts will be probably extended for cleaning also fuels coming from bioresources. The catalytic activity of such systems continuously increases in the last decades due to a better control of the preparation of the corresponding oxide precursors and of the required consecutive sulfidation process. The aim of this work was to give a detailed description of the sulfidation procedure and to the influence of some additives added to the oxide precursors on the sulfidation of the promoter.

A conventional alumina supported CoMo catalyst was used for this study. Sulfidation was performed in the gas phase using an H<sub>2</sub>-15%H<sub>2</sub>S mixture at atmospheric pressure. The initial oxidic precursor was stepwise heated up to 673 K. At each step, the resulting solid was characterized using several techniques such as XPS, HREM, ESR etc...[1]. In situ QEXAFS experiments were performed in order to better analyze the sulfidation of the promoter [2]. Data shown that sulfidation follows a complex multisteps mechanism:

1. A fast O-S exchange started at almost room temperature without changing the initial Mo VI oxidation state,
2. An intramolecular redox phenomenon occurs leading to a partial reduction of MoVI into MoV and the concomitant oxidation of S<sup>2-</sup> anions into S<sub>2</sub><sup>2-</sup> species
3. Sulfur is then further incorporated into the system and a second redox process takes place leading to the formation of MoOS<sub>2</sub><sup>2-</sup> moieties where the Mo cation is still at V oxidation state.

These four steps do not modify the initial Mo symmetry and they all occurred at quite low temperature. At 473 K, S<sub>2</sub><sup>2-</sup> species are reduced leading to some elemental sulfur and S<sup>2-</sup>

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species bridging two adjacent Mo cations. This step provokes a drastic structural rearrangement conducting to the formation of the well known MoS<sub>2</sub> lamellar structure even if Mo is still in an O-S environment. A further increase of the sulfidation temperature is required to completely transformed the Mo ions in a IV oxidation state.

Cobalt sulfidation is faster than Mo. A fraction of Co atoms is already sulfided at room temperature and sulfidation is complete at about 473 K temperature at which the MoS<sub>2</sub> structure is not formed. This clearly demonstrated that the active CoMoS phase is formed with a pre-existing “CoS” phase.

The addition of carbon on the oxide precursors does not greatly affect the overall mechanism of sulfidation. Coke formation may increase slightly the dispersion of the active phase leading to more active catalysts either in the hydrodesulfurisation of model molecules or real feedstocks [3].

When a straight run GO spicked with DMDS (or a model feed of DMDS and n-hexadecane) is used under conditions mimicking industrial activation procedures, slight differences are observed. The mechanism remains the same but there is no sulfidation at low temperature (until H<sub>2</sub>S is produced by decomposition of DMDS) [4]. Again several techniques will be used to identify the mechanism of sulfidation and the role of additives (like TriEthylenGlycol) on this activation procedure. The presence of TEG impregnated on the oxidic phase slows down the activation of the catalyst helping the formation of so called CoMoS phase.

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**RECENT DEVELOPMENTS AND PERSPECTIVES OF THE DIRECT CATALYTIC  
CONVERSION OF NATURAL GAS TO FUELS, INTERMEDIATES AND  
CHEMICALS**

**Parmaliana A.**

*Department of Industrial Chemistry and Material Engineering, University of Messina,  
Salita Sperone, 31, I-98166, Messina, Italy  
E-mail: [adolfo.parmaliana@unime.it](mailto:adolfo.parmaliana@unime.it)*

Since environmental concerns, low quality and shortage of oil, increasing demand of cleaner fuels and intermediate chemicals are posing a continuous adjustment in the structure of the petrochemical industry, the use of natural gas (NG) as alternative feedstock appears an adequate, sought and viable strategy. In this context, the direct conversion of NG into commodity chemical products actually constitutes one of the hottest and challenging topics in catalysis. Indeed, the disclosure of innovative and clean process routes employing novel catalytic approaches with a low-cost feedstock result in significant economic advantages over current technologies being then a potential breakthrough for the future of the chemical and petrochemical industries.

This contribution refers on the state of the art of the R&D activity on the direct NG conversion highlighting the various research approaches proposed during the last two decades and the achieved milestones. An overall overview of catalyst formulations, reactor configurations and process schemes along with hurdles and drawbacks to be overcome will be accomplished. An account of the running research strategies, scientific and technological key issues and perspectives of this research area will be outlined.

**CATALYSTS LIVE AND UP CLOSE: PROBING CATALYTIC SOLIDS WITH  
IN SITU MICRO-SPECTROSCOPY**

**Weckhuysen B.**

*Inorganic Chemistry and Catalysis group, Department of Chemistry, Faculty of Beta  
Sciences, Utrecht University, Utrecht, The Netherlands  
E-mail: b.m.weckhuysen@chem.uu.nl*

Catalysts are the workhorses of chemical industry: more than 80 % of chemicals have come into contact with at least one catalyst material during their manufacturing process. Catalytic solids can also be extremely complex: solids with high surface areas, for example, possess many different potential active sites in their structure. Determining the active site in these catalysts and elucidating their related reaction mechanism remain intellectual challenges and are of paramount importance for the road to the so-called rational design of catalysts, offering prospects of improved formulations of existing catalysts, and the possibility to create more effective and selective catalysts from scratch. Rational design remains in most cases a pipe dream: the experimental tools available for monitoring catalysts as they work are still, in the main, too rudimentary. Nevertheless, this area of research – often referred to as in-situ or operando spectroscopy – has seen tremendous progress over the last decade, partially as a result of improvements in analytical instrumentation. The aim of the lecture is to give an overview of the field of in-situ spectroscopy of catalytic solids and more in particular illustrate with specific examples what the laboratory at Utrecht University has been doing over the last 5 years in this area. The lecture starts with a potential roadmap for future in-situ studies, outlining the challenges, limitations and possibilities of this research approach. Two areas of interest will be discussed in detail: (1) the development of time-resolved combined in-situ spectroscopy and (2) the development of in-situ micro-spectroscopy. These two approaches will be illustrated with case studies including supported metal (oxide) catalysts as well as zeolites.



## QUANTUM CHEMISTRY AS A NANOTECHNOLOGY: HOW TO TAILOR A CATALYST WITH DEFINED PROPERTIES?

**Witko M.**

*Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,  
ul. Niezapominajek 8, 30 239 Cracow, Poland  
E-mail: ncwitko@cyf-kr.edu.pl*

At present, a main goal of catalytic science is to tailor the most active and selective catalyst for a particular reaction. This requires understanding of a mechanism of the reaction and of the catalyst role, which cannot be obtained without a detailed knowledge of its physical and chemical properties. Such a goal demands synergy between two parallel and complementary approaches: experimental and theoretical, and gives the opportunity to manufacture catalyst for a particular reaction. In the following the role of theory will be illustrated on the example of V-O systems.

Vanadia-based catalysts are used in many different processes that belong to various types of chemical reactions. Their wide application follows from a fact that  $V_2O_5$  crystallites may exhibit two structurally different types of faces: surface built of chemically saturated atoms and those built of unsaturated cations and anions. Both show different behavior in catalytic reactions by performing a complex multi-step operation on the reacting molecule through activation of some of the bonds within reactant and hindering those interactions, which could result in unwanted product.

In the lecture the energetic stability of low-indices (010), (100) and (001) $V_2O_5$  surfaces will be compared based upon periodic DFT calculations. The electronic structure and activity of structurally different surface oxygen sites will be discussed using both cluster and periodic approaches. Adsorption of hydrogen leading to the formation of surface hydroxyl and water species will be considered. Then adsorption of ammonia on acidic surface OH sites will be accounted for. Creation of surface oxygen vacancies will be undertaken and followed by their re-oxidation through the gaseous oxygen.

**NEW GENERATION OF CATALYST SYSTEMS BASED ON  $\alpha$ -DIIMINE,  
BIS(IMINO)PYRIDINE AND PHENOXY-IMINE COMPLEXES**

**Ivanchev S.S.**

*St-Petersburg Department of the Boreskov Institute of Catalysis of the Siberian Branch of the  
Russian Academy of Sciences, St-Petersburg, Russia*

*E-mail: ivanchev@SM2270.spb.edu*

The data on the synthesis of post-metallocene catalysts systems based on  $\alpha$ -diimine-Ni and bis(imino)pyridine-Fe complexes containing cycloalkyl substituents in the ortho-position of the aryl group are studied in ethylene polymerizations in both homogeneous and SiO<sub>2</sub> or MgCl<sub>2</sub> supported conditions are summarized. A series of novel phenoxy-imine-Ti and Zr complexes is also studied.

The activity of the considered catalyst systems is determined by their ligand structure. The optimum structures of these complexes and temperature conditions for obtaining high quality polyethylenes with high- and superhigh molecular weights and good thermophysical properties are defined.

The data on the synthesis of post-metallocene catalysts and study of their activity in homogeneous and heterogeneous ethylene polymerization performed at St-Petersburg Department of the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences in cooperation with Vorozhtzov Institute of Organic Chemistry (Novosibirsk) are summarized.

The following new catalytically active compounds were obtained:

1. A series of  $\alpha$ -diimine and bis(imino)pyridine ligands containing cycloalkyl substituents in the ortho-position of the aryl ring adjoining to the imine nitrogen were synthesized to subsequently prepare the corresponding complexes;

2. Oligomeric bis(imino)pyridine ligands and relating Fe(II) complexes were prepared for the first time;

3. More than 20 novel phenoxy-imine ligands with various structure and corresponding Ti-complexes are synthesized.

The catalyst activity studies for the synthesized MAO activated  $\alpha$ -diimine-Ni and bis(imino)pyridine-Fe complexes in homogeneous ethylene polymerizations indicated a significant increase of their effective performance temperatures relating to the counterparts without ortho-cycloalkyl substituents in the aryl rings. These experimental data were confirmed by quantum chemical calculations.

The oligomeric bis(imino)pyridine-Fe(II) complexes were found to effectively catalyze ethylene polymerization at elevated temperatures (70-80 °C) yielding polymers with high molecular weights ( $M_n \sim 400000$ ).

MAO activated mixtures (“reactor blends”) of  $\alpha$ -diimine-Ni and bis(imino)pyridine-Fe complexes in homogeneous ethylene polymerizations are studied for the first time in homogeneous ethylene polymerizations and the synergistic (non-additive) effect of their catalyst behavior is revealed.

The kinetic features of ethylene polymerization catalysis using SiO<sub>2</sub> supported new  $\alpha$ -diimine-Ni and bis(imino)pyridine-Fe complexes as well as their mixtures are studied.

The analysis of the catalyst behavior for the MAO activated novel phenoxy-imine catalyst systems revealed the effect of their ligand structure, particularly substituents in the phenoxy group and at imine nitrogen, upon their ethylene polymerization activity and temperature range of their effective functioning. Quantum chemical calculations of the changes in the heat effects of elementary reactions involved in the polymerization process afforded the explanation of the differences in ethylene polymerization kinetics using phenoxy-imine complexes of various structure.

A series of phenoxy-imine catalyst systems mostly promising for obtaining high quality polyethylenes with the required thermophysical properties under technologically appropriate conditions is determined.

The studies are performed with the participation of researchers from Vorozhtzov Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences (acad. G.A. Tolstikov, I.I. Oleinik, I.V. Oleinik et al.), Institute of Macromolecular Compounds (A.V. Yakimansky), Konstantinov Institute of Nuclear Physics (Prof. V.A. Trunov) and Lomonosov Moscow State University (Prof. V.B. Rybakov).

**Yablonsky G.S., Gleaves J.T.**

*Washington University in St.Louis, USA*

*E-mail: gy@che.wustl.edu*

New frontiers in the TAP-area represent a combination of the new technique of catalyst preparation and new methodology of non-steady-state kinetic characterization. A new approach for precisely tailoring the surface of complex catalytic particles at the atomic level is presented. An apparatus of original construction that combines an atomic beam deposition (ABD) system with a temporal analysis of products (TAP-2) reactor system is described. Catalyst samples were prepared by directly adding metal atoms in sub-monolayer amounts to the surface of micron-sized particles. The approach is illustrated by the examples of CO oxidation over a series of Pd/PdO catalysts. The Pd deposits were characterized using XPS, SEM and TEM. CO<sub>2</sub> production during TPR experiments exhibited oscillatory behavior. The goal of combining ABD with TAP experiments in a single apparatus is to develop a method of establishing direct, reproducible correlations between changes in surface composition and changes in catalyst activity.

Precise kinetic characterization (non-steady-state and steady-state) was performed using pulse response methods, temperature-programmed reaction (TPR), etc. ‘State-by-state’ catalyst kinetic screening is illustrated by the example of hydrocarbon selective oxidation. A new non-steady-state kinetic catalyst characterization procedure is described. Denoted the Y-procedure, it is based on TAP-response experiments using a thin-zone TAP-reactor (TZTR). The main idea of the Y-procedure is to use the diffusional flow as a ‘measuring stick’ to determine the concentration and reaction rate in a narrow zone of catalytic material. The described results in atomic level catalyst design assisted by precise kinetic characterization open new possibilities for inferring the working structure of the catalytic active site and revealing mechanistic details of complex reactions based on a battery of non-steady-state and steady-state kinetic measurements using the ‘interrogative kinetics’ methodology.

## THEORETICAL AND EXPERIMENTAL ASPECTS OF USING STRUCTURED CATALYTIC SYSTEMS

**Noskov A.S.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: noskov@catalysis.nsk.su*

The paper deals with the development of theoretical and experimental bases of applying structured catalytic systems to the creation and optimization of catalytic processes.

Solutions of the following problems are used as examples:

1. Theoretical and experimental studies of heat (mass) exchange processes in structured systems and optimization of catalytic honeycomb monoliths.
2. Development of mathematical methods and experimental tools to control grain structures in catalytic reactors.
3. Characterization of catalytic properties and creation of catalysts for structured systems.

The heat (mass) transfer processes in honeycomb and fiber catalysts were studied using NMR tomographic and computational hydrodynamic techniques. Measurements of the proton density (moisture content) in the samples allowed the evaporation rate to be determined as dependent on the geometrical parameters and gas phase flow rate. Theoretical calculations were based on solution of the Navier-Stokes equation to demonstrate that the unsteady gas flow at the inlet fragments of the honeycomb monolith results in an increase in the mass exchange coefficients.

The obtained theoretical and experimental data on mass exchange processes in honeycomb monoliths were used for theoretical optimization (determination of the minimal concentration of an active component, for example, platinum) of the catalyst to provide the needed conversion of the initial reactant. The theoretical solution of this problem required the development of new methods for analysis of mathematical models of catalytic reactors. The problem of optimization of the active component distribution was reduced to the solution of special Euler equation.

In general, the results obtained for irreversible catalytic reactions can be described as follows: The optimized active component distribution allows the precious metal content to be decreased by 30–50 % at the same conversion.

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At present, intensive studies are focused on synthesis of catalysts based on structured fiber materials. These are materials with unique catalytic properties in a number of chemical reactions. Specific hydrodynamics of gas flow in the fiberglass systems were estimated in two-dimensional approximation using the Navier-Stokes equation. It was demonstrated for the case of gas flowing at the rate of 0.1 m/s and the distance of 10  $\mu\text{m}$  between individual fibers that the mass exchange coefficients are negligible in the yarns inside the fiber but large enough in the external yarns. Such a mass exchange behavior makes it necessary to use fiberglass-based reactors of special design. The mass exchange in fiberglass systems was studied in more detail using up-to-date physical methods (NMR tomography) and computational hydrodynamics based on the three-dimensional fiberglass model.

Materials based on quartz fibers are promising for creation of catalytically active filters to trap and oxidize soot particles in exhaust gases of diesel engines. Oxide catalysts for oxidation of soot particles were developed at the Institute of Catalysis, which allow the ignition temperature of model soot to be reduced from 435  $^{\circ}\text{C}$  (without contact with a catalyst) down to 200–250  $^{\circ}\text{C}$  (at the contact with the catalyst). A mathematical model developed for theoretical analysis of the soot filter operation includes non-stationary equations for gas-phase concentrations of soot particles,  $\text{O}_2$  and  $\text{CO}_2$ , for the solid-phase soot content, for the filter temperature, as well as an equation for pressure drop in the filter. The main results were modeling of dynamic regimes of filling with soot and oxidative regeneration of the filter based on the fiber material with the supported catalyst. The calculations allowed estimation of the parameters of dynamic regimes of the catalytic soot filter operation (temperature, degree of trapping soot particles etc.) to provide effective cleaning (80–85 %) of the exhaust gases of diesel engines.

In catalytic reactors with fixed granular beds, the high efficiency is provided by the volume-uniform structure and stability of the bulk bed under its operation in an industrial reactor. The theoretical and experimental studies made it possible to understand the dynamics of the formation of granulated beds in adiabatic and tube catalytic reactors. The results obtained were used for designing special loading facilities to create granular catalyst beds with controlled properties.

A new set of characteristics of the granulated catalyst beds, such as the uniform structure for the filtering flow, a higher density of catalyst packing, stability under variable stresses, provided a 5–10 % increase in the efficiency of industrial reactors and a longer catalyst service life. The results obtained were demonstrated by operation of more than 30 industrial reactors.

In fluidized catalyst bed reactors, there occurs the turbulent mode of fluidization that is characterized by low-sized gas bubbles, small amplitudes of pressure fluctuations in the bed and high rates of interphase mass exchange. The properties of the turbulent fluidized bed were used for development of a new large-scale process for synthesis of nitrous oxide through selective oxidation of ammonia. For this process, supported magnesium-bismuth oxide catalysts were developed. The catalysts are highly selective for  $N_2O$  (up to 90 %) over a wide range of experimental conditions and provide a low yield of  $NO$ . Employing of the turbulent mode of fluidization allowed the catalyst loading to be decreased by a factor of 2.5 in comparison to that in the traditional bubble-forced fluidization.

The studies gave rise to creation of the first pilot plant for synthesis of up to 10 t/y of nitrous oxide through ammonia oxidation in the fluidized catalyst bed. When a concentrated reaction mixture is used (50 vol %  $NH_3$  and 50 vol %  $O_2$ ), the reaction products contain 85 vol % of  $N_2O$  and no more than 2 ppm of remnant  $NO_x$ .

In general, the reported results can be classified into two groups. First, these are the studies and development of methods for effective application of regular-structured catalysts (honeycomb monoliths, fiber materials). On the other hand, the structures (turbulent fluidized bed, dense packed granular structures in fixed bed reactors) can be controllably created in the catalytic reactors to make more effective through application and managing of these structures. The obtained scientific results are applied both in the existing industrial processes and in the new catalytic technologies.

**THE MODERN HIGHLY EFFECTIVE CATALYSTS FOR OLEFIN  
POLYMERIZATION. EVALUATION OF THE PROSPECTS OF CATALYSTS OF  
VARIOUS TYPES AND COMPOSITION FOR POLYOLEFIN PRODUCTION**

**Zakharov V.A.**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: zva@catalysis.ru*

The results obtained in Boreskov Institute of Catalysis at research and development of highly efficient catalysts of various types and compositions (supported Ziegler-Natta catalysts, catalysts based on zirconocene complexes and bis-iminopyridyl complexes of Fe, Co, V, Cr) are presented. Possibilities and prospects of the catalysts of different types and compositions for production of polyolefins are discussed on the base of these data.

The great amount of the new highly active catalysts for olefin polymerization based on the metallocene and postmetallocene complexes of Ti, Zr and Hf, bis-iminopyridine complexes of Fe, Co, V, Cr and some another metallocenes have been found and studied during last two decades. These new catalysts allow to control more precisely the molecular structure of polyolefins and design the new polymer materials. But at the same time many interesting results have been obtained to improve the well known supported Ziegler-Natta catalysts (especially supported titanium-magnesium catalysts which contain titanium chlorides on the support-highly dispersed magnesium chloride and some special additives). Nowadays these catalysts dominate at production of isotactic polypropylene and high density polyethylene. Some results obtained in our lab on the study of the supported titanium-magnesium catalysts (TMC) and development of the new modifications of these catalysts are discussed in this presentation.

The experimental data on the composition and structure of the surface species formed in these catalysts, on the number and reactivity of active centers, on the molecular structures and morphology of polymer produced with these catalysts are presented.

The new original method for preparation of these catalysts is found. This method allows to produce various types of the supported TMC with different composition and optimal morphology needed for productions of different grades of polyolefins.

The new homogeneous catalysts based on zirconocene complexes and bis-iminopyridine complexes of Fe, Co, V, Cr are studied at ethylene polymerization. It is necessary to transform these homogeneous catalysts to the supported ones to use in the commercial scale. We have studied the interaction of zirconocene with different supports and clarified the effect



of the acidic sites of the supports and effect of different aluminorganic activators on the formation of active sites of the supported catalysts.

We have found that bis-iminopyridine Fe (II) complexes are very flexible and suitable active component for preparation of the highly active supported catalysts with different supports and different activators. Data on the activity of these catalysts and molecular structures of PE produced are presented.

**CATALYSIS AND PROCESS DESIGN WITH WALL-COATED MICROCHANNEL  
REACTORS - USE IN FUEL PROCESSING AND MORE**

**Hessel V.<sup>1,2</sup>, de Croon M.<sup>2</sup>, Guan G.<sup>1</sup>, Kolb G.<sup>1</sup>, Löwe H.<sup>1,3</sup>, Rebrov E.<sup>2</sup>, Schouten J.<sup>2</sup>,  
Zapf R.<sup>1</sup>**

<sup>1</sup>*Institut für Mikrotechnik Mainz GmbH (IMM), Mainz, Germany*

<sup>2</sup>*Eindhoven University of Technology (TU/e), Eindhoven, the Netherlands*

<sup>3</sup>*Johannes-Gutenberg-Universität Mainz, Mainz, Germany*

*E-mail: hessel@imm-mainz.de*

Microstructured reactors provide both an entirely new reactor and processing concept with highly intensified mass and heat transfer, whereas their construction and operation may result in higher technical expenditure as compared to traditional reactors such as fixed-bed reactors. Thus, in order to fully exploit their beneficial properties at the expense of the drawbacks and the risk of facing the “unknown”, the development of tailored catalysts and the reactor system design are and remain the major issues. Following today’s dominant application, which is fuel processing for fuel cells, the main issues are described - catalyst and catalytic reactor development as well as system-level analysis.

The finding of *highly active catalytic systems* is the major issue for alcohol fuels such as methanol and ethanol, since the operating temperature of the reformer itself is significantly lower compared to hydrocarbon reforming. On the contrary, catalyst activity typically is given for high-temperature micro-fuel processor operation, but then to have *catalyst stability* is most relevant. This holds for propane, butane and mixtures such as LPG. The higher operating temperature, normally exceeding 700°C, promotes catalyst deactivation, e.g. by sintering procedures. WHSV values of up to 2400 Ndm<sup>3</sup>/(h g<sub>cat</sub>) were achieved for the partial oxidation of propane. For gasoline, deactivation by coking gets more an issue compared to light hydrocarbons. The addition of air to the reformer feed is one viable option to cope with coking problems. Advanced *catalyst coating- and reactor material technology* is crucial for steam reforming of higher hydrocarbon fuels such as diesel due to the very high reaction temperature exceeding 800°C. A microstructured heat-exchanger / reactor was developed and operated for more than 40 hours already, which completely converts diesel fuel.

While much attention has so far been paid to the above mentioned reactor and process engineering as well as experimental catalyst studies, a *bottom-up engineering of the catalyst itself* for micro-channel layers is missing, with the goal to achieve a counterpart in regularity and functionality on the nano-scale to the microengineered reactor: ‘structured reactors –

structured catalysts'. As one first step, *highly homogeneous sub-micronscale catalyst structures* were prepared. These inverse-opal silica and alumina coatings owe uniform pore size, interconnected pore network with ordered structure and regular pore wall, and tailored surface properties and are being tested for preferential carbon monoxide oxidation and propane catalytic combustion.

System integration is the final challenging task and will be exemplified by integrated plate heat-exchanger reactors for the combined propane steam reforming / propane combustion, diesel steam reforming / combustion and for the steam generation fed by hydrocarbon combustion. These devices are operated at temperatures  $>750^{\circ}\text{C}$  and up to a size range of  $5 \text{ kW}_{\text{el}}$  of the fuel cells supplied. Cooling capabilities have been introduced into reactors designed for the partial oxidation of propane, the water-gas shift and the preferential oxidation of carbon monoxide. Balance-of-plant components such as cross-flow heat-exchangers working up to  $900^{\circ}\text{C}$ , evaporators, condensers and pre-heaters for fuel cells and fuel processors complete this list. At IMM, a complete fuel processor capable of feeding a  $5 \text{ kW}_{\text{el}}$  fuel cell and working with autothermal reforming of iso-octane as a model for gasoline has been successfully put into operation. At TU/e, issues of *heat management* were largely resolved for the preferential oxidation, which resulted in a tailored integrated design with three microstructured heat exchangers and one reactor. *Flow distribution* issues were addressed for the same purpose. Recently, an exergy analysis and a performance benchmarking to fixed-bed reactors were given.

Meanwhile, together with the Truma Gerätetechnik Company, Europe's largest manufacturer in the field of liquid gas heaters for leisure vehicles and boats, a complete fuel processor was developed which converts LPG into electricity [8]. This is used in conjunction with a fuel cell system that is specific for the recreational vehicle area with a view to the environment and efficient usage. First commercial systems will be launched 2008 in selected numbers.

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**SYNTHESIS, STRUCTURE AND PROPERTIES OF THE NOVEL NITROGEN  
DOPED NANOSTRUCTURED CARBON MATERIALS FOR PEMFC CATHODE  
CATALYSTS**

**Ismagilov Z.R.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: zri@catalysis.ru*

The use of novel nanocarbon supports: carbon nanofibers (CNF) and amorphous microporous carbons (AMC) for synthesis of Pt and non-Pt cathode catalysts for PEMFC was investigated. Different structural types of CNF and AMC formed from different organic precursors were prepared and characterized by XRD, TEM, XPS and adsorption methods. Pt cathode catalysts with 5-30 wt.% Pt loading were synthesized and studied by XRD, TEM, CO adsorption and EXAFS. The activity of the catalysts was studied in a MEA cell with a low Pt loading level of 0.02-0.09 mg/cm<sup>2</sup>. The MEA testing showed that the Pt cathode catalysts on CNF had similar performance in comparison with a catalyst on conventional carbon support Pt/Vulcan XC-72R, while the catalyst prepared on AMC had better output in MEA even at a lower Pt loading.

A series of nitrogen containing N-CNF and N-AMC were prepared for synthesis of non-platinum cobalt catalysts. These carbons characterized by XRD, electron microscopy XPS and adsorption methods. The state of cobalt in the catalysts on N-CNF or N-AMC was studied by TEM and XPS. It was found that supported Co is present in the catalysts both as polydisperse metal particles of different types and N-bound Co cations. The study of the catalysts by rotating disc method showed that the oxygen reduction activities generally increase with the nitrogen content of the support.

**IONIC LIQUIDS: CATALYSIS, ORGANIC SYNTHESIS, ELECTROCHEMISTRY, ...  
WHAT NEXT?**

**Kustov L.M.**

*N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow Russia*

*E-mail: LMK@ioc.ac.ru*

Ionic liquids, i.e. the low-temperature molten salts containing an organic fragment of N-alkylammonium (pyridinium, imidazolium) or other heterocyclic or aliphatic moiety as a cation and any type of the anion including halide, metalhalide as well as other anions ( $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$ ,  $\text{BF}_4^-$ ,  $\text{OTf}^-$ ,  $\text{NTf}_2^-$ ,  $\text{OAc}^-$ ,  $\text{NO}_3^-$ ) are now being studied extensively in diverse processes of organic synthesis as ecologically friendly (“green”) solvents, catalytic media and electrolytes.

Such systems have been synthesized and studied in the reactions including, inter alia

- Metathesis of olefins, including functionalized olefins,
- Alkylation of aromatic substrates with olefins,
- Alkylation of butanes with isobutenes,
- Oligomerization of olefins,
- Isomerization of paraffins and naphthenes,
- Cracking of hydrocarbons,
- Isomerization and disproportionation of alkylaromatic hydrocarbons,
- Gatterman-Koch carbonylation of aromatic hydrocarbons,
- Synthesis of hydrocarbons from CO and hydrogen
- Removal of sulfur- and nitrogen-containing compounds from hydrocarbon mixtures.

Ionic liquids form a two-phase system, which facilitates the separation of products from the catalyst. Furthermore, ionic liquids can be reused without any loss of the activity and with no necessity of regeneration. One more advantage of the specific class of ionic liquids – those based on metal halide anions – is their extremely strong acidity, which makes it possible to convert hydrocarbons at as low temperatures as 0-20 °C, unlike many well known acid catalysts.

The use of perfluorocarbons («blue blood») as a component of the reaction mixture together with ionic liquids allows one to increase the solubility of gases ( $\text{CO}$ ,  $\text{O}_2$ ) and to

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enhance the reactivity of metal-complex catalysts by 2-10 times, in particular in the Fischer-Tropsch process.

New data were accumulated on the use of ionic liquids in the process of paraffin isomerization under mild conditions, alkylation of aromatic hydrocarbons, synthesis of conducting polymers. Ionic liquids have been used in a variety of electrocatalytic and electrochemical processes, such as removal of S- and N-containing compounds, deposition of metals, preparation of electro- and proton-conducting polymers, application in Li-batteries.

The review of the literature and own data related to the use of ionic liquids in the processes of capturing and storage of CO<sub>2</sub> and other gases and purification of gases from different impurities is presented in the lecture.

## CATALYTIC ACTIVATION OF CO<sub>2</sub> – THE USE OF RECYCLED CO<sub>2</sub> IN CHEMICALS PRODUCTION

**Keiski R.L.**

*University of Oulu, Department of Process and Environmental Engineering, POB 4300,*

*FIN-90014 University of Oulu, Oulu, Finland*

*E-mail: riitta.keiski@oulu.fi*

The present-day demand to decrease CO<sub>2</sub> emissions requires increased energy efficiency and actions for separation, storage and utilization of CO<sub>2</sub>. The role of catalysis in the reduction and utilization of CO<sub>2</sub> is widespread [1]. It covers more efficient production of low and non-carbon fuels and electrolytic cells, more effective catalytic converters for lean burn engines, more efficient conversion of renewable resources such as biomass to fuels, and more effective utilization of CO<sub>2</sub>. Aresta and Dibenedetto [2] have also called for the methods to use CO<sub>2</sub> both to reduce emissions and to generate profit for a company. To accomplish all of these goals, new more active and selective catalysts are still needed.

The total production of CO<sub>2</sub> based chemicals accounts for over 100 Mt per year. The commercial utilization of CO<sub>2</sub> is, however, marginal in comparison with the global CO<sub>2</sub> flows, but the utilization is expected at least to triple in short term [2]. The use of CO<sub>2</sub> as the C1 feedstock is discussed widely in the literature [3-4]. The most potential utilization areas are found in the production of urea, salicylic acid, inorganic carbonates and polycarbonates, and methanol. In chemicals production, urea production is the highest in volume and production of methanol has the second largest potential [1]. In the synthesis of methanol, CO<sub>2</sub> is commonly used to adjust the feed composition, since CO<sub>2</sub> consumes more hydrogen than CO. Since CO<sub>2</sub> can be directly converted with hydrogen into methanol with higher selectivity than CO and at lower temperatures, the methanol synthesis directly from CO<sub>2</sub> and hydrogen has gained a wide attention during the last decade. Reports on the use of CO<sub>2</sub> as a solvent for chemical synthesis have expanded, motivated by the implementation of benign processes [5-7]. A particular use of scCO<sub>2</sub> is as a solvent and reagent. One relevant example that benefits the scCO<sub>2</sub> as a C1 source is found in the synthesis of cyclic carbonates [8-9] and dimethyl carbonate (DMC) [10-16].

Our research group has studied widely the possibilities to use CO<sub>2</sub> in synthesis gas and chemicals production by utilizing the CO<sub>2</sub> content of flue and process gases. The main research areas have been dry reforming and methanol and DMC syntheses [17-21]. CO<sub>2</sub>

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hydrogenation to methanol over Cu/ZrO<sub>2</sub> catalysts has been investigated at CO<sub>2</sub>/H<sub>2</sub>=1/3, p~30 bar, and T~500 K and a performance comparison has been done using a commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst as a reference. The effect of different variables in the stages of catalyst preparation and calcination on the catalyst performance has been studied thoroughly in this study. The direct synthesis of DMC using carbon dioxide as a solvent (scCO<sub>2</sub>) and reagent for its fixation from methanol has been studied by using di-*n*-utyldimethoxystannane as a catalyst in order to get insight into the reaction mechanism for catalyst activity improvements. This study has provided information on the new mechanistic routes and reactive species for the green DMC formation.

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## CURRENT STATUS AND PROSPECTS FOR DEVELOPMENT OF CATALYSTS AND CATALYTIC PROCESSES FOR OIL PROCESSING

**Kapustin V.M.**

*Gubkin Russian State Oil & Gas University, Moscow, Russia*

*E-mail: vkapustin@vnipineft.ru*

A role of catalysts in solving the task of switching to Euroquality petroleum products was discussed. The contemporary market of oil-refining catalysts in Russia was reviewed, including catalysts for such large-scale processes as catalytic cracking, reforming, and hydrocracking. To reduce the catalyst import to Russia, it is necessary to establish a catalyst holding dedicated to pursue a common marketing and scientific & engineering policy in production, application and development of domestic catalysts.

A role of catalysts in solving the task of switching to Euroquality petroleum products, one of major tasks of Russian oil-refining industry at present, was discussed.

The contemporary Russian market of oil-refining catalysts was reviewed, including catalysts for such large-scale processes as catalytic cracking, reforming, and hydrocracking. The situation is aggravated by tough competition from leading foreign companies that dominate at the Russian market of catalysts at present. As of today, up to 50-70 percent of oil-refining catalysts, depending on a specific process, is supplied by such companies as Axens, Albemarle, Sud-Chemie, Grace Davidson, Criterion, UOP, Haldor Topsoe, Engelhardt.

The status of catalytic cracking catalyst production was reviewed. At present, two types of silica-alumina zeolite-containing catalysts are in use at Russian refineries, namely, bead catalysts for DCC units and microspheroidal catalysts for FCC units. In the USSR, the bead catalysts were produced in Grozny, Ufa, Baku and Salavat. Nowadays, about 50 percent of the market is occupied by and 50 percent by a Russian company Katakhim. The Russian market of microspheroidal catalysts is divided among Grace Davidson, Engelhardt and Albemarle. Omsk Catalyst Plant covers a requirement of Omsk Refinery catalytic crackers only.

In Russia, reforming catalysts are produced by three manufacturers, namely, Promyshlenniye Katalizatory, Angarsk catalyst plant and ZAO Nizhegorodskiye Sorbenty.

A share of domestic catalysts used at Russian refineries is about 30 percent. 70 percent of the market is occupied by UOP, Axens, and Criterion.

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The hydrocracking catalyst market is divided among Axens, Grace Chevron, Haldor Topsoe, and UOP.

To reduce the catalyst import to Russia, it is necessary to establish a catalyst holding dedicated to pursue a common marketing and scientific & engineering policy in the field of production, application and development of domestic catalysts.

NANOSTRUCTURE OF LOW TEMPERATURE  $\text{Al}_2\text{O}_3$  POLYMORPHSTsybulya S.V.<sup>1,2</sup><sup>1</sup>*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*<sup>2</sup>*Novosibirsk State University, Novosibirsk, Russia**E-mail: tsybulya@catalysis.nsk.su*

Low temperature alumina polymorphs,  $\gamma$ -,  $\eta$ -,  $\chi$ - $\text{Al}_2\text{O}_3$ , were synthesized and studied by high resolution transmission electron microscopy and X-ray powder diffraction along with computer simulation of the diffraction patterns. It was found that  $\gamma$ -,  $\eta$ - and  $\chi$ - $\text{Al}_2\text{O}_3$  differ from each other by the crystallographic shape of the building blocks (nanodomains), character of their stacking with each other and types of the faulting arising upon their assembly into extended nanostructure.

$\text{Al}_2\text{O}_3$ , traditionally referred to as alumina, plays high technological importance since it is widely used for producing different kinds of ceramics, wide set of catalysts for numerous industrial chemical processes, adsorbents, coatings, soft abrasives, etc. Only  $\alpha$ - $\text{Al}_2\text{O}_3$  (corundum) is the stable oxide whereas  $\gamma$ -,  $\delta$ -,  $\eta$ -,  $\theta$  -,  $\chi$  - and  $\kappa$  - derivatives are considered to be metastable; they are formed gradually upon the dehydration of different hydroxides and oxyhydroxides [1]. Low temperature alumina polymorphs,  $\gamma$ -,  $\eta$ -,  $\chi$ - $\text{Al}_2\text{O}_3$ , were synthesized and studied by high resolution transmission electron microscopy and X-ray powder diffraction along with computer simulation of the diffraction patterns. An approach to the investigation of highly imperfect nanocrystalline compounds based on the simulation of X-ray powder diffraction pattern and involving a model of one-dimensionally disordered crystal [2] has been used. Planar defects lying on the  $\{111\}$ ,  $\{110\}$  and  $\{100\}$  planes and being the origin of the broadening of X-ray diffraction peaks in different forms of aluminium oxide have been revealed. In addition to providing strong experimental support for the imperfect character of the specimens structure, these results demonstrate the possibility of using nanosized crystalline domain with similar spinel structure of  $[\text{Al}_3\text{O}_4]^+$  content, regularly shaped and having specified developed face and bounding surfaces, for description of the structure of whole variety of low temperature aluminas. Defects appearing in the process of assembling of these blocks into extended nanostructure may yield specific ratios of vacancies necessary for maintaining the  $\text{Al}_2\text{O}_3$  stoichiometry. Definite kinds of the line shape broadening observed in the X-ray diffraction patterns of these materials originate from the different types of packing of nanocrystalline domains accompanied by subsequent formation of planar defects inside oxide particles. It was found that  $\gamma$ -,  $\eta$ - and  $\chi$ - $\text{Al}_2\text{O}_3$  differ from each

## KLS-I

other by the crystallographic shape of the building blocks (nanodomains with size about 2 - 3 nm), character of their stacking with each other and types of the faulting arising upon their assembly into extended oxide structure.

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## FISCHER-TROPSCH SYNTHESIS: RELATIONS BETWEEN STRUCTURE OF COBALT CATALYSTS AND THEIR CATALYTIC PERFORMANCE

**Khodakov A.Y.**

*Unité de Catalyse et de Chimie du Solide - UMR 8181 CNRS, Université des Sciences et Technologies de Lille, Bat C3, Cité scientifique, 59655 Villeneuve d'Ascq, France*

*E-mail: andrei.khodakov@univ-lille1.fr*

Fischer-Tropsch synthesis has been experiencing a strong revival in recent years, due to the resource utilization considerations and environmental concerns. Because of their stability and high hydrocarbon productivity, cobalt supported catalysts represent the optimal choice for synthesis of long-chained hydrocarbons. Information about the nature of active sites is crucial for the design of cobalt Fischer-Tropsch catalysts. This lecture reviews recent research work about the relations between the structure of cobalt supported catalysts and their catalytic performance in Fischer-Tropsch synthesis. Several specific requirements to the design of efficient cobalt Fischer-Tropsch catalysts are formulated and discussed.

Fischer-Tropsch synthesis produces clean fuels from syngas, which can be generated from natural gas, coal and biomass. The first experiments on catalytic hydrogenation of carbon monoxide were carried out by Sabatier in 1902. In 1922, Hans Fischer and Franz Tropsch proposed the Synthol process, which gave a mixture of aliphatic oxygenated compounds via reaction of carbon monoxide with hydrogen over alkalized iron chips.

In eighties, expensive investments in the Fischer-Tropsch R&D programs have picked up in major petroleum companies. The global resurgence of the interest in Fischer-Tropsch synthesis has been primarily driven by the problems of utilization of stranded gas, by diversification of sources of fossil fuels and environmental concerns [1, 2]. Synthetic liquid fuels generally have very low content of sulfur and aromatic compounds compared to gasoline or diesel from crude oil. The abundant reserves of natural gas in many parts of the world have made it attractive to commission new plants based on Fischer-Tropsch technology. In 1993, the Shell Bintulu 12,500 barrels-per-day (bpd) plant came into operation. In June 2006, the Sasol Oryx 34,000 bpd plant was inaugurated. SasolChevron is currently building its Escarvos GTL plant in Nigeria. Shell and Exxon signed the agreement on building 140,000 bpd and 150,000 bpd GTL-FT plants in Qatar. Thus, after several decades of research and development, Fischer-Tropsch technology has finally come to the stage of full scale industry and worldwide commercialization.

Catalyst is a vital part of any industrial Fischer-Tropsch process. Because of their stability and high hydrocarbon productivity, cobalt supported Fischer-Tropsch catalysts

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represent the optimal choice for synthesis of long-chained hydrocarbons. Information about the nature of active sites is crucial for the design of cobalt Fischer-Tropsch catalysts.

There is currently a consensus in the literature [3, 4] that Fischer-Tropsch synthesis proceeds on cobalt metal particles, which size can vary in a wide range [5]. Fischer-Tropsch catalysts could also contain several other cobalt species: cobalt carbide, cobalt oxides, cobalt support mixed compounds [6]... These species are probably not directly involved in Fischer-Tropsch synthesis. Additional active sites for Fischer-Tropsch synthesis could be present in promoted cobalt catalysts [7]. One of the specificities of Fischer-Tropsch synthesis is that the reaction rates and hydrocarbon selectivities significantly evolve [8, 9] with time on-stream on cobalt supported catalysts.

The lecture reviews the state of the art related to the influence of several important parameters of catalyst structure on Fischer-Tropsch reaction rates, hydrocarbon selectivity and catalyst stability. These parameters include:

- mean cobalt metal particle size and cobalt particle size distributions in the catalysts;
- phase composition of cobalt metal particles;
- catalyst texture;
- promotion with noble metals and metal oxides;
- catalyst oxidative and reductive pretreatments;
- cobalt precursors and presence of other cobalt species.

Possible mechanisms of catalyst deactivation and modification of cobalt active sites during the reaction are also discussed. After detailed analysis of the relations between the structure and catalytic performance, several specific requirements to the design of cobalt Fischer-Tropsch catalysts are formulated.

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**QUANTUM-CHEMICAL STUDY OF THE STATE AND REACTIVITY  
OF METAL NANOPARTICLES IN ZEOLITES**

**Mikhailov M.N.**

*N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia*

*E-mail:mik@ioc.ac.ru*

A quantum chemical model is developed that serves to unravel the nature of interaction of a platinum nanoparticle with FAU and MFI zeolites. The interaction of the metal cluster with the support surface decreases the electronic density on the metal particle and suppresses both Lewis and Brønsted acidity of the support. Adsorption on basic sites of supports favors the formation of electron enriched metal clusters. The catalytic significance of unusual electronic structure of metal particle for alkane isomerization is outlined.

Fine metal particles supported on zeolites are an important class of catalytic systems. The character of metal-support interaction affects stability and activity of catalysts. However, the mechanism governing the metal-support interaction is far from being understood. In this work the behavior of Pt particles adsorbed on FAU and MFI zeolites is described.

To model the zeolite supports the cluster approach was used. The cluster electronic structure was computed at the density functional theory level using the Becke's three parameters exchange functional combined with the Lee-Yang-Parr and Vosko-Wilk-Nusair correlation functionals. The SBKJC effective core potential and corresponding basis set augmented with polarization functions were used on all atoms. All the calculations were performed with the PC GAMESS program package.

From the calculations it can be inferred that the Pt nanoparticle interacts ( $E_{\text{ads}} = 5\text{-}25$  kcal/mol) with basic framework oxygens and Brønsted acid sites of zeolite. Adsorption on basic sites of supports favors the formation of electron enriched metal clusters. The reason for appearance of the negative charge is a redistribution of electronic density from Si and Al atoms through framework oxygens to metal particle. Electronic density on Al and Si atoms slightly reduces and that on acid sites increases. The platinum particle can be additionally stabilized due to donation of the excess of electronic density to acid sites. The transfer of Brønsted protons onto platinum surface leads to the formation electron-deficient metal particle. This process is of exothermic nature and proceeds with the activation energies of 0-15 kcal/mol. The introduction of platinum into the zeolite results in a considerable reduction of Brønsted acidity. Moreover the interaction of platinum with extraframework aluminums is accompanied by the suppression of Lewis acidity.

## **KLS-YS**

From the results outlined above it can be concluded that the electronic structure of metal particle is strongly affected by the interaction with basic framework oxygens and acid sites of support. The interaction of the platinum cluster with the acid sites decreases the electronic density on the metal particle and neutralizes acidity of the zeolite support. These data throw some light into the structure of active sites of Pt-zeolite isomerization catalysts. It is generally accepted that alkane dehydrogenation occurs on a metal particle whereas acid site promotes isomerization step. This approach excludes the interaction between metal and acid site. An alternative explanation can be offered that involves the metal cluster – Brønsted proton adduct as an active site for the alkane isomerization over the Pt-zeolite catalysts.



# ORAL PRESENTATIONS

**SECTION I            MECHANISMS OF HETEROGENEOUS  
AND HOMOGENEOUS CATALYSIS AT  
MOLECULAR LEVEL**

**SECTION II           DESIGN OF HETEROGENEOUS AND  
HOMOGENEOUS CATALYSTS**

**SECTION III          ENVIRONMENTAL AND INDUSTRIAL  
CATALYSIS**





**BORESKOV'S CONCLUSION ON ALMOST CONSTANCY OF THE SPECIFIC  
CATALYTIC ACTIVITY AS AN IMPORTANT FACTOR FOR UNDERSTANDING  
THE PARADOX OF HETEROGENEOUS CATALYSIS**

**Ostrovskii V.E.**

*Karpov Institute of Physical Chemistry, Moscow, Russia*

*E-mail: [vostrov@cc.nifhi.ac.ru](mailto:vostrov@cc.nifhi.ac.ru); [ostrovv@rol.ru](mailto:ostrovv@rol.ru)*

Fundamental importance of Boreskov's conclusion on almost constancy of the specific catalytic activity inherent in different catalysts of the same chemical composition is confirmed. It is shown that combined consideration of this conclusion and of the causes of Boudart's paradox of heterogeneous catalysis leads to clarification of the problems that are of particular importance for the theory of catalysis and for the methodology of studies of intermediate surface substances occurring in the course of catalytic processes.

In the paper [1], G.K. Boreskov had generalized the studies performed by him together with V.S. Chesalova, V.A. Dzis'ko, A.G. Filippova, M.G. Slin'ko, and others and by A.E. Agronomov, W. Hofer, U. Hofman, W. Schmidt, J. Siller, and others and had arrived at the following fundamental conclusions. (1) The specific activity of solid catalysts of any definite chemical composition in any stationary reaction is almost the same independently of the method of their preparation; i.e., catalytic activities are basically dictated by chemical properties rather than by some special state or special structural elements of surfaces. (2) To develop an efficient theory of catalysis, comprehensive physicochemical studies of the surface substances occurring during catalytic processes are necessary.

G.K. Boreskov wrote that "...the interaction of gas molecules with catalyzing surfaces significantly modifies the properties of surfaces and influences the binding energy for the gas molecules adsorbed after formation of intermediate surface particles much stronger than the initial non-homogeneity of some surface regions does." This conclusion contradicts the opinion on the decisive effect of surface heterogeneity on the catalytic activity; G.K. Boreskov did not write that no surface heterogeneity exists, but his results testified clearly that this is not the property to control the catalytic activity.

Somewhat later, M. Boudart [2] called the catalylists' attention to "the paradox of heterogeneous catalysis" implying that the catalytic kinetics can be, on frequent occasions, satisfactorily described with different kinetic equations deduced on the basis of the suppositions on either homogeneity or heterogeneity of the catalyst surface and with different kinetic equations deduced on the basis of different reaction mechanisms; i.e., the dilemma whether the surface is homogeneous or heterogeneous and the problem on the actual catalytic

## OP-I-1

mechanism are as if "things in themselves" for those who would like to decide them by kinetic methods.

For 50 years, these studies have been the focus of discussions, the most extensive ones being given [3, 4, 5, 6, 7], and the author of this work. However, these discussions are not exhaustive and their results are not universally recognized.

Here, we consider the following questions emerging from [1] and [2].

(1) If, for a number of reactions and catalysts, it is stated that the specific activity of a catalyst in a reaction is almost constant independently of catalyst preparation procedures and if the reaction kinetics is describable by equations deduced with preconditions of homogeneity and heterogeneity of the catalyst surfaces, the questions arise as to whether it is necessary to search for proofs of surface heterogeneity or we should fix that the surfaces reveal themselves as matrixes with averaged properties and whether any independent proofs of surface heterogeneity exist.

(2) If the kinetics of a catalytic reaction is describable by different equations deduced on the basis of different reaction mechanisms, the question arises as to whether this means that information on the intermediate surface substances cannot be obtained from kinetic data.

The above-formulated questions are considered on the basis of generalization of the results and conclusions published till now and original experimental and theoretical data. Following Boreskov's conclusion on the primary importance of studies of intermediate surface interactions, we consider the adsorption techniques intended to study the chemical compositions and properties of the intermediate particles adsorbed at the surfaces being in the states approximating those occurring in the course of catalytic processes.

It will be shown that Boreskov's conclusion that "...the principal factor controlling the specific catalytic activity is the chemical composition and chemical structure of catalysts" is confirmed by numerous studies, and the causes of the fact that just these factors rather than the catalyst preparation procedure and other features control the specific catalytic activity will be analyzed.

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# SIZE-CONTROLLED PALLADIUM NANOPARTICLES ANCHORED TO STRUCTURED CARBON SUPPORTS IN LIQUID- AND GAS-PHASE SELECTIVE HYDROGENATIONS

**Kiwi-Minsker L., Semagina N., Ruta M.**

*Ecole Polytechnique Fédérale de Lausanne EPFL-GGRC Station 6 CH-1015 Lausanne,  
Switzerland*

*E-mail: liubov.kiwi-minsker@epfl.ch*

## **Introduction**

Microemulsion (ME) technique is widely used for the preparation of metal nanoparticles for catalytic applications [1]. It provides easy control over nanoparticle size and monodispersity. Catalyst preparation usually consists in mixing of nanoparticle-containing ME with a support (tetrahydrofuran is often added to release nanoparticles) with following washing and calcination to remove surfactant. This often results in particles sintering. A big challenge is also recovering a reverse ME non-polar phase (hydrocarbon) and a surfactant.

Here we propose a simple method for purification of ME-derived metal nanoparticles which allows obtaining monodispersed particles of the controlled size and recovering ME hydrocarbon and a surfactant. Palladium nanoparticles are shown to be used either per se in liquid-phase selective hydrogenations or deposited on structured carbon supports for liquid- and gas-phase hydrogenations. They represent also a new catalytic tool to study size-sensitivity of catalytic reactions.

## **Experimental**

Pd nanoparticles of 6, 8, 11, 13 nm diameter were synthesized in the reverse MEs of water/AOT/isooctane and purified via evaporation of hydrocarbon, methanol addition (to flocculate nanoparticles and dissolve surfactant) and centrifugation [2]. Obtained precipitate was either easily immediately suspended in the catalytic reaction mixture [2], or dried under vacuum and used after storage, or deposited onto a support from its aqueous suspension [3, 4]. As supports, activated carbon fiber (ACF) fabrics [3, 4] or carbon nanofibers grown on sintered metal filters (CNF/SMF) [5] were used. Calcination step was not employed for the catalysts preparation. Nanoparticles after purification and the supported catalysts were characterized by XRD, AAS, XPS, EDX, HR-TEM, CO chemisorption.

## OP-I-2

Size-sensitivity of 2-methyl-3-butyn-2-ol (MBY) selective hydrogenation was studied with the suspended nanoparticles [2]. Liquid-phase 1-hexyne hydrogenation was carried out either with dried nanoparticles or deposited on ACF with drying at 393 K [3, 4]. Pd nanoparticles on CNF/SMF were tested in gas-phase acetylene hydrogenation at 423 K [5].

### Results and discussion

Nanoparticles' purification allowed preserving their size and monodispersity ( $\pm 20\%$ ). Fig. 1 shows HR-TEM images of f.c.c. nanoparticles of 6, 11 and 13 nm diameter suspended in MBY and a histogram of size distribution. No agglomeration was found neither for suspended nor for the dried or carbon-deposited nanoparticles.  $>99.5\%$  of the surfactant was removed by washing with methanol, and residuals stabilize nanoparticles against agglomeration.

Structure-sensitivity of liquid-phase MBY hydrogenation was studied in the presence of suspended nanoparticles of 6-13 nm diameters [2]. The initial TOF calculated per mole of surface Pd atoms was duplicated when particle size was increased from 6 to 13 nm but remained constant when accounted per number of specific Pd atoms on Pd(111) facets. Reaction was shown to be a structure-sensitive but size-independent for Pd particles of 6–13 nm size. Selectivity to olefinic alcohol of 96% was not size-dependent, but an increase in particle size decreased the byproduct ratio of dimers to saturated alcohol. Thus, control of Pd size allows controlling the reaction rate and the byproduct distribution.

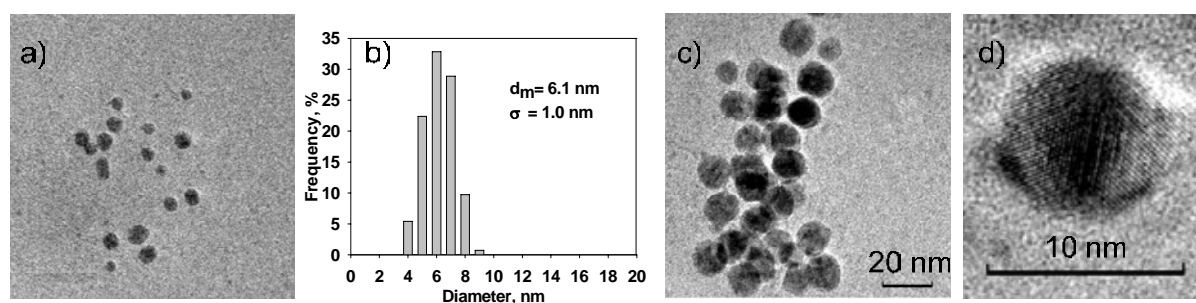


Fig. 1. HR-TEM images of Pd nanoparticles of 6 nm diameter (a) with a particle size distribution histogram (b), 13 nm (c) and 11 nm (d) diameter suspended in MBY

Nanoparticles of 8 nm supported on ACF (0.45 wt% Pd) were studied in liquid-phase 1-hexyne hydrogenation [4]. The selectivity to 1-hexene of  $>96\%$  up to 90% conversion was observed. The catalyst showed better catalytic performance than a traditional Lindlar catalyst both in solvent-assisted and solvent-free hydrogenation. Catalyst reusability was shown in 6 successive runs [3], thus, the material is suitable for performing multiphase reactions in the

reactors with structured catalytic beds. Dried 13 nm-particles were shown to efficiently suppress the overhydrogenation of 1-hexene to 1-hexane.

Pd nanoparticles deposited on the structured CNF/SMF support were employed also in gas-phase acetylene hydrogenation and showed higher activity and selectivity than Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. Surfactant residuals do not suppress the catalyst activity, thus the catalyst prepared without a calcination step may be also successfully used for gas-phase reactions.

## Conclusions

ME-based method for preparation of monodispersed Pd nanoparticles of the controlled size was elaborated. It allows recovering ME hydrocarbon and surfactant. Nanoparticles may be used per se to study structure-sensitivity of catalytic reactions, or used for the supported catalysts preparation both for liquid- and gas-phase hydrogenations.

## Acknowledgements

Financial support from the Swiss National Science Foundation (SNSF) and Commission for Technology and Innovation (CTI) is gratefully acknowledged.

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**THE OSCILLATION BEHAVIOR IN CO OXIDATION ON THE  
POLYCRYSTALLINE AND NANOSIZED PALLADIUM**

**Boronin A.I., Slavinskaya E.M., Kuznetsov P.A., Zaikovskii V.I., Stadnichenko A.I.,  
Amosov Yu.I.**

*Borovskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: boronin@catalysis.nsk.su*

At present a number of data on catalytic reactions characterized by the self-oscillation behavior have been accumulated in the catalysis literature [1]. The catalysts of the processes with the self-oscillation behavior are both simple (monocrystalline or polycrystalline metals) and the complicated systems (metallic particles supported on oxides, zeolites etc). Most frequently the self-oscillations are observed for the oxidation reactions of CO and hydrocarbons. The palladium catalysts are intensively investigated because they demonstrate the self-oscillation kinetics in many reactions. Also, Pd catalysts are most important for practical catalysis. The study of the mechanism of the self-oscillation behavior in heterogeneous reactions is of big interest for the catalysis theory.

The investigation of the catalytic activity of the Pd supported catalysts in the regime of cyclic light-off testing showed the appearance of chaotic oscillations during the sample cooling after on reaching the maximum of CO conversion at  $T > 300$  °C (Fig.1). It was revealed that self-oscillations of the reaction rate are observed on the supported  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> oxide, where palladium is in highly dispersed nanosized state. No oscillations of the reaction rate were observed, when the palladium was supported on the surface of other oxides like ZrO<sub>2</sub>, CeO<sub>2</sub> and their mixed compositions with alumina. The catalysts Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were prepared by the impregnation of pseudoboehmite or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by Pd nitrate solution with the following drying at 80 °C and calcination on air at 400 °C, 600 °C and 800 °C.

The kinetic measurements were performed in the flow reactor with the high time resolution 0.7 sec. The measurements showed that the self-oscillations appeared during the sample cooling around the temperature 270 °C and continued to be observed down to 170 °C. The self-oscillation existence correlates with the decrease of CO conversion. The temperature range for the self-oscillating regime of reaction depends on the calcination temperature. When the calcination temperature increases (and the size of the supported Pd particles increases, too) the self-oscillation temperature range is narrowed and this phenomenon occurs within 220 °C – 170 °C. In Fig. 1 the typical self-oscillating behavior of CO oxidation reaction is presented for the catalyst Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> calcined at 800 °C.



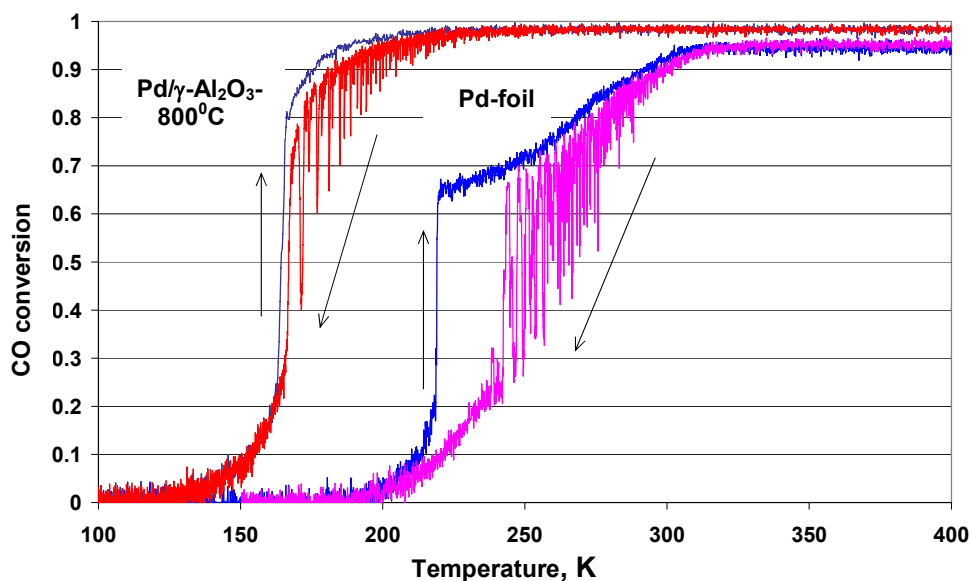


Fig. 1. The dependence of CO conversion on temperature ( $P(\text{CO})/P(\text{O}_2)=1/5$ ) under the slow heating and cooling ( $5^\circ\text{C}/\text{min}$ ) of the flow reactor.

In order to establish the mechanism of self-oscillations and the state of palladium in the course of the reaction the complex of physicochemical methods was applied such as XPS, XRD and HRTEM. The investigation of the samples treated by the reaction media at different kinetic regimes showed that the appearance of the self-oscillations is accompanied with the changes of morphology and the oxidation state of palladium. During the oscillating regime the formation of metallic nanoclusters covering the surface of ordered PdO particles is observed.

For investigation of the particle size effect on the self-oscillation behavior the comparison with polycrystalline foil was performed. The self-oscillations on the foil surface are also observed (Fig. 1). The temperature range for these self-oscillations is shifted towards high temperature side on about 1000 C. XPS and SEM data showed the formation of the strong surface roughness and the formation of oxide particles PdO with a mean size about  $500 \text{ \AA}$ . In this case the surface of polycrystalline palladium represents as a cover of PdO particles, which form dynamically under the action of reaction media.

In the present work the possible mechanisms of the self-oscillations in CO oxidation on palladium are discussed. The influence of some parameters as partial pressures of reagents, disordering of the surface, the oxidation/reduction rate of palladium, the interaction of Pd nanoparticles with the support are discussed in this work. Using the equipment capability to measure kinetics with the high time resolution, it was shown that the temperature factor is not the main parameter accounting for the appearance of self-oscillations.

This work was supported by Federal Agency on Science and Innovations, grant IN.12.6/003.

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**ISOTOPIC TRACER STUDIES OF THE FISCHER-TROPSCH SYNTHESIS  
REACTION**

**Davis Burtron H.**

*Center for Applied Energy Research, University of Kentucky, 2540 Research Park Dr.,  
Lexington, KY, 40511, USA  
E-mail: davis@caer.uky.edu*

Results for use of stable and radioactive isotopes to define the mechanism for the Fischer-Tropsch synthesis will be covered. The extent that secondary reactions impact the mechanism will be defined from the results of tracer studies. The labeled compounds formed after switching from hydrogen to deuterium will be utilized to define the extent that diffusion impacts the results.

Emmett and coworkers in the US and Eidus, Roginskii and coworkers in Russia pioneered the use of isotopic tracers to define the mechanism of the Fischer-Tropsch Synthesis (FTS). While these early studies provided significant advances in the understanding of the reaction mechanism, limitation in the analytical capabilities limited the highest carbon numbers that could be accurately analyzed. Advances in the instrumentation now allows one to analyze radioactivity in products up to about carbon number twenty and the g.c.-m.s. capabilities allow the utilization of deuterium up to similar carbon numbers.

Results of carbon-14 and deuterium isotopic studies using current instrumentation will be utilized to better define the reaction mechanism for the FTS reaction. As an example, the results using deuterium are outlined below.

Conventional wisdom indicates that the use of deuterium for study of Fischer-Tropsch (FT) synthesis mechanism studies would be of limited utility since it is expected that exchange would occur in the alkane and alkene products. However, we have demonstrated that the exchange of alkanes does not occur to a measurable extent under FT synthesis conditions. Moreover, while exchange occurs in the vinyl alkene positions the exchange in the remainder of the molecule is much slower.

Conversions have been carried out in continuous stirred tank reactors (CSTR) initially using a mixture of  $D_2/CO = 0.7$  until a steady-state CO conversion was obtained. The feed was then switched to a  $H_2/CO = 0.7$  mixture and the CO conversion decreased. Following several days of synthesis with  $H_2$  the feed was changed back to  $D_2/CO = 0.7$  and the CO conversion again increased. Switching again to  $H_2/CO = 0.7$ , the CO conversion decreased.

The isotopic tracer data obtained using fixed bed and CSTR for iron catalysts are summarized in Table 1.

While there are differences among the data, there is general agreement that there is an inverse kinetic isotope effect on the rate of conversion of CO. Previous reports of a kinetic isotope effect for the methanation of CO have appeared and there is no general agreement as to the mechanism that causes a negative isotope effect. A part of the differences in the above data is likely due to the use of the fixed bed reactor at Berkeley and the CSTR at the CAER.

There is likewise an inverse isotope effect for synthesis using the cobalt catalyst. Data using different cobalt catalysts at Berkeley (fixed bed reactor) and CAER (CSTR) are compared in Table 2.

Thus, both iron and cobalt catalysts exhibit an inverse isotope effect, and these effects are of similar magnitude. Thus, the hydrogenation of CO is more rapid with deuterium than with hydrogen but the hydrogenation to produce methane and the retention of alkene is slower in deuterium than in hydrogen.

One explanation for these observations is that the rate of conversion of CO depends upon the stability of the intermediate that leads to the initial transition state and that the stability of this transition state structure determines the rate of CO conversion. In this view, the free energy of the reactants are the same for both deuterium and hydrogen and the free energy of the transition state of the deuterium containing species is more stable than the hydrogen containing species.

Conv. Level, CO%	Fixed Bed Reactor <sup>a</sup>		CSTR <sup>b</sup>	
	Low (18%)	High (65%)	Low (20%)	High (80%)
$k_H/k_D$ for CO conv.	0.55	0.55	0.90 (200h) 0.91 (1400h)	0.88 (300h) 0.86 (570h)
$k_H/k_D$ for WGS	1.2	1.2	ca. 1.0	0.94
$k_H/k_D$ for CH <sub>4</sub> prod.	0.75	0.55	0.84	1.3
$k_H/k_D$ for C <sub>2</sub> <sup>=</sup> /C <sub>2</sub>	1.0	1.0	0.35	0.38
$k_H/k_D$ for C <sub>3</sub> <sup>=</sup> /C <sub>3</sub>	1.4	1.4	0.64	0.69
$k_H/k_D$ for C <sub>4</sub> <sup>=</sup> /C <sub>4</sub>	1.6	1.8	0.65	0.70

a. Catalyst: Zn:Fe=0.1, K/M=0.02, Cu/M=0.01; 235°C, 21.4 atm, H<sub>2</sub>/CO or D<sub>2</sub>/CO = 2.0. (Final Rpt, DE-FC26-98-FT40308; work conducted at UCB).

b. Catalyst: 100Fe:4.6Si:1.44K; 270°C; 11.6 atm., H<sub>2</sub>/CO or D<sub>2</sub>/CO = 0.67 (work at CAER).

**OP-I-4**

Table 2. Kinetic Isotope Effect for Cobalt Catalyst Using Fixed Bed and CSTR		
	Berkeley (fixed bed) <sup>a</sup>	CAER (CSTR) <sup>b</sup>
$k_H/k_D$ for CO conv.	0.8	0.73
$k_H/k_D$ for CH <sub>4</sub> formation	1.1	1.2
$C_3^=/C_3$ , H(D)	---	1.9 (2.2)
$C_4^=/C_4$ , H(D)	---	1.3 (1.5)
a. 21.9% CO/silica; 473 K; 2 MPa; H <sub>2</sub> /CO (D <sub>2</sub> /CO) = 2.		
b. 19.2% CO/silica; 483 K; 2.13 MPa; H <sub>2</sub> /CO (D <sub>2</sub> /CO) = 2		

**Acknowledgment**

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**UNUSUAL REACTION OF O<sup>•-</sup> SPECIES WITH WATER ON FeZSM-5.  
THE MECHANISM AND POSSIBLE IMPACT ON CONFLICTING DATA  
IN THE LITERATURE**

**Starokon E.V., Dubkov K.A., Pirutko L.V., Paukshtis E.A., Panov G.I.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: starokon@catalysis.nsk.su*

Water was found to interact with anion radicals O<sup>•-</sup> on FeZSM-5 zeolite, which led to O<sub>2</sub> evolution into the gas phase. Isotopic and spectral studies showed that the reaction proceeds by the mechanism involving abstraction of hydrogen atom from H<sub>2</sub>O and is accompanied by reduction of O<sup>•-</sup> anions to hydroxyl groups: 4Fe<sup>3+</sup>O<sup>•-</sup> + 2H<sub>2</sub>O → 4Fe<sup>3+</sup>OH<sup>-</sup> + O<sub>2</sub>. The similar OH groups form upon interaction of O<sup>•-</sup> with H<sub>2</sub> and CH<sub>4</sub>.

It is known that iron introduced into the zeolite matrix may form special Fe<sup>2+</sup> complexes (the so-called α-sites) that are inert toward O<sub>2</sub>, but can be readily oxidized by N<sub>2</sub>O to yield the anion-radical species of adsorbed oxygen, O<sup>•-</sup> [1]:



Similar to radicals observed on V and Mo oxides, the O<sup>•-</sup> particles on FeZSM-5 (α-oxygen, O<sub>α</sub>) are involved in isotopic exchange with O<sub>2</sub> and interact with CO, methane and other hydrocarbons even at room temperature. α-Oxygen is responsible for remarkable catalytic performance of FeZSM-5 zeolites in selective oxidation reactions (for example, benzene to phenol oxidation) and in N<sub>2</sub>O decomposition. This is why α-oxygen is the subject of numerous experimental and theoretical studies.

Thermodesorption experiments demonstrate that O<sub>α</sub> is stable up to 250–300 °C. However, as was found in ref. [2], adsorption of H<sub>2</sub>O at 250°C results in the evolution of O<sub>2</sub> (in the amount approximately equal to 0.25 of the oxygen amount loaded from N<sub>2</sub>O). Table 1 shows that dioxygen forms even at much lower temperatures, 25–200 °C. An assumption about O<sub>α</sub> displacement is not confirmed by isotopic experiments. At 25 °C, mainly the water oxygen is evolved, although no isotopic exchange of O<sub>2</sub> take place in the presence of water. Upon subsequent TPD of a sample treated with water, desorption of O<sub>2</sub> is observed at temperatures above 400 °C.

It is seen from Table 1 that amounts of oxygen formed upon water adsorption and at subsequent TPD are approximately equal for all temperatures tested. Atomic fraction of <sup>18</sup>O

## OP-I-5

isotope in the gas phase ( $f_g$ ) increases as the temperature grows, with distribution of isotopes in the gas phase being non-equilibrium in all cases ( $K$  is below 4).

Table 1. Experiments on  $H_2O$  adsorption over a sample by  $\alpha$ -oxygen ( $C(O_\alpha) = 1.7 \times 10^{19}$  at./g) at different temperatures

t, °C	$O_2$ formed at $H_2O$ adsorption, at./g $\times 10^{-18}$	$f_g(^{18}O)$ , %	$O_2$ formed at subsequent TPD, at./g $\times 10^{-18}$	$K = \frac{[^{16}O^{18}O]^2}{[^{16}O_2] \times [^{18}O_2]}$
25	5.8	23.9	9.2	2.1
50	6.6	36.0	8.8	2.2
100	7.9	51.4	10.0	2.2
125	7.1	58.7	9.5	2.4
200	7.2	69.5	9.7	2.7

Figure 1 shows the IR spectra of FeZSM-5 zeolite.  $O_\alpha$  loading by reaction (1) (spectrum b) is not accompanied by any changes as compared to spectrum (a) of the parent sample, whereas further adsorption of  $H_2O$  leads to qualitative changes in spectrum (c). The appearance of a new intense adsorption band at  $3674 \text{ cm}^{-1}$  is clearly seen in the difference spectrum (d).

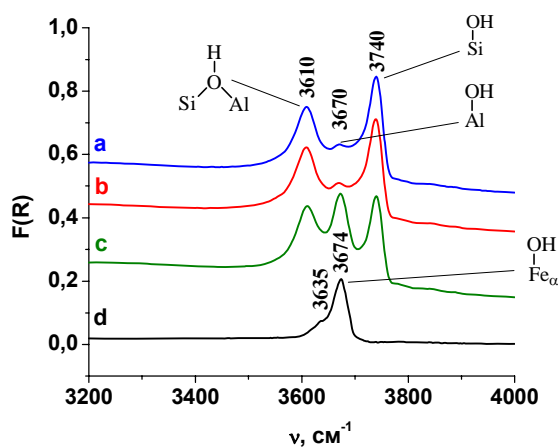
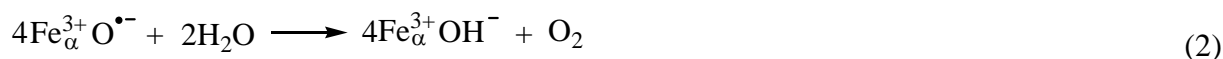


Fig. 2. IR spectra of FeZSM-5 zeolite in the OH vibration region: a) after standard pretreatment, b) after  $O_\alpha$  loading, c) after  $H_2$  interaction with  $\alpha$ -oxygen at 20 °C, d) the difference spectrum.

This indicates the occurrence of  $H_2O$  interaction with  $O_\alpha$ , leading to the formation of new OH groups on the zeolite surface. It seems interesting that the same spectra are obtained for the reaction of  $H_2$  with  $O_\alpha$ . Therefore, these OH groups can be considered as identical and located at the  $\alpha$ -site iron.

Thus,  $O_\alpha$  interacts with water according to the following scheme:



Judging from the isotopic composition of  $\text{O}_2$  evolved, the mechanism is quite complicated and may include several competitive steps, with their contribution depending on temperature:



The  $\text{HO}^\bullet$  radicals being formed, entering further transformations (probably, via intermediate formation of  $\text{H}_2\text{O}_2$ ), yield  $\text{O}_2$  and water.

Fast reaction of  $\text{O}_\alpha$  with water (as well as with  $\text{H}_2$  and hydrocarbon impurities) and formation of low-reactive OH groups in the process could explain some contradictions in the literature data. In particular, the fact that in vacuum setups the reactions with  $\text{O}_\alpha$  can be observed at room and lower temperatures, whereas in flow setups, which are commonly used for catalytic studies, such reactions are observed only at temperatures above  $200^\circ\text{C}$ . Presumably, in the latter case, when a considerable amount of gases is passed through the catalyst, long-term cooling will lead to a loss of  $\text{O}_\alpha$  due to reaction with impurities, even if they are present in minor concentrations.

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**THE MECHANISM OF THE SELECTIVE CATALYTIC REDUCTION  
OF NITROGEN OXIDES WITH PROPYLENE OVER Pt,Cu/ZrO<sub>2</sub>-CONTAINING  
PILLARED CLAY**

**Tretyakov V.F., Matyshak V.A.<sup>1</sup>, Burdeynaya T.N., Lermontov A.S., Korchak V.N.<sup>1</sup>,  
Sadykov V.A.<sup>2</sup>**

*A.V. Topchiev Institute of Petrochemical Synthesis RAS, Moscow, Russia*

<sup>1</sup>*N.N. Semenov Institute of Chemical Physics RAS, Moscow, Russia*

<sup>2</sup>*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: tretjakov@ips.ac.ru*

The results of a spectrokinetic study on the mechanism of the SCR of NO<sub>x</sub> with propylene in an excess of oxygen on a ZrO<sub>2</sub>-pillared clay catalyst are presented. It was found that the catalytic properties of nanosized ZrO<sub>2</sub> particles as the pillar constituents of ZrO<sub>2</sub>-pillared clay and bulk ZrO<sub>2</sub> are quite different, due to presence of different nitrate and carbon-containing species adsorbed on their surfaces.

Pillared clays containing nanosized zirconium dioxide particles (ZrO<sub>2</sub>-pillared clays) are promising catalysts for the selective catalytic reduction (SCR) of nitrogen oxides (DeNO<sub>x</sub>) with hydrocarbons in an excess of oxygen [1–3]. The activity of pillared clays depends on the size, shape, and structure of nanosized ZrO<sub>2</sub> pillars arranged between aluminosilicate layers.

The goal of this study was to find the reaction paths of formation and consumption of nitroorganic compounds, which are well-known key intermediates in this reaction. Also during this work the comparison of the adsorption and catalytic properties between bulk ZrO<sub>2</sub> and nanosized ZrO<sub>2</sub> pillars in pillared clay was performed.

The interactions of reaction components and their mixtures of various compositions with sample surfaces were studied in the course of reaching a steady state using transmission Fourier transform IR spectroscopy (a Spectrum RX I FT-IR System spectrometer from Perkin-Elmer).

It was found that the adsorption and catalytic properties of nanosized ZrO<sub>2</sub> particles as the pillar constituents of ZrO<sub>2</sub>-pillared clay and bulk ZrO<sub>2</sub> are quite different. The interaction of NO with the surface of bulk ZrO<sub>2</sub> resulted in the formation of three types of nitrate complexes. Only two nitrate species were formed on ZrO<sub>2</sub>-pillared clay (the monodentate species was absent). Only an acetate complex was formed in the interaction of a mixture of propylene and oxygen with the surface of bulk ZrO<sub>2</sub>, whereas an isopropoxide complex was the main propylene activation species on ZrO<sub>2</sub>-pillared clay. On the surface of ZrO<sub>2</sub>-pillared clay, isopropoxide and nitrate intermediates formed a complex structurally similar to adsorbed



dinitropropane. On the surface of bulk  $ZrO_2$ , acetate and monodentate nitrate complexes formed a complex structurally similar to adsorbed nitromethane. The dinitropropane complex on  $ZrO_2$ -pillared clay was consumed in reactions with surface nitrates. The decomposition reaction of a dinitropropane compound with the formation of acetate complexes and ammonia predominated on the surface containing no nitrate complexes in the absence of  $NO + O_2$  from a gas phase. The found differences in reactant activation species and their thermal stabilities explained differences in the activities of bulk  $ZrO_2$  and nanosized  $ZrO_2$  particles as pillars in pillared clay in the course of the selective catalytic reduction of nitrogen oxides with propylene in an excess of oxygen.

It was found that only bridging and bidentate nitrate complexes were formed on the surface of Pt,Cu/ $ZrO_2$ -pillared interlayered clay ( $ZrO_2$ -PILC) upon the interaction with a flow of the (0.2%  $NO + 2.5\% O_2$ )/ $N_2$  mixture, whereas monodentate and nitrosyl complexes were not detected. The concentration of nitrate complexes on Pt,Cu/  $ZrO_2$ -PILC was higher and the strength of their bond to the surface was weaker than those on unmodified  $ZrO_2$ -PILC. Isopropoxide and acetate complexes and coordinatively bound acetone were formed on the surface in the interaction of Pt,Cu/  $ZrO_2$ -PILC with a flow of the (0.2%  $C_3H_6 + 2.5\% O_2$ )/ $N_2$  mixture. The supporting of Pt and Cu onto zirconium dioxide pillars resulted in considerable changes in the concentration and the temperature region of existence of hydrocarbon surface compounds, as compared with  $ZrO_2$ -PILC. Under reaction conditions at relatively low temperatures, isopropoxide and nitrate intermediates on the surface of Pt,Cu/  $ZrO_2$ -PILC formed a complex structurally similar to adsorbed dinitropropane. At elevated temperatures, a surface nitromethane complex was formed in the interaction of the acetate complex with nitrate species. The spectrokinetic measurements demonstrated that the apparent rate constants of consumption of nitrate and nitroorganic complexes considerably increased on going from  $ZrO_2$ -PILC to Pt,Cu/  $ZrO_2$ -PILC. Moreover, the constants of consumption of nitroorganic and nitrate complexes were similar for either of the catalysts. This fact suggests that, on the test catalysts, nitroorganic complexes were reaction intermediates in the selective catalytic reduction of  $NO_x$  ( $NO_x$  SCR) with hydrocarbons. The found differences in the active species and thermal stabilities of reactants can explain different activities of  $ZrO_2$ -PILC and Pt,Cu/  $ZrO_2$ -PILC in the SCR reaction of  $NO_x$  with propylene in an excess of oxygen.

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**SELECTIVITY- AND ACTIVITY-DETERMINING FACTORS IN SELECTIVE  
OXIDATIVE DEHYDROGENATION OF PROPANE AND ETHANE  
- A COMBINED OPERANDO CHARACTERISATION AND TRANSIENT  
MECHANISTIC APPROACH**

**Ovsitser O., Kondratenko E.V., Dingerdissen U.**

*Leibniz-Institut für Katalyse e. V. Berlin, Germany*

*E-mail: olga.ovsitser@catalysis.de*

Operando UV/Vis spectroscopy, transient techniques (SSITKA, TAP-reactor) in combination with overall steady-state kinetic analysis were applied to derive insights into individual steps of selective oxidative dehydrogenation of propane (ODP) and ethane (ODE) with O<sub>2</sub> and N<sub>2</sub>O over differently structured VO<sub>x</sub> aggregates and alkali-earth metal oxide catalysts. Catalyst ability for generation of active oxygen species of certain nature as well as the ratio of the rates of catalyst reduction and reoxidation were identified as key factors determining alkene selectivity in the reactions studied.

Oxidative conversion of light alkanes to respective olefins and oxygenates is a challenging approach in oxidation catalysis not only from a fundamental but also from an applied point of view. The main challenge is, however, to minimize the formation of carbon oxides (CO<sub>x</sub>). Therefore, deep fundamental understanding of catalytic reactions at near to elementary reaction steps is of prime importance for catalyst development. The main aim of the present study was to elaborate a strategy enabling to couple microscopic mechanistic and physicochemical knowledge of selective conversion of low alkanes (C<sub>2</sub>-C<sub>3</sub>-hydrocarbons) to C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> with macroscopic observations in chemical reactors. To this end we applied a complex methodology consisting of micro kinetic transient analysis with isotopic traces, overall steady-state kinetics as well as transient and steady-state in-situ UV-Vis spectroscopic analysis. This relationship is essential for developing new effective catalytic materials or for improving the existing ones. Vanadium-, and alkali-earth metals-based oxide materials were used as model catalysts.

The influence of reaction conditions on catalyst composition was studied by means of operando UV/Vis and XRD analysis as well as ex-situ XPS. Transient operando UV/Vis measurements were applied to determine kinetics of reduction and reoxidation of VO<sub>x</sub> species. Mechanistic insights into O<sub>2</sub>, N<sub>2</sub>O and C<sub>3</sub>H<sub>8</sub> activation as well as into product formation were derived from transient isotopic experiments in the TAP (temporal analysis of products reactor) reactor and SSITKA (steady-state isotopic transient kinetic analysis) set up.

Under ambient pressure steady-state conditions, propene selectivity in the oxidative dehydrogenation of propane (ODP) over nano-sized  $\text{VO}_x$  species and polymerized  $\text{V}_2\text{O}_5$  aggregates was always higher with  $\text{N}_2\text{O}$  than with  $\text{O}_2$  at comparable degrees of propane conversion. Two important improving effects of  $\text{N}_2\text{O}$  on the ODP reaction should be especially emphasized: i) a higher primary  $\text{C}_3\text{H}_6$  selectivity is achieved and ii) the decrease in  $\text{C}_3\text{H}_6$  selectivity with increasing degree of propane conversion is less marked. Taking into account the results of operando catalyst characterization, it is concluded that steady-state catalytic performance is not determined by the initial catalyst composition but a new catalyst composition created under the reaction conditions. Due to the lower oxidizing ability of  $\text{N}_2\text{O}$  than  $\text{O}_2$ , the oxidation state of vanadium reduces from 5+ to 4+ and 3+ in the presence of  $\text{N}_2\text{O}$  ( $X(\text{C}_3\text{H}_8) < 5\%$ ,  $X(\text{O}_2) < 10\%$ ,  $X(\text{N}_2\text{O}) < 10\%$ ). The degree of catalyst reduction under conditions of the ODP reaction is concluded to be an essential factor for achieving high propene selectivity. However, the nature of oxygen species formed from  $\text{O}_2$  and  $\text{N}_2\text{O}$  may also influence the ODP performance as indicated by transient experiments with isotopic traces ( $^{18}\text{O}_2$ ). Lattice oxygen of  $\text{VO}_x$  clusters participates in  $\text{C}_3\text{H}_6$  and  $\text{CO}_x$  formation using  $\text{N}_2\text{O}$  and  $\text{O}_2$ . Additionally, adsorbed oxygen species take part in  $\text{CO}$  and  $\text{CO}_2$  formation. These species are assumed to be of molecular nature and formed from  $\text{O}_2$  only.

In contrast to vanadium-based catalysts, no improving effect of  $\text{N}_2\text{O}$  on catalytic performance of alkali-earth metal oxides in the autothermal oxidative dehydrogenation of ethane to ethylene was observed. Ethylene yields up to 60 % were achieved with  $\text{O}_2$ . Differences between redox and non-redox catalytic systems for oxidative dehydrogenation of ethane and propane are explained in the presentation.

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**COMBINED INFLUENCE OF OXIDATION-REDUCTION AND ACID-BASE PROPERTIES OF CATALYSTS IN REDOX-CONVERSIONS OF NITROGEN OXIDES AND METHANE****Orlyk S.N.***L.V. Pisarzhevskii Institute of Physical Chemistry of NAS Kyiv, Ukraine**E-mail: orlyk@inphyschem-nas.kiev.ua*

The results of development of the concept about influencing of acid-base and oxidation-reduction properties of catalysts in reactions of SCR of nitrogen(I, II) oxides by C<sub>1</sub>-C<sub>4</sub>-hydrocarbons, partial oxidation of C<sub>2</sub>-C<sub>3</sub>-hydrocarbons by nitrogen(I, II) oxides, carbon dioxide reforming and deep oxidation of methane are submitted.

The heightened interest to heterogeneous-catalytic oxidation reactions is called by their practical value as expedient method of industrial synthesis of valuable products, and also relevance of their implementation for environmental catalysis. Up to 60-70 years of XX cent. an item determining in such reactions the bond energy oxygen-catalyst, redox-properties of catalyst was considered. G.I.Golodets has put forward a rule about the relevant role of acid-base properties of catalyst in redox-processes [1] with development of the concept in [2]. In the given paper the outcomes of usage of these approaches are submitted at the development of catalysts and processes of nitrogen oxides and methane conversion, in particular: a SCR of nitrogen(I, II) oxides by C<sub>1</sub>-C<sub>4</sub>-hydrocarbons, partial oxidation of C<sub>2</sub>-C<sub>3</sub>- hydrocarbons by nitrogen(I, II) oxides, oxidative conversion of methane (deep oxidation and carbon dioxide reforming).

The enhancement of the redox properties of the Rh-M<sub>x</sub>O<sub>y</sub>/ZrO<sub>2</sub> catalysts upon the introduction of rhodium does not alter their bifunctional nature and provided further evidence for the importance of the bifunctional nature of the catalysts (existence of both redox and strong Brønsted acid sites) for the manifestation of SCR activity [3]. Modification by Fe and Mn improves the catalytic behavior of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> as a result of the increase of the concentration of active sites [4].

Activation of N<sub>2</sub>O on Fe-containing pentasils is connected with the presence of α - centers, consisting of iron atoms, with formation of surface oxygen of a high reactivity. Activation of alkanes is connected with the availability on a surface of catalyst of atomic oxygen and acid-base centers. According to the data of NH<sub>3</sub>-TPD and IR-spectroscopy the activity of Fe-zeolite catalysts in SCR of N<sub>2</sub>O by hydrocarbons correlates with availability on

their surface of strong acid **B**-centers [5]. In partial oxidation of C<sub>3</sub>-C<sub>4</sub>-alkanes by nitrogen(I, II) oxides on zirconium dioxide modified by various heteropolyacids (HPA) the activity of catalysts depends on the amount of deposited P-Mo-HPA, and the reaction selectivity to the partial oxidation products correlates with the concentration of weak acid sites [6].

So, in reactions of nitrogen(I and II) oxides conversion the greatest activity and selectivity is shown by bifunctional catalysts. Due to definite combination of redox- and acid properties of a surface of catalysts on the base of zirconia (Rh) -M<sub>x</sub>O<sub>y</sub>/ZrO<sub>2</sub> (M=Co, Cr, Ce), HPA/ZrO<sub>2</sub> and zeolites Fe/H-zeolite (Mordenite, ZSM-5), they show high activity upon selective reduction of nitrogen oxides up to nitrogen with the help of C<sub>1</sub>-C<sub>4</sub>-hydrocarbons, and in reactions of partial oxidation of lower alkanes up to oxygenates [3-6].

Modifying of a surface of the silver catalysts (supported on ceramic honeycomb monoliths) by the additives of alkali metals Ag/(Cs, K, Na)/synthetic cordierite, that is the definite change of acid-base properties of a surface, results in achievement of promoting effect during epoxidation of ethylene by nitrogen(I) oxide – an increase in 1.5-2 times of the yield of target product – ethylene oxide [7].

The activation of methane during deep oxidation at rather low temperatures (280-350 °C) is connected with availability of reactive oxygen and strong acid centers on a surface of composite oxide, in particular of cobalt-zirconium catalysts (Co<sub>x</sub>O<sub>y</sub>/ZrO<sub>2</sub>) [8], that is consistent with modern ideas about the mechanism of deep oxidation of methane on oxide catalysts (capability of methane C-H bond activation on the acid centers of catalysts).

The increasing of stability performance of the structured nickel catalysts of carbon dioxide reforming of methane NiO-Al<sub>2</sub>O<sub>3</sub>-(Li, Na, K)/synthetic cordierite is reached by regulation of acid-base properties of their surface.

The obtained outcomes are development of the concept about combined influence of oxidation-reduction and acid-base properties of catalysts in oxidation-reduction catalytic processes. At selection of catalysts for such processes it is necessary to estimate not only energy binding oxygen - catalyst, but also acid-base properties of their surface.

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**EXPERIMENTAL EVIDENCE OF THE LOW TEMPERATURE DECOMPOSITION  
OF HYDROGEN SULFIDE INTO HYDROGEN AND ELEMENTAL SULFUR**

**Startsev A.N., Voroshina O.V., Bauman Yu.I., Pashigreva A.V., Babushkin D.E.,  
Plyasova L.M., Zakharov I.I., Kiwi-Minsker L.<sup>1</sup>, Parmon V.N.**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>1</sup>*Ecole Polytechnique Fédérale de Lausanne, GGRC-EPFL, CH-1015, Lausanne, Switzerland*

*E-mail: startsev@catalysis.nsk.su*

The low temperature decomposition of hydrogen sulfide into hydrogen and elemental sulfur can proceed *via* a surface stoichiometric reaction between two adjacent H<sub>2</sub>S molecules adsorbed on two neighboring catalytic sites. The decomposition results in the formation of H<sub>2</sub>S<sub>2(ads)</sub> and evolution of one hydrogen molecule into the gas phase [1]:



Note, that the gas phase reaction



is thermodynamically prohibited ( $\Delta_r H_{298}^0 = 13.6$  kcal/mol,  $\Delta_r S_{298}^0 = -3.9$  cal/mol.K,  $\Delta_r G_{298}^0 = 14.1$  kcal/mol). On the contrary, the surface stoichiometric reaction (1) occurs at room temperature spontaneously over common sulfide (Co,Mo)/Al<sub>2</sub>O<sub>3</sub> catalysts. The surface compound {H<sub>2</sub>S<sub>2(ads)</sub>} was identified in the following way. After adsorption of H<sub>2</sub>S at room temperature and evolution of hydrogen in the gas phase, the sulfide catalyst was heated to 100-200 °C and the desorption products were collected sequentially in benzene and zinc acetate solution. No hydrogen sulfide was detected in acetate solution, while the <sup>1</sup>H NMR spectrum of the benzene solution shows a line at  $\delta = 2.23$  ppm, which is attributed to disulfane H<sub>2</sub>S<sub>2</sub>.

Thus, the rate-limiting step of the hydrogen sulfide decomposition into hydrogen and elemental sulfur appears to be the decomposition of the key surface intermediate {H<sub>2</sub>S<sub>2(ads)</sub>} into hydrogen and elemental sulfur, evolution of the second hydrogen molecule to the gas phase and the recombination (oligomerization) of molecular sulfur S<sub>2</sub> into cyclooctasulfur S<sub>8</sub>. As the result, according to DFT calculations [2], the overall reaction of the H<sub>2</sub>S decomposition can be described by the following equation:



One of the principal approach to accelerate the limiting step of the overall reaction (3) is locating of the solid catalyst in an appropriate solvent [3]. In this case, the expected intermediates and reaction products can be dissolved in the solvent, which accelerates the recombination of molecular sulfur  $S_2$  into cyclooctasulfur  $S_8$ .

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**TRANSIENT OPERATION OF Fe-ZEOLITE BASED NH<sub>3</sub>-SCR CATALYSTS,  
EXPERIMENTS AND KINETIC MODELING**

**Malmberg S.<sup>1</sup>, Schuler A.<sup>1,2</sup>, Votsmeier M.<sup>1</sup>, Gieshoff J.<sup>1</sup>, Drochner A.<sup>2</sup>, Vogel H.<sup>2</sup>**

<sup>1</sup>*Umicore AG & Co. KG, Hanau, Germany*

<sup>2</sup>*Technical University Darmstadt, Darmstadt, Germany*

*E-mail: martinumi@gmx.de*

The response of a Fe-Zeolite based NH<sub>3</sub>-SCR catalyst to step changes in inlet concentration has been measured. It is shown that the transient behaviour of the catalyst can well be reproduced by a kinetic model that takes into account NH<sub>3</sub> storage on the catalyst and the inhibition of the SCR reaction by NH<sub>3</sub>.

**Introduction**

Upcoming stringent legislation will require NO<sub>x</sub> exhaust treatment of Diesel vehicles. One alternative for the removal of NO<sub>x</sub> from lean exhaust gas is ammonia-SCR where the ammonia is produced from urea in the exhaust system. Fe-exchanged zeolites are attractive materials for automotive exhaust ammonia-SCR since they show a high selectivity towards the desired products N<sub>2</sub> and H<sub>2</sub>O, particularly at elevated temperatures [1, 2].

The application potential of a dynamic SCR-catalyst model for the layout of exhaust system and for an improved urea dosing system has been recently demonstrated by Chatterjee and co-workers [3] for vanadium based catalysts. It is the objective of the current contribution to characterize the dynamic operation of Fe-zeolite catalysts experimentally and to set up a model describing the observed behaviour.

**Materials and Methods**

Gas mixtures containing NO, NO<sub>2</sub>, NH<sub>3</sub>, O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O were prepared using a standard flow controller setup and conversion was measured over a coated monolith sample of ~ 40 ml volume. Reactor temperatures were in the range of 150 - 400 °C and hourly space velocities in the range 12500 1/h to 25000 1/h. Gas concentrations were measured with an FTIR detector. The transient test procedure consists of step changes in NH<sub>3</sub>, NO and NO<sub>2</sub> concentration at a fixed temperature. The test sequence is designed in a way so that all relevant information for the characterization of steady state and transient performance of the catalyst can be collected in 24 hours.



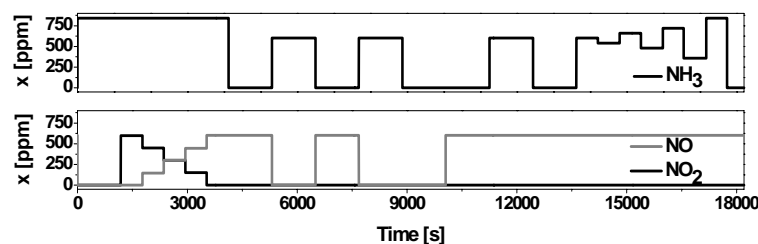


Fig. 1. NO, NO<sub>2</sub>, and NH<sub>3</sub> inlet concentration during the test sequence. This sequence is repeated for different temperatures.

## Results and Discussion

A kinetic model is set up that takes into account the storage and release of NH<sub>3</sub> on the zeolite catalyst and the different reactions of NH<sub>3</sub> with NO alone, NO<sub>2</sub> alone and combined NO/NO<sub>2</sub>. NH<sub>3</sub> oxidation by O<sub>2</sub> is found to be negligible. The Analysis of the results shows that ammonia storage/release and inhibition of the SCR reactions by NH<sub>3</sub> are the key processes for an understanding of the transient performance of the SCR catalyst. The dynamic behavior of the Fe-Zeolithe catalyst proves surprisingly similar to the vanadium based catalyst.

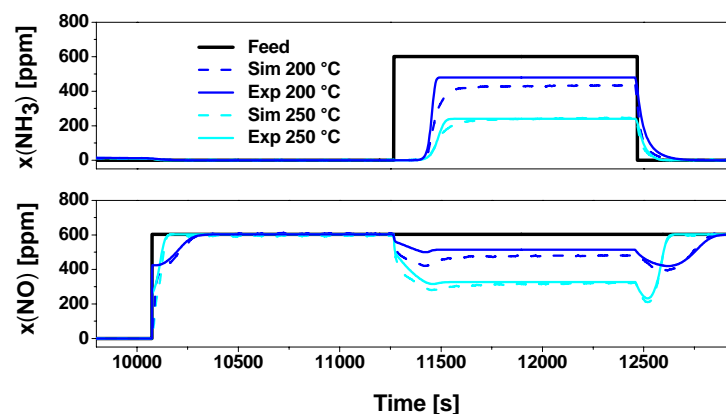


Fig. 2. Comparison of measured and computed outlet concentrations for a NH<sub>3</sub>/NO pulse sequence.

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**XPS STUDIES OF REACTIONS OF NO<sub>x</sub> WITH METALLIC PARTICLES  
SUPPORTED ON OXIDES: Pt ON Al<sub>2</sub>O<sub>3</sub>**

**Smirnov M.Yu., Kalinkin A.V., Bukhtiyarov V.I.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: smirnov@catalysis.ru*

The reaction of platinum deposited on alumina with a mixture of NO and O<sub>2</sub> has been studied using XPS. The reaction at room temperature causes accumulation of nitrate-ions on the alumina surface and oxidation of platinum. Platinum is also oxidized when it is deposited onto the pre-nitrated alumina surface. The reaction with surface nitrates is proposed to be a possible way of platinum oxidation under the treatment of Pt/Al<sub>2</sub>O<sub>3</sub> in NO<sub>x</sub> mixtures.

Reactions of nitrogen oxides with supported metal and oxide catalysts is of significance in view of development of NO<sub>x</sub> storage reduction catalysts for automotive exhaust aftertreatment. This work begins a series of our works, where the interaction of metallic particles supported on oxides with NO<sub>x</sub> mixtures will be studied. The work is implemented using X-ray Photoelectron Spectroscopy (XPS). Samples of Pt/Al<sub>2</sub>O<sub>3</sub> model catalysts were prepared by evaporation of platinum onto a thin alumina film grown on a tantalum foil. The prepared samples were treated in a preparation chamber of photoelectron spectrometer with NO<sub>x</sub> mixture composed of O<sub>2</sub> (2 Torr) and NO (10 Torr) and then transferred into an analyzer chamber for spectra measurement.

Platinum deposited onto the freshly prepared alumina surface are characterized by a Pt4f doublet with a Pt4f<sub>7/2</sub> binding energy (BE) ranging within 72.0-71.6 eV, increase in the amount of platinum deposited reducing the BE value. Heating the sample in vacuum reduces the intensity of Pt4f spectrum and shifts the spectrum to the BE value of 71.2 eV (Fig. 1), which is typical of bulk platinum metal. This behavior is in agreement with literature data and indicates the formation of small metallic Pt particles on the alumina surface, sizes of which are increased with raising the amount of deposited platinum and temperature of subsequent annealing in UHV.

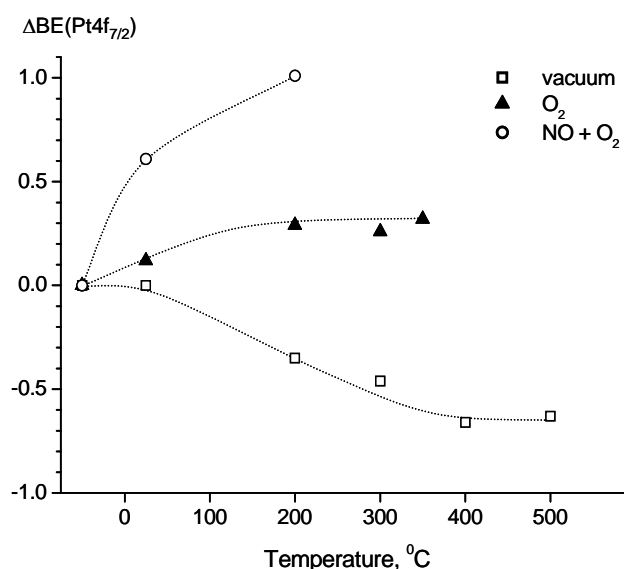
Practically no changes are observed in the Pt4f spectrum after interaction of Pt/Al<sub>2</sub>O<sub>3</sub> with O<sub>2</sub> at 10 Torr and room temperature, whereas increase in BE(Pt4f<sub>7/2</sub>) by 0.3 eV occurs when reaction temperature rises to 350 °C (Fig. 1). The moderate shift without line broadening allows us to assume that oxygen dissolves in platinum with more or less uniform distribution of oxygen atoms in the bulk of Pt particles. Heating the sample in vacuum to T ≥ 200°C shifts the Pt4f line down to 71.2 eV pointing to the removal of dissolved oxygen at these temperatures.

The reaction of Pt/Al<sub>2</sub>O<sub>3</sub> with NO<sub>x</sub> at room temperature accumulates nitrate-ions on the surface of alumina that is established by appearance of N1s and O1s lines at 407.5 eV and

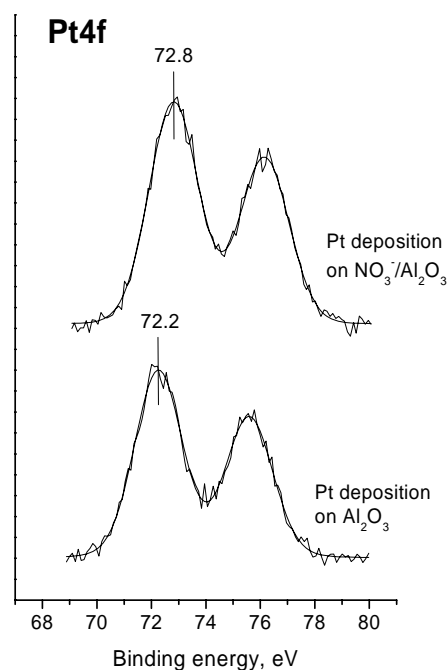
533.1 eV, respectively. In parallel, the Pt4f line shifts upward by  $\sim 0.6$  eV (Fig. 1). The shift is increased to 0.9 eV when the reaction temperature rises to 200 °C. This rather large shift to higher BE indicates that contrary to pure oxygen treatment, the interaction of Pt/Al<sub>2</sub>O<sub>3</sub> with NO<sub>x</sub> mixture causes deeper oxidation of platinum, perhaps, with the formation of platinum (II) oxide. It has been also found that the smaller is the mean size of Pt particles, the easier is their oxidation with NO<sub>x</sub>.

To test the role of surface nitrate-ions in oxidation, platinum was evaporated onto the surface of the alumina film pre-treated with NO<sub>x</sub> mixture at room temperature. The pre-treatment produces nitrate-ions on the surface of alumina. Deposition of platinum onto the nitrated alumina surface attenuates the nitrate N1s and O1s lines. Fig. 2 compares Pt4f spectra recorded after deposition of equal amounts of platinum onto the pure and nitrated alumina surfaces. It is seen that the BE(4f<sub>7/2</sub>) is about 0.6 eV higher when platinum is deposited on the nitrated surface. The results obtained indicate that nitrate-ions on the alumina surface are able to oxidize supported platinum particles.

In conclusion of this work, we can infer that at least one route for oxidation of platinum supported on Al<sub>2</sub>O<sub>3</sub> is the reaction of platinum with nitrate-ions formed on the surface of the oxide support. As a development of the work, we are planning to study the reactions of NO<sub>x</sub> mixture and surface NO<sub>3</sub><sup>-</sup> with different metals (Pd, Rh, Au) supported on alumina and on other oxides.



**Fig. 1.** The Pt4f<sub>7/2</sub> binding energy shift in the course of Pt/Al<sub>2</sub>O<sub>3</sub> heating in vacuum, O<sub>2</sub> or NO<sub>x</sub> (2 Torr NO + 10 Torr O<sub>2</sub>).



**Fig. 2.** Pt4f spectra for platinum deposited onto the pure (the bottom spectrum) and pre-nitrated (the upper spectrum) alumina surfaces.

**HYDROGEN PEROXIDE OXIDATION OF ORGANIC COMPOUNDS CATALYZED  
BY MANGANES COMPLEXES WITH 1,4,7-TRIMETHYL-1,4,7-  
TRIAZACYCLONONANE IN THE PRESENCE OF A CARBOXYLIC ACID**

**Mandelli D., Matthes M.G., Aoyagi Jonatas L.T., Shul'pin G.B.<sup>1</sup>**

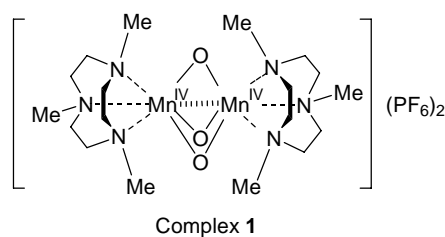
*Pontifícia Universidade Católica de Campinas, Faculdade de Química, Rod. D. Pedro I,  
km 136, Pq. das Universidades, Campinas, SP, 13086-900, Brazil*

<sup>1</sup>*N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia*

*E-mail: dalmo\_mandelli@mail.ru*

Dinuclear manganese(IV) complex [(TMTACN)Mn(O)<sub>3</sub>Mn(TMTACN)](PF<sub>6</sub>)<sub>2</sub> (TMTACN = 1,4,7-trimethyl-1,4,7-triazacyclononane,) catalyzes the efficient oxidation of alkanes, olefins and alcohols with hydrogen peroxide at room temperature only if a carboxylic acid is present as a co-catalyst. Oxidations of cyclohexane and cyclohexanol were studied in detail. The reactions were carried out both in acetonitrile and without any solvent. The oxidation of cyclohexane in acetonitrile gave rise to formation of cyclohexyl hydroperoxide which was transformed in the course of the reaction into cyclohexanol and cyclohexanone. In the absence of acetonitrile the oxidation of cyclohexanol gave cyclohexanone and in the oxidation of cyclohexane both cyclohexanol and cyclohexanone were produced. The oxidation of isopropanol affords acetone with turnover numbers up to 40000 after 5 hours in the absence of a solvent.

It has been discovered earlier that the system consisting of dinuclear manganese(IV) complex [LMn(O)<sub>3</sub>MnL](PF<sub>6</sub>)<sub>2</sub> (L = TMTACN; catalyst, complex 1), carboxylic acid (co-catalyst) and aqueous H<sub>2</sub>O<sub>2</sub> efficiently oxidizes various organic compounds (alkanes, alcohols, sulfides, olefins) in acetonitrile at room temperature [1].



In the present work, kinetic features have been found to be different for the oxidations of cyclohexane with H<sub>2</sub>O<sub>2</sub> catalyzed by 1 in homogeneous solution in acetonitrile in the presence of co-catalysts: acetic acid on the one hand and oxalic acid on the other hand. The obtained results are used in a detailed kinetic analysis of these oxidations, and a possible mechanism of the reaction has been proposed. We also studied oxidation of cyclohexanol to cyclohexanone

by the H<sub>2</sub>O<sub>2</sub>–oxalic acid system in acetonitrile solution. We found that cyclohexanol is efficiently oxidized into cyclohexanone at room temperature in the absence of any organic solvent. Conversion is very high after 5 minutes. After this time concentration of formed cyclohexanone decreases gradually due to the transformation of cyclohexanone into over-oxidation products. Under analogous conditions cyclohexane is rapidly oxidized to produce cyclohexanol and cyclohexanone. Concentrations of these products decrease at time > 15 minutes due to the formation of over-oxidation products.

### Acknowledgments

This work was supported by the Russian Basic Research Foundation (grant No. 06-03-32344-a). The authors thank also the State of São Paulo Research Foundation (Fundação de Amparo a Pesquisa do Estado de São Paulo, FAPESP), the Brazilian National Council on Scientific and Technological Development (Conselho Nacional de Desenvolvimento Científico e Tecnológico, CNPq, Brazil) for support. D. Mandelli thanks CNPq (grant No. 300984/2004-9), M. G. Matthes is grateful to FAPESP (grant No. 05/51579-2), J. L. T. Aoyagi to PIBIC/CNPq. G. B. Shul'pin expresses his gratitude to the FAPESP (grants No. 2002/08495-4 and 06/03984-8), the CNPq (grant No. 300601/01-8) for support and the Faculdade de Química, Pontifícia Universidade Católica de Campinas for making it possible for him to stay at this University as invited Professor and to perform a part of the present work.

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**CYCLIC TRIMERIZATION AND LINEAR OLIGOMERIZATION OF  
PHENYLACETYLENE BY CYCLOPENTADIENYL NICKEL(I) COMPLEXE**



**Saraev V.V., Kraikovskii P.B., Vil'ms A.I., Kuzakov A.S., Yunda A.Yu., Matveev D.A.,  
Lammertsma K.<sup>1</sup>**

*Irkutsk State University, Irkutsk, Russia*

<sup>1</sup>*Vrije University, Amsterdam, the Netherlands*

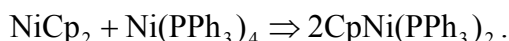
*E-mail: saraev@chem.isu.ru*

Research by EPR method of the interaction of Ni(I) complex CpNi(PPh<sub>3</sub>)<sub>2</sub> with phenylacetylene and its catalytic activity in cyclic trimerization and linear oligomerization of phenylacetylene.

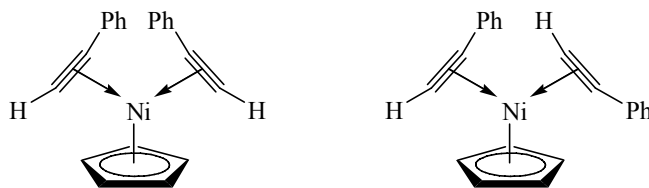
Nickelocene NiCp<sub>2</sub> in combination with organolithium compounds LiR is an effective catalyst for oligomerization and polymerization of alkynes [1]. The catalyst formation involves reduction of nickelocene giving the high reactive Ni(I) monocyclopentadienyl complexes that in the absence of stabilizing ligands transform to bi-, tri-, tetra-, and polynuclear clusters [2].

This paper reports the results of the EPR study of the interaction of (η<sup>5</sup>-cyclopentadienyl)nickel(I) complex CpNi(PPh<sub>3</sub>)<sub>2</sub> with phenylacetylene (PA) and its catalytic activity in cyclic trimerization and linear oligomerization of phenylacetylene.

The CpNi(PPh<sub>3</sub>)<sub>2</sub> complex was prepared through contradisproportion reaction between NiCp<sub>2</sub> and Ni(PPh<sub>3</sub>)<sub>4</sub> complexes in toluene solutions:



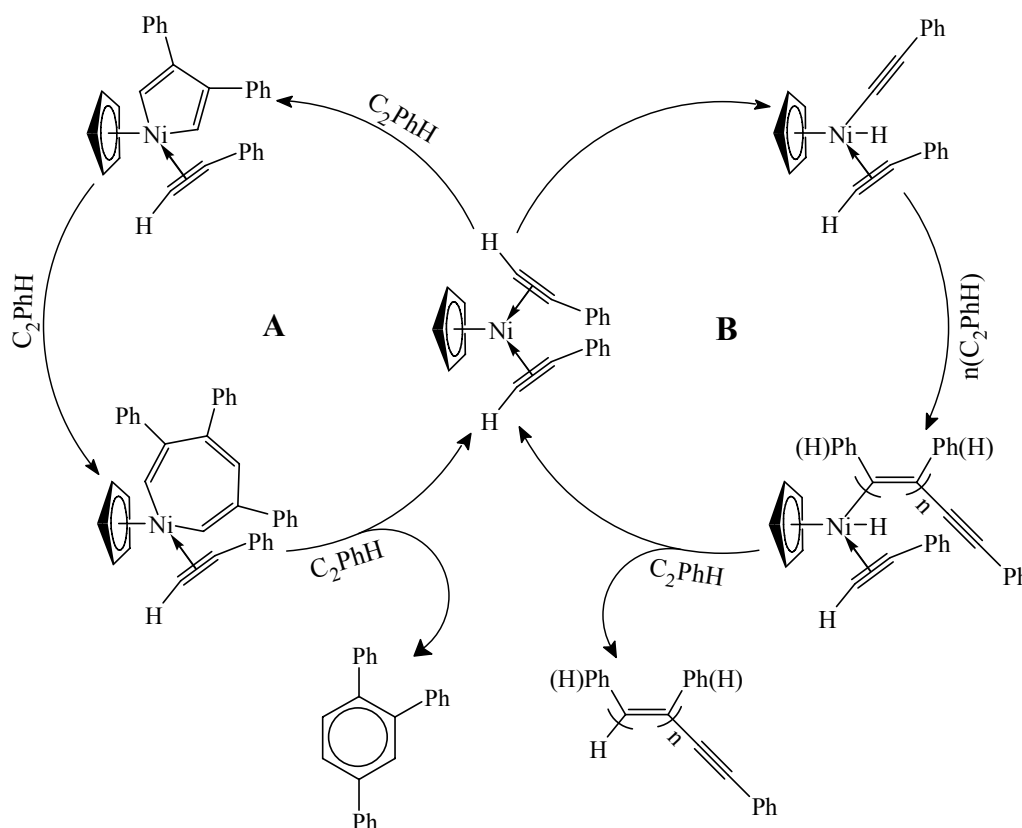
It was shown that phenylacetylene reacts with the CpNi(PPh<sub>3</sub>)<sub>2</sub> complex (molar ratio PA/Ni = 1-2) via the substitution of phosphine ligands by phenylacetylene to form the π-alkyne complex CpNi(PhC≡CH)<sub>2</sub> which in toluene solutions according to EPR data exists in the forms of two isomers different in the mutual orientation of the coordinated molecules:



In time the π-alkyne Ni(I) complex turns to diamagnetic cluster structures.

It was established that when phenylacetylene is taken in an excess relatively to the  $\text{CpNi}(\text{PPh}_3)_2$  complex (molar ratio  $\text{PA}/\text{Ni} = 200$ ) the monomer is actively oligomerized at ambient temperature to give largely cyclic trimers (predominantly 1,2,4-triphenylbenzene) and linear oligomers containing, on average, 9-10 monomeric units. The reaction products were characterized by NMR ( $^{13}\text{C}$  and  $^1\text{H}$ ) and mass spectra. The condition for the 97 % yield of 1,2,4-triphenylbenzene were found. A proportional dependence between the oligomerization activity and the concentration of the  $\pi$ -alkyne complex  $\text{CpNi}(\text{PhC}\equiv\text{CH})_2$  in the system was found.

Schema for the cyclic trimerization and linear oligomerization is proposed:



According to the suggested schema, an active particle in catalytic cycles of trimerization (**A**) and linear oligomerization (**B**) is Ni(I)  $\pi$ -alkyne complex stabilized by substrate molecules.

The work is supported by the funds NWO (the Netherlands) and RFBR (Russia) (international grant No 047.015.014).

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**MECHANISM OF THE OXYHYDRATIVE SCISSION  
OF 1-BUTENE TO ACETIC ACID IN THE PRESENCE OF WATER**

**Suprun W.Ya., Sadovskaya E.M.<sup>1</sup>, Muzykantov V.S.<sup>1</sup>, Papp H.**

*Universität Leipzig, Leipzig, Germany*

<sup>1</sup>*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: suprun@chemie.uni-leipzig.de*

**Introduction.** Acetic acid (AcOH) is produced on industrial scale mainly by carbonylation of methanol and liquid phase oxidation of ethylene and butane. Gas phase oxidation of n-butenes on VO<sub>x</sub> catalyst is a potential route for the production of AcOH on a smaller industrial scale [1]. The mechanism of butene oxidation to AcOH is still a matter of discussion. Seiyama et al. proposed an oxyhydrative scission mechanism involving water as a reactant [2]. In contrast, Kaneko et al. suggested a reaction mechanism without the participation of water [3]. This investigation is aimed at elucidating the reaction pathway for oxidation of 1-butene using isotopic transient methods in order to obtain information on the reaction mechanism.

**Experimental.** VO<sub>x</sub> containing catalysts were prepared by spray-drying of a slurry of TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and Sb<sub>2</sub>O<sub>3</sub>. The catalytic experiments were carried out at atmospheric pressure in a continuous flow reactor in the temperature range of 120 to 360 °C. The influence of various reaction conditions on reaction was also studied. The detailed results of the catalyst characterization (H<sub>2</sub>-TPR, O<sub>2</sub>-TPD, XPS,..) and description of the catalytic equipment are given in [4].

**Results and Discussion.** More than 20 products were identified by on line MS and GC-MS in the oxidation of 1-butene including C<sub>1</sub>-C<sub>5</sub> carboxylic acids and anhydrides with AcOH as the main product. Along with these products, C<sub>1</sub>-C<sub>4</sub> alcohols, C<sub>1</sub>-C<sub>4</sub> mono- and dicarbonyl compounds and C<sub>1</sub>-C<sub>4</sub> carboxylic acid were identified. It was observed that the selectivity to AcOH increased with the increase in residence time and concentration of O<sub>2</sub> and water.

By SSITKA measurements the distribution of <sup>16</sup>O and <sup>18</sup>O in the oxidation products was determined after single or periodic switching of <sup>16</sup>O<sub>2</sub> to <sup>18</sup>O<sub>2</sub>. During the oxidation of 1-butene in the presence of water, it was found that the isotope exchange rate was fast but limited. The degree of isotope exchange in AcOH and in the presence of H<sub>2</sub>O was ca. 10% at 160°C and increased an 25-35% with increase in reaction temperature to 260°C. Isotopic transient experiments with H<sub>2</sub><sup>18</sup>O revealed that <sup>18</sup>O from H<sub>2</sub><sup>18</sup>O (Fig. 1b,c) was more readily incorporated into acetic acid than <sup>18</sup>O from <sup>18</sup>O<sub>2</sub>. These results clearly indicate that water participates in the reaction and O-isotope exchange takes place between oxygen and adsorbed water molecules on the catalyst surface. These results indicated additionally that during catalytic oxidation of butene in presence of H<sub>2</sub><sup>16</sup>O a transfer of oxygen from water to acetic



acid occurred. From the numerous isotope transient experiments the following kinetic models for O-transfer are discussed: (i) direct isotope exchange between adsorbed oxygen and OH-group, (ii) reversible adsorption of AcOH and isotope exchange with OH-groups; (iii) direct oxygen-transfer from OH to AcOH. It was proven that the formation of AcOH proceeds with the participation of OH-groups.

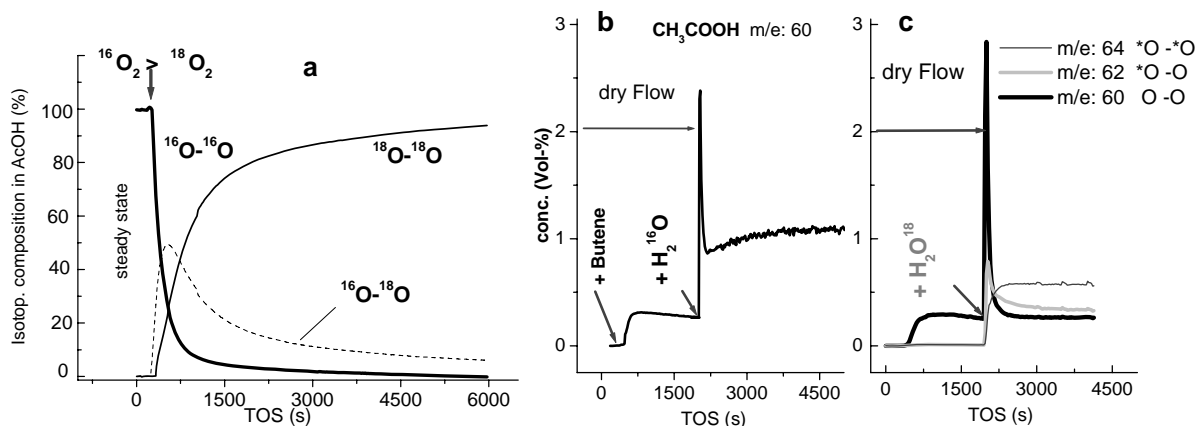


Fig. 1: O-isotopes exchange in acetic acid during the oxidation of 1-butene at 260°C in absence of water (a) and after addition of  $^{16}\text{O}$ -water (b) or  $^{18}\text{O}$ -water to the feed (c).

Water was involved in the reaction steps such as the formation of 2-BuOH and/or AcOH. The alternative mechanisms of the  $^{16}\text{O}$ - $^{18}\text{O}$ -isotope exchange during the oxidation of 1-butene in the absence and presence of water are proposed.

In addition to the isotopic tests, the reactivity of various intermediates such as acetaldehyde (AcH), propionaldehyde (PrA), methylethylketone (MEK), 2-butanol (BuOH) and  $\text{C}_1$ - $\text{C}_3$ -carboxylic acid were studied towards catalytic oxidation under similar reaction conditions. The selectivity to acetic acid from intermediates decreased in the order: AcH > MEK > PrA > 2-BuOH > n-butene [4]. Furthermore, selective oxidation of  $\text{C}_2$ - $\text{C}_3$  aldehydes to the corresponding carboxylic acid depended on the kind of aducts and the reaction conditions [5]. As a result AcOH can be formed: (i) by oxidative cleavage of MEK formed from 2-BuOH, and (ii) from AcH via selective oxidation and/or oxidative scission of propionaldehyde or propionic acid. Reaction temperature and the presence of water strongly influenced the formation of AcOH and other products shifting the reaction to a different pathway.

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**THE SCOPE OF HOMOGENEOUS CATALYTIC OXIDATION IN THE PRESENCE  
OF Mo-V-PHOSPHORIC HETEROPOLY ACIDS**

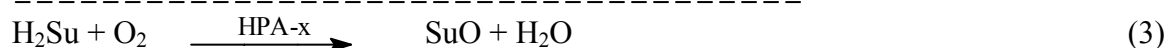
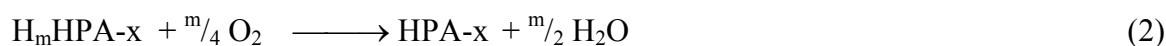
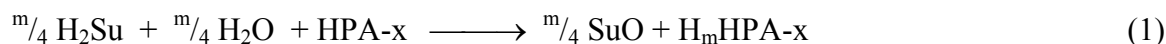
**Zhizhina E.G., Odyakov V.F., Simonova M.V., Matveev K.I.**

*Borekov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: zhizh@catalysis.nsk.su*

Different substrates can be oxidized by O<sub>2</sub> in the presence of solutions of Mo-V-phosphoric heteropoly acids having composition H<sub>3+x</sub>PV<sub>x</sub>Mo<sub>12-x</sub>O<sub>40</sub> (HPA-x). Olefins C<sub>2</sub>-C<sub>4</sub> are oxidized to carbonyl compounds in solutions of Pd+HPA-x with selectivity S=97-99 %. Alkylphenols of benzene and naphthalene series are oxidized in two-phase systems to para-quinones with S=90-99 %. So, 2,3,6-trimethylphenol is oxidized to 2,3,5-trimethyl-1,4-benzoquinone which is a key semiproduct of vitamin E synthesis. 2-Methyl-1-naphthol is oxidized to 2-methyl-1,4-naphthoquinone (vitamin K<sub>3</sub>). Using HPA-x solutions, Diels-Alder reaction and oxidation of its adduct can be realized as an one-pot process. So, 9,10-anthraquinone can be produced starting from hydroquinone, benzoquinone, or naphthoquinone. Vitamin K<sub>3</sub> can be produced similarly from *o*-cresol.

Solutions of Mo-V-phosphoric heteropoly acids having composition H<sub>3+x</sub>PV<sub>x</sub>Mo<sub>12-x</sub>O<sub>40</sub> (HPA-x, x is a number of V atoms in HPA-x) are reversibly acting oxidizers. They are used as catalysts in various oxidation processes (3). Oxidation of various substrates H<sub>2</sub>Su is carried out via reactions (1) and (2):



Here, H<sub>m</sub>HPA-x is a form of HPA-x reduced by m electrons.

Processes (3) can be realized in one stage, but they are usually carried out in two stages for increasing of their selectivity and guaranteeing of non-explosion-proof. Regeneration of catalyst via reaction (2) is a common stage of all processes (3).

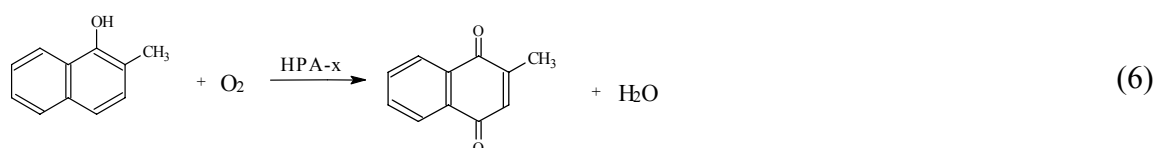
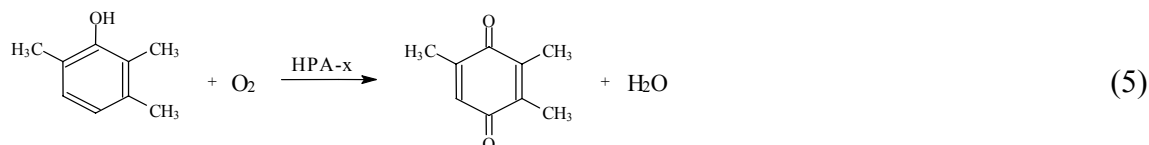
Olefins C<sub>2</sub>-C<sub>4</sub> are oxidized to carbonyl compounds (acetaldehyde, acetone, methylethylketone) in solutions of Pd+HPA-x with S = 97-99 % via reaction (4).



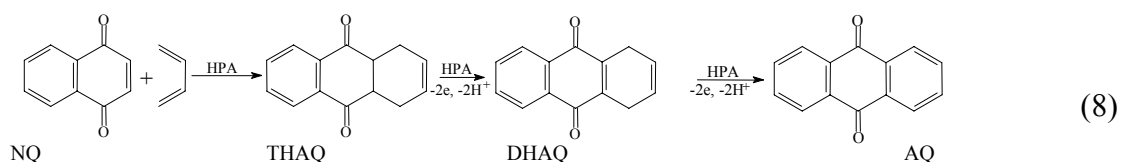
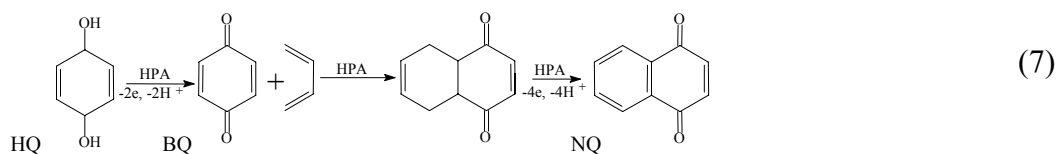
After stripping of reaction product at 100 °C, the catalyst is regenerated at 150-160 °C under pressure of O<sub>2</sub> (2-4 atm) via reaction (2).

Alkylphenols of benzene and naphthalene series are oxidized to corresponding para-quinones with high selectivity in the presence of HPA-x in two-phase systems (water +

organic solvent). These quinones are important products of fine chemistry. So, 2,3,6-trimethylphenol is oxidized via reaction (5) to 2,3,5-trimethyl-1,4-benzoquinone (S=99 %) which is a key semiproduct of vitamin E synthesis. 2-Methyl-1-naphthol is oxidized via reaction (6) to 2-methyl-1,4-naphthoquinone (vitamin K<sub>3</sub>, S=90 %). These methods of the quinone production are friendly to environment.



Aqueous solutions of HPA-x are also used as bifunctional catalysts for Diels-Alder reaction and followed oxidation of obtained adducts. So, we succeeded to produce 9,10-anthraquinone (AQ) at 60–80°C in 1,3-butadiene atmosphere starting from hydroquinone (HQ), 1,4-benzoquinone (BQ), or 1,4-naphthoquinone (scheme (7)+(8)). The Diels-Alder reaction and followed oxidation are realized as one-pot process.



In the processes (7) and (8) at atmospheric pressure, a mixture of AQ and its partly hydrogenated compounds 1,4,4a,9a-tetrahydro-9,10-anthraquinone (THAQ) and 1,4-dihydro-9,10-anthraquinone (DHAQ) is formed. A yield of AQ reaches to 54 % from naphthoquinone (NQ, scheme (8)) or 20% from HQ (schemes (7)+(8)). It is important that reactions via schemes (7)+(8) proceed without organic solvents. Slightly soluble reaction products AQ+THAQ+DHAQ are almost quantitatively separated by filtering from reduced solution of HPA-x. The mixture AQ+THAQ+DHAQ is an important product and can be used as a catalyst for delignification of wood.

Joining the Diels-Alder reaction with the oxidation of obtained adducts in HPA-x solution, vitamin K<sub>3</sub> can be produced with S=38-40 from 2-methylphenol or 2-methylaniline which are quite available compounds.

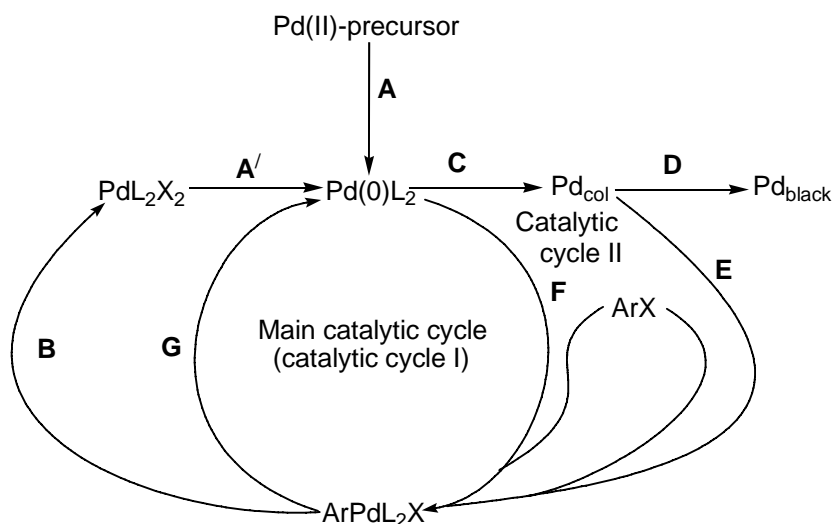
**INTERPLAYS BETWEEN REACTIONS WITHIN AND WITHOUT CATALYTIC  
CYCLE OF THE HECK REACTION**

**Schmidt A.F., Smirnov V.V., Ayman Al.H.**

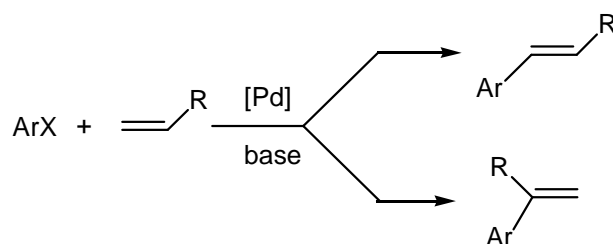
*Irkutsk State University, Irkutsk, Russia*

*E-mail: aschmidt@chem.isu.ru*

In this report we present our concepts concerning the studied pathways of catalyst transformation without the main catalytic cycle (Scheme 1) of the Heck reaction [1, 2] as well as a short description of the experiments allowing some conclusions on the mechanism of these processes.



**Scheme 1.** Key processes without the main catalytic cycle (cycle I) in the Heck reaction.



**Scheme 2.** Heck reaction (X=I, Br, Cl).

It has been shown that an explanation for the observed trends of the Heck reaction kinetics (Scheme 2) is impossible without considering catalyst transformation that occurs off the main catalytic cycle. As a main result of our studies, it has been established that a catalyst transformation without the main catalytic cycle occurs in four mutually compensative directions (Scheme 3): (i) reduction Pd(II)  $\rightarrow$  Pd(0) (A,A'); (ii) oxidation Pd(0)  $\rightarrow$  Pd(II) (F,B

and **E,B**); (iii) agglomeration  $\text{Pd}(0) \rightarrow \text{Pd}_{\text{col}} \rightarrow \text{Pd}_{\text{black}}$  (**C,D**); (iv) dissolution (via oxidation)  $\text{Pd}_{\text{col}} \rightarrow \text{Pd}(\text{II})$  (**E**) [3].

The experimental data obtained in our studies of both model and real catalytic reactions are wholly consistent with one another in the context of Schemes 1. Mechanisms of the palladium transformations without the main catalytic cycle, i.e. reduction, agglomeration and oxidation (as a result of ArX homocoupling), are of a so-called non-linear type. Since such a type of mechanism involves steps, the rates of which depend non-linearly on the concentration of intermediates, the agglomeration and reduction exhibit autocatalytic kinetics; the rate of oxidation is proportional to the square of the total catalyst concentration. The main catalytic cycle alone is of a linear mechanism but this cycle is subjected to the catalyst non-linear transformations. The mechanistic finding and analysis of the coupling of non-linear processes are a real challenge. However, our experiment results provide us with enough evidence to predict an influence of some factors on the Heck reaction and to arrange the principles of the catalytic system organization. These principles can be used to help attaining reasonable rates, TOF and TON in the Heck reaction. One piece of evidence for advantages of such a rational approach for the optimization of the synthetic protocol is a significant increase in efficiency of the phosphane-free catalytic system in the reactions with non-activated aryl bromides and even non-activated aryl chlorides. It was not until now that an implementation of these reactions without the traditional additives of phosphines was conceivable. The low catalyst loading, the availability and the low prices of the components of the catalytic system, together with the absence of an inert atmosphere, make the suggested approach attractive for application at a larger scale.

Acknowledgement: *This work was supported by the Russian Foundation for Basic Research (Project No. 05-03-32222)*

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## SITE ISOLATION BASED DESIGN OF SELECTIVE OXIDATION CATALYSTS

Mamedov E.

*Sabco Technology Center, 1600 Industrial Boulevard, Houston, Texas 77478, USA**E-mail: emamedov@americas.sabco.com*

The incorporation of catalytically low active elements to the VSb and VMo oxides promoted the structural isolation of V, Sb and Mo species in their body. These diluted catalysts displayed substantially higher selectivity in partial oxidations of C<sub>2</sub>-C<sub>3</sub> paraffins than their undiluted counterparts. The performance of diluted catalysts was further improved by loading the surface with appropriate promoters.

In an effort to isolate V, Mo and Sb species in oxide catalysts, catalytically low active elements, such as Mg, Al, Zr, Si, Hf, Ti and Nb, were introduced to their body by co-precipitation technique. Many of these so-called diluted oxides turned out to be more selective catalysts than their undiluted analogues. This was the case for ethane oxidation to ethylene and acetic acid on Nb-diluted VMo oxide catalyst (Figure 1), propane oxidative dehydrogenation on Al-diluted FeVSb oxide catalyst (Figure 2) and propane ammoxidation on VSb oxides diluted with Mg, Al and Zr (Figure 3). Niobium added to the VSb oxide did not increase catalyst intrinsic selectivity but essentially reduced the acrylonitrile overoxidation. The behavior of diluted catalysts was dependent on the nature and amount of diluent material. In particular, both activity and selectivity went through the maximum with increasing the extent of catalyst dilution.

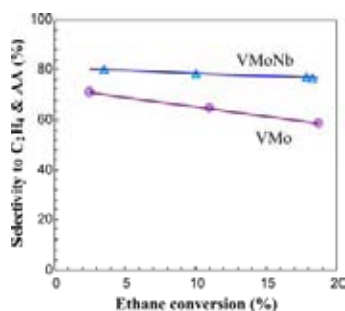


Fig. 1. Ethane oxidation at 260 °C

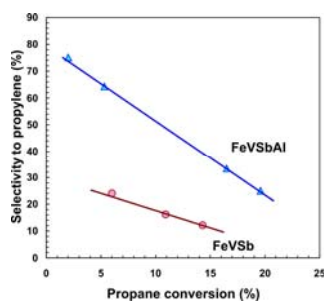


Fig. 2. Propane oxidative dehydrogenation at 350 °C

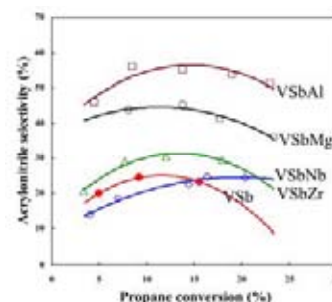


Fig. 3. Propane ammoxidation at 500 °C

Diluted catalysts differed from undiluted ones also structurally. Undiluted VSb oxides with excess antimony consisted of  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> and defect rutile phase of approximate composition VSbO<sub>4</sub>. The surface was enriched in antimony which was Sb<sup>5+</sup>. The average oxidation state of vanadium was 4+. Diluted oxides did not contain rutile or any other vanadium-containing phase. Instead, they contained oxide compounds of antimony with

diluent element, such as  $\text{AlSbO}_4$ ,  $\text{MgSb}_2\text{O}_6$  or  $\text{Nb}_3\text{Sb}_3\text{O}_{13}$ , and small amounts of individual oxides of antimony and diluent element. At the surface vanadium and antimony were present as  $\text{V}^{5+}$  and  $\text{Sb}^{5+}$ , and their relative concentrations were close to those in the bulk. Diluent elements were always present in highest oxidation states. It appears that catalytically low active elements incorporated to the bulk of the VSb oxide structurally isolated vanadium and antimony species. This should reduce the number of  $\text{V} - \text{O} - \text{Sb}$  chains considered to be degradation sites for hydrocarbons and increase the number of  $\text{V} - \text{O}$  moieties which are believed to have catalyzed propane conversion to propylene. Antimony cations surrounded with low active Mg, Al, Nb or Zr were the sites that catalyzed ammoxidation of the intermediate propylene to acrylonitrile. These sites should function more selectively than the antimony having vanadium in close proximity as the latter might oxidize propylene instead of ammoxidizing it. These argumentations infer that the structural isolation of antimony species with catalytic low active elements was the factor that increased the nitrogen-insertion activity of the VSb oxide catalysts.

Further improvement in behavior of diluted catalysts was achieved by tuning their surface property. Selectivity of the FeVSbAl oxide catalyst in the oxidative dehydrogenation of propane to propylene was substantially improved by loading its surface with potassium. This procedure did not change catalyst texture, phase composition and reducibility but decreased surface acidity. On less acidic surface, propane and propylene adsorbed most likely weaker to result in lower rate of their total oxidation. Selectivity of the VSbAl oxide catalyst in propane ammoxidation to acrylonitrile was increased by putting tungsten on its surface. Adding tungsten increased the number of acid sites without altering their strength. Due to this change in acidity, promoted catalyst adsorbed more ammonia that reduced degradation and enhanced ammoxidation of the intermediate propylene. Using the same approach, selectivity of ethane oxidation to acetic acid over VMoNb oxide catalyst was increased by two times at the expense of selectivity to ethylene. In all these cases, surface modification was more efficient than the bulk modification.

**KINETIC OF HOMOMOLECULAR LOW TEMPERATURE ISOTOPE EXCHANGE  
OF HYDROGEN AS AN INSTRUMENT FOR RESEARCH OF CORRELATION  
BETWEEN CATALYTIC AND ELECTRONIC PROPERTIES OF  
REM,Hf,Zr,Ni,Ru,Pt,Pd,Rh, IMS LnCu<sub>n</sub>, Hf(Cu,Ag,Au)<sub>n</sub> AND FOR  
DETERMINATION OF COMPOSITION AND BOND ENERGY OF IMC**

**Zhavoronkova K.N., Boeva O.A.**

*Mendelejev University of Chemical Technology, Moscow, Russia*

*E-mail: chekmarv@rctu.ru*

Results of investigation of reaction  $H_2 + D_2 = 2HD$  at low temperatures (77 – 200 K) on films of REM,Hf,Zr,Ni,Ru,Pt,Pd,Rh,IMS LnCu<sub>n</sub>, Hf(Cu,Ag,Au)<sub>n</sub> are reported. It was proved that at lower temperatures exchange goes by Eley mechanism and at higher T it occurs by Ridial mechanism. Correlations between catalytic properties and electronic structure of metals were discussed. The nature of activation energy at very low T ( $77 - T_{br}$ ) –  $E_1$  was understood. It was proved that correlation between the preexponential factor  $B_1$  and sublimation energy of pure metals ( $\Delta H_s$ ) allows to use factor  $B_1$  for bond energy in IMC and supported catalysts finding and also for the composition of IMC on the surface determining.

This work is devoted to summing up results of wide investigation of the kinetic of model reaction of isotope exchange in molecular hydrogen at low temperatures (77-200 K) on films condensed in high vacuum of all rare earth metals, Hf, Zr, Ni, Ru, Pt, Pd, Rh and intermetallic compounds like LnCu<sub>n</sub>, Hf( Cu, Ag, Au )<sub>n</sub>. Conclusions about mechanisms of reaction in two temperature ranges ( $77 - T_{br}$ ,  $T > T_{br}$ ,K) were made, and its connection with electronic structure of metals was discussed.

It was shown that activation energy  $E_1$  of the exchange which takes place at very low temperatures by Eley mechanism and has meanings 0 – 4 kJ/mol can be expressed as

$$E_1 = 0,01 \Delta H_s - E_c \quad (1)$$

where  $\Delta H_s$  ( $E_b$ ) is the sublimation energy (or bond energy  $E_b$ ) of metal. The first member of equation can be understood as the energy of M--H bond breaking and  $E_c$  – as the energy of new forming bond M—H(D), e.g. the energy which compensates bond breaking energy. Consequently  $E_1$  is the value of not full compensation in the process of turning of the activated complex of Eley mechanism. That is why it has so low meanings.  $E_c$  depends on the nature of metals. The degree of the compensation is:  $\alpha = E_c / 0,01 \Delta H_s$ .

Results of investigation of the pressure dependence of specific catalytic activity  $K_m$  (0,1—3 Torr) in the range of not so low temperatures ( $T_{br}$ —200K) (Ridial mechanism) gave the opportunity to calculate heats of adsorption of  $H_2^+$ -form on REM- films. It appeared that



the dependence of  $\Delta H_{H_2}$  on the place in REM row is the same as the dependence of the energy of excitation of f-electrons to Fermi-level.

Strait line dependence between  $\lg B_1$  and  $\Delta H_s (E_b)$  was found for 20 in 23 examined pure metals – REM and transition:  $\lg B_1 = 0,0072\Delta H_s + 11,4$ . (2)

REM have quite low specific catalytic activity. The next element – Hf is about two orders more active: 70 times more active then Lu, 380 times more active then Pr, Sm, Tb, Ho at 77 K, having only one addition 5d-electron. REM-Cu alloys are also about two orders more active then pure REM. There  $K_m$  is near to  $K_m$  of Hf. The conclusion could be done that upon forming intermetallic compound  $LnCu_n$  the partial transition of 4s electrons of Cu to 5d-level of Ln takes place. The reason of IMC  $K_m$  increasing is mainly B-factor increasing, and this fact in its own turn is connected with M—M bond energy ( $E_b$ ) increasing in IMC in comparison with pure REM. With the help of equation (2)  $E_b(\Delta H_s)$  were calculated for IMC compounds. The parts of d-electrons in bond of IMC were calculated by Gordienko-method:  $\%d_b = (E_b^{ims} - \Delta H_s^{Eu(Yb)}) / (\Delta H_s^{La} - \Delta H_s^{Eu})$ . This part is markedly higher than that for pure REM.

IMS  $Hf(Cu, Ag, Au)_n$  in contrary are somewhat less active then pure Hf, factors  $B_1$  have lower meanings and consequently meanings of  $E_b$  are lower too. It means that shift of the 5d-electron density from Hf to 1B-metals occurs.

The dependence of  $\Delta H_s(E_b)$ --  $T_m$ (melting point) of the most of metals was build. Having determined of  $E_b$  of IMC it was possible to determine  $T_m$ , and with the help of phase diagram of  $M_1—M_2$  – system the composition of IMC on the surface of alloy could be determined.

### Conclusions:

1. With the help of a typical catalytic parametr, namely--predexponential factor  $B_1$  of low temperature isotope exchange in molecular hydrogen on bimetallic alloys or supported metal catalysts it is possible to find the bond energy in this alloys or supported metal catalyst. This will give the opportunity to predict catalytic properties of this objects in some other reactions.

2. The same parametr -  $B_1$ - combined with  $E_b$ -- $T_m$  dependence and phase diagram allows to determine the composition of IMC on the surface.

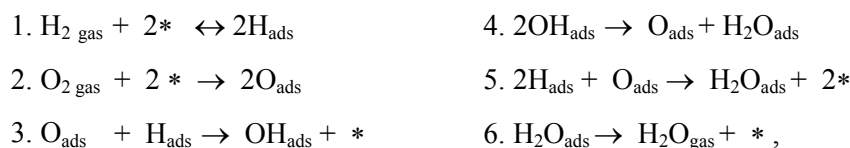
**EXPERIMENTAL STUDY OF HYDROGEN OXIDATION OVER PLATINUM  
GROUP METALS: INTERMEDIATES, SPILLOVER AND SURFACE WAVES****Gorodetskii V.V.***Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia**E-mail: Gorodetsk@catalysis.ru*

HREELS, XPS, UPS, TDS, FEM, FIM have been applied to the study of the titration  $\text{H}_2 + \text{O}_{\text{ads}}$  and isothermal, non-linear dynamic processes of the  $\text{H}_2 + \text{O}_2$  reactions on single crystals (Pt, Pd) and tip (Pd, Rh, Ir, Pt) surfaces. The formation of face-specific adsorption islands and the mobility of a sharp reaction fronts has been observed. The contribution of spillover phenomena ( $\text{H}_{\text{ads}}/\text{Pd} \rightarrow \text{O}_{2\text{ads}}/\text{Ti}^{3+}/\text{TiO}_2$ ) on the overall rate of  $\text{H}_2$  oxidation has been studied as well.

In the late 1950s Boreskov stated a chemical approach to the kinetics of heterogeneous catalysis by metals based on the effect of the reaction mixture and reaction conditions on the properties and chemical composition of the catalyst. For a long time oxidation on the platinum group metals has been considered as a catalytic model reaction that can produce valuable information on the mechanism of such effects. The aim of our study has been: 1) to gain the further understanding of the  $\text{H}_2$  oxidation kinetics at low temperatures on platinum group metals (Pt, Ir, Rh, Pd) varying from single crystal surfaces up to model sharp tip catalysts ( $\sim 10^3 \text{ \AA}$ ) on a near-atomic and molecular scale, 2) to determine the contribution of spillover effect ( $\text{H}_{\text{ads}}/\text{Pd}$  (nanoparticles  $\sim 20 \text{ \AA}$ )  $\rightarrow \text{O}_{2\text{ads}}/\text{Ti}^{3+}/\text{TiO}_2$ ) on the overall rate of  $\text{H}_2$  oxidation, and 3) to study of oscillatory behavior as a result of differences in the underlying mechanisms of the formation of spatiotemporal structures (oscillations, chemical waves) like surface reconstruction and subsurface oxygen formation. It will help to bridge the structure and pressure gap between single crystals and supported metal particles. A different mesoscopic (HREELS, XPS, UPS, TDS, WF) and microscopic (FEM, FIM) analytical tools have been applied to the study of the intermediates during  $\text{H}_2$  oxidation.

**Intermediates.** The Pt(100) surface presented by  $1 \times 1$  phase is catalytically active due to its ability to dissociate  $\text{H}_2$  and  $\text{O}_2$  molecules. The reactivity of molecular peroxo  $\text{O}_{2\text{ads}}^{2-}$  with  $\nu(\text{OO})$  at  $850\text{-}950 \text{ cm}^{-1}$  and atomic  $\text{O}_{\text{ads}}$  with  $\nu(\text{PtO})$  at  $490 \text{ cm}^{-1}$  states towards  $\text{H}_2$  has been studied on a Pt(100) and Pt(111) single crystals by HREELS and TDS. An atomic state of oxygen with *extremely high* activity has been found to be responsible for a low-temperature reaction at 100 K. At present, the  $\text{H}_{\text{ads}} + \text{O}_{\text{ads}}$  process may be proposed for the formation of  $\text{OH}_{\text{ads}}$ , which is an important intermediate species at the  $\text{H}_2 + \text{O}_2$  reaction on platinum surfaces.

HREEL spectra show two characteristic bands at 3500 and 725  $\text{cm}^{-1}$ , respectively.  $\text{OH}_{\text{ads}}$  – species are highly active due to the rapid attachment of the second hydrogen atom,  $\text{H}_{\text{ads}}$ , producing water molecules through a sequence of six reaction steps:



**Spillover.** The role of defects ( $\text{Ti}^{3+}$  sites) in the adsorption centres formation, their stabilization by the palladium nanoparticles and then defects participation in  $\text{H}_2+\text{O}_2$  reaction has been studied on the  $\text{TiO}_x$  surface. A series of activity sets:  $\text{Ti}^{3+}/\text{TiO}_2 \ll \text{Pd} \sim \text{Pd-Ti}^{3+}/\text{TiO}_2$  have been determined. It was demonstrated, that the activity of the  $\text{Pd-Ti}^{3+}/\text{TiO}_2$  model catalysts in  $\text{H}_2$  oxidation could be attributed to active sites both on the support and on Pd particles through the hydrogen spillover from Pd to  $\text{Ti}^{3+}/\text{TiO}_2$ . One of the important functions of Pd nanocrystallites in  $\text{H}_2$  oxidation is to atomize hydrogen and oxygen molecules and than to supply the  $\text{H}_{\text{ads}}$  atoms to  $\text{O}_{2\text{ads}}/\text{Ti}^{3+}/\text{TiO}_2$  by *spillover* phenomena. The combination of metallic (Pd) and ionic sites ( $\text{Ti}^{3+}$ ) provides the catalyst with molecular oxygen storage capacity and with two different parallel reactions through the atomic and molecular oxygen states for  $\text{H}_2$  oxidation.

**Surface waves.** Present experimental work shows that FEM with a resolution of  $\sim 20 \text{ \AA}$  and FIM with a resolution of  $\sim 6 \text{ \AA}$  can also serve as an *in situ* catalytic flow reactor. A very sharp metal tip,  $\sim 1000 \text{ \AA}$  in radius, exposes different surface nanoplanes with different structures.  $\text{H}_2_{\text{gas}}+\text{O}_{\text{ads}} \rightarrow \text{H}_2\text{O}_{\text{gas}}+\text{H}_{\text{ads}}$  titration reaction and isothermal, non-linear dynamic processes of the  $\text{H}_2+\text{O}_2$  reaction have been studied on Pd, Rh, Ir and Pt tips in the  $10^{-7}$  to  $10^{-3}$  torr total pressure regime. An example of surface waves is shown, Fig. 1. Here the surface is first saturated with oxygen,  $\text{O}_{\text{ads}}$ , which then reacts with  $\text{H}_2$  via a reaction front in a face-specific reaction sequence starting

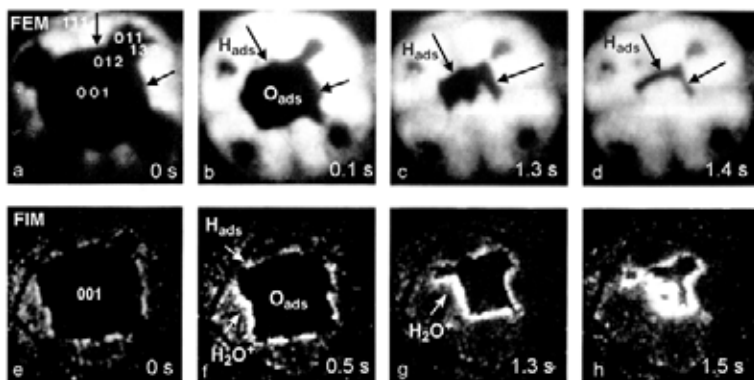


Fig. 1. FEM images (a–d) and FIM images (e–h) during the titration reaction of  $\text{O}_{\text{ads}}$  with hydrogen,  $P_{\text{H}_2} = 4.6 \times 10^{-7}$  mbar,  $T = 395$  K. In FEM, the disappearance of the  $\text{O}_{\text{ads}}$  layer (black) is characterized by the formation of the  $\text{H}_{\text{ads}}$  layer (white); time value  $\sim 1.4$  s. In FIM a bright reaction front is imaged by  $\text{H}_2\text{O}^+$  ions moving from  $\{133\}$ ,  $\{111\} \rightarrow \{012\} \rightarrow \{001\}$ ; time value  $\sim 1.5$  s.

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(at  $\tau = 0$ ) on the peripheric  $\{111\}$  planes and ending (after 1.4 s) on the (001) apex plane. In Fig. 1a-d the sequence of FEM images shows the dark  $O_{\text{ads}}$  layer ( $\Delta\Phi \approx 1.1$  eV) being transformed into a bright  $H_{\text{ads}}$  layer ( $\Delta\Phi \approx 0.2$  eV). The same titration reaction has also been studied by FIM (Fig. 1e-h). A bright reaction front is imaged here by the product water molecules ( $H_2O^+$  ions). Isothermal, non-linear dynamic processes of the  $H_2+O_2$  reaction on Pd and Pt tips have been studied simultaneously with the formation of face-specific adsorption islands and the mobility of reaction/diffusion fronts.

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## STRUCTURE AND CHEMICAL ACTIVITY OF TRANSITION METAL AND METAL OXIDE CATALYSTS: A THEORETICAL DFT STUDY

**Zhanpeisov N.U.**

*Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*

*E-mail: nurbosyn@orgphys.chem.tohoku.ac.jp*

We report here on the results of DFT calculations for the formation of oxygen vacancy site on TiO<sub>2</sub>(110) and its interaction with molecular oxygen, on the mechanism of the selective oxidation of methanol to formaldehyde over vanadia supported on silica and titania catalysts, as well as on NO and bromine interactions with the Pt(111) surface.

On the chosen above three examples the importance of proper modeling of structure and chemical activity of target catalysts will be discussed. Our calculations reproduce satisfactorily the known adsorption modes of water as well as difficulty in binding molecular oxygen on non-defect sites of TiO<sub>2</sub>(110). However, they did not support conclusions and the results of other similar theoretical study.<sup>1</sup> Accordingly, the experimental TPD observation on triply exceeding concentration of O<sub>2</sub> per vacancy site in saturation coverage can be well explained without making an assumption on the formation of O<sub>4</sub> particle at the vacancy site if one properly address the mechanism of formation of precursor defect sites on rutile TiO<sub>2</sub>(110).

We will show also that an improper use of cluster models mimicking an intrinsic support structure may result in the failure to explain the experimental findings on selective oxidation of methanol to formaldehyde over vanadia modified oxide catalysts.<sup>2</sup> In addition, an attractive bonding interaction not only for bromine and Pt(111) but also for all the three adsorption modes of NO on the Pt(111) surface will be explained.<sup>3</sup> In agreement with experimental observations, the calculations predict that the first peak in the IR spectra appears at ca. 1515 cm<sup>-1</sup> at the initial stage of low NO coverage, while it would shift to 1707 cm<sup>-1</sup> at high NO coverage. Finally, some discrepancies with the results of other theoretical studies in literature will be critically pointed out.

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**CHEMICAL BONDING AND ELECTRONIC STATES OF Mn AND O IONS IN  
ORTHORHOMBIC  $\text{LaMnO}_3$  AND  $\text{La}_{0.75}\text{MnO}_3$  LATTICES. BAND STRUCTURE  
CALCULATIONS**

**Tapilin V.M.**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: tapilin@catalysis.nsk.su*

Band structure, density of states, charges and magnetic moments at ions have been calculated in LSDA+U approximation. Structures of  $\text{La}_{0.75}\text{MnO}_3$  lattices were obtained by geometry optimization. It was found two different lattices of  $\text{La}_{0.75}\text{MnO}_3$ . La removing leads to decrease of valence electrons in the unit cell and results, first of all, in reduction of electronic populations of O. Only in one of two lattices, which has lower energy,  $\text{Mn}^{4+}$  ions appeared. In both structures Mn ions, as well as OI and OII ions, are charged and magnetic non-equivalent.

Catalytic activity of lanthanum manganites depends on concentration of  $\text{Mn}^{4+}$  appeared upon replacement of some La atoms by atoms of lower valence. The appearance of these ions is detected by redox titration or Mn core level energy shifts. Both of the techniques give poor information about electronic states of Mn in the samples and to fill the gap we performed band structure calculations of orthorhombic  $\text{LaMnO}_3$  and  $\text{La}_{0.75}\text{MnO}_3$  lattices.  $\text{La}_{0.75}\text{MnO}_3$  was obtained by removing one of four La atoms from the unit cell and chosen to maximize the valence electron reduction occurring in doped samples. After La removing the geometry optimization among the rest 19 atoms of the unit cell is performed.

La manganites are known as a system with strong electron-electron correlation in d-shells of Mn. To treat this correlation properly we used density functional theory in LSDA+U approximation for band structure calculation of lattices with optimized geometry, while to reduce calculation expenditures geometry optimization itself was performed in LDA approximation. Beside band structure calculations, the density of electron states (DOS), charges and magnetic moments at ions calculations were performed also.

Band structure calculation shows that stoichiometric  $\text{LaMnO}_3$  is an insulator with indirect energy gap of 0.5 eV width and antiferromagnetic magnetic moments alignment. Magnetic moment of Mn ions is  $3.78 \mu_B$ . The valence band is formed by 2p-states of O and 3d-states of Mn with approximately equal contribution in total DOS what witnesses of covalent bonding between O and Mn. The absence of La states in this energy region points at ionic bonding of La in the lattice. Due to direct transition occurs in optical electron excitations the edge of

optical absorption is greater 1eV. The calculated Lowdin charges at Mn are 0.58, at OI are -0.47, at OII are -0.48, and at La 0.96 |e|.

Two stable lattices of  $\text{La}_{0.75}\text{MnO}_3$  were obtained. In the first one Mn ions remain in the planes parallel to  $ac$ -plane of the orthorhombic lattice even the distances between Mn and La planes are changed. The valence electron reduction leads to shift the Fermi level down into valence band. As a result O lose electrons and their charges change between  $-0.34$  and  $-0.44$  |e|. In spite of expectations, only one of Mn ions slightly increase its charge, 0.59 |e|, while the others charges became 0.55, 0.56 and 0.57 |e|. Mn ions as well as both types of O ions become charge and magnetic non-equivalent.

The total energy per unit cell for the second  $\text{La}_{0.75}\text{MnO}_3$  lattice is 0.68 eV lower than for the first one. Each of two Mn planes of the unit cell splits into two sub-planes with sub-plane separation 0.7 and 0.24  $\text{\AA}$ . The Fermi level, as in the first lattice, crosses the valence band. One of Mn ion of the unit cell has the charge 0.65 |e| and it is a candidate for  $\text{Mn}^{4+}$  ion. The charges at the rest of Mn ions are 0.52, 0.53 and 0.57 |e|. The charges of O ions are in the region  $-0.35 \div 0.45$  |e|. As for the first lattice Mn ions as well as O ions charge and magnetic non-equivalent.

**KINETIC MONTE-CARLO MODELS OF SURFACE WAVE DYNAMICS  
AND OSCILLATIONS DURING CARBON MONOXIDE OXIDATION  
ON PLATINUM METALS**

**Elokhin V.I., Matveev A.V., Latkin E.I., Gorodetskii V.V.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: elokhin@catalysis.ru*

We shall compare the specific features of the stochastic models for imitating the oscillatory and autowave dynamics during CO oxidation over Pt(100) and Pd(110) differing by the structural properties of catalytic surfaces. The synchronous oscillations of the reaction rate and surface coverages are exhibited within the range of the suggested model parameters. The possibility for the appearance of the cellular, target and turbulent patterns, spiral and elliptic waves on the surface in the cases under study has been shown.

Chemical wave patterns corresponding to moving surface concentration patches are the result of coupling of surface diffusion, surface reconstruction and surface reaction. Depending on the reaction condition, such spatiotemporal phenomena can also lead to an oscillatory behaviour of the overall reaction rate. We constructed and studied the statistical lattice (Monte-Carlo) models that imitate the oscillation and wave dynamics in the adsorbed layer for the reaction of CO oxidation over the Pt(100) and Pd(110) single crystals, differing by the structural properties of catalytic surfaces. It is well-known that Pt(100) undergoes the reversible adsorbate-induced surface structure transformation  $hex \leftrightarrow 1 \times 1$  under the influence of the adsorbed species. The lifting of the  $hex$  reconstruction is accompanied by an increase in the oxygen sticking coefficient from  $\approx 0.001$  ( $hex$ ) to  $\approx 0.1$  ( $1 \times 1$ ). The competition of the  $O_2$  and CO adsorption in combination with the processes of the surface structure transition  $hex \leftrightarrow 1 \times 1$  is a driving force for self-oscillations. Contrary to Pt(100) the surface of Pd(110) single crystal does not reconstruct in the course of reaction. In this case the oscillatory behaviour of the  $CO + O_2$  reaction can be attributed to the periodic formation and decomposition of subsurface oxygen (Pd(110):  $O_{ad} \rightleftharpoons O_{ss}$ ). In both cases the synchronous oscillations of the reaction rate and surface coverages are exhibited in simulations within the range of the suggested model parameters (under the conditions very close to the experimental observations). These oscillations are accompanied by various wave processes on the lattice that models single crystalline surfaces. The boundaries of oscillatory behaviour and hysteresis effects have been recognized. The effects of the size of the model lattice and the intensity of  $CO_{ads}$  diffusion on the synchronization and the form of oscillations and surface waves are



studied. The presence of a narrow zone of the reaction when the oxygen wave front propagates along the metal surface has been revealed in simulations. This is supported by the results obtained by the methods of field electron microscopy (FEM) and field ion microscopy (FIM). We found that the inclusion in the stochastic model of  $\text{CO}_{\text{ads}}$  diffusion anisotropy, which reflects the real symmetry of the single crystal Pd(110) surface, does not affect the dynamics of oscillations of the integral characteristics of the reaction (the rate and the surface coverage), but it leads to the formation of ellipsoid spatiotemporal structures on the surface, which were observed experimentally with modern physical methods for surface science studies. It was shown that it is possible to obtain a wide spectrum of chemical waves (cellular and turbulent structures, spiral, ring, ellipsoid and stripe oxygen waves on the surface) using the lattice models developed. These waves have been observed in different experimental studies of oscillatory dynamics of catalytic reactions.

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## FROM BIOMASS TO FUELS: HYDROTREATING OF OXYGENATED COMPOUNDS

**Gandarias I., Barrio V.L., Requies J., Arias P.L., Cambra J.F., Güemez B.**

<sup>1</sup> *School of Engineering (UPV/EHU, Chemical and Environmental Engineering Department,  
c/ Alameda Urquijo s/n, 48013 Bilbao, Spain*

*E-mail: pedroluis.arias@ehu.es*

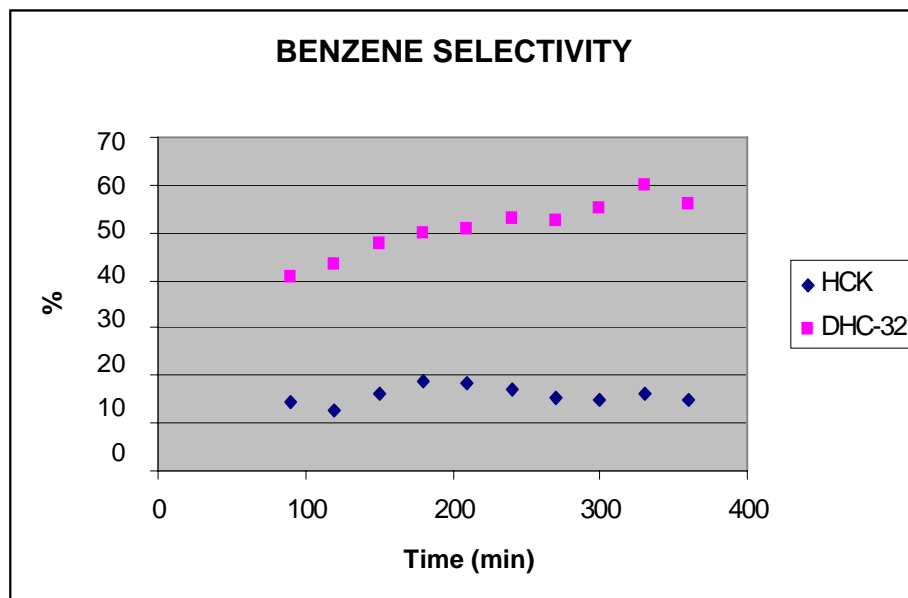
Biomass is a renewable alternative to fossil raw materials in the production of liquid fuels and chemicals. Pyrolysed biomass contains an abundance of oxygen-containing molecules that need to be removed to improve the stability of the liquids. A hydrotreating process, hydrodeoxygenation (HDO), is commonly used for this purpose. Thus, the aim of this work is to examine the role of new catalysts used for HDS purposes in HDO. In addition, products distribution and catalyst stability are studied against changes in the feed composition, the solvent, and the catalyst pre-treatment.

The biofuel obtained from the fast pyrolysis of biomass has high oxygen content. Ketones, aldehydes, acids, esters, ethers and alcohols have been detected in significant quantities. Because of the reactivity of oxygenated groups, the main problem of the fuel is the instability. Therefore study of the deoxygenation of biofuel is needed.

In the present work the hydrodeoxygenation (HDO) of biofuel in the presence of NiMo catalysts supported on alumina is described. The effect of catalyst preactivation on the activity and products distribution during hydrotreating of phenol is also studied. The catalyst pre-treatment strongly increases the HDO activity, as it could be expected. Moreover, the effects of temperature and feed composition on the catalyst' activity and stability are examined. Phenol is representative of the oxygen-containing compounds in pyrolyzed biomass. The liquid feed containing 3 wt.% of phenol is introduced in the reactor at a rate of 10 g/h. The reaction conditions are: P= 1.5 MPa; T= 523-623 K. Phenol HDO is generally accepted to proceed via two parallel reaction pathways: the bond between the oxygen atom and the aromatic carbon can be broken giving aromatic products (direct hydrogenolysis route), or the aromatic ring can be hydrogenated before the rupture of the oxygen-carbon bond (combined hydrogenation-hydrogenolysis route) [1]. In the latter route, alicyclic products are formed and the corresponding alicyclic alcohols are probably formed as short-lived intermediates.

As it can be observed in the figure, the maximum benzene selectivity occurs for the DHC-32 catalyst. Thus, it seems that for this catalyst the direct hydrogenolysis route has been favoured. For the HCK catalyst c/hexane is the major compound of the product stream.

Taking into account the H<sub>2</sub> consumption of both pathways, this makes the direct hydrogenolysis pathway of HDO, favoured by the DHC-32 catalyst, more advantageous in fuel production. Nevertheless, environmental legislation is nowadays limiting the concentration of aromatics in liquid fuels.



The main goal of this work is to hydrodeoxygenate the biofuel obtained from pyrolyzed biomass. Thus, this process implies the transformation of the phenol, model compound, to more stable products. Moreover, the catalyst formulation enables to favour the HDO reaction pathway of the direct hydrogenolysis, and consequently the products formed.

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NOVEL CATALYTIC METHODS OF CELLULOSE AND FINE CHEMICALS  
PRODUCING FROM PLANT BIOMASS

**Kuznetsov B.N., Taraban'ko V.E., Kuznetsova S.A.**

*Institute of Chemistry and Chemical Technology SB RAS, Krasnoyarsk, Russia*

*E-mail: bnk@icct.ru*

The presentation describes some results of the recent study in the area of catalytic intensification of the processes of valuable chemicals producing from plant biomass: cellulose, microcrystalline cellulose, thermally reversible gels from wood raw material, aromatic aldehydes from lignin, levulinic acid, ethers of levulinic acid and 5-hydroxymethylfurfural, biodestructive polymers from polysaccharides.

Catalytic methods are used in the industrial processes of plant polysaccharides conversion to glucose and furfural, in the synthesis of fragrant compounds from triterpene, vanillin from liginosulfonates etc. Catalyst application in the processes of cellulose production is restricted only by anthraquinone and some its derivatives.

Main problems of catalysts application in the chemical transformations of plant polymers are discussed. They are connected with the realization of effective interaction between catalysts and polymer surface, with catalyst deactivation and regeneration problems.

The development of new generation of ecologically friendly catalytic methods promoting the chemical conversions of lignin and polysaccharides to valuable products is the urgent task in the field of renewable plant biomass processing.

Some examples of successive use of homogeneous and heterogeneous catalysts of acidic and oxidation types in the novel processes of cellulose and fine chemicals producing from plant lignin and polysaccharides are presented in this paper.

The influence of catalyst and plant raw material nature on the yield and composition of lignin oxidative depolymerization and polysaccharides acidic conversion products was studied. The main regularities of catalytic delignification of coniferous and deciduous types of wood in the media "acetic acid – water – hydrogen peroxide" were established. The effective methods were suggested for the regulation of cellulosic products yield and composition. These methods are based on the variation of catalyst nature ( $H_2SO_4$ ,  $TiO_2$ ,  $H_2MoO_4$ ), wood type (silver-fir, aspen, larch, birch) and delignification process parameters (temperature, reaction mixture composition, water/wood ratio, time, catalyst concentration).

For all studied types of wood the optimal conditions of delignification process were selected. They supply the production with a high yield the chemical pulp with a low content of residual lignin. Based on these studies, the new sulfur-free and chlorine-free methods of wood sawdust and straw conversion to pulp for chemical processing and to microcrystalline cellulose were developed. The method of thermally-reversible gels producing from wood sawdust was suggested, based on the stages of sawdust catalytic delignification by mixture “acetic acid – hydrogen peroxide – water”, alkaline treatment and methylation of the pulp.

Novel catalytic methods of aromatic aldehydes producing from wood lignin were developed. The significant increase of vanillin and syringaldehyde yields was observed in the processes of wood lignin and lignosulphonates oxidation by molecular oxygen in an alkaline medium in the presence of copper catalyst. At selected conditions the yield of vanillin is by 2-3 times higher and the total duration of the process is about 10 times shorter in the comparison with the industrial non-catalytic process of vanillin production from lignosulphonates.

The scheme of levulinic acid formation from wood cellulose in the presence of acidic catalyst was established: cellulose  $\rightarrow$  glucose  $\rightarrow$  levoglucosenone  $\rightarrow$  hydroxymethylfurfural  $\rightarrow$  levulinic acid.

Sulfuric acid catalyst can be effectively used under the moderate temperature (98 °C) to produce levulinic acid with the yield exceeding 35 % mol. for glucose and 50 % mol. for sucrose. In the two-phases system “water – butanol” the continuous removal of polysaccharides conversion products from water phase by means of alkylation and extraction processes increases significantly (by 8-9 times) the yield of ethers of levulinic acid and hydroxymethylfurfural at high concentration of carbohydrates in the water solution.

New approach to the preparation of new type of biodestructive polymers was suggested which includes the hexoses catalytic conversion to  $\alpha$ -angelicalactone and its polymerization through the lactone cycle opening. The polymerization of  $\alpha$ -angelicalactone in the presence of sodium butylate gives polymeric material containing 50 % of bonds monomer – monomer which were formed by lactone cycle opening.

**NEW CATALYTIC SYSTEM FOR CONJUGATED OXIDATION OF CARBON  
MONOXIDE, AND HYDROCARBOXYLATION OF ALKENES**

**Bruk L.G., Timashova E.A., Kozyavina O.V., Gorodsky S.N., Oshanina I.V., Temkin O.N.**

*M.V. Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia*

*E-mail: lbruk@rol.ru*

Principle of kinetic conjugation of reactions can help to create catalytic systems providing synthesis of desirable products under mild conditions

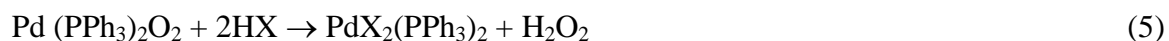
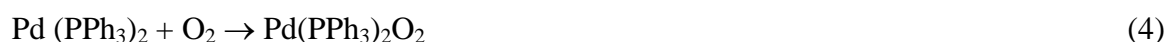
Conjugated reactions are subject of theoretical and practical interest for creation of the new catalytic systems [1]. The oxidation of carbon monoxide by molecular oxygen is one of the simple available model reactions suitable for studying fundamental regularities of the conjugated processes [2, 3]. This reaction may be used as “basic” one to produce key intermediate for reactions with thermodynamic or kinetic limitations. For example, reaction (1) is impossible under usual conditions.



But hydrogen peroxide may be obtained from water and oxygen according to coupled reaction (2)



It was shown at first by Likholobov's group in the system Pd(Ac)<sub>2</sub>-PPh<sub>3</sub>-CF<sub>3</sub>COOH [2] due the conjugation of reactions (3-5). Palladium (0) complex Pd(PPh<sub>3</sub>)<sub>2</sub> was the key intermediate.



Our group have shown, that another mechanism of conjugated reaction (2) is possible (6-8) [4].



This report deals with the mechanistic study results of the conjugated reactions of carbon monoxide, water, and organic solvent oxidation, and cyclohexene hydrocarboxylation to cyclohexane carboxylic acid in catalytic systems: PdBr<sub>2</sub>-1,4-dioxane-H<sub>2</sub>O,

PdBr<sub>2</sub>- tetrahydrofuran-H<sub>2</sub>O, PdI<sub>2</sub>-LiI-1,4-dioxane-H<sub>2</sub>O, PdBr<sub>2</sub>-CuBr<sub>2</sub>-tetrahydrofuran-H<sub>2</sub>O under very mild conditions (1 atm, 30°)

The effects of the nature of solvent, of anion, as well as the effects of inhibitors, and kinetics were studied. The hypothetical mechanisms of conjugated reactions in the above-mentioned systems were selected (discriminated). The best mechanism includes formation and transformations of hydride palladium complex (scheme 1). This hydride palladium complex is responsible for conjugation of the reactions of carbon monoxide, water, and solvent oxidation. Experimental kinetic equation (9) does not contradict to proposed mechanism (scheme 1).



$$r_{\text{CO}_2} = k_1[\text{Pd}]_{\Sigma}[\text{H}_2\text{O}] P_{\text{CO}} / ([\text{H}^+](1 + k_2 P_{\text{CO}})) \quad (9)$$

The correctness of this hypothesis was tested by experiments with addition of cyclohexene in the system PdBr<sub>2</sub> – tetrahydrofuran – H<sub>2</sub>O. It is well known, that hydride complexes of palladium are truthful catalysts of alkene carbonylation reactions in the solutions of palladium complexes. The synthesis of cyclohexane carboxylic acid is carried out in this system under mild conditions (30°, atmospheric pressure of CO and O<sub>2</sub> mixture) with rate up to 0.3 mol/l·h and with selectivity on cyclohexene up to 95 %.

A number of alkenes were tested as substrates of hydrocarboxylation in these systems: oktene-1, hexene-1, styrene, 4-vinyl-cyclohexene, norbornadiene, norbornene. In the cases of majority alkenes the products of hydrocarboxylation reactions were identified.

It is possible to design catalytic systems for reactions with thermodynamic or kinetic limitations using information about probable mechanism of these reactions. We term this approach “principle of kinetic conjugation of reactions”.

**Acknowledge** Financial support of RFBR (Grants NN 05-03-08134, 04-03-33014).

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## HYDROCARBONS TRANSFORMATIONS AT SUPERCRITICAL CONDITIONS

**Bogdan V.I.**

*N.N. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia*

*E-mail: bogdan@ioc.ac.ru*

Supercritical conditions have some advantages for the heterogeneous reactions involved processes of isomerization, alkylation, oligomerization, cracking and aromatization. The catalytic transformations of light hydrocarbons at the supercritical conditions is characterized by much more prolonged catalyst life-time and productivity in comparison with the conventional gas phase reaction.

The performance of heterogeneous catalytic reactions under supercritical conditions is very perspective. Supercritical reaction engineering is believed to overcome limitations of heterogeneously catalyzed gas phase reactions since the intermediates formed and coke precursors could be desorbed from the catalyst surface faster due to their higher solubility in supercritical fluids than in the case of gas reactions. Application of supercritical fluids either as solvents or reactants provides the following attractive opportunities:

- i. sharp enhancement of rate of desirable reactios
- ii. strong increase of the catalyst lifetime
- iii. mild conditions for the catalysts regeneration

Catalytic reactions of hydrocarbons including isomerization, alkylation, oligomerization, cracking and aromatization were studied over sulfated zirconia, titania-supported heteropolyacids and tungstia, hydrogen forms and modified zeolites in a flow type reactor in the wide range of pressures changing from 0.1 to 19.0 MPa in the reaction temperatures. At gas phase conditions stability and productivity of these catalysts are too low due to their fast deactivation by deposition on their surface of coke precursors. In contrast performance of the corresponding reactions at supercritical conditions allows to solve this problem. Under supercritical conditions the activity and productivity of the catalysts are invariable for a long time provided that the density of hydrocarbons transformed is liquid-like.

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## DEVELOPMENT OF CATALYSTS FOR HYDROGEN GENERATION FROM HYDRIDE COMPOUNDS

**Simagina V.I., Storozhenko P.A.<sup>1</sup>, Netskina O.V., Komova O.V., Odegova G.V.,  
Kochubey D.I.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>1</sup>*State Research Institute of Chemistry and Technology of Organoelement Compounds,  
Moscow, Russia*

*E-mail: netskina@catalysis.nsk.su*

Investigation of hydrogen generation from  $\text{NaBH}_4$  and  $\text{NH}_3\text{BH}_3$  over catalysts has been carried out. It was shown, that the nature of a support and an active component of the catalyst affects the rate of  $\text{H}_2$  generation. According to data obtained by physicochemical methods, surface complexes of the precursor of an active component with the support are formed. Differences of these complexes depend on the nature of the support. The further reduction of catalysts in a medium of hydride results in the formation of metal clusters with various reaction properties.

During the last two decades it became obviously, that intensive evolution of industry and transport would lead to energy crisis. Fast decrease of fossil fuel promotes a search of alternative energy sources. It is a received idea, that hydrogen is a perspective energy carrier. Taking into account modern rates and scales of energy evolution, the world civilization should pass to hydrogen energy in the near future. Today, the main problem of using hydrogen consists in its storage, safety, transportation and distribution. The requirement to  $\text{H}_2$  storage systems are determined by character of commercial applications. So, the large volumetric and gravimetric hydrogen density of  $\text{H}_2$  fuel is very important for mobile devices. The highest volumetric  $\text{H}_2$  density is found in chemical hydrides. Among the hydrides, sodium borohydride and ammonia-borane are desirable due to high hydrogen content and the excellent stability.

According to many researchers, catalytic hydrolysis of  $\text{NaBH}_4$  is a promising method for hydrogen generation for use in portable fuel cells of mobile devices. The hydrolysis of  $\text{NaBH}_4$  provides the amount of hydrogen twice more than in case of thermal decomposition of the hydride. At room temperature the  $\text{NaBH}_4$  alkaline solution is stable, but the using of catalysts leads to generation of hydrogen in controlled conditions. Different catalytic systems have been suggested for the  $\text{NaBH}_4$  hydrolysis reaction. In recent publications, one can find information on the use of ruthenium catalysts supported on anion-exchange resins (A-26,

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IRA-400), platinum group metals on various supports, cobalt borides, nickel boride and finely dispersed metallic nickel and cobalt in this reaction. In the last few years, several publications on the use of catalysts containing platinum group metals supported on  $\text{LiCoO}_2$  appeared in the literature. However, systematical studies of the catalytic properties of different system are not reported.

Our investigation shown, that the nature of a support and an active component of the catalyst affects the rate of hydrogen generation. We found that the activity of catalysts on all of the tested supports decreases in the order  $\text{Rh} > \text{Pt} > \text{Ru} > \text{Pd}$ . The rhodium catalysts based on Sibunit,  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{TiO}_2$  exhibits the highest activity. It is likely that difference in the reactivity of rhodium catalytic systems is related to the interaction of the precursor of an active component with the support. According to data obtained by physicochemical methods (UV-vision, XPS, TEM, EXAFS and IR-spectroscopy), complexes of the precursor of an active component with the support are formed in the course of rhodium chloride supporting. Differences in the composition and structure of surface complexes depend on the nature of the support. The further reduction of these complexes in a reaction medium of sodium borohydride results in the formation of metal clusters, which exhibit various reaction properties.

Paradoxical results are obtained for Pt and Rh catalysts supported on untraditional  $\text{LiCoO}_2$  carrier having very low specific surface ( $1\text{-}3 \text{ m}^2/\text{g}$ ). These catalytic systems possess the maximal activity in a number of systems investigated by us with the advanced specific surface ( $100\text{-}500 \text{ m}^2/\text{g}$ ). The effect of the  $\text{LiCoO}_2$  synthetic method and its phase composition, structure, dispersity on the activity of catalysts in the  $\text{NaBH}_4$  hydrolysis was investigated. A significant change of phase composition of the lithium cobalt oxide support after an interaction with the reaction mixture was observed. This was associated with partial surface interaction of  $\text{LiCoO}_2$  particles with a  $\text{NaBH}_4$  solution bringing to formation of glass-like lithium boron oxide and cobalt boride.

Similar researches of hydrogen generation from ammonia-borane over catalysts have been carried out. Perspectives of its using as a source of hydrogen for fuel cell have been demonstrated.

Carried out studies have permitted to develop the optimized design of hydrogen generators with automatic control system. During the testing it was shown that generator with mass of 300 g can provide work of 100 Watt portable fuel cell during 1 hour under one-time refueling by 150 ml of a sodium borohydride solution.

## APPLICATION OF MECHANOCHEMISTRY IN CATALYSIS

**Molchanov V.V., Buyanov R.A., Goidin V.V.**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: molchanov@catalysis.ru*

Wasteless and energy-saving preparation methods of a number of catalysts were developed. It was experimentally proven that defects of the catalyst crystalline structure strongly affect specific activity of the catalyst. A recently developed trend of mechanochemical catalysis has shown much promise for hydrogenation, oxidation, amination, and hydroalumination. Catalytic reactions were performed for the first at the mechanochemical activation conditions, elevated temperature and increased gas pressure.

The mechanism of formation of different catalytic systems during mechanochemical activation (MCA) and subsequent treatments was established. The mechanism was used to develop a number of wasteless and energy-saving preparation methods of hydrogenation catalysts based on intermetallide hydrides, hydrocarbon decomposition catalysts for production of nano fibrous carbon and hydrogen, V-Ti selective oxidation catalysts and heteropoly acids. The above methods are characterized by short synthesis times, few reaction stages, low power consumption, absence of waste waters, and resulting catalysts with high catalytic activity.

The experimental data strictly evidence the influence of crystalline structure defects on the catalyst activity, which is exhibited as linear dependences of specific catalytic activity versus concentration of definite-type defects. Such dependences were obtained for zinc oxide, titanium dioxide and zinc ferrite in the CO oxidation.

The oxygen atoms located or chemisorbed in the places of outcropping of crystalline structure defects on the crystal grain surface are the catalytically active centers which are responsible for an increase of CO specific oxidation rate.

It was shown for the first time that if crystalline structure defects are the places where catalytically active centers are located, these centers are also responsible for an increase of reactivity of complexes in simple chemical reactions and an increase of sorption ability of materials. Such universal influence of the defects on the reactivity permits one to consider that the main reason of increasing reactivity is that increasing thermodynamic potentials of the catalysts.

The main idea of the mechanochemical catalysis trend is performance of catalytic reactions under mechanochemical activation conditions. Energy is supplied to catalysts and

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reagents as mechanical energy. Pulse mechanical action results in the formation of a dissipation system where a new catalyst state is formed, which permits the performance of catalytic reactions at the MCA conditions.

Mechanochemical catalysis exhibits high efficiency in the selective reduction of unsaturated bonds and functional groups in the solid phase, esterification of boric acid, destruction of chlorine-containing dioxins, conversion of not-readily soluble materials with low reactivity (betulin, ursolic acid), hydroaluminizing of unsaturated hydrocarbons.

Our experimental results can serve as the basis for development of new technologies of catalytic fine organic synthesis.

We have developed new methods of the MCA performance at increased pressure in the gas phase and high temperatures, which permits one to perform unique transformations/conversions in the inorganic and fine organic synthesis. Mechanochemical reactions were performed for the first time at the above conditions.

## DEHYDROGENATION OF C<sub>2</sub>-C<sub>3</sub> ALKANES TO ALKENES AS AUTOCATALYSIS PROCESS

**Snytnikov V.N., Snytnikov V.I., Mischenko T.I., Sklyar O.P., Parmon V.N.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: snyt@catalysis.ru*

Using technique “wall-less reactor” was created gas homogeneous conditions for research C<sub>2</sub>-C<sub>3</sub> alkanes dehydrogenation. Reagents activation was realized by continuous CO<sub>2</sub>-laser radiation that was adsorbed by ethylene and reproduced to the reaction volume. Ethylene is one of the primary reaction product, It allows to regard this process as “energy catalysis”.

The mechanism of the endothermic dehydrogenation of ethane to ethylene is usually associated with generation of radicals. In the thermal cracking of ethane, the radicals are most probably generated and perish on the reactor inner walls through which the energy is supplied. While considering pyrolysis in reactors, it is of great interest to distinguish between homogeneous reactions of hydrocarbons in the reactor volume and heterogeneous processes on the reactor walls, as well as to study the gas-phase thermal reactions in order to improve further the industrially important methods for synthesis of C<sub>2</sub>-C<sub>3</sub> and other olefins.

Dehydrogenation of ethane was studied under conditions of a wall-less reactor when heterogeneous processes are excluded. We designed a reactor of 6.5 cm<sup>3</sup> in volume where the heat energy was supplied directly to the gas at atmospheric pressure using a continuous CO<sub>2</sub> laser with the radiation power up to 120 W at the power density up to 10<sup>4</sup> W/cm<sup>2</sup>. Since ethane does not absorb radiation of the CO<sub>2</sub> laser, it was mixed with ethylene or propylene which are characterized by a strong absorption band at 10.6 μm. In our experiments, the vibration energy of radiation-excited olefin molecules was transferred to ethane molecules due to fast relaxation through collisions. The reactor design ensured the gas bifunctionality, i.e. a part of the high-dense mixture behave as a heat insulator between the quartz walls at the temperature not higher than 125 °C and the reaction zone at the temperature not higher than 1000 °C.

The product analysis using chromatographic technique revealed that the absorption of the laser radiation by the ethane-ethylene mixture containing more than 5 vol % of ethylene gave rise to the chemical reaction of dehydrogenation of ethane into ethylene to generate hydrogen. The ethane conversion depended on the radiation energy and reached 90 %. The selectivity for ethylene decreased from 90 % to 70% as the energy supply increased. The decrease in the selectivity was accounted for by synthesis of methane. Propylene was formed in amount of

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1–1.5 vol % under any conditions of the ethane pyrolysis. At a low laser energy supply, butane was detected in trace amount among the products nearby the point of initiating the chemical reactions; it disappeared as the ethane conversion increased. Acetylene was detected at high conversions of ethane. No other product was detected.

The possibility of the autocatalytic effect to occur in the system is discussed along with the radical chain mechanisms of the ethane pyrolysis to be used in technological applications. The obtained experimental data on ethane dehydrogenation in the wall-less reactor demonstrate applicability of the selective CO<sub>2</sub>-laser radiation to control endothermic chemical reactions.

**PREPARATION OF CATALYSTS FOR DEHYDROGENATION OF LOWER  
PARAFFINS USING PRODUCTS OF THERMAL ACTIVATION OF GIBBSITE**

**Pakhomov N.A., Molchanov V.V., Isupova L.A., Nadtochii V.I.<sup>1</sup>, Zolotovskii B.P.<sup>2</sup>,**

**Tikhov S.F., Tanashev Yu.Yu., Babenko V.S., Buyanov R.A.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>1</sup> *NGKC Ltd, Novy Urengoi, Russia*

<sup>2</sup> *VNIIGAS Ltd, Moscow, Russia*

*E-mail: pakhomov@catalysis.ru*

The dehydrogenation of paraffins on Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts is a widely exploited way for large-scale production of pure olefins. Two types of Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts are now used in industry: (i) granulated catalysts for the dehydrogenation in a fixed bed under low partial pressure and (ii) microspherical catalysts for the dehydrogenation of isobutane, isopentane or propane in a fluidized bed [1].

In literature, there are a lot of different methods for preparing aluminium hydroxides and oxides for these catalysts. In this work we consider the unified approach to the preparation of alumina based supports and Cr<sub>2</sub>O<sub>3</sub> –based catalysts, for which the products of gibbsite thermal activation are used as starting materials. These products possess a high reactivity and, under fixed conditions, can be rehydrated with formation of “active” aluminium hydroxides [2]. Large-scale manufacture of the activated gibbsite is possible through its “thermochemical activation” (TCA) in a flow flash reactor [2] or by the method of “centrifugal thermal activation” (CTA) in a centrifugal flash reactor (CEFLAR<sup>TM</sup>) [3]. The physico-chemical properties of TCA and CTA products are similar but they can sufficiently differ from each other if considering their activity in the rehydration process [4].

Phase composition, textural and strength characteristics of support as well as granules form are determined by the type of catalytic process (fixed or fluidized bed and the nature of dehydrogenated hydrocarbon). We have shown that the key stages determining the support properties are: (1) the stage of gibbsite thermal activation, and (2) the stage of hydration of the thermally activated product. The conditions of each of these stages can play a dominant role in catalyst design. For example, when studying the regularities of the microspherical catalyst formation we have found that, under similar conditions of the preparation, the catalyst prepared from the CTA product is more active and selective than that prepared from the commercial TCA product, f.e. the output of isobutylene and selectivity of isobutane dehydrogenation may be increased by 2 to 5 abs.%. The value of activity rising directly depends on conditions of the CTA product manufacturing.

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The nature of dehydrogenized component in paraffin dehydrogenation processes plays an important role at developing of carrier preparation technology for granulated catalysts. We have found that the preparation of support for catalysts of isobutane or propane dehydrogenation (Catofin process) may be done by wasteless technology which is based on granulation of TCA / CTA powdered product using the plate granulator with consequent hydration of spherical particles by water vapor. The quality of the spheres obtained, their textural and strength characteristics are determined by fractional and phase composition of used thermal activated products. The samples of  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalyst prepared using spherical alumina have been lab tested in the reaction of isobutane dehydrogenation, their catalytic properties are similar to that of the best commercial catalysts tested under similar conditions.

Very exacting requirements to the phase composition of support and its porous structure are made to the extruded catalyst of the one-step dehydrogenation of n-butane to butadiene (Catadien process). We have shown that the support must be  $\gamma\text{-Al}_2\text{O}_3$  with surface area about  $100 \text{ m}^2/\text{g}$  and optimal volume ratio of mesopores, macropores and transport pores. The manufacture of alumina with desired properties is possible only through regulation of the hydration conditions for TCA / CTA products; mild synthesis of pseudoboehmite as a binder is combining with more strict hydrothermal synthesis aimed to the preparation of macrocrystalline boehmite.

The new quality has been obtained when wide-porous ceramic-metal composite  $\text{Al}_2\text{O}_3\text{-Al}$  (cermet) prepared from metal Al and TCA product is used as a support. Introduction of TCA product into the initial raw materials influence the textural and mechanical properties of cermets and lead to decrease of their cost. The optimal composition of the raw material providing the preparation of support with the best combination of textural, strength and catalytic properties has been determined.  $\text{Cr}_2\text{O}_3$  - based catalyst prepared using  $\text{Al}_2\text{O}_3\text{-Al}$  cermet as support has been tested in reactions of dehydrogenation of lower  $\text{C}_3\text{-C}_4$  paraffins. As prepared catalyst has been shown to be very active and even more selective as compared with the best analog [5].

Thus, it is shown that the products of the thermal activation of gibbsite can be widely used for the preparation of different  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  dehydrogenation catalysts, the corresponding technologies are low-waste or practically wasteless. Properties of catalyst were shown to be strongly depending on the process of thermal activation.

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**MOLECULAR DESIGN OF NEW TYPE OF SUPPORTED CATALYSTS MODIFIED  
BY Sn AND Ge PREPARED VIA ANCHORING TECHNIQUE**

**Borbáth L., Margitfalvi J.L., Somodi F., Gőbölös S., Hegedűs M., Vilella I.M.J.<sup>1</sup>,  
de Miguel S.R.<sup>1</sup>, Scelza O.A.<sup>1</sup>**

*Chemical Research Center, Institute of Surface Chemistry and Catalysis, Hungarian Academy  
of Sciences, 1025 Budapest, Pusztaszeri út 59-67, Hungary*

<sup>1</sup>*Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), Facultad de Ingeniería  
Química (Universidad Nacional del Litoral)-CONICET. Santiago del Estero 2654, (3000)  
Santa Fe, Argentina*

*E-mail: borbath@chemres.hu*

Upon using a two-step anchoring process we have prepared new types of supported E-M catalysts (M= Pt, Pd, Rh, Ru and E= Sn, Ge) with high E/M ratios. In the first step slab-like Surface Organometallic Species (SOMS) are formed followed by stepwise decomposition of these species. The decomposition of SOMS in hydrogen or oxygen resulted in either supported alloy-type E-M surface species or EO<sub>x</sub>-type Lewis-acid sites anchored onto the active metal, respectively. Catalysts prepared in this way showed unique properties in different reactions.

A two-step process using Controlled Surface Reactions (CSRs) between metal tetraalkyls (ER<sub>4</sub>) (E= Ge, Sn; while R= CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) and hydrogen adsorbed over different supported metals (M= Pt, Pd, Rh, Ru) were used to prepare various types of supported bimetallic catalysts, with exclusive modifier-active metal interaction [1-5]. In these studies Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and functionalized active carbon were used as support materials.

Kinetic investigation of the initial period of anchoring reaction using two different types of supported Pt catalysts provided new information about the elementary steps involved in anchoring of tin [3]. In this process the key issue is the formation of *multilayered* surface organometallic species (SOMS) anchored exclusively onto the supported metal. Based on the analysis of Temperature Programmed Reaction (TPR) profiles the formation of multilayered (slab-like) SOMS has been suggested. The excess of both hydrogen and ER<sub>4</sub> was highly favorable for the formation of multilayered SOMS. The “fingerprint” character of TPR curves can also be used for catalyst characterization [1-3].

Upon changing conditions of CSRs used for tin anchoring variety of tin containing entities, such as (i) tin enriched platinum, (ii) Sn-Pt alloy phases, (iii) SnO<sub>x</sub> species anchored directly to the Pt surface, (iv) SnO<sub>x</sub> species at the Pt-support interface, (v) SnO<sub>x</sub> species on the

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support, can be formed. The formation of the above species has been evidenced by chemisorption of CO, H<sub>2</sub> and O<sub>2</sub>, titration, Mössbauer and FTIR spectroscopy [4-5]. *In situ* characterization by EXAFS and Mössbauer spectroscopy have shown that tin is easily oxidized and reduced. In reduced catalysts tin is directly coordinated with Pt, while after oxidation tin is primarily in a form of highly dispersed and reactive tin oxide over the Pt-Sn nano-cluster. This SnO<sub>x</sub>-type surface species can be reduced both by H<sub>2</sub> and CO even at room temperature [5]. Upon using chemisorption methods two forms of surface Sn and Pt was distinguished.

The high activity and selectivity of these catalysts in variety of reactions can be attributed to the atomic proximity of Lewis-acid sites and the active metal [2, 4, 5].

Catalytic systems containing Ge are more complex as compared to systems containing Sn. Two methods of modification of monometallic platinum catalyst supported on functionalized active carbon were used for the preparation of Ge-Pt/C bimetallic catalysts: (i) conventional impregnation (CI) and (ii) CSRs. All results, namely the study of germanium anchoring reaction, two test reactions (cyclohexane dehydrogenation (CHD) and cyclopentane hydrogenolysis (CPH)) and CO chemisorption, indicate that the modification of Pt with Ge using CSRs was highly selective, i.e., almost 100 % of Ge introduced was anchored to platinum. The introduction of germanium into the platinum by CSRs resulted in pronounced decrease of both the initial rates and the activation energy in CHD. The changes in the activation energy values indicates on an electronic modification of Pt by Ge, while the initial rate decrease was attributed to the geometric modifications of Pt caused by the dilution of Pt surface by anchored germanium. On the other hand results showed that in catalysts prepared by CI method Ge was located mainly on the support.

In this lecture details on the (i) design, (ii) preparation, (iii) characterization of new catalytic compositions, containing highly active “metal ion-metal nanocluster” type active site ensembles and (iv) testing of this catalysts will be demonstrated and discussed.

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**DESIGN OF REFORMING CATALYSTS. CREATION OF NEW TECHNOLOGIES  
OF MOTOR FUEL PRODUCTION ON THEIR BASIS**

**Belyi A.S.**

*Institute of Hydrocarbons Processing SB RAS, Omsk, Russia*

*E-mail: belyi@ihcp1.oscsbras.ru*

The results of the research of platinum state in alumina-platinum reforming catalysts (RC) carried out in the Institute of Hydrocarbons Processing SB RAS during last 20 years have been summarized. The primary result of this investigation is the ascertainment of an important role of non-metallic platinum state ( $Pt^{\sigma}$ ) in the adsorption processes and in catalysis of reforming reactions.

The results of studies of model reactions of benzene hydrogenation, cyclohexane dehydrogenation and heptane dehydrocyclization have been presented. On the basis of the analysis of the obtained results modified classic model of RC has been suggested. According to this model  $Pt^{\sigma}$ -centers and  $Pt^0$ -centers are presented on the alumina surface. This catalytic system is highly active and promotes the behavior of aromatization reaction with high selectivity.

The results of research of modifying influence of S, Se, Te, Sn and Re on the catalytic properties of  $Pt^{\sigma}$ -centers have been summarized. The obtaining results of changes of kinetic parameters of model reactions have been discussed from the position of ligand-effects. Considerable increasing of selectivity and stability of RC in the reforming reactions is the demonstration of modification effects.

The data of study of  $Pt^{\sigma}$ -centers and  $Pt^0$ -centers distribution throughout the oxide supporter pores with different size (microdistribution) are adduced. Close interconnection among the sorption mechanism of an active component precursor (chlorides Pt (IV)), microdistribution and platinum state in catalysts has been revealed. Analysis of a large group of model catalysts has allowed to establish general regularity. The area of  $Pt^{\sigma}$  localization is displaced in comparison with  $Pt^0$  to the area of minor size mesopores with the radius  $< 5.0$  nm in all cases. At the RC preparation addition in a solution some substances displacing front of platinum sorption to the area of minor size pores promotes  $Pt^{\sigma}$  formation.

On the basis of the obtained results the cardinal principles of development of high-performance catalysts, technologies of their production and exploitation in the industrial

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conditions have been stated. The data of industrial operation of new marks of RC on 7 industrial-scale reforming units at the regime of reforming- gasoline manufacture (about 3 million tons per year) with the octane number 96-100 p. RON are adduced.

Investigation of new catalysts properties has allowed to reveal the fundamentally new possibility of their using in the process of joint treatment of light alkanes and C<sub>5+</sub>-alkanes into typical components of high-octane motor fuels. The development of three modifications of new production technology of high-octane environmentally appropriate gasolines with the selectivity of formation of desired product close to 100 % has become the realization of this possibility.

### Conclusion

The investigations results of active centers state in alumina-platinum catalysts have been summarized. The main results are the following:

- 1) the ideas about regularities of formation and role of platinum ionic forms in hydrocarbons adsorption and conversion catalysis;
- 2) the establishing of general regularities of catalysts design;
- 3) the development of high-effective catalysts, catalysts technology and catalysts exploitation in production processes of engine fuels and aromatic hydrocarbons.

The first data about the industrial exploitation of a new reforming catalyst ПП-51/04 (ПП-71) and industrial approbation of a new process of engine fuels production by combined conversion of C<sub>3</sub>-C<sub>4</sub> hydrocarbons and gasoline fractions ("Biforming" process) are presented.

**GALLIA AND GERMANIA SUPPORTED PLATINUM, RUTHENIUM AND  
IRIDIUM CATALYSTS IN REACTION OF SELECTIVE HYDROGENATION OF  
CROTONALDEHYDE - COMPARISON OF PHYSICOCHEMICAL AND  
CATALYTICAL PROPERTIES**

**Gebauer-Henke E., Rynkowski J.**

*Institute of General and Ecological Chemistry, Technical University of Łódź,*

*90-924 Łódź, ul. Żeromskiego 116, Poland*

*E-mail: jacryn@mail.p.lodz.pl*

Hydrogenation of crotonaldehyde in a gas phase at atmospheric pressure over Pt/support, Ru/support, Ir/support (support= $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>,  $\alpha$ -GeO<sub>2</sub>) catalysts was studied. Two types of active phase precursor were used: non-chloride (Pt(acac)<sub>2</sub>, Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, Ir(acac)<sub>3</sub>) and chloride (H<sub>2</sub>PtCl<sub>6</sub>, RuCl<sub>3</sub>, IrCl<sub>3</sub>). In all cases better results were obtained for catalysts obtained from non-chloride precursors. The best catalytic properties among all tested catalysts shows 5 wt. % Ir/ $\alpha$ -GeO<sub>2</sub> for which 100 % of selectivity to desired product - crotyl alcohol, at high and stable activity equal to 198  $\mu\text{mol s}^{-1} \text{g}_{\text{Ir}}^{-1}$  was obtained.

The selective hydrogenation of  $\alpha$ ,  $\beta$  – unsaturated aldehydes over supported metal catalysts to unsaturated alcohols is difficult to achieve because the C=C double bond hydrogenation is both thermodynamically and kinetically favoured. However, an elaboration of effective catalysts is of considerable practical interest due to the use of the unsaturated alcohols as intermediates in the synthesis of a variety of fine chemicals [1, 2].

In our previous studies we examined gallia and germania supported platinum, ruthenium and iridium catalyst, showing their promising catalytic performance in the reaction of selective hydrogenation of crotonaldehyde in a gas phase. In this work we summarize and compare results obtained till now, pointing the great potential of Ga<sub>2</sub>O<sub>3</sub> and GeO<sub>2</sub> as the supports of noble metals catalysts for the hydrogenation of  $\alpha,\beta$  - unsaturated aldehydes to unsaturated alcohols. Physicochemical characterization of these catalytic systems was carried out by means of BET, XRD, TPR SEM, TEM FTIR and TOF-SIMS methods. Catalysts were calcined for two hours at 200 °C (for platinum and iridium catalysts) and 400 °C (for ruthenium catalysts). Reaction of selective hydrogenation was carried out at 80 °C for all catalysts after one hour reduction at temperature range from 80 to 700 °C.

After optimization of the pre-treatment parameters (calcination, reduction temperature) most of tested catalysts showed very promising selectivity and high activity. The best results

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from all tested catalyst were obtained for systems containing 5 wt. % of active phase. Results are presented in table 1.

Table 1. The best results for Pt, Ru, Ir/support for reaction carried out at 80 °C, at conversion equal to 10 %.

Catalysts	Selectivity to crotyl alcohol [%]	Activity [ $\mu\text{mol s}^{-1} \text{g}_{\text{active phase}}^{-1}$ ]
5 % wt. Pt/ $\alpha$ -Ga <sub>2</sub> O <sub>3</sub>	89	150
5 % wt. Pt/ $\beta$ -Ga <sub>2</sub> O <sub>3</sub>	80	100
5 % wt. Pt/ $\alpha$ -GeO <sub>2</sub>	70	200
5 % wt. Ru/ $\alpha$ -Ga <sub>2</sub> O <sub>3</sub>	86	293
5 % wt. Ru/ $\beta$ -Ga <sub>2</sub> O <sub>3</sub>	80	162
5 % wt. Ru/ $\alpha$ -GeO <sub>2</sub>	73	122
5 % wt. Ir/ $\alpha$ -Ga <sub>2</sub> O <sub>3</sub>	90	130
5 % wt. Ir/ $\beta$ -Ga <sub>2</sub> O <sub>3</sub>	95	155
5 % wt. Ir/ $\alpha$ -GeO <sub>2</sub>	100	198

Optimal pre-treatment parameters for catalysts:

- platinum catalysts: calcination temperature 200 °C, reduction temperature 300 C, independently of kind of used support,
- ruthenium catalysts: calcination temperature 400 °C, reduction temperature 250 °C for catalysts supported on gallium oxide and 200 °C for catalysts supported on germanium oxide,
- iridium catalysts: calcination temperature 200 °C, reduction temperature 200 °C for catalysts supported on gallium oxide and 100 °C for catalysts supported on germanium oxide.

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**NANOSTRUCTURED POLYOXIDE AND Pt-Ru METAL CLUSTERS OVER CeO<sub>2</sub> PROMOTED ALUMINA FOR METHANE CONVERSION TO SYNTHESIS-GAS**

**Dossumov K., Salakhova R.Kh., Popova N.M., Tungatarova S.A., Grigorieva V.P.,  
Komashko L.V., Baishumanova T.S., Massalimova B.K.**

*D.V. Sokolsky Institute of Organic Catalysis and Electrochemisrty MS&HE RK,*

*Almaty, Republic of Kazakhstan*

*E-mail: tungatarova58@mail.ru*

The catalyst 0.5%Pt-0.5%Ru/2%Ce/( $\theta+\alpha$ )-Al<sub>2</sub>O<sub>3</sub> reduced by H<sub>2</sub> at 1173 K presents a mixture of Pt and Ru (3-30 nm) nanoparticles in reduced and partially oxidised states surrounded by large size formations of surface CeAlO<sub>3</sub> compound with perovskite structure and Ce<sub>6</sub>O<sub>11</sub> oxide (15-80 nm). High CH<sub>4</sub> conversion and selectivity to CO and H<sub>2</sub> (close to 100 %) at short contact times (2.35-8·10<sup>-3</sup> s) were observed on this catalyst in partial oxidation of CH<sub>4</sub> to synthesis-gas at 1173 K and atmospheric pressure. Methane is activated on Pt<sup>0</sup>, while oxygen is activated on Ce oxide nanostructures and Ru metal clusters.

The activity of the catalyst 0.5%Pt-0.5%Ru/2%Ce/( $\theta+\alpha$ )-Al<sub>2</sub>O<sub>3</sub> after pre-reduction at 1173 K was studied in the reaction of partial oxidation of methane, at 1173 K and short contact times ( $\tau$ ) 2.35-8 ms. Dependencies of CH<sub>4</sub> conversion ( $X_{CH_4}$ ), selectivity to CO ( $S_{CO}$ ) and H<sub>2</sub> ( $S_{H_2}$ ), and H<sub>2</sub>/CO ratio on duration of experiments are presented in Table 1. It was shown that CPO of CH<sub>4</sub> proceeds with selective formation of synthesis-gas (H<sub>2</sub>/CO=1.99-2.13) but decrease of methane conversion from 84.2 to 57.1 % was observed. The highest conversion of methane (100 %) and selectivity to CO and H<sub>2</sub> formation (99,6 and 100 %) were observed at  $\tau = 3.25$  ms ( $W = 1.17 \cdot 10^6$  h<sup>-1</sup>). Insignificant amount of CO<sub>2</sub> ( $S_{CO_2} = 0.4\%$ ) was detected in the reaction products.

Table 1. Variations of CH<sub>4</sub> conversion, selectivity to CO, H<sub>2</sub> and CO<sub>2</sub>, and H<sub>2</sub>/CO ratio depending on duration of experiments at T=1173 K and  $\tau=2,5$ ms on the 0.5%Pt-0.5%Ru/2%Ce/( $\theta+\alpha$ )-Al<sub>2</sub>O<sub>3</sub> catalyst.

Time, hour	$X_{CH_4}$ , %	$S_{CO}$ , %	$S_{H_2}$ , %	$S_{CO_2}$ , %	H <sub>2</sub> /CO
0.2	84.3	95.8	98.7	4.2	2.06
0.6	77.1	97.2	96.8	2.8	1.99
1.0	72.9	95.1	99.5	4.9	2.09
1.7	58.6	93.9	100	6.1	2.13
2.7	57.1	87.5	100	12.5	2.13

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According to XRD data the 0.5%Pt-0.5%Ru/2%Ce/( $\theta$ + $\alpha$ )-Al<sub>2</sub>O<sub>3</sub> reduced by H<sub>2</sub> at 1173 K was shown to be a mixture of CeO<sub>2</sub>, Ce<sub>6</sub>O<sub>11</sub>, surface CeAlO<sub>3</sub> compound with perovskite structure and nanostructural clusters of Pt and Ru in reduced and partially oxidised states,

According to TEM, the large-sized aggregates comprised by semi-transparent 6-8 nm sized particles of Ce<sub>6</sub>O<sub>11</sub> phase, narrowly distributed 3-4 nm sized particles of Pt and dense nanoparticles of metallic ruthenium ( 10-20 nm) are distributed on the surface of the support. Enlargement of Ce<sub>6</sub>O<sub>11</sub> nanoparticles up to 80 nm was observed after processing under reaction conditions at reducing atmosphere.

An increase of contact time slightly decreased the conversion of CH<sub>4</sub> (82%) and selectivity to CO and H<sub>2</sub>. The ratio of H<sub>2</sub>/CO was close to 2. Such ratio is the most appropriate for synthesis of methanol and hydrocarbons. Obtained results confirmed well-known data on high selectivity of ruthenium in the case of addition of CeO<sub>2</sub> into the catalyst at CPO of CH<sub>4</sub> with XCH<sub>4</sub>=74% [1]. In our investigation, it was shown that the use of Ru promoted by Pt and supported on stabilised 2%Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> increased the methane conversion up to 10 % at high selectivity to CO and H<sub>2</sub> at short contact times. EM data indicated formation of Pto, Ru<sub>o</sub>, Ce<sub>6</sub>O<sub>11</sub>, and CeAlO<sub>3</sub> clusters. We propose that an improvement of reaction parameters over mixed Pt-Ru catalyst supported on 2%Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> is caused by combination of different activation mechanisms of reactants: CH<sub>4</sub> is activated on Pto, oxygen – on Ru<sub>o</sub> and Ce<sub>6</sub>O<sub>11</sub>. The perovskite CeAlO<sub>3</sub> on the surface is likely promotes stabilisation of Pt and Ru on the support (2% Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>).

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**EFFECT OF MANGANESE OXIDE AND NOBLE METAL PRECURSOR ON  
CATALYTIC PROPERTIES OF Pt(Pd)-MnO<sub>x</sub>- ALUMINA CATALYSTS:  
DIESEL EXHAUST AND CATALYTIC COMBUSTION**

**Yashnik S.A., Ismagilov Z.R., Rogov V.A., Ushakov V.A., Ovsyannikova I.A.**

**Porsin A.V.<sup>1</sup>, Denisov S.P.<sup>1</sup>, Danchenko N.M.<sup>1</sup>**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>1</sup>*Ural Electrochemical Integrated Plant, Novoural'sk, Russia*

*E-mail: yashnik@catalysis.ru, zri@catalysis.ru*

In the current communication we shall review the XRD composition and redox properties of the binary Pt(Pd)-MnO<sub>x</sub>-alumina catalysts and compare them with catalytic properties in hydrocarbon oxidation. Both catalysts, Pt-MnO<sub>x</sub>-alumina and Pd-MnO<sub>x</sub>-alumina, will be shown to reduced at low temperature in TPR experiment, which may contribute to unique catalytic properties of Pt-MnO<sub>x</sub>-alumina catalysts in diesel test and Pd-MnO<sub>x</sub>-alumina catalysts in catalytic methane combustion.

The catalysts containing composition of noble metals (Pt, Pd, Rh) and transition metal oxides (MnO<sub>x</sub>, CuO, Co<sub>3</sub>O<sub>4</sub>) are usually characterized by a non-additive increase of catalytic activity of noble metal catalysts and transition metal oxide catalysts in the reaction of oxidation of different type hydrocarbons, such as methane, propane/propene, butane, and others [1-7]. Such catalytic systems are more perspective for application in catalytic close-coupled converters of diesel engine operated at high temperatures [8], because it allows decreasing the noble metal loading and improving the thermal stability.

The catalytic properties of Pt-MnAlO and Pd-MnAlO catalytic systems in deep hydrocarbon oxidation will be summarized in this presentation. The magnitude of the synergetic effect observed for Pt-MnAlO and Pd-MnAlO catalytic systems were found to depend on the nature of oxidized hydrocarbon and catalytic composition, in particularly the types of the manganese oxides and noble metal precursor. We observed the synergetic effect of manganese oxides and Pt in monolithic MnAlO catalysts modified with small Pt additions (0.1-0.3 wt.%) for the reaction of ethylene and butane oxidation, and standard DIESEL test runs with mixture of propane/propene, CO and NO [5, 6]. The synergetic effect in methane oxidation was resided only to Pd-MnAlO catalysts [5, 7], especially for Pd-Mn<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> and Pd-MnLaAl<sub>11</sub>O<sub>19</sub> catalysts calcined at high temperatures (1000-1200 °C).

We study the XRD-composition, textural and redox properties of the Pt-MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalytic systems simulated a washcoated layer of monolithic catalysts and identify their

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effect on catalytic properties in light hydrocarbon oxidation. The redox properties of Pt-MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts is found to depend from the precursors of alumina ( $\gamma$  and  $\chi$ ), manganese oxides (MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>) and Pt (H<sub>2</sub>PtCl<sub>6</sub>, H<sub>2</sub>[Pt(OH)<sub>6</sub>], Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> or PtX). It has been shown that the TPR profile of all MnAlO catalysts are changed in the presence of small Pt loading. Binary Pt-MnAlO-catalysts containing spinel-type oxide, for example solid solution of Mn<sup>3+</sup> cations in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>, are almost completely reduced at the temperature (up to 300 °C), at which the reduction of the MnAlO samples is only starting. The lower reduction temperature of MnO<sub>x</sub> in the binary samples is usually explained by two reasons; both require strong interaction between Pt and MnO<sub>x</sub>. First, noble metals catalyze the reduction of MnO<sub>x</sub> by hydrogen spill-over during the TPR experiment. Second, the mobility of the lattice oxygen in MnO<sub>x</sub> is increased.

Redox properties of Pt-MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts are shown to be correlated with catalytic activity in light hydrocarbon oxidation. At similar Pt loadings (1.06 g/l), the catalytic activity of Pt-MnAlO monolithic catalysts in butane oxidation and DIESEL tests increases in the order H<sub>2</sub>PtCl<sub>6</sub> ~ H<sub>2</sub>[Pt(OH)<sub>6</sub>] < PtX. The capability of these catalysts to be reduced by hydrogen in TPR experiment is also increased in this order.

The precursors of manganese oxides (MnO<sub>2</sub>, Mn<sub>3</sub>O<sub>4</sub>, MnLaAl<sub>11</sub>O<sub>19</sub>) and Pd (H<sub>2</sub>PdCl<sub>4</sub>, Pd(NO<sub>3</sub>)<sub>2</sub> or Pd(CH<sub>3</sub>COO)<sub>2</sub>) are found to have an effect on the reversible PdO/Pd transformation observed during high-temperature calcination of Pd-MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, and the redox and catalytic properties of Pd-MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst in methane oxidation. The redox properties of Pd-MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> are correlated with their catalytic properties in methane oxidation.

The synergistic effect in catalytic activity of Pt(Pd) and MnAlO catalytic system can be explained by three reasons: 1) formation of a metastable spinel Mn<sub>3</sub>O<sub>4</sub>; 2) stabilization of fine-dispersed PtO<sub>x</sub>/PdO particles or formation of fine-dispersed metallic Pd<sup>0</sup>; and 3) strong interaction of PtO<sub>x</sub>/PdO(Pd) particles with MnO<sub>x</sub> particles. All reasons result in the increase of redox properties of Pt(Pd)-MnAlO catalytic systems.

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**FORMATION OF NANO-SIZED COBALT CRYSTALLITES ON SILICA-ALUMINA  
SUPPORTS ACTIVE FOR FISCHER-TROPSCH SYNTHESIS – A MECHANISTIC  
STUDY**

**Botha J.M., Datt M.S., Visagie, J.L., Larina T.V.<sup>1</sup>, Zaikovskii V.I.<sup>1</sup>, Cubar A.V.<sup>1</sup>,  
Aristov Yu.I.<sup>1</sup>, Fenelonov V.B.<sup>1</sup>, Paukshtis E.A.<sup>1</sup>, Balzhinimaev B.S.<sup>1</sup>**

*Sasol Technology R&D, Klasie Havenga road 1, Sasolburg, 1947, South Africa*

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: thys.botha@sasol.com*

Over the past two decades, Fischer-Tropsch synthesis (FTS) has received renewed interest as a step in gas-to-liquids (GTL) technology. Development of supported nano-sized cobalt crystallites on SiO<sub>2</sub>, TiO<sub>2</sub>, C, Al<sub>2</sub>O<sub>3</sub>, etc. continues to be of utmost importance in FTS. The effect of metal precursor, support, support pre-treatment, calcination, reduction, promoters, etc. on metal dispersion (i.e. cobalt crystallite size) has been studied in detail. However, the consensus view is that when making use of the most common route to catalyst preparation, namely some form of aqueous impregnation using Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O followed by drying, calcination and reduction, the cobalt crystallites so produced engage in a poorly understood chemical interaction with the catalyst support.

The aim of this study therefore was to focus on the mechanism of cobalt crystallite formation on silica-alumina catalyst supports for application in FTS. Techniques such as IR spectroscopy, UV-Vis, DSC, HREM, etc. were used in combination in order to put forward a mechanism for the formation of cobalt nitrate “droplets” on the surface of catalyst support during catalyst manufacturing. The effect of these cobalt nitrate “droplets” on the physical as well as chemical properties of the FTS catalysts manufactured as well as reducibility and morphology of calcined cobalt oxide was studied and will be presented.

**UNUSUALLY STABLE SUPPORTED NANOSIZE CATALYSTS FOR  
CHLOROBENZENE HYDRODECHLORINATION**

**Lokteva E.S., Kachevsky S.A.<sup>1</sup>, Stakheev A.Yu., Rostovshchikova T.N., Smirnov V.V.,  
Yavsin D.A.<sup>2</sup>, Gurevich S.A.<sup>2</sup>, Kozhevnikov V.M.<sup>2</sup>**

*Lomonosov Moscow State University, Moscow, Russia*

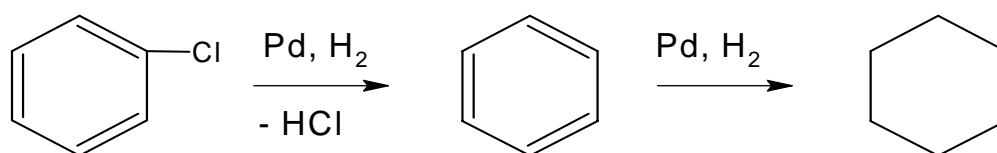
<sup>1</sup>*Ioffe Physiko-Technical Institute of RAS, St.-Petersburg, Russia*

<sup>2</sup>*N.N. Zelinskii Organic Chemistry Institute of RAS, Moscow, Russia*

*E-mail: les@kge.msu.ru*

New unusually stable and efficient catalysts based on Pd and Ni nanoparticles for chlorobenzene hydrodechlorination were fabricated by means of laser electrodispersion technique. The catalyst structure was studied by means of TEM and XPS. The unique catalytic properties of the nanostructured metal films are associated both with the small size of amorphous metal particles and particle self-organization on the surface of silicon or carbon supports.

Method of laser electrodispersion which is based on cascade fission of metallic microdrops in laser torch plasma [1] was used for fabrication of Pd and Ni nanoparticles deposited on surface oxidized silicon and sibunite. Different types of sibunite with granule size at the range between 0.6-3.0 mm were used. Prepared films were tested as catalysts for chlorobenzene conversion to benzene and cyclohexane:



Hydrodechlorination was carried out in a fixed-bed flow reactor under the excess of hydrogen at 100 – 250 °C at atmospheric pressure using 0.05 g of catalyst. The products were analyzed by means of gas chromatography. Fresh and worked-out Pd and Ni catalysts having different surface particle density were studied by TEM, XPS and electrophysical methods. In accordance with these studies the particle size is about 2 nm for Pd and 2.5 nm for Ni with very narrow size distribution <10 % in all catalysts, the metal particles are amorphous and fully reduced. The catalysts are very stable to oxidation.

The efficiency and selectivity of process strongly depend on the content of metal on a support surface or surface particle density and support type. The 90-100 % chlorobenzene conversion was observed for Pd catalysts at 150-200 °C. The Pd nanoparticles deposited on sibunite having large granule size 2.5-30 mm were the most active in hydrodechlorination.

The specific catalytic activity achieves the maximal value  $6.5 \times 10^5$  mol P/ mol Pd x h at 200 °C at the very low content of metal ( $<10^{-3}$  weight %) on the sibunite surface. For usual supported catalysts the activity is three orders lower. Hydrodechlorination on the most active catalysts supported on sibunite results in only benzene formation. The use of catalysts supported on silicon gives rise to benzene and cyclohexane. Their ratio depends on metal content in the catalyst, time-on-stream and temperature. The Pd catalysts fabricated by means of laser electrodispersion technique keep the high efficiency for a long time. The Ni catalysts were less active, only 50 % chlorobenzene conversion was observed at 250 °C.

In accordance with XPS data the Pd valence state does not change in the course of hydrodechlorination. Only an average size of Pd particles increases during the reaction. The growth of particle size may be a reason for the catalyst activation during catalytic reaction. During the catalytic reaction Pd does not undergo both oxidation and chlorination resulting in palladium oxide or chloride formation. Small particle size as well as their amorphous state may be reasons for this phenomenon.

These data together with our previous results obtained for other types of chlorohydrocarbon reactions and hydrogenation [2, 3] let us conclude that the extremely high activity, the strong dependence of activity on the metal content in catalyst and the high stability are the common features of nanostructured catalysts fabricated by means of laser electrodispersion technique. These results are of exceptional importance for development of new hydrodechlorination catalysts because the fast catalyst poisoning is the main unresolved problem in technology of toxic polychlorinated chemicals utilization. New laser electrodispersion technique for fabrication of highly active and stable catalysts makes possible a solution of this problem.

This work was supported by ISTC (2955).

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**CATALYTIC PROPERTIES OF INVERTASE IMMOBILIZED  
ON MODIFIED MESOSTRUCTURED SILICA CELLULAR FOAMS**

**Szymańska K.<sup>1</sup>, Kostrzewa E.<sup>1</sup>, Bryjak J.<sup>2</sup>, Mrowiec-Białoń J.<sup>3</sup>, Jarzebski A.B.<sup>1,3</sup>**

<sup>1</sup>*Silesian University of Technology, Department of Chemical Engineering, Gliwice, Poland*

<sup>2</sup>*Wrocław University of Technology, Faculty of Chemistry, Wrocław, Poland*

<sup>3</sup>*Polish Academy of Sciences, Institute of Chemical Engineering, Gliwice, Poland*

*E-mail: Andrzej.Jarzebski@polsl.pl*

The properties of invertase covalently attached to mesostructured silica cellular foams (MCF) modified with 2-aminoethyl-3-aminopropyltrimethoxysilane and next with glutaraldehyde, were investigated in detail. Such biocatalysts showed very attractive properties. They behaved identically as a native enzyme when compared in the Arrhenius plot and in the batch experiments. Yet they were notably more stable and could be reused. The pH range of high invertase activity expressed in sucrose conversion was considerably broader (3.5-5.5) than of native enzyme (4-5) but optimum reaction temperature was changed only slightly.

Immobilization of enzymes on various water insoluble supports attracts considerable attention and polymeric organic materials are the most common carriers applied to date. More recently, however, the mesoporous silica materials obtained by templating method were shown to be even more promising enzyme supports. Quite recently we have demonstrated that wide pore siliceous mesostructured cellular foams (MCF) with the surface modified with alkylamines are particularly attractive carriers for trypsin, invertase and glucoamylase [1]. Their properties were far superior to the counterparts supported on Eupergit C, a specialty polymeric enzyme carrier, and also wide pore silica gels modified in the same way. Here we report the results of studies focussed on the investigation of catalytic properties of invertase immobilized on MCFs modified with 2-aminoethyl-3-aminopropyltrimethoxysilane (AEAPTS) and further with glutaraldehyde (GLA), a cross linker, i.e. the system which proved to be the most efficient among those tested earlier.

Immobilization of invertase was carried out in the same way as described before [1] and AEAPTS load was 1.5 mmol/g of silica. We studied in more detail the effect of:

- reaction conditions (pH and temperature) on the expressed activity of MCF-bound invertase to determine the optimum conditions for the conversion of sucrose to glucose and fructose,
- enzyme load on the activity of immobilized invertase and its dependence on the concentration of a native enzyme used in immobilization,
- immobilization conditions on the biocatalysts activity, stability, etc.

The MCF-bound invertase appeared to be equally active as the native enzyme in batch experiments. Yet the former could be used repeatedly without significant loss in activity. The behaviour of the two preparations in the Arrhenius plot (reaction rate vs  $1/T$ ) was quite similar which clearly indicates that mass transport limitation of the MCF-based catalysts activity was insignificant.

The experiments performed showed that immobilized invertase remains highly active in a notably broader range of pH (3.5-5.5) than the native enzyme (4-5) and its activity is notably higher at weakly acidic conditions than the neutral pH.

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## THE COBALT NANOPARTICLES IN CO-SUPPORTED FISHER-TROPSCH CATALYSTS BY WATER VAPOUR

**Chernavskii P.A., Pankina G.V., Mougtsimov A.V., Lunin V.V.**

*Lomonosov Moscow State University, Chemistry Department, Moscow, Russia*

*E-mail: chern@kge.msu.ru*

The Co nanoparticles oxidation by water vapour formed during Fischer-Tropsch synthesis (FTS) takes place under high conversions. This process influences on selectivity of FTS. It was stated that Co crystallites interacts with water vapour in the range from room temperature to 250<sup>0</sup>C and atmospheric pressure. Oxidation kinetics was investigated by means of vibration magnetometer of original construction. It was shown that pre-adsorbed hydrogen strongly retards Co nanoparticles oxidation by water vapour. In contrast the pre-adsorbed CO doesn't influence on the oxidation process.

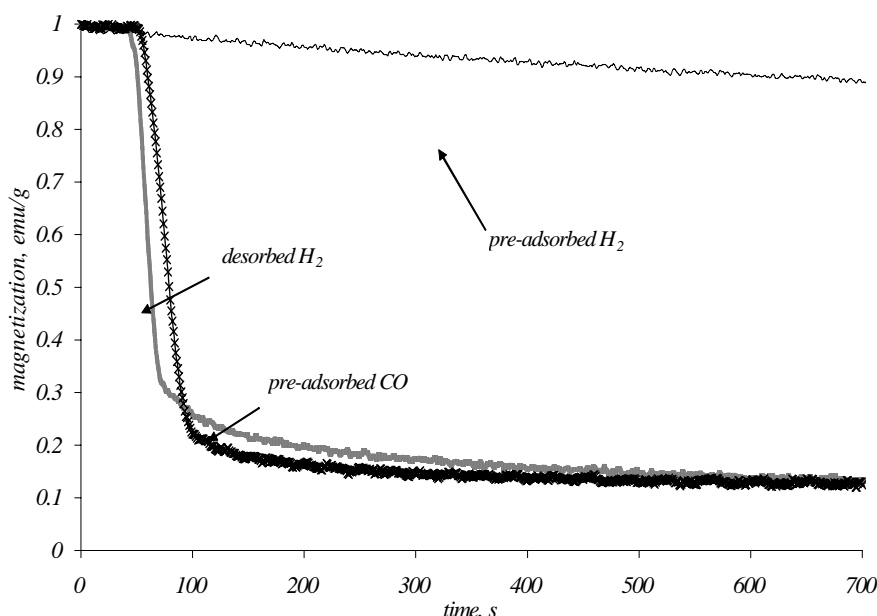


Fig. The magnetization-time dependance of Co nanoparticles (4 nm) oxidation by water-vapour.

The oxidation of Co-supported nano-particles by the O<sub>2</sub> trace amounts was also investigated. Low-temperature oxidation of cobalt nanoparticles leads to the size-dependent effects, related to the selective nucleation of oxide at the edges and the corners of cobalt crystallites. It was suggested that the initial oxidation rate is proportional to the coverage of nanoparticles by atomic oxygen. Complete oxidation leads to formation of hollows in cobalt oxide nanoparticles. Magnetic measurements of particle size distribution are in good agreement with the results of transmission electron microscopy.



**PALLADIUM-MANGANESE SYSTEMS CHARACTERIZATION: CATALYTIC  
PROPERTIES IN METHANE COMBUSTION**

**Requies J., Barrio V.L., Arias P.L., Cambra J.F., Güemez M.B., Alvarez-Galvan M.C.<sup>1</sup>,  
V. A. de la Peña O'Shea<sup>1</sup>, Fierro J.L.G.<sup>1</sup>**

*Dep. of Chemical and Envir. Eng., School of Engineering (UPV/EHU), 48013 Bilbao, Spain*

<sup>1</sup>*Institute of Catalysis and Petrochemistry, CSIC, Cantoblanco, 28049 Madrid, Spain*

*E-mail: [jesus.requies@ehu.es](mailto:jesus.requies@ehu.es)*

Catalytic combustion is known to possess a number of advantages compared to conventional flame combustion. Thus, catalytic combustion of methane has been studied for Pd and Pd-Mn structured catalysts at several experimental conditions. Characterization of these catalytic systems was done by XRD and XPS analysis in order to study the surface and to establish the influence of the surface structure on the catalytic activity. The Mn-Pd monolithic catalysts enhance a good stability and a full conversion of methane at high temperature and at different  $\lambda$  and pressure.

### **Introduction**

The main advantage of the catalytic combustion is that it allows combustion at temperatures below the NO<sub>x</sub> formation and at the same time achieves ultra low emissions of CO and unburned hydrocarbons. Other advantages of this process are the stability of the combustion and the ability to combust fuel outside the flammability limits. For these reasons the catalytic combustion is a suitable alternative to conventional flame combustion in gas turbines.

### **Experimental**

Commercial cordierite monoliths (Corning, 400 cpsi) were coated using a modified dip-coating procedure with an alumina stabilised layer. Pd- and Mn- precursors were deposited on the stabilised alumina washcoat through impregnation with an aqueous solution. Several dip-coating followed by drying during several hours were necessary to obtain a 25 % weight of catalyst material. Catalysts were calcined in air at 1000 °C during 2 hours.

The catalytic activity was tested in a conventional bed-fixed reactor, working at different pressures (5-12 bar), lambdas ( $\lambda = \text{air/methane ratio} = 3-9$ ) and temperatures (550-750 °C). The composition of the product gas was analyzed by an on-line gas chromatograph equipped with a TCD and FID detectors. For the catalyst characterization XRD and XPS measurements were performed.

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### Results and discussion

The addition of manganese to the palladium monolithic catalysts improves the catalyst stability. In figure 1, the effect of the temperature has been presented at 5 bar of pressure and a lambda of 3. As it can be observed at lower temperatures (<700 °C) very little methane conversion was observed. Even though at higher temperatures the methane conversion was complete and a not phenomenon of deactivation is observed during the measured time on stream. For higher lambdas ( $\lambda=9$ ) the methane conversion decreased. In figure 2 experiments at higher pressures are compiled for the 5Mn-0,5Pd catalyst. As it can be seen a small diminution in activity was observed when the pressure was increased for methane combustion.

Physicochemical characterization of catalytic samples by XPS and XRD showed differences in chemical state, metal-support interactions and properties of palladium and manganese particles, indicating the importance of the morphological and surface properties of the metal phases in driving the activity of the monolithic catalysts.

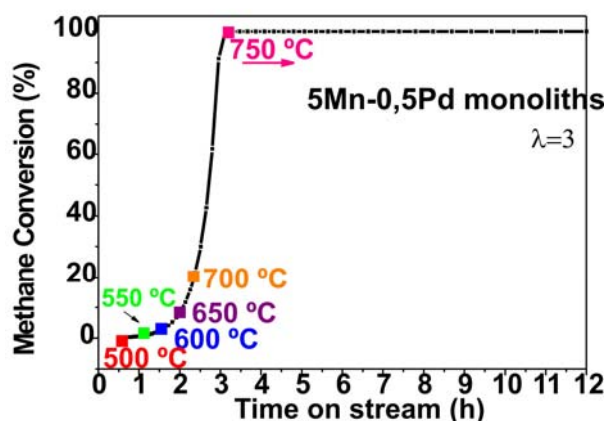


Fig. 1. Effect of temperature for 5Mn-0,5Pd

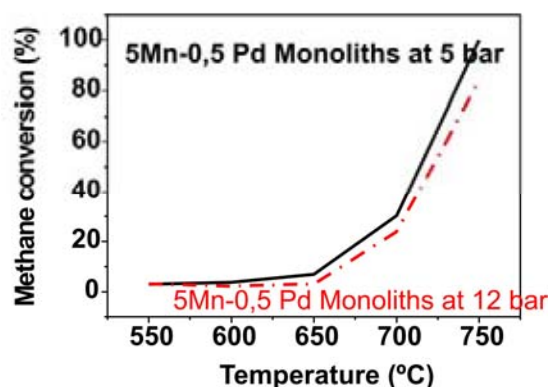


Fig. 2. Effect of pressure for 5Mn-0,5Pd

### Conclusions

A test facility has been used for assessing the activity of different palladium-manganese structured catalysts for methane combustion. From these experiments, the following conclusions may be drawn: the addition of manganese to the palladium monolithic catalyst has a positive effect: a) on the activity, especially at higher temperatures (750 °C) the methane conversion is full, and b) on the stability, because not deactivation is observed for the time on stream measured.

### Acknowledgements

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## SURFACE SELFPROPAGATING THERMOSYNTHESIS OF SUPPORTED CATALYSTS

**Tsyruľ'nikov P.G.**

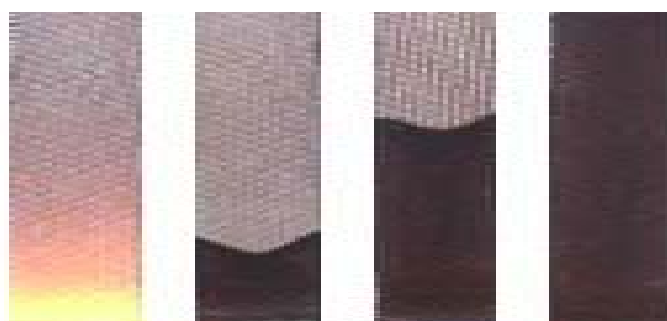
*Institute of Hydrocarbons Processing SB RAS, Omsk, Russia*

*E-mail: tsyr@incat.okno.ru*

Surface selfpropagating thermosynthesis (SSTS) of supported catalysts was developed. The preparation technique consists of: 1) impregnation of various carriers by the solution of precursors which can be oxidized (burned) with oxygen (air) or supported oxidizers; 2) drying the sample, and 3) initiating by the heat pulse the surface flameless combustion. The acetates and nitrates of  $\text{Co}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Ce}^{+3}$ ,  $\text{Pd}^{+2}$  and air oxygen as oxidizer were used as fuel pairs. The regularities of SSTS and activity of catalysts were investigated. It was shown that the catalysts activity is higher in comparison with commonly prepared catalysts.

In contrast with well-known SHS of various materials (catalysts) the temperatures of SSTS reached in the heat front are much lower. The short time influence of the middle temperature heat front on the reagent substances gives the dispersive and catalytically active phases.

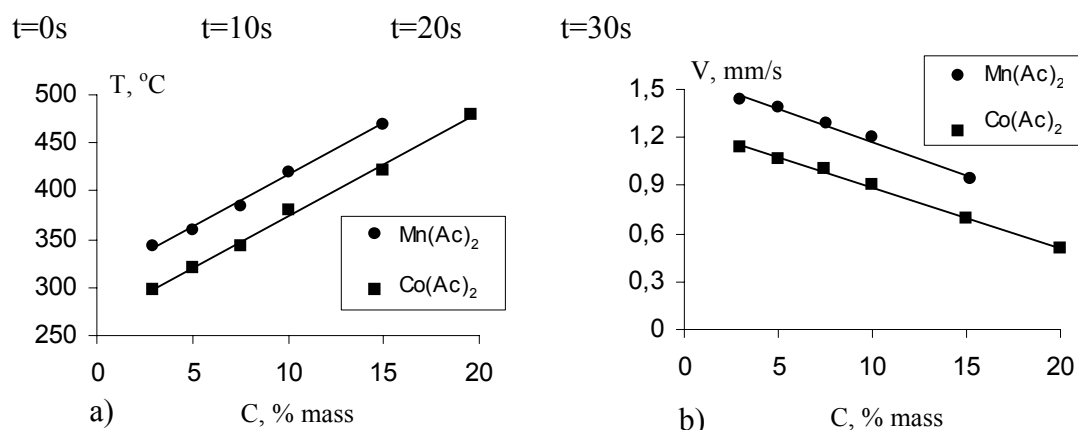
The glass fabric, cordierite monolith ( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ), armored Ti-Si and Ni-Al-Si porous plates, porous titanium,  $\gamma\text{-Al}_2\text{O}_3$  grains were used as carriers. The example of SSTS and some its parameters are presented in the Fig. 1 and 2.



**Fig. 1.** The dynamics of the heat front of 5% $\text{Co}_3\text{O}_4$ /glass fabric at the SSTS. The  $\text{Co}_3\text{O}_4$  precursor is cobalt acetate, the oxidizer –  $\text{O}_2$  (air).

$T_{\max} : 380^\circ\text{C}$

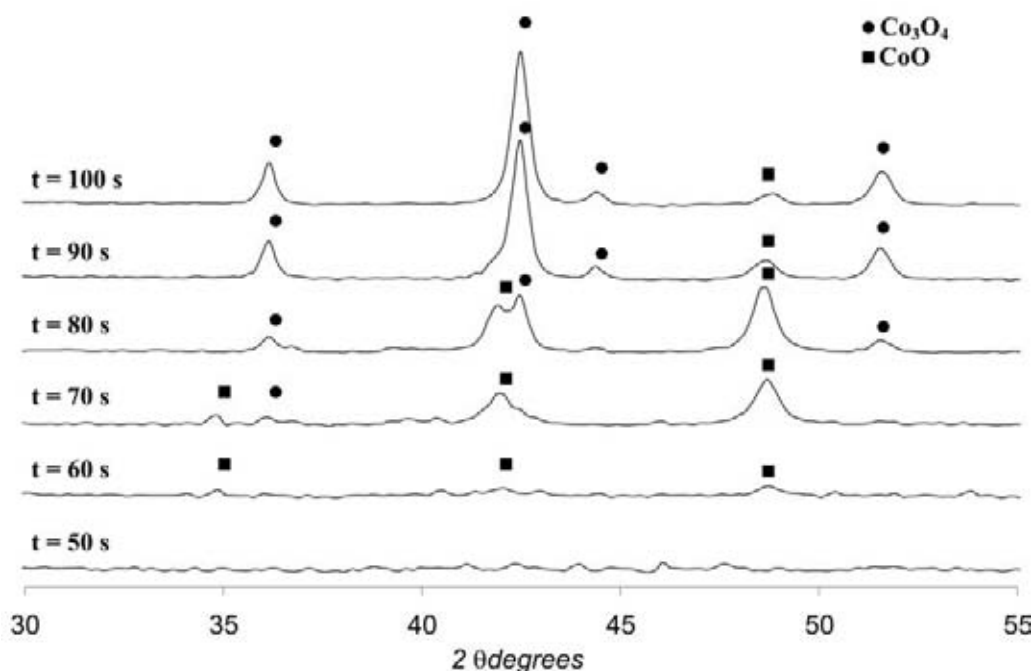
Heat front rate: 0.9 mm/s



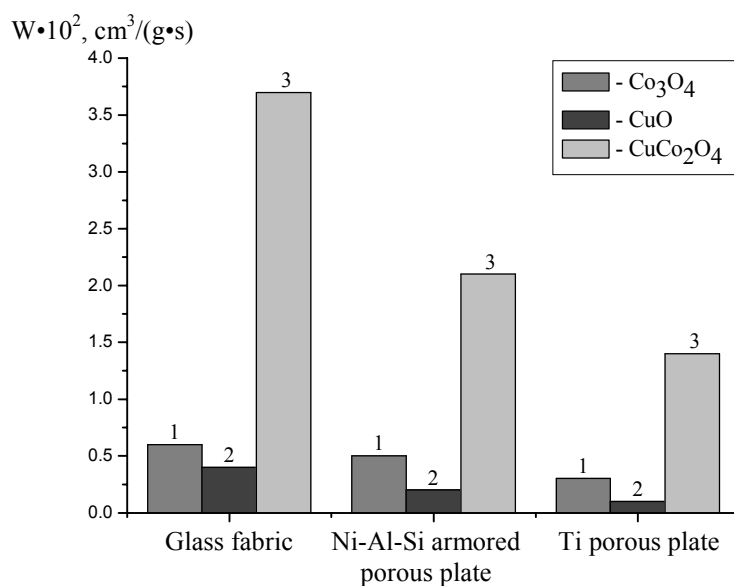
**Fig. 2.** The dependence of heat front temperature (a) and heat front movement rate (b) on the precursor and its content on support. The initial samples thermo stating is  $100^\circ\text{C}$ .

## OP-II-11

In order to check the phase transformation the method of X-ray diffraction in situ with time resolution was used. The time of survey of one diffractogram was 5 s. Approximately 20 pattern have been taken during the heat front passing. Some results are given in the Fig. 3.



**Fig.3.** Heat front diffractograms for the catalyst 40% mass.  $\text{Co}_3\text{O}_4$ /glass fabric. The precursor -  $\text{Co}(\text{CH}_3\text{COO})_2$ ; the intermediate phase -  $\text{CoO}$ ; the final phase -  $\text{Co}_3\text{O}_4$ .



**Fig. 4.** The activities of Cu- and Co- containing oxide catalysts on various carriers in deep oxidation of methane. Oxides content: 10% mass. The flow – circular setup,  $C_{\text{CH}_4}$  inlet 0,5% vol.,  $X = 50\%$ ,  $T = 500^\circ\text{C}$ .

As it is seen the combined supporting of Cu- and Co-acetates following by SSTS leads to the synergic effect in activity connected with the  $\text{CuCo}_2\text{O}_4$  formation.

The author appreciates his co-workers U.F. Zavyalova, N.B. Shitova, A.I. Nizovskii, A.N. Shmakov, A.Y. Gladkiy, N.D. Ryzhova for fruitful collaboration.

## CHARACTERIZATION AND CATALYTIC ACTIVITY OF COBALT SUPPORTED MONTMORILLONITE K10

**Ghattas M.S.**

*Catalysis Department, Petroleum Refining Division, Egyptian Petroleum Research*

*Institute (EPRI), Nasr City, Cairo 11727, Egypt*

*E-mail: msg\_epri@yahoo.com*

Cobalt supported montmorillonite K10 catalysts with different cobalt concentrations (3, 6, 9 & 18 wt % Co) were prepared by impregnation technique. Quartz and montmorillonite metal were detected beside  $\text{Co}_3\text{O}_4$  species in X-ray diffractogram. The latter was increased as cobalt content increases. More than one peak were observed in temperature programmed reduction profile, first one corresponding to the reduction of residual precursor cobalt nitrate, second to reduction of  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$  and third to reduction of  $\text{CoO}$  to cobalt metal and the forth in the reduction temperature region from 600 up to 980 °C corresponding to several species which have certain mode of interaction between cobalt and support as cobalt silicate and cobalt aluminate. The intensity of these peaks increased with increase of cobalt concentration. The hysteresis loop, pore size distribution, pore volume and BET surface area were greatly affected by cobalt loading. New bands at 1384, 800 and 669  $\text{cm}^{-1}$  were linked to the cobalt species present in the cobalt / montmorillonite K10 catalysts not to the support. The catalysts under investigation have higher catalytic activity toward n-hexane, cyclohexane, toluene and benzene cracking.

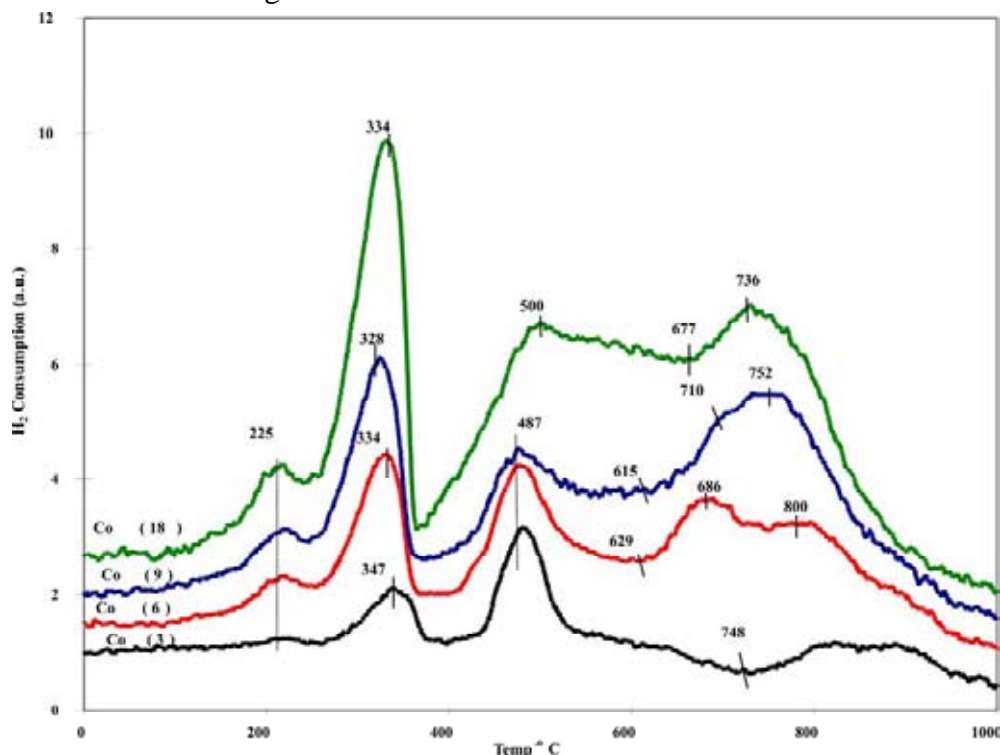


Fig.: TPR for Cobalt Oxide / MK 10 Catalysts

**GOLD-ALUMINA AND GOLD-CERIA NANOSIZED CATALYSTS FOR CO OXIDATION: EVIDENCES FOR METAL-SUPPORT INTERACTION**

**Moroz B.L., Pyrjaev P.A., Zaikovskii V.I., Ruzankin S.F., Larina T.V.,  
Anufrienko V.F., Bukhtiyarov V.I.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: moroz@catalysis.nsk.su*

Catalysts containing Au nanoparticles on non-reducible ( $\delta$ -Al<sub>2</sub>O<sub>3</sub>) and reducible (CeO<sub>2</sub>) oxides were synthesized by anionic adsorption of Au(III) hydroxycomplexes followed by calcination in air at 400 °C and characterized by XRD, XPS, HRTEM and diffuse reflectance UV/vis spectroscopy. They showed high and stable catalytic activity in oxidation of CO (1 %) in air containing 2 % steam at 40-70 °C. The experimental evidences for the strong interaction between metal and the both supports *via* formation of Au-O-Al(Ce) bonds are reported.

During last 15 years, gold nanoparticles of both unsupported and supported on oxide carriers were found to reveal surprisingly high catalytic activity in various oxidation reactions including the low-temperature CO oxidation. Gold catalysts are tested for practical application to environmental protection from CO and removal of CO from hydrogen fuel for fuel cell. Type of support strongly affects the catalytic properties of gold. However, the reasons of the effect of support are not clear yet. Here, based on the results of studying the Au/Al<sub>2</sub>O<sub>3</sub> and Au/CeO<sub>2</sub> catalysts we demonstrate that the strong gold-support interaction may occur both in the case of reducible (CeO<sub>2</sub>) and non-reducible (Al<sub>2</sub>O<sub>3</sub>) oxide carriers and be a reason for the improved catalytic performance of Au nanoparticles in CO oxidation.

The catalysts containing 1.5% wt.% Au were prepared by anionic adsorption of Au(III) hydroxycomplexes from the alkalized HAuCl<sub>4</sub> solution onto  $\delta$ -Al<sub>2</sub>O<sub>3</sub> (Sasolchemie;  $S_{BET} = 110 \text{ m}^2/\text{g}$ ) and CeO<sub>2</sub> of the same  $S_{BET}$  synthesized in Prof. V.A. Sadykov's group (BIC) by modified Pechini method. After calcination in air at 400 °C, XRD patterns of the samples display the broadened reflections related to metallic gold, at that no changes in the unit cell parameter  $a$  for  $\delta$ -Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> are observed. HRTEM micrographs demonstrate Au particles from 2 to 10 nm in size, the majority of particles are 2-3 and 5-6 nm in diameter for the Au/ $\delta$ -Al<sub>2</sub>O<sub>3</sub> and Au/CeO<sub>2</sub> samples, respectively. The supported Au particles are somewhat flattened, the crystal faces adjoining to the support surface are the most extensive as compared with the other faces of the Au crystallite (Fig. 1). The symmetry of Au crystallite faces is the same as the symmetry of the support crystallite faces. It strongly suggests an epitaxial

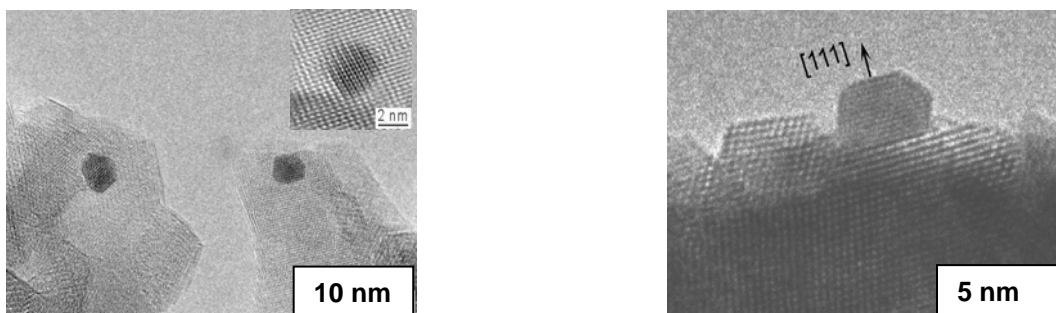


Figure 1. HRTEM images of Au nanoparticles located on the  $\delta$ -Al<sub>2</sub>O<sub>3</sub> (left) and CeO<sub>2</sub> (right) surface.

interaction between supported Au particles and the support surface with the formation of Au–O–Al(Ce) bonds.

The UV/vis spectrum of the Au/ $\delta$ -Al<sub>2</sub>O<sub>3</sub> catalyst contains the intense peak at 19000 cm<sup>-1</sup> and the broad shoulder at 25000-32000 cm<sup>-1</sup> which can be assigned to the plasmon absorption of metal Au nanoparticles and to the O2p → Au5d charge transfer (CT) in the surface gold species with Au-O-Au bonds, respectively [Anufrienko V.F., Moroz B.L., Larina T.V. et al., Dokl. Russ. Akad. Nauk, 413(2007) № 4]. For the Au/CeO<sub>2</sub> catalyst, the spectrum exhibits the plasmon band of metallic gold at 14000 cm<sup>-1</sup> apart from the bands at >32000 cm<sup>-1</sup> (O2p → Ce4f CT) and ~28000 cm<sup>-1</sup> (most probably, Ce<sup>4+</sup> → Ce<sup>3+</sup> transition) belonging to the CeO<sub>2</sub> support. Simulation of the plasmon absorption of Au nanoparticles within the discrete dipole approximation showed that the plasmon frequency ( $\omega_{max}$ ) which depends on the dielectric constant of the surrounding medium ( $\epsilon_m$ ) is equal to 20000 cm<sup>-1</sup> for the unsupported Au particles in a vacuum ( $\epsilon_m=1$ ) and should shift towards the experimental  $\omega_{max}$  values (19000 or 14000 cm<sup>-1</sup>) at the values of  $\epsilon_m$  characterized the dielectric properties of Al<sub>2</sub>O<sub>3</sub> ( $\epsilon_m=2.2$ ) and CeO<sub>2</sub> ( $\epsilon_m=9.0$ ). This fact also confirms the strong interaction between the metal and support in the catalysts studied.

The nanosized Au/Al<sub>2</sub>O<sub>3</sub> and Au/CeO<sub>2</sub> catalysts show high catalytic activity in CO oxidation at 25-70 °C and 0.1 MPa of CO:H<sub>2</sub>O:O<sub>2</sub>:N<sub>2</sub>=1:2:20:77 gas mixture. Heating the catalysts in air at temperature as high as 700°C does not result in Au particle sintering, and they still keep their improved catalytic performance. Strong gold-support interaction may be a reason for high thermal stability of Au catalysts that was observed in our tests.

The work was supported by the NWO (project No. 047.015.003) and the Integration interdisciplinary program of the Siberian Branch of RAS (project No. 79).

**MOLYBDENUM CARBIDE COATINGS PREPARED BY ELECTROCHEMICAL SYNTHESIS IN MOLTEN SALTS FOR APPLICATION IN MICROSTRUCTURED FUEL PROCESSORS**

**Rebrov E.V., Dubrovskiy A.R.<sup>1</sup>, Kuznetsov S.A.<sup>1</sup>, De Croon M.H.J.M., Schouten J.C.**

*Laboratory of Chemical Reactor Engineering, Eindhoven University of Technology,  
5600 MB Eindhoven, the Netherlands*

<sup>1</sup>*Institute of Chemistry, Kola Science Centre RAS, Apatity, Murmansk region, Russia*

*E-mail: e.rebrov@tue.nl*

The activity and stability of two types of molybdenum carbide coatings deposited on molybdenum substrates (Mo<sub>2</sub>C/Mo) were compared in the water gas shift reaction at 230 – 350 °C. If molybdenum carbide is present as a thin layer over a molybdenum substrate (Mo<sub>2</sub>C/Mo), the catalytic activity is enhanced compared to that of the pure Mo<sub>2</sub>C phase.

In the reforming of gasoline or natural gas, a hydrogen rich gas is produced with a carbon monoxide concentration of 10-12 vol.%. Because CO is a poison for a proton exchange membrane fuel cell catalyst, the water-gas shift (WGS) reaction is used to reduce its concentration to below 1 vol.%, increasing H<sub>2</sub> yield. Bulk molybdenum carbides exhibits promising catalytic activity for the water gas shift reaction (WGS), which is superior to that of the commercially used catalysts [1, 2]. The aim of this study was the development of new generations of highly active and stable catalytic coatings for the WGS reaction by application of high-temperature electrochemical synthesis in molten salts.

Two carburization series were carried out on 40x10 mm<sup>2</sup> molybdenum substrates with a thickness of 0.1 mm. The first series was carried out in a melt containing 5 wt.% Li<sub>2</sub>CO<sub>3</sub>, while the second one in a melt containing 5 wt.% of Li<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>MoO<sub>4</sub> at a Mo/C molar ratio of 2 in an equimolar NaCl-KCl mixture. Synthesis of Mo<sub>2</sub>C coatings was performed at 850 °C for 7 h with a cathodic current density of 5 mA cm<sup>-2</sup>. The glassy carbon crucible served as anode. The specific surface area of coatings, determined by BET method, was ca. 20 m<sup>2</sup> g<sup>-1</sup>. Hexagonal Mo<sub>2</sub>C was the only phase present in the coatings.

The kinetics of the WGS and backward WGS reactions was measured on a Mo<sub>2</sub>C/Mo coatings inserted in a microstructured reactor in the temperature range of 230-350 °C. The reactor has an AISI 316 stainless steel housing with standard tube connections and can be heated up to 650 °C with an electrical furnace. Twenty cavities of 130 × 400 μm<sup>2</sup> were microfabricated by electrical discharge machining (EDM) in the side walls of each reactor



compartment along the length of the reactor. The activity tests were carried out at atmospheric pressure either with four, eight, or sixteen Mo<sub>2</sub>C/Mo plates inserted in the microstructured reactor.

The activity remained stable for at least 700 hours on-stream at 300 °C in a composition containing 1-3 vol.% CO, 1-3 vol. % CO<sub>2</sub>, 5-10 vol. % H<sub>2</sub>O and 30-50 vol.% H<sub>2</sub> balanced by He. There was no evidence of methanation activity for the Mo<sub>2</sub>C/Mo coatings in the whole range of temperatures studied. A combined Power-Law Eley-Rideal kinetic model is proposed to describe the reaction in the 530 – 600 K range. This model accurately predicts the equilibrium CO conversion and can be used at H<sub>2</sub>O/CO ratios above 1.5, which are typical conditions applied in a fuel processor for fuel cell applications. A comparison was made between an adiabatic fixed bed reactor with the Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst and an isothermal microstructured reactor, operating at the top limit of the temperature range used in commercial technology, viz. 250 °C. The Mo<sub>2</sub>C/Mo catalysts show higher CO removal rates per unit of reactor volume when temperature gradient was applied in a microreactor.

The high-temperature electrochemical synthesis methods are being further developed towards the synthesis of molybdenum carbides on microstructured molybdenum substrates. The application of microstructured substrates with semi-cylindrical microchannels with a diameter of 300 microns will considerably enhance the geometrical area available for coating deposition comparing to that of flat plates.

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## NANOSTRUCTURED CATALYSTS BASED ON MESOPOROUS METAL-SILICATES

**Trusova E.A., Bondarenko G.N., Chalykh A.E.**<sup>1</sup>

*A.V. Topchiev Institute of Petrochemical Synthesis RAS, Moscow, Russia*

<sup>1</sup>*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia*

*E-mail: trusova@ips.ac.ru*

Formation mechanisms of meso- and micro-mesoporous silicates at alkali and acidic catalysis conditions in organic-aqueous medium, genesis of supramolecular architectures in gelation and formation of ultradispersed solid systems, methods of modification of mesoporous surface by catalytically active forms of metals, and testing of generated nanostructured catalysts in any model reactions of hydrocarbons conversion are discussed in report.

Recent years results obtained during the development of synthesis method of nanostructured catalysts based on meso- and micro-mesoporous metal-silicates are summarized in the report. Fundamental aim of the investigation and its scientific novelty are consist in establishing of mechanisms of structures formation of meso- and micro-mesoporous SiO<sub>2</sub> doped by metal ion (Al, Ge, Fe, Ti, Zr), in the synthesis conditions proceeded by wet method, and in determination of catalytic properties dependence of obtained systems from synthesis condition and structure. Method is based on the combined catalytic hydrolysis of silicon and metal derivatives in organic-aqueous medium in the presence of templates at temperatures 80-150°C and autogenic pressure. The group OH<sup>-</sup> or H<sup>+</sup> play a role of catalyzing the formation of polymer organic-inorganic structures.

Urgency of subjects in the petrochemical profile institute caused by rising of requirement in catalysts that are improve efficiency of naphtha processing, need of feed base for obtaining of high-octane gasoline and as consequence improving of transport ecologation. The practical significance of work reported consist in modern technology development for obtaining of new catalysts generation based on meso- and micro-mesoporous silicates containing nanostructured metal nanoparticles in their pores.

Polyfunction is important peculiarity of developing systems based on SiO<sub>2</sub>. On the one hand they are able to be high active low-temperature catalysts of hydrocarbon processing. From the other hand their mesopores play role of the nanoreactor, in which surface catalytically active metals as isolated ions, microcrystals or cluster, oftenly connected with surface via strong interaction like metal-surface, are incorporated.

As-synthesized highly dispersed powders presented the Me-silicates (Me = Al, Ge, Fe, Ti and Zr, ratio Si/Me =3-30) in which silicon ions in meso-(3-14 nm) or micro-mesoporous SiO<sub>2</sub> were isomorphously substituted by Me-ions (FT-IR spectroscopy showed 960-970 cm<sup>-1</sup> band shifted to 1000-1100 cm<sup>-1</sup>). The BET surface area of the powders was 100-200 m<sup>2</sup>/g. We succeeded to synthesize Me-silicates with a big part (up to 100 %) of mesopores (3-10 and 8-14 nm) under moderate temperatures (≤150 °C), atmospheric pressure and mild drying conditions (without supercritical conditions). The characteristic feature of the method applied is approach that used for structure stabilization problem. It allowed preventing structure collapse under thermal treatment at 500 °C for 5 h. In the case of alkaline hydrolysis the influence of initial OH<sup>-</sup>/SiO<sub>2</sub> ratio on the size and texture of titanium-silicates microspheres was established by comparison results of SEM and semi-contact AFM. It was cleared this ratio is one of the main factor of molecule spatial arrangement in supramolecular gel architecture, which remain intact in further formation of powder microstructure. Bulk weight of different sample series was 0.3-0.7 g/cm<sup>3</sup>.

Titanium-silicate with a formula Ti<sub>0.03</sub>Si<sub>0.97</sub>O<sub>2</sub> was synthesized as spherical microgranules with diameter of 30-40 μm, consisting of nanotubes with diameter of 30-40 nm. Mesoporous aluminosilicate with ratio Si/Al = 3 as spherical microgranules with diameter of 20-35 nm connected with each other in chain were synthesized.

The opportunities of method developed are not only directed formation of silicate architecture but the structured nanoparticles formation and coating of Ti- and Al-silicates mesopore surface by I, III and VI-VIII groups metal. It was possible to manage catalytic coating formation in order to obtain

- nanoparticles (0D) inside of mesopores
- uniform 10-15Å thickness coating (2D), which fully follows mesopore surface relief
- catalytic coating, which could increase initial silicate surface area up to 25-30 %

Thus, obtained catalysts were tested in different hydrocarbons conversion reactions, showed high activity, selectivity and moreover unique catalytic properties of nanostructured systems.

The authors thank Prof. S.N. Khadzhiev for helpful discussions.

**INFLUENCE OF MOLECULAR STRUCTURE OF CARBON-SUPPORTS ON  
CATALYTIC PROPERTIES OF COMPLEX CARBON-METAL OXIDE  
CATALYSTS**

**Strelko V.V., Zazhigalov V.A., Zaitsev Yu.P., Brazhyk D.V., Kuts V.S.**

*Institute for Sorption and Problems of Endoecology, NAS of Ukraine, Kyiv, Ukraine*

*E-mail: vstrelko@ispe.kiev.ua*

Active carbons possessed  $\pi$ -conjugated system, which shows the electron-donor ability attract attention as perspective support for catalysts. Introduction of heteroatoms or deposition of metal oxides on carbon surface can lead to essential change of electronic properties of the system and its catalytic activity.

In this communication the influence of the content of O and N heteroatoms in carbon matrix and the dimensions of supported clusters of V, Co, Fe oxides on their catalytic properties in selective oxidation of  $H_2S$  and CO was considered. The prepared catalysts were studied by means of porosimetry, DTA, XRD, XPS and AFM methods. The surface electronic structure of the samples was estimated by semi-empirical quantum chemical method AM1.

It was established that the introduction of oxygen or nitrogen heteroatoms in carbon matrix allows to change catalytic activity of carbon catalysts in hydrogen sulfide oxidation to elemental sulfur. The quantum chemical calculations show that the presence of 4-6 % of oxygen or 2-3 % nitrogen in carbon matrix leads to essential increase of electron-donor ability of carbons. These results well correlate with catalytic properties of the carbons. XPS data show that catalytic activity of these carbons is connected with formation on their surface of oxygen in the form of a superoxide-ion  $O_2^*$ . The prepared modified carbons can oxidize 51-57 mmol  $H_2S$  per g catalyst without their deactivation.

Introduction of metals or metal-oxides on carbon surface leads to redistribution of electron density between carbon matrix and metal atom. The last obtains excess of electron density which can transfers to oxygen atoms. It was shown that the method of metal oxides deposition influences on the size of formed oxide clusters. It was established that catalytic activity of supported on these carbons vanadium-containing catalysts is determined by the dimensions of formed oxide clusters (Fig.). The carbon catalysts with nano-sized vanadia (50-70 nm) demonstrate maximum activity in hydrogen sulfide oxidation (130 mmol  $H_2S/g$  catal.). The increase of the size of vanadia cluster decreases catalytic activity of the sample up to level of carbon-support.

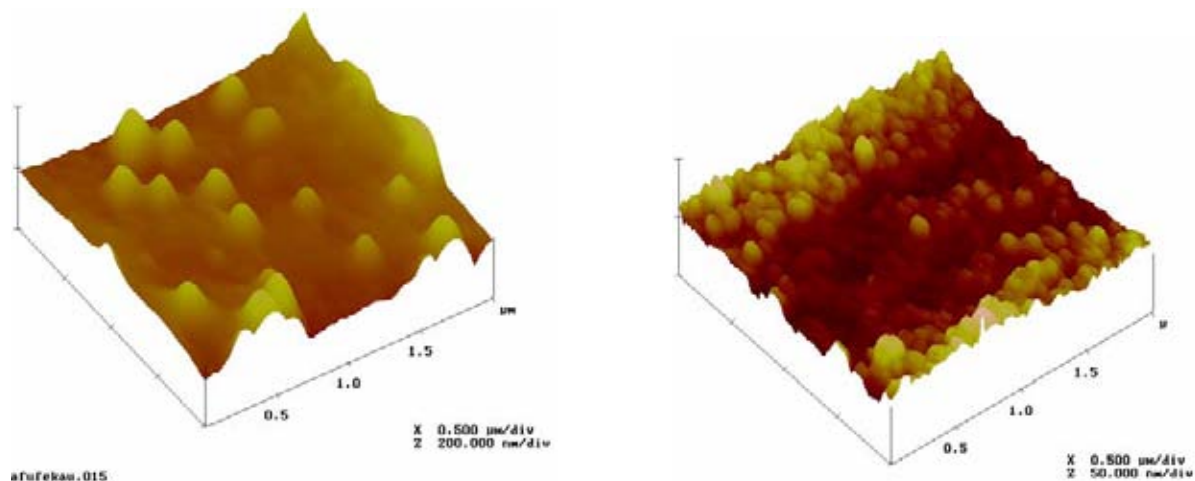


Fig. The surface of MeO<sub>x</sub>/C catalysts (AFM)

Reduction of CoO<sub>x</sub>/C samples increases their activity in CO oxidation. The results of calculation show that in system Co/C essential transfer of electron density on cobalt atoms takes place. The reduced CoO<sub>x</sub>/C catalysts demonstrate high activity and selectivity in CO oxidation in hydrogen excess. Preliminary introduction of nitrogen atoms in carbon matrix increases activity and stability of Co<sub>x</sub>/C catalysts in this reaction, which proceeds below to 100 °C.

**NEW METHODOLOGICAL APPROACHES TO THE ANALYSIS OF THE SIZE  
AND STRUCTURE OF NANOSIZED OBJECTS**

**Tuzikov F.V., Tuzikova N.A., Parmon V.N.**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: tuzikov@catalysis.ru*

Under discussion are new theoretical and methodical approaches to expand potentialities of diffraction methods for analysis of the size and structure of nanoparticles under static conditions and under conditions of multistage equilibrium interactions between macromolecules and complexes. These approaches are used to characterize a variety of dispersed constituents of catalytic systems (in solutions, gels, sols, powders, films etc.), as well as to study mechanisms of multistage complex formation through intermediate complexes at equilibrium stages. New instrumentation methods for measurements and correction of small-angle XRD patterns are developed, as well as effective design for units of a small-angle X-ray diffractometer.

The studies of nanoparticles with molecular weights larger than 1000 Da remain of unflinching interest to catalytic scientists. For this reason, the development of new informative physicochemical methods to study nanoparticles and extension of possibilities of in-depth inspection of their structural features is of importance. Both inorganic and organic active components of catalysts and enzymes are indeed chemically reactive nanostructures.

In the presentation, it is emphasized that the diffraction methods of X-ray, neutron, light etc. small-angle (diffuse) scattering are most suitable and effective for analysis of namely nanoparticles. The wide application of these methods has been as yet restrained due to the gap in effective procedures for identification of the diffraction patterns. New methodological approaches to analysis of small-angle X-ray and light scattering data are described which can be used for studying the size and structure of nanoparticles of very different chemical compositions at different aggregate states. Potentialities of the unique procedures for experimental analysis of nanosize objects, including catalytically active systems, are illustrated by mathematical models and by experimental data on real chemical and biological catalytic systems and processes. The developed methodological approaches are expected to be helpful for studying a variety of supramolecular components of catalytic systems and processes based thereon, as well as for chemical and biological technologies and medicine.

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## HETEROPOLY ACIDS AS CATALYSTS FOR VAPOUR-PHASE HYDROGENATION OF CARBOXYLIC ACIDS

**Benaissa H., Davey P.N.<sup>1</sup>, Kozhevnikov I.V.**

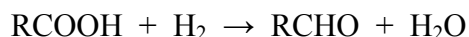
*Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK*

<sup>1</sup>*Quest International, Ashford, Kent, TN24 0LT, UK.*

*E-mail: kozhev@liverpool.ac.uk*

Keggin heteropoly acids (HPAs)  $H_{3+n}[PMo_{12-n}V_nO_{40}]$  ( $n = 0, 1, 2$ ) and their  $Cs^+$  salts are active catalysts for the vapour-phase hydrogenation of propanoic and hexanoic acids to the corresponding aldehydes. It is demonstrated that the hydrogenation activity and selectivity of HPA catalysts depend on their acid and redox properties in a manner that is well established for partial oxidation catalyzed by HPA

Heteropoly acids (HPAs) possess controllable acid and redox properties and are widely used as acid and oxidation catalysts in homogeneous and heterogeneous systems [1, 2]. The Keggin HPAs  $H_{3+n}[PMo_{12-n}V_nO_{40}]$ , where  $n = 0, 1, 2$ , and their Cs salts are well known as catalysts for partial oxidation in the gas phase, e.g. the oxidation of methacrolein to methacrylic acid and oxidative dehydrogenation of isobutyric acid [1]. In this work, these HPAs were studied as catalysts for the vapour-phase hydrogenation of propanoic and hexanoic acids to the corresponding aldehydes. Hydrogenation of carboxylic acids to aldehydes over oxide catalysts has attracted significant interest [3].

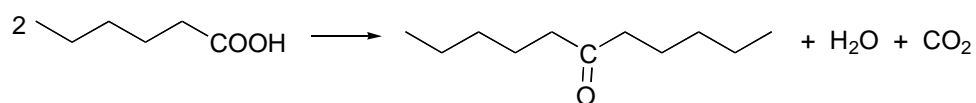


The hydrogenation of acids was carried out in a fixed-bed flow microreactor with on-line GC analysis. The reactor was packed with 0.2 g catalyst (typically a bulk HPA). Prior to reaction, the catalyst was treated in situ in a hydrogen flow, ramping the temperature to 400 °C at a rate of 10 °C/min then dwelling at 400 °C for 2 h. The hydrogenation of acids was carried out at 300-400 °C, 1 bar  $H_2$  pressure, 40-80 mL/min gas flow rate and an acid concentration in the gas flow of 2 vol.%. Usually it took about 1 h for the reaction to reach steady state. During that time the selectivity to aldehydes gradually increased.

It was found that the hydrogenation activity and selectivity of HPA catalysts strongly depend on their acid and redox properties in a manner that is well established for partial oxidation catalyzed by HPA [1, 2]. The acid and redox properties of HPAs can be controlled by varying their composition. Partial substitution of Mo(VI) by V(V) in the  $PMo_{12}O_{40}^{3-}$  anion, enhancing the redox properties of the polyanion [1, 2], was found to improve catalyst activity



and selectivity to aldehydes. Heteropoly acids  $H_{3+n}[PMo_{12-n}V_nO_{40}]$  exhibited high catalytic activities but low selectivities to aldehydes, yielding  $C_3$ - $C_8$  (predominantly  $C_6$ ) hydrocarbons as the main products. The hydrocarbons probably resulted from reduction of carboxylic acids followed by acid-catalyzed cracking and alkylation. Partially substituted  $Cs^+$  heteropoly salts showed high selectivities (up to 80 %) to aldehydes, which indicates that this reaction requires only a moderate acidity of the catalyst. Neutral  $Cs^+$  heteropoly salts,  $Cs_3PMo_{12}O_{40}$ ,  $Cs_4PMo_{11}VO_{40}$  and  $Cs_5PMo_{10}V_2O_{40}$ , gave mainly ketones, 3-pentanone and 6-undecanone from propionic and hexanoic acid respectively. The ketonisation of carboxylic acids over metal oxide catalysts has been observed previously [3, 4].



The HPA catalysts were characterized before and after reaction by XRD, FTIR, TG/DSC and surface area/porosity analysis. Catalyst surface area was found significantly decreased after reaction. From FTIR, the Keggin (primary) structure of catalysts remained intact during the reaction. In contrast, the secondary structure of HPA changed, as XRD showed that initially crystalline catalysts became amorphous after reaction.

The hydrogenation of propanoic acid was found to be zero order in propanoic acid and had an activation energy of 85 kJ/mol (320-380 °C). The reaction rate did not depend on the flow rate at constant GHSV. It is suggested that the reaction occurs in chemical regime via a Mars – van Krevelen mechanism [3].

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**TITANIUM-MAGNESIUM CATALYSTS FOR STEREOSPECIFIC PROPYLENE  
POLYMERIZATION: SYNTHESIS AND MECHANISM OF THEIR ACTION**

**Bukatov G.D., Sergeev S.A., Zakharov V.A.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: bukatov@catalysis.ru*

At moment the polypropylene (PP) production is mainly based on supported Ziegler-Natta, high activity and high stereospecificity of which do not require removing the catalyst residue and atactic polymer from PP produced. At the same time the morphology of catalyst particles is very important peculiarity because it determines the morphology of PP particles due to the “replication” effect at polymerization.

We elaborated the original method of synthesis of titanium-magnesium catalysts (TMC) with the control morphology of catalyst particles. TMC produce PP with high yield (over 20 kg PP/g cat (or over 800 kg PP/g Ti) at 7 bars for 2 h) and high isotacticity (97 – 98 %). Catalysts have a narrow particle size distribution with the averaged particle size controlled in the range from 10 to 100 microns for any polymerization process (slurry, bulk or gas phase).

Effect of propylene prepolymerization with TMC on final PP morphology is studied. The number of active centers and propagation rate constant for stereospecific and non-stereospecific sites are determined. The chain transfer rate constants and the contribution of different chain transfer reactions at slurry and bulk polymerization are determined too.

TMC performance is similar (activity, stereospecificity) or higher (morphology of particles: no fines, higher density, etc.) compared to that for the best commercial PP catalysts.

## HOMOGENEOUS AND SUPPORTED CATALYSTS BASED ON IRON, COBALT, VANADIUM AND CHROMIUM BIS(IMINO)PYRIDYL COMPLEXES

**Semikolenova N.V., Zakharov V.A., Echevskaya L.G., Matsko M.A.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: nvsemiko@catalysis.nsk.su*

Data about catalytic activity at ethylene polymerization of homogeneous catalysts formed by interaction of bis(imino)pyridyl complexes with close ligand framework and different transition metal center ( Fe, Co, Cr, V) with MAO and  $AlR_3$  co-catalysts and the molecular structure ( MM and MWD) of the obtained polymers are reported. Catalytic properties of the supported catalysts, prepared by anchoring of bis(imino)pyridyl complexes on the oxide supports (  $SiO_2$ ,  $Al_2O_3$ ) and data on the PE structure were compared with that of correspondent homogeneous catalysts.

New catalytic systems based on tridentate bis(imino)pyridyl complexes of transition metals of the VIII group (late transition metal catalysts) proved to be highly active catalysts for ethylene polymerization [1-5]. Catalysts of these type are of growing scientific and industrial attention now and the supported catalysts, where bis(imino)pyridyl complexes are anchored on the surface of a solid carrier, is the point of extreme interest [6, 7].

In the present work the ethylene polymerization with homogeneous catalysts based on a series of bis(imino)pyridyl complexes with close ligand framework and different metal center (Fe, Co, Cr, V): 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridineiron (II) and cobalt (II) chlorides (2,6-Me<sub>2</sub>-LMCl<sub>2</sub>, M=Fe, Co), 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine vanadium (III) chloride (2,6-Et<sub>2</sub>-LVCl<sub>3</sub>) and 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine chromium (III) chloride (2,4,6-Me<sub>3</sub>-LCrCl<sub>3</sub>) were studied. Data about catalytic activity of the systems, formed by interaction of bis(imino)pyridyl complexes with MAO and  $AlR_3$  co-catalysts, and the molecular structure ( MM and MWD) of the obtained polymers are reported.

When activated in the appropriate conditions ( activator nature, activator/complex molar ratio, concentration), bis(imino)pyridyl complexes exhibited high initial activity at ethylene polymerization that rapidly falls down. The rate of deactivation depended on the activator nature and complex composition. The catalysts based on vanadium and chromium complexes were active at high polymerization temperatures (60-70 °C), whereas the active species formed in the systems with bis(imino)pyridyl complexes of iron and cobalt were noticeably less thermally stable and were almost inactive at temperature higher 40 °C.

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All investigated catalytic systems produced highly linear polyethylene (PE), but MM and MMD values substantially depend on the transition metal. PE samples obtained with 2,6-Me<sub>2</sub>-LCoCl<sub>2</sub> and 2,4,6-Me<sub>3</sub>-LCrCl<sub>3</sub> complexes were characterized by low MM ( $M_w=1.5-2\times 10^3$ ) and narrow MMD ( $M_w/M_n = 1.8-2$ ), evidencing that only one type of active centers is formed in these catalytic systems and they can be considered as single-site catalysts.

In presence of the catalysts based on 2,6-Et<sub>2</sub>-LVCl<sub>3</sub> activated with MAO, polymers with higher MM and broader MMD than that in case of cobalt and chromium complexes, were obtained ( $M_w=8-12\times 10^3$ ,  $M_w/M_n =3-5$ ). PEs with relatively high MM ( $M_w=50-140\times 10^3$ ) and broad MMD ( $M_w/M_n = 5-10$ ) were produced by (2,6-Me<sub>2</sub>-LFeCl<sub>2</sub>) with MAO, AlMe<sub>3</sub>, Al(i-Bu)<sub>3</sub> as activators. Thus, a set of active centers with different reactivity are formed in the catalysts based on bis(imino)pyridyl iron and vanadium complexes.

By anchoring of bis(imino)pyridyl complexes on the oxide supports ( SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) the correspondent supported catalysts were prepared. Catalytic properties of the supported catalysts at the ethylene polymerization in presence of Al(i-Bu)<sub>3</sub> as activator and data on the PE structure were compared with that of correspondent homogeneous catalysts.

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**Fe(III), Ti(IV), Zr(IV)-CATALYZED ASYMMETRIC OXIDATIONS OF THIOETHERS AND PRODUCT SEPARATION VIA ENANTIOSELECTIVE SORPTION ON CHIRAL METAL-ORGANIC FRAMEWORKS**

**Bryliakov K.P., Nuzhdin A.L., Talsi E.P.**

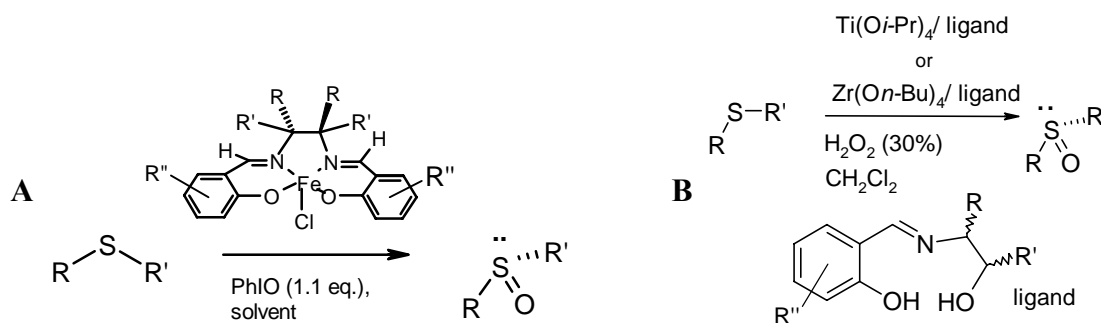
*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: bryliako@catalysis.ru*

New homogeneous catalytic systems for asymmetric oxidation of sulfides to sulfoxides with high chemoselectivity and moderate-to-high *ees* based on iron(III), titanium(IV) and zirconium(IV) complexes with chiral Schiff bases are presented, and the mechanisms of their catalytic action are discussed. The resulting enantiomeric sulfoxides can be separated by enantioselective column chromatography using new chiral Zn-organic frameworks as chiral stationary phases.

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. The need in new cheap, effective and environmentally benign catalytic systems encourages the search for replacements of the classical Kagan-Modena systems (based on  $\text{Ti}(\text{O}i\text{-Pr})_4/\text{diethyl tartrate}$  combinations) which suffer from low turnover numbers, low chemoselectivity and the need in expensive alkylhydroperoxides as oxidants. Besides, elaboration of new effective techniques for isolation of single enantiomers from enantiomeric mixtures is also a task of high importance.

In this work, we present a series of iron(III)-Schiff base complexes (Scheme, A), titanium(IV)- and zirconium(IV)-Schiff base complexes (Scheme, B) capable of stereoselective oxidation of alkyl aryl sulfides. The reaction mechanisms are discussed.



It has been found that homochiral porous Zn-organic frameworks, like  $\{[\text{Zn}_2(\text{bdc})(L\text{-lac})(\text{dmf})]\cdot\text{dmf}\cdot\text{H}_2\text{O}\}_n$  (*bdc* = *p*-benzenedicarboxylate, *L-lac* = *L*-lactate), are capable of size- and enantioselective sorption of alkyl aryl sulfoxides. In this work, we

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present the use of such MOFs as chiral stationary phases for enantioselective chromatographic separation of sulfoxides.

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**APPLICATION OF THE WEAKLY NUCLEOPHILIC POLYFLUORINATED  
ORGANOBORON COMPOUNDS FOR THE PALLADIUM - CATALYZED  
CROSS-COUPLING REACTIONS**

**Adonin N.Yu., Bardin V.V.<sup>1</sup>, Frohn Hermann-Josef<sup>2</sup>**

*Borshchov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>1</sup>*N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS, Novosibirsk, Russia*

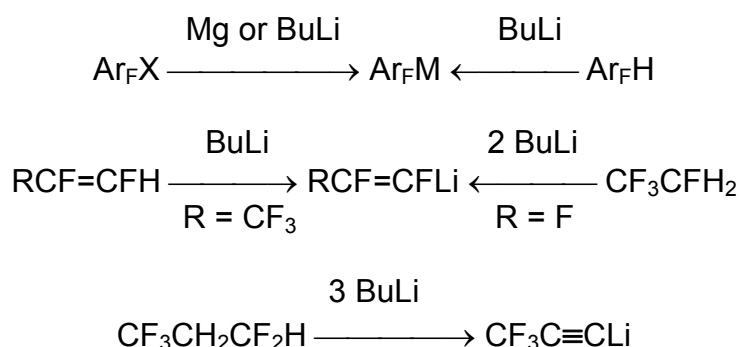
<sup>2</sup>*University of Duisburg-Essen, Duisburg, Germany*

*E-mail: nic-adonin@yandex.ru*

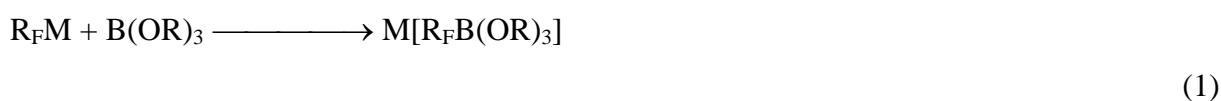
The recent achievements in the synthesis of polyfluoroorganoboron compounds and their application for the palladium - catalyzed cross-coupling reactions are presented.

### 1. Synthesis of polyfluoroorganoboron compound

The key polyfluoroorganoborates,  $M[R_F B(OR)_3]$ , were prepared by the nucleophilic addition of polyfluorinated organometallics (Scheme 1) to trialkoxyborates (eq. 1).



*Scheme 1*



$\text{R}_F = \text{Ar}_F, \text{RCF}=\text{CF}, \text{CF}_3\text{C}\equiv\text{C}$

The fluorinated organotrialkoxyborates can be easily transformed into the corresponding organoboronic acids as well as to potassium organotrifluoroborates (Scheme 2).

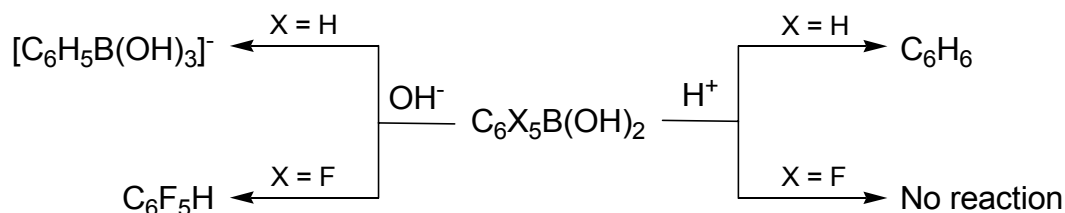


*Scheme 2*

### 2. Principal distinguishes of fluorinated organoborates from their non-fluorinated analogs

Some principal distinguishes are shown in the scheme 3.

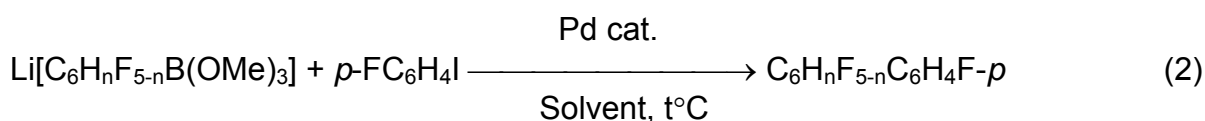
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Scheme 3

### 3. Cross-coupling reactions with polyfluoroorgano(trialkoxy)borates

A number of fluorinated biphenyls were obtained by the Pd-catalyzed cross-coupling reaction of lithium polyfluorophenyltrimethoxyborates with p-fluoroiodobenzene in moderate yield. The influence of the nature of Pd catalyst as well as promoting additives on the yield of desired products were studied.

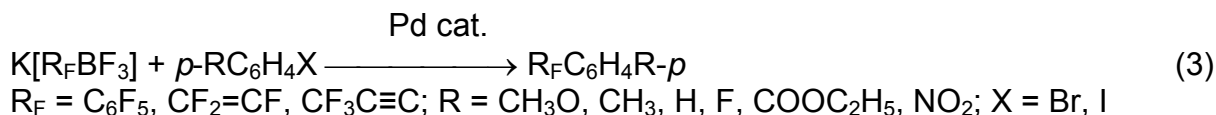


$n = 0-3$

### 4. Cross-coupling reactions with potassium polyfluoroorganotrifluoroborates

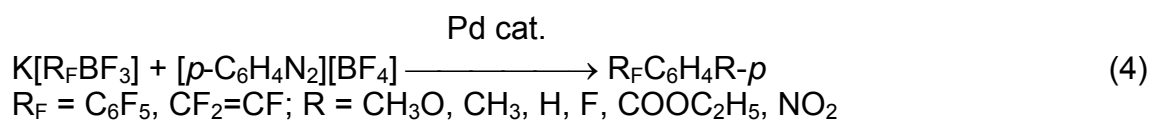
a) with aryl iodides

In the case of aryl iodides and bromides the cross-coupling products were obtained in high yields



b) with arenediazonium tetrafluoroborates

Arenediazonium tetrafluoroborates react with potassium polyfluorophenyl- and trifluorovinyltrifluoroborates giving the corresponding cross-coupling products in moderate yields.



The mechanistic aspects of the tremendous specificity of polyfluorinated organoborates in cross-coupling reaction relative to their hydrocarbon analogues are discussed.



## RHODIUM CATALYZED HYDROFORMYLATION OF MONOTERPENES

**Gusevskaya E., Barros H., da Silva J., dos Santos E.**

*Departamento de Química, Universidade Federal de Minas Gerais, Belo Horizonte*

*31270-901, MG, Brasil*

*E-mail: elena@ufmg.br*

Rhodium catalyzed hydroformylation of various monoterpenes, such as  $\beta$ - and  $\alpha$ -pinenes, 2- and 3-carenes, myrcene, linalool, etc., as well as isoprene (as a model molecule) will be discussed in the present communication. A special attention will be given to the design of efficient homogeneous and biphasic catalytic systems by tuning the nature of auxiliary phosphorous ligands. A good control of chemo-, regio- and diastereoselectivity has been achieved through the appropriate choice of the ligand and adjusting the reaction variables.

Rhodium catalyzed hydroformylation represents a versatile and one of the least expensive synthetic pathways to aldehydes. Diversification of substrates by using special olefins can afford aldehydes bearing additional functional groups and other oxygen containing molecules hardly accessible by conventional methods. These hydroformylation products can be used as bi- or poly-functionalized building blocks for organic syntheses thus opening new entries to many valuable compounds. The hydroformylation of monoterpenes is an important route to add value to these olefins easily available from biomass. A number of their functionalized derivatives have olfactory and biological activity and can be interesting for the pharmaceutical and fragrance industries. In recent years, we have been systematically studying the hydroformylation of various monoterpenes, including functionalized ones [1-5]. These substrates may contain one, two or even three different olefinic functionalities: exocyclic, endocyclic, conjugated, allylic substituted, terminal or/and internal, etc.; thus the development of fast and selective processes of their hydroformylation is a quite challenging task. In the present communication, we will review our new and recently published results in this field. A special attention will be given to the design of efficient homogeneous and biphasic catalytic systems by tuning the nature of auxiliary ligands (monophosphines, diphosphines, phosphites). We have achieved a good control of the chemo-, regio- and, usually, diastereoselectivity through the appropriate choice of the ligand and adjusting the reaction variables. The hydroformylation of such monoterpenes as  $\beta$ - and  $\alpha$ -pinenes, 2- and 3-carenes, myrcene, linalool, camphene, etc., as well as isoprene (as a model molecule) will be discussed. In particular, the hydroformylation of isoprene as well as myrcene (both

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containing conjugated olefinic bonds) has showed unusual kinetics and other remarkable trends, opposite to those usually observed with simple olefins: the reactions are strongly accelerated by the increase in the ligand concentration and/ or ligand basicity. These findings allowed us to develop efficient processes occurring under mild conditions (80-100°C, 40-80 atm) using rhodium catalysts promoted by triphenylphosphine, the most accessible, low cost and stable phosphorous ligand employed in hydroformylation.

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**TITANIUM- AND ZIRCONIUM-MONOSUBSTITUTED POLYOXOMETALATES  
AS ‘SINGLE-SITE’ MODELS FOR STUDYING OXIDATION MECHANISMS**

**Kholdeeva O.A., Maksimovskaya R.I., Trubitsina T.A., Maksimov G.M., Poblet J.M.<sup>1</sup>**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>1</sup>*Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, 43005 Tarragona,  
Spain*

*E-mail: khold@catalysis.nsk.su*

Recent developments in the application of Ti- and Zr-monosubstituted Keggin-type polyoxometalates (Ti- and Zr-POMs) as molecular models for studying mechanisms of H<sub>2</sub>O<sub>2</sub>-based selective oxidation catalysis are reviewed. The similarity in the spectroscopic and catalytic behavior of Ti- and Zr-POMs and heterogeneous Ti(IV) and Zr(IV) single-site catalysts is demonstrated. The progress on the synthesis of Ti- and Zr-POMs, studying their interaction with H<sub>2</sub>O<sub>2</sub>, and characterization of the peroxo species formed are surveyed, with special emphasis being placed on the role of protons in the activation of the peroxo groups.

Mechanistic and structure/activity studies based on model systems are becoming increasingly important in the catalyst designing area. POM units can function as inorganic multidentate, hydrolytically and oxidatively resistant ligands for redox-active ions. This provides advantages of POM-based model systems for studying regularities governing the reactivity of heterogeneous ‘single-site’ catalysts compared to model systems based on complexes with organic or organometallic ligands, which are prone to oxidative and/or hydrolytic degradation [1, 2].

Titanium and zirconium ‘single-site’ catalysts are among the most efficient ones for the selective oxidation of organic compounds with aqueous H<sub>2</sub>O<sub>2</sub>. Ti-POMs, containing Ti(IV) isolated in inorganic matrix, [Bu<sub>4</sub>N]<sub>7</sub>[(PTiW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>OH] (**1**), [Bu<sub>4</sub>N]<sub>8</sub>[(PTiW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>O] (**2**), [Bu<sub>4</sub>N]<sub>4</sub>[PTi(OH)W<sub>11</sub>O<sub>39</sub>] (**3**), [Bu<sub>4</sub>N]<sub>4</sub>[PTi(OMe)W<sub>11</sub>O<sub>39</sub>] (**4**), [Bu<sub>4</sub>N]<sub>4</sub>[PTi(OAr)W<sub>11</sub>O<sub>39</sub>] (**5**), and [Bu<sub>4</sub>N]<sub>5</sub>[PTi(O)W<sub>11</sub>O<sub>39</sub>] (**6**) have been prepared and comprehensively characterized [3,4]. The reactivity of different Ti–L bonds, including Ti–OH, Ti=O, Ti–OMe, and Ti–O–Ti, towards H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> and ArOH has been assessed. A two-step mechanism of the reaction of Ti-POMs with H<sub>2</sub>O<sub>2</sub>, which involves hydrolysis of the Ti–L bonds to yield **3** followed by fast interaction of **3** with H<sub>2</sub>O<sub>2</sub> producing the monoprotinated titanium peroxo complex [Bu<sub>4</sub>N]<sub>4</sub>[HPTi(O<sub>2</sub>)W<sub>11</sub>O<sub>39</sub>] (**I**), has been suggested. Peroxo complex **I** has been first isolated and characterized using both experimental and computational techniques. A compilation of UV-vis, IR, RR, <sup>31</sup>P and <sup>183</sup>W NMR, cyclic voltammetry, potentiometric titration and

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elemental analysis data supported a monomeric Keggin structure of **I** bearing one peroxy ligand in a  $\eta^2$ -coordination fashion [3]. The RR deuterium labeling experiments and DFT calculations revealed that in solid state the activating proton is localized at Ti–O–W bridging oxygen rather than at the peroxy group; however, both Ti–OH–W and TiOO–H protonated species could coexist in solution. Peroxy complex **I** reacts with organic substrates via homolytic, most likely, electron-transfer mechanisms. The oxidation mechanism becomes heterolytic when the amount of protons in the peroxy complex increases from 1 to 2 [5]. In sharp contrast to **I** and **II**, the unprotonated peroxy complex  $[\text{Bu}_4\text{N}]_5[\text{PTi}(\text{O}_2)\text{W}_{11}\text{O}_{39}]$  is inert toward organic substrates.

The previously unknown dimeric Zr-POMs,  $(n\text{-Bu}_4\text{N})_7\text{H}[\{\text{PW}_{11}\text{O}_{39}\text{Zr}(\mu\text{-OH})\}_2]$  (**7**),  $(n\text{-Bu}_4\text{N})_8[\{\text{PW}_{11}\text{O}_{39}\text{Zr}(\mu\text{-OH})\}_2]$  (**8**), and  $(n\text{-Bu}_4\text{N})_9[\{\text{PW}_{11}\text{O}_{39}\text{Zr}\}_2(\mu\text{-OH})(\mu\text{-O})]$  (**9**), differing in their protonation state have been prepared, and their structure has been established by elemental analysis, potentiometric titration, X-ray single crystal structure, IR, Raman,  $^{31}\text{P}$  and  $^{183}\text{W}$  NMR spectroscopy [6]. The DFT calculations proposed that protonation at Zr–O–Zr bridging site is more favorable than protonation at Zr–O–W sites and that the doubly-bridged hydroxo structure is thermodynamically more stable than singly-bridged oxo structure, in marked contrast with analogous Ti-POM. The model study based on Zr-POMs has demonstrated that the presence of acid protons is also crucial for the activity of zirconium single-site catalysts, but in contrast to titanium, only homolytic oxidation mechanisms may operate with Zr.

The POM-based model studies allowed us to explain a number of phenomena observed for heterogeneous Ti- and Zr-catalyzed oxidations and to predict catalytic behavior of the corresponding single-site catalysts.

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## NATURE OF ACTIVE SITES OF H-BETA ZEOLITES IN THE FRIES REARRANGEMENT OF PHENYL ACETATE

Adryan P., Roessner F., Ismail R.<sup>1</sup>

*Industrial Chemistry 2, Carl von Ossietzky University, 26111 Oldenburg, Germany*

<sup>1</sup>*Woman's Research & Training Center, University of Aden, Khormaksar, P.O. Box, 6312, Yemen*

*E-mail: frank.roessner@uni-oldenburg.de*

The Fries rearrangement of phenyl acetate was used to study the nature of the involved acidic sites. By re-exchanging H-beta zeolite with monovalent cations a straight decline in activity in dependence on the cation content was found indicating on the dominating role of Brönsted acidic sites as well as on their catalytic uniformity. The unusual behaviour of bivalent cations was explained in terms of cation-oxo-species.

### Introduction

The application of heterogeneous catalysts in liquid phase reactions becomes more and more important. However, the separation of different structural parameters influencing the catalytic activity is not so intensively studied as for gas phase reactions. Therefore, the Fries rearrangement of phenyl acetate, an established reaction for the formation of hydroxyacetophenones, was used as test reaction. Typically, the reaction is performed on H-beta zeolites. Even though this reaction is well understood, there are controversial discussions about the nature of the catalytic active centers. Although the bridging Si-OH-Al groups are supposed to have dominating influence on the conversion of phenyl acetate, their role in the reaction is not experimentally determined. If they are indeed involved in the reaction then there should be a linear correlation between their number and the observed catalytic activity.

The aim of this work was to study the influence of the degree of cation re-exchange on the conversion. A special emphasis was placed on valency of the extra-framework cation.

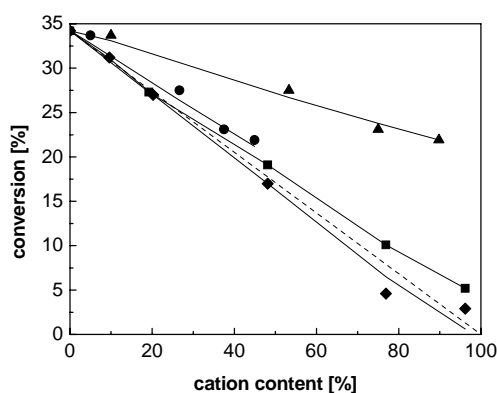
H-beta zeolite (Si/Al=25) was re-exchanged by Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> cations via solid state reaction. The liquid phase Fries rearrangement was carried out in a soxhlet-based reaction set-up with 2 g of catalyst and 0.35 mol phenyl acetate without any solvent. The acidic properties were studied by desorption of ammonia.

### Results and Discussion

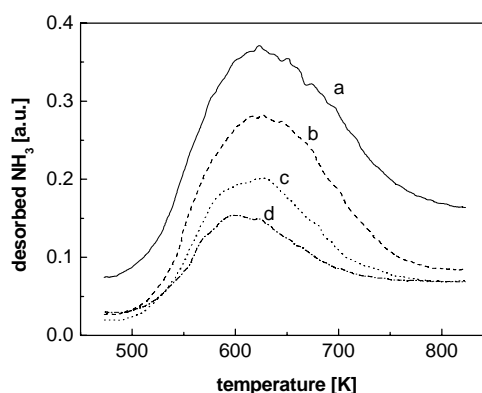
Beside phenol *p*-acetoxyacetophenone, *o*- and *p*-hydroxyacetophenones were formed as main products. After 90 min the increase of conversion was drastically retarded by product inhibition as shown previously. Therefore, the conversion after six hours was used to compare

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the activity of H-beta zeolites re-exchanged with sodium, potassium and calcium cations (Figure 1). The conversion decreases linearly with decrease of proton content. For the sodium and potassium ion exchanged zeolites the decline of conversion follows the theoretical value corresponding to the number of remaining protonic centers in the zeolite (dotted line). In case of H-beta zeolites re-exchanged with calcium ions the obtained conversions are higher than expected, if it is assumed that one bivalent calcium ion replaces two protons. However, when a 1:1 stoichiometry is assumed the results fit to the theoretically expected values. Therefore, a question about the compensation of the excess charge arises. The discussion in terms of condensation of hydroxocations, as observed for Y zeolites, accompanied with the formation of bridged calcium-oxygen-species seems to be a suitable explanation.



**Fig. 1.** Influence of the exchange degree on the conversion (♦ Na<sup>+</sup>, ■ K<sup>+</sup>, ▲ Ca<sup>2+</sup> (M<sup>II</sup>), ● Ca<sup>2+</sup> (M<sup>I</sup>)).



**Fig. 2.** NH<sub>3</sub>-TPD spectra of modified beta zeolites (a: 0 % K<sup>+</sup>, b: 19 % K<sup>+</sup>, c: 48 % K<sup>+</sup>, d: 77 % K<sup>+</sup>).

The modified catalysts were further characterized by XRF, FTIR and NH<sub>3</sub>-TPD. In Figure 2 NH<sub>3</sub>-TPD spectra are given for zeolites H- and KH-beta with different re-exchange degree. It can be seen that the amount of desorbed NH<sub>3</sub>, corresponding to the number of acidic centers, is decreasing with increasing proton content. Therefore it can be concluded that entirely Brønsted acid centers, which have an equal specific catalytic activity, are involved in the reaction. No influence of Lewis acid sites (*e.g.* cations or extra-framework species) was detected.

**BIFUNCTIONAL HOMOGENEOUS CATALYSTS FOR ORGANIC COMPOUNDS  
OXIDATION IN TWO-PHASE SOLUTIONS**

**Pai Z.P., Tuzikov F.V., Kochubei D.I., Berdnikova P.V., Tuzikova N.A., Kustova G.N.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: zpai@catalysis.ru*

Oxidative catalysis is a field of chemistry where transition metal complexes have found a wide utility. The use of the catalytic properties of metal complexes is of particular importance in the performance of liquid-phase reactions in two-phase solutions.

It is of common knowledge that peroxopolyoxotungstates (PPOT) formed in systems  $\text{H}_2\text{O}_2 - \text{H}_3\text{PO}_4 - \text{Na}_2\text{WO}_4$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40} - \text{H}_2\text{O}_2$  [1] are usually used for oxidation of various organic substrates (such as olefins, alcohols, aromatic hydrocarbons) by hydrogen peroxide. *In situ* catalyst synthesis results in the formation of a mixture of  $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ ,  $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$  and  $\{\text{HPO}_4[\text{WO}(\text{O}_2)_2]_2\}^{2-}$ . Note that  $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$  (tetra(oxodiperoxotungsto)phosphate) exhibits the highest catalytic activity. We synthesized and characterized a number of catalysts based on the above efficient anion and quaternary ammonium salts (QAS) activyl as phase-transfer catalysts. The application of such catalytic systems permits one to develop new efficient synthesis methods of valuable aliphatic and aromatic epoxides as well as mono -, di - and polycarboxylic acids by direct oxidation of different organic substrates with hydrogen peroxide.

Catalytic systems were synthesized using the Keggin-type tungstophosphorus heteropoly acid (of the 12<sup>th</sup> order) and QAS containing different anions as fluoride, chloride or bromide.

Raman and IR spectroscopy studies showed that spectra of the fluoride and chloride QAS complexes correspond to anion  $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ . For bromide QAS, a Br ion provides destruction of the peroxo complexes and IR spectra do not contain absorption bands typical of peroxo groups. However, if a Br ion is introduced into the reaction mixture as QAS during *in situ* formation of catalytic complexes in the oxidation reactions, the rate of oxidation holds rather high. This is probably associated with the fact that hypobromite HOBr, formed in the reaction mixture due to oxidation of a bromide ion by  $\text{H}_2\text{O}_2$ , can act as an active oxidizer. This suggestion agrees with the conclusions made elsewhere [2].

The PPOT based catalytic systems were characterized by the low-angle X-ray scattering method in solutions. It was shown that the catalyst samples are formed by assemblies of

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particles (electron density non-uniformities). Moreover, peroxocomplex samples synthesized with use of  $[(n\text{-Bu})_4\text{N}]^+$  cation approximates to a monodispersed complex, and with use of  $[\text{Me}(n\text{-C}_8\text{H}_{17})_3\text{N}]$ -cation the product representing a binary mixture of two fractions is formed. The observed differences are most probably associated with different natures of the used QAS.

The prepared peroxopolyoxotungstophosphate catalysts were studied by structural analysis using the EXAFS method permitting exploration of the neighboring atom surrounding upon treatment of the fine structure of the X-ray absorption spectra of these atoms in the substance. Spectra were taken on a VEPP-3 electron storage ring (EXAFS spectroscopy station of the Siberian Synchrotron Radiation Center) with the electron energy 2 GeV and the current 90 mA, which operated in the "fluorescence" mode.

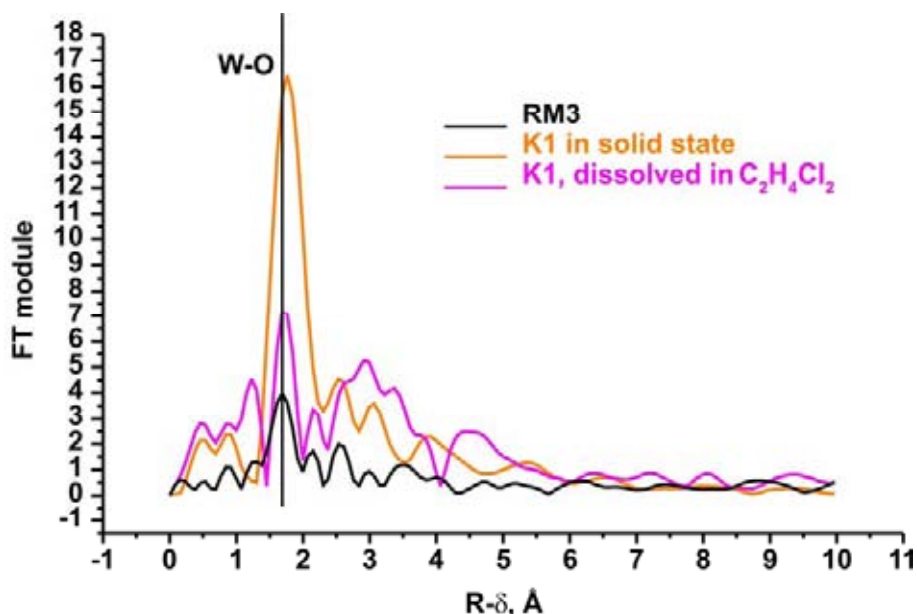


Fig. 1. Curves of radial atom distribution for the reaction mixture of oxidation of cyclohexene and PPOT based catalysts:

*Sample RM3: Organic phase of a reaction mixture ( $\text{C}_2\text{H}_4\text{Cl}_2$ ,  $\text{C}_6\text{H}_{10}$ ,  $\text{H}_2\text{O}_2$ ,  $[(n\text{-Bu})_4\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$  after 60 minutes of reaction)*

*Sample K1:  $[(n\text{-Bu})_4\text{N}]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$*

Data on the structural analysis obtained by EXAFS spectroscopy suggest that structures of tungstophosphate peroxopolyoxo complexes do not undergo transformation or destruction under conditions of oxidation of cyclohexene by hydrogen peroxide. Data on the IR, low-angle X-ray scattering and EXAFS study of the particular organometallic catalysts can serve as a basis for advanced planning of research activities aimed at elucidating of molecular mechanisms of interaction between catalyst nano particles and substrates in oxidation reactions.



Thus, the bifunctional homogeneous catalysts exhibited high efficiency in the oxidation of organics by hydrogen peroxide in the two-phase solutions (organic phase – aqueous phase). The reaction predominantly proceeds in the organic phase. Peroxopolyoxotungstate complexes containing an organic cation are very soluble in the organic phase and act as active transport agents of oxygen to a substrate. Regeneration of these complexes proceeds on the interphase during interaction with hydrogen peroxide. An increase in the interfacial area is obtained by vigorous mixing of the two-phase system in the “catalytic duck” type reactor.

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**HOMOGENEOUS CATALYTIC SYSTEMS FOR DIRECT OXIDATION OF SATURATED HYDROCARBONS: DESIGN AND MECHANISTIC SCENARIO**

**Chepaikin E.G., Bezruchenko A.P., Menchikova G.N., Moiseeva N.I.<sup>1</sup>, Gekhman A.E.<sup>1</sup>,  
Moiseev I.I.<sup>1</sup>**

*Institute of Structural Macrokinetic and Materials Science RAS, Chernogolovka, Russia*

*<sup>1</sup>N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, Russia*

*E-mail: grig@ism.ac.ru, echep@ism.ac.ru*

The use of homogeneous catalytic systems is the most prospective way for natural gas processing. The catalytic systems composed of  $\text{RhCl}_3$  and copper or iron compounds as cocatalysts were designed. By analogy with biocatalysts action  $\text{CO}$ ,  $\text{H}_2$  or their mixture was added as the reducing agents for dioxygen activation. C – C bonds activation occurs in  $\text{C}_2$  –  $\text{C}_4$  hydrocarbons and products with a lesser number in carbon atoms than in the initial hydrocarbons are formed. Based on the kinetic data and the results of isotopic investigation ( $\text{CD}_4$ ,  $^{18}\text{O}_2$ ,  $\text{H}_2\text{O}$ ) mechanistic scenario was proposed.

The conventional methods for the use of natural gas in the chemical and petrochemical industry are multi-stage, power-consuming and raw material intensive. Natural gas resources, taking into account hydrate resources on a bottom of the great oceans, are large yet but not unlimited. In this connection a development of the qualified methods for natural gas processing are of the great scientific and industrial interest.

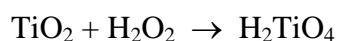
We designed the homogeneous complex metal systems for the catalytic oxidation of saturated hydrocarbons by dioxygen. Activation of saturated hydrocarbons was carried out with rhodium complexes. Copper or iron compounds were used as cocatalysts for dioxygen activation. These compounds, in the low oxidation level, interact with dioxygen under certain condition to form hydrogen peroxide so facilitated a cleavage of the first bond in dioxygen. By analogy with biocatalysts action a reducing agent should be added to the system [1]. For the systems designed the appropriate reducing agents are carbon monoxide, hydrogen, and their mixture which return an oxidized form of the cocatalyst to a reduced one under catalysis by rhodium compounds. In certain interval one can operate the process selectivity by means of the conditions variation.

In aqueous trifluoroacetic acid the catalytic systems allow transform methane to methanol, methyl trifluoroacetate, formic acid, and, in the presence of carbon monoxide, into acetic acid. The initial activity of the systems was  $100 \div 150$  mol  $\text{CH}_4$ /mol Rh·hour in the closed volume under  $95^\circ\text{C}$  and pressure (MPa)  $\text{CH}_4$  (6.0),  $\text{O}_2$  (0.56),  $\text{CO}$  (0.5  $\div$  2.5). Some

kinetic regularities of the process were studied. The use of trifluoroacetic acid as co-solvent is a good way for protection of alcohol, which is generated in this reaction, against further oxidation owing to esters generation [2]. At the same time alkyl trifluoroacetates are easily hydrolyzed.

Ethane and propane were oxidized both in C – H and C – C bonds. Butane and isobutane were oxidized mainly in C – C bonds. In such a way the products with a lesser number of carbon atoms than in initial hydrocarbons are formed. All the products were identified.

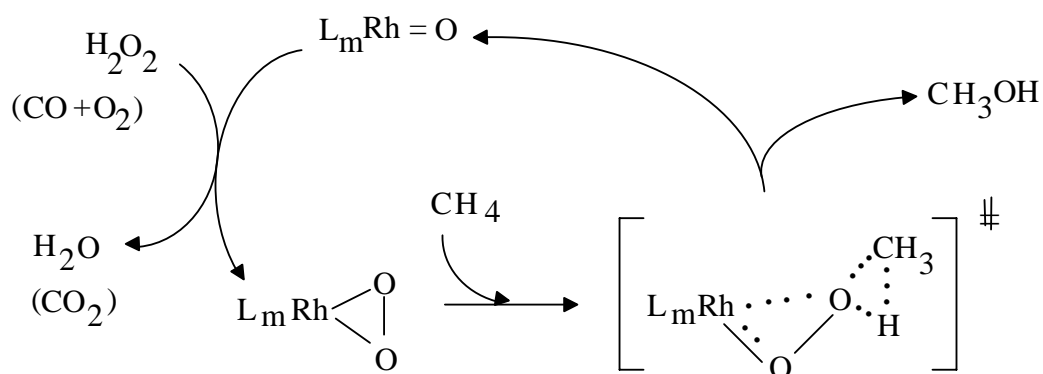
Participation of hydrogen peroxide or its equivalents as the intermediate active oxidants were proved by the following data. Under conditions of hydrocarbon oxidation metallic titanium was oxidized in the presence of the catalytic systems. At first protective oxide film was destroyed according to reaction:



Furthermore, 2,2'-dimethylbutane oxidation by rhodium – copper – chloride catalytic system in the presence of dioxygen and carbon monoxide, and the same reaction catalyzed by  $\text{RhCl}_3$  in the presence of hydrogen peroxide (gradually added), resulted in the same products.

It was found the kinetic isotopic effect  $k_{\text{CH}_4}/k_{\text{CD}_4}$  to be  $4 \pm 0.15$ . With the use of the compounds labelled  $^{18}\text{O}$  (dioxygen, water, and trifluoroacetic acid) oxygen was shown to insert into oxygenates mainly from dioxygen.

The possible mechanisms for the reaction were considered. We concluded that the mechanism with peroxocomplex participation is the most likely one.



The work was supported by the Russian Foundation for Basic Research (grant # 02-03-33153 and 05-03-32489)

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**THE CREATION OF EFFECTIVE VPO CATALYSTS FOR  $n\text{-C}_5\text{H}_{12}$  SELECTIVE OXIDATION TO ANHYDRIDES (PHTHALIC, MALEIC, CITRACONIC) ON THE BASE OF PROCESS MECHANISM CONCEPTION**

**Cheburakova E.V., Zazhigalov V.A.**

*Institute for Sorption and Problems of Endoecology, National Academy of Sciences of  
Ukrainian, Kiev, Ukraine  
E-mail: VPO@ispe ldc.net*

The preparation of the catalysts for selective oxidation of hydrocarbons with preferential formation only one of the partial oxidation products is interesting and important problem of development of the catalysis. A solution of this problem can be realized on the base of conception of the process mechanism that permits to substitute a casual selection of catalysts by the purposeful synthesis of catalysts with determined physicochemical properties.

One of interesting objects for such investigation is the reaction of  $n\text{-C}_5\text{H}_{12}$  partial oxidation on vanadium-phosphorus catalysts (VPO) which leads to the formation of three important products: phthalic (PhA), maleic (MA) and citraconic (CA) anhydrides. Recently we proposed the scheme of the  $n\text{-C}_5\text{H}_{12}$  oxidation mechanism. In accordance to this scheme an abstraction of the methyl group from  $n\text{-C}_5\text{H}_{12}$  molecule leads to formation of unsaturated  $\text{C}_4$ -hydrocarbons which oxidized consecutively in MA. The PhA formation is connected with Diels-Alder reaction between MA and intermediate  $\text{C}_4$ -olefins and low stationary concentration of the lasts limits this process. Primary isomerization of  $n\text{-C}_5\text{H}_{12}$  leads to the formation of  $i\text{-C}_5\text{H}_{12}$  and its oxidation to CA.

The investigation of the VPO catalysts properties with a various content of dopants (Bi, Zr, La, Fe, Ti, W, Mo, Te), which differ by acidic properties permits to confirm the consequences from proposed mechanism. It was shown that the selectivity to CA increased simultaneously with a growth of total acidity of the catalysts surface. A change of the Brönsted and Lewis acid centers ratio regulates the selectivity to MA and PhA. The increase of the catalysts Lewis acidity permits to stabilize intermediate unsaturated  $\text{C}_4$ -compounds on the catalyst surface and this leads to rise of the PhA selectivity. Naturally, because MA participates in PhA formation the selectivity to MA decreases. The increase of the MA selectivity observes at augmentation of the Brönsted acidity of catalysts surface.

Thus the proposed scheme of  $n\text{-C}_5\text{H}_{12}$  oxidation and obtained results determine the pathways which permit to regulate the catalytic properties of VPO catalysts in reaction of  $n\text{-C}_5\text{H}_{12}$  partial oxidation for obtaining high selectivity to one of the anhydrides.

**CATALYTIC CYCLOMETALLATION OF CYCLOALKYNES WITH  $R_nAlCl_{3-n}$   
AND  $RMgX$  IN THE PRESENCE OF Zr COMPLEXES**

**D'yakonov V.A., Zinnurova R.A., Galimova L.F., Ibragimov A.G., Dzhemilev U.M.**

*Institute of Petrochemistry and Catalysis of RAS, Ufa, Bashkortostan, Russia*

*E-mail: ink@anrb.ru*

Bicyclic 1-ethylaluminacyclopentenes (**1**) with annulated to double bonds cycloalkane fragments were obtained via the interaction between cycloalkynes (cyclooctyne, cyclodecyne, cyclododecyne) and equimolar amount of triethylaluminium in the presence of  $Cp_2ZrCl_2$  (5 mol %) as a catalyst under mild conditions (20–21 °C, 8 h) in high yields (> 85%) and selectivity (> 95%).

Cycloaluminum of cycloalkynes with  $RAiCl_2$  (R = Et,  $NEt_2$ , OBU) affected by catalytic amounts of  $Cp_2ZrCl_2$  in the presence of activated Mg (acceptor of halogenide ions) was carried out in ethereal solvents to yield novel types of unsaturated tricyclic organoaluminium compounds (**2**).

The OAC (**1**) under the action of dimethyl sulfate were transformed into spiro[2,n]alkanes. Demetallation of the OAC (**2**) using thionyl chloride led to sulfolenes.

Cyclomagnesiumation of cycloalkynes with  $RMgX$  affected by  $Cp_2ZrCl_2$  catalyst was found to afford bi- (**3**) or tricyclic (**4**) magnezacyclopentadienes.

As it is known,<sup>1</sup> tri- and tetracyclic organoaluminium compounds (OAC) can be obtained in high yields and selectivity by cycloaluminum of norbornadienes with  $Et_3Al$  in the presence of Zr complexes.

In this paper we propose a novel synthetic method for bi- and tricycloalanes by cycloaluminum of cyclic acetylenes with trialkyl alanes or alkyl halogenalanes under the action of Zr-containing catalysts.

Bicyclic 1-ethylaluminacyclopentenes (**1**) with annulated to double bonds cycloalkane fragments were found to obtain via the interaction between cycloalkynes (cyclooctyne, cyclodecyne, cyclododecyne) and equimolar amount of triethylaluminium in the presence of  $Cp_2ZrCl_2$  (5 mol %) as a catalyst under mild conditions (20–21 °C, 8 h) in high yields (more than 85%) and selectivity (more than 95%).

Cycloaluminum of cycloalkynes with  $RAiCl_2$  (R = Et,  $NEt_2$ , OBU) affected by catalytic amounts of  $Cp_2ZrCl_2$  in the presence of activated Mg (acceptor of halogenide ions) first was carried out in ethereal solvents to yield novel types of unsaturated tricyclic organoaluminium compounds (**2**).

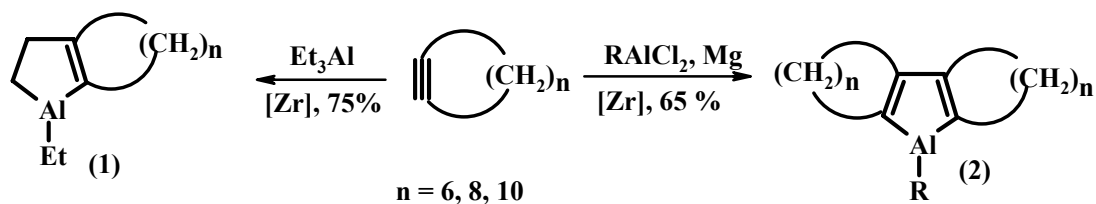
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<sup>1</sup> U.M.Dzhemilev, A.G.Ibragimov, A.P.Zolotarev, L.M.Khalilov and R.R.Musluchov. Izv.. AN SSSR. Ser. Khim., 1992, P. 386

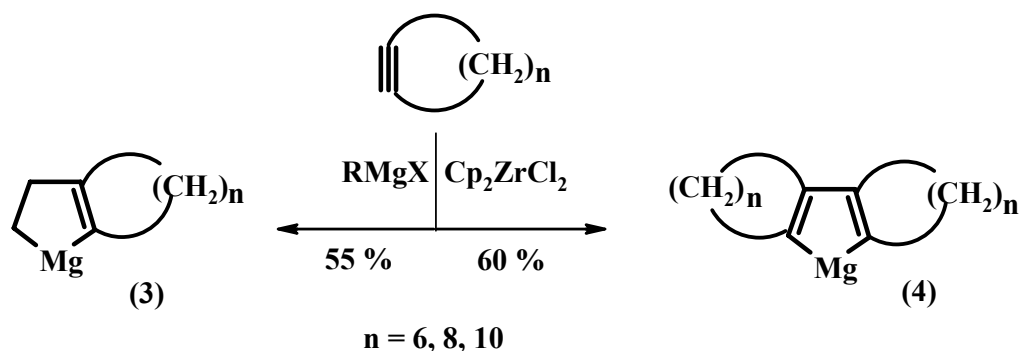
## OP-II-29

The OAC (**1**) under the action of dimethyl sulfate was transformed into spiro[2,n]alkanes. Demetallation of the OAC (**2**) using thionyl chloride led to sulfolenes.

The probable formation mechanism for cyclic OAC, which involves the generation of ethylenezirconium or cyclopropanezirconium intermediates under the reaction conditions, is discussed. Subsequent insertion of one or two molecules of starting cycloalkyne and transmetallation of generated *in situ* zirconacyclopent-2-enes or zirconacyclopenta-2,4-dienes with halogenalanes are proposed for related di-(**1**) or tricycloalanes (**2**).



Cyclomagnesiation of cycloalkynes with  $RMgX$  affected by  $Cp_2ZrCl_2$  catalyst, in an analogous fashion, was found to afford bi- (**3**) or tricyclic (**4**) magnezacyclopentadienes.



The research work was financially supported by grants of RF President (NSh-7470.2006.3) and the Russian Foundation for Basic Research (Project No. 05-03-32367).

**CATALYTIC SYSTEMS ON THE BASIS OF CARBON SUPPORTS  
FOR AMBIENT TEMPERATURE CO OXIDATION**

**Radkevich V.Z., Senko T.L., Khaminets S.G.,<sup>1</sup> Wilson K., Yegiazarov Yu.G.**

*Institute of Physical-Organic Chemistry of the National Academy of Science, Minsk, Belarus*

<sup>1</sup>*Department of Chemistry, University of York, Heslington, York, UK*

*E-mail: radkevich\_vz@ifoch.bas-net.by*

A range of palladium-copper-iron catalysts for the ambient temperature oxidation of CO have been prepared using stone-fruit activated coal and fibrous carbon support materials. The influence of the nature of the carbon support, composition of active component and its content as well as preparation conditions on catalytic CO oxidation efficiency was studied. "Carbopon" carbon fiber supports are found to give rise to the most active catalytic system, with 90 % conversion of CO observed under a respiratory regime at 20 °C. The catalyst retains its activity upon keeping in reaction media or storage in the moist air for a long period of time.

Post reaction (0.5 % CO in air) analysis of these catalysts by XPS reveals palladium is in the oxidized condition, mainly as Pd<sup>+</sup>, copper and iron - as Cu<sup>2+</sup> and Fe<sup>3+</sup> respectively.

Air purification and removal of CO in spite of numerous researches, conducted in recent decades, is still a challenging problem and requires the development of new catalysts for CO oxidation, which are active at low temperatures and not poisoned by water vapor. Carbon materials possessing high surface area and resistance towards different treatments [1] are regarded as effective supports for such catalysts.

In present work stone-fruit activated coal (SAC, granule diameter near 1-2 mm, sorption of water 0.72 cm<sup>3</sup>/g, S<sub>sp</sub> by nitrogen absorption 950 m<sup>2</sup>/g) and fibrous carbon materials "carbopon" and "busofit" (fiber diameter near 5-10 μm, sorption of water 0.64 and 0.17 cm<sup>3</sup>/g, S<sub>sp</sub> by nitrogen adsorption 780 and 670 m<sup>2</sup>/g, respectively), manufactured by "Khimvolokno" association (Svetlogorsk, Belarus) were used as initial supports for catalytic systems for the ambient temperature oxidation of CO. Functionalised forms of SAC were prepared by treating with aqueous solutions of hydrogen peroxide, nitric acid or with gaseous ammonia at 300 °C. Final catalysts were prepared by impregnation of the carbon supports with aqueous solutions of palladium, copper and ferric iron salts (chlorides, acetate and bromides) under pH 3.0 to 4.5. After impregnation the catalysts were dried in air at 25 °C for 16 hours.

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The influence of the nature of the carbon support, composition and content of the active component as well as preparation conditions on the efficiency of the catalytic system in CO oxidation was subsequently studied. SAC supports modified with functional groups were found to have decreased catalytic activity for CO oxidation. It was shown that supports with lower hydrophilicity or reactions where the gaseous mixture was dried result in decreased catalyst activity. The role of water and oxygen in the reduction-oxidation processes took place in palladium-copper-iron containing heterogenised catalytic system will be discussed.

Carbon fiber (carbofon) catalytic system was prepared, and found to provide 90 % conversion of CO under a respiratory regime at 20 °C. The catalyst is found to retain its activity after even keeping in reaction media or storage in moist air for a long period of time.

The specific activity of the palladium based catalyst with 0.55 wt. % Pd, 2.75 wt. % Cu and 0.22 wt. % Fe, is found to be  $60.2 \times 10^3$  CO molecules/s/Pd atom, is 1.5 times higher than the best SAC supported catalyst and 2.7 times higher than the best previous reported carbon supported system [2], which contains 0.2 wt. % Pd and 11.5 wt. % Cu. Post reaction (0.5 % CO in air) analysis of these catalysts by XPS reveals palladium is in the oxidized condition, mainly as Pd<sup>+</sup>, copper and iron - as Cu<sup>2+</sup> and Fe<sup>3+</sup> respectively.

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**SUPPORTED Zr- AND Hf-CENE CATALYSTS FOR PROPYLENE  
POLYMERIZATION**

**Novokshonova L.A., Ushakova T.M., Lysova M.V., Kudinova O.I.,  
Krasheninnikov V.G., Lyubimtsev A.I.<sup>1</sup>**

*N.N. Semenov Institute of Chemical Physics, RAS, Moscow, Russia*

<sup>1</sup>*Moscow State University, Moscow, Russia*

*E-mail: lnov@chph.ras.ru*

The influence of fixation of *ansa*-metallocene precatalysts, differing by the symmetry type, the nature of bridges,  $\eta$ -bonded ligands, substitutes in the ligands, metal (Zr, Hf), on a support solid surface on the catalytic properties of formed supported catalysts in propylene polymerization (activity, molecular mass characteristics and microstructure of obtained polypropylene) in comparison with properties of analogous homogeneous systems was investigated.

As the supports-activators of metallocenes, the alkylaluminoxanes, synthesized directly on a montmorillonite (MMT) surface in a reaction of partial hydrolysis of the aluminum alkyls ( $\text{AlMe}_3$ ,  $\text{Al}(i\text{-Bu})_3$ ) by a mobile support water  $\text{MMT-H}_2\text{O/AlR}_3$  were used. The support-activator  $\text{MMT-H}_2\text{O/Al}(i\text{-Bu})_3$  generates with all employed *ansa*-zirconocenes the more effective in propylene polymerization surface metal-alkyl complexes than  $\text{MMT-H}_2\text{O/AlMe}_3$ . Besides,  $\text{MMT-H}_2\text{O/Al}(i\text{-Bu})_3$  is an effective activator for Hf-cene precatalysts in contrast to  $\text{MMT-H}_2\text{O/AlMe}_3$ .

The modification of  $\text{MMT-H}_2\text{O/Al}(i\text{-Bu})_3/\text{Zr}$  (Hf)-cene by  $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  gives the significant increase of catalyst activity in propylene polymerization at reduced Al/Mt ratio. The action of borate shows itself also as stabilization of catalytic complexes, especially for the supported Zr- and Hf-cenes of  $\text{C}_2$  symmetry.

**“GREEN” TECHNOLOGY FOR OLEFIN/ PARAFFIN ALKYLATION**

**Angevine P., Gaffney A., D’Amico V., Yeh C.Y., van Broekhoven E.<sup>1</sup>**

*ABB Lummus Global, Inc., Bloomfield, NJ, U.S.A.*

<sup>1</sup>*Albemarle Catalysts, Amsterdam, The Netherlands*

*E-mail: chuen.y.yeh@us.abb.com*

Refiners have long used alkylation for high-octane gasoline. High purity makes alkylate ideal as a clean, gasoline-blending component. Since existing hydrofluoric and sulfuric acid based technologies have environmental and safety issues, people have sought a solid catalyst of equivalent performance. Unfortunately, until now the catalysts investigated have not met the goals of activity, selectivity, stability and economic feasibility.

This paper describes the basic chemistry of a new solid acid catalyst process (AlkyClean<sup>®</sup>) and explains key catalyst and process innovations that make this a scientific jump to a ‘green’ technology for clean gasoline.

Worldwide, refiners remain challenged to provide motorists with cleaner fuels that meet increasingly demanding environmental regulations. These initiatives have been enacted to improve air quality through the reduction of harmful vehicle emissions. Alkylate – the gasoline boiling range product of the reaction of isobutane with light olefins (C<sub>3</sub>-C<sub>5</sub>) – has high octane, low vapor pressure, no toxic aromatics or reactive olefins, and generally neither sulfur nor nitrogen compounds. As such, it is an ideal “clean fuels” gasoline blend stock, which is both in increased demand and of growing importance to the refining industry.

Along with the mandate for cleaner fuels, today’s refiner must also contend with increased political and regulatory pressures to employ more environmentally friendly technologies. For over 50 years, only corrosive and potentially hazardous hydrofluoric (HF) and sulfuric (H<sub>2</sub>SO<sub>4</sub>) liquid acid catalyzed alkylation processes have been available to refiners. While both of these technologies have proven to be generally reliable, there remains a strong focus on the environmental and safety risks associated with the use of these toxic liquid acids. Over the last two decades this has resulted in rising expenditures for monitoring and risk mitigation, along with increased permitting difficulties for both new and revamped/expanded units. In the extreme, existing alkylation plants have even been mothballed in response to pressures against their continued operation near densely populated areas. As a result, industry interest remains strong to find a competitive, true solid acid catalyst (SAC) technology that would provide a much more environmentally friendly (“green”) alternative for this critical refinery process. Unfortunately, up to now the catalysts investigated have not met the goal of activity, selectivity, stability and economic feasibility.

This paper describes the basic chemistry of a new solid acid catalyst process (“AlkyClean®”) and explains key catalyst and process innovations that make this a scientific jump to a green technology for clean gasoline. Liquid acid and solid acid chemistries are compared and contrasted; and other discussion topics include the major pathways, rate determining steps, thermodynamic issues, and impact of operating variables.

In addition to the chemistry of alkylation, a brief history of the AlkyClean process development is provided. This first-of-its-kind technology development was a collaborative effort among three diverse organizations: a catalyst manufacturer, an engineering company, and a refiner. These three companies provided the balanced expertise and perspective to enable the project’s success as it moved from discovery to development to commercial demonstration.

ALTERNATIVE FLUE GAS CLEANING BY CATALYSIS, ELECTROCATALYSIS  
AND SELECTIVE GAS ABSORPTION

**Due-Hansen J.<sup>1</sup>, Rasmussen S.B.<sup>1</sup>, Huang J.<sup>1</sup>, Riisager A.<sup>1</sup>, Eriksen K.M.<sup>1</sup>,  
Fehrmann R.<sup>1</sup>, Hamma H.<sup>1,2</sup>, Rogez R.<sup>2</sup>, Winnick J.<sup>3</sup>, Wasserscheid P.<sup>4</sup>**

<sup>1</sup>*Department of Chemistry and Center for Sustainable and Green Chemistry, Technical  
University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

<sup>2</sup>*Laboratoire TECSSEN, Faculté des Sciences et Techniques de St Jérôme, 13397 Marseille  
Cedex 20, France*

<sup>3</sup>*School of Chemical Engineering, Georgia Institute of Technology, GA 30332, USA*

<sup>4</sup>*Lehrstuhl für Chemische Reaktionstechnik, Universität Erlangen-Nürnberg, D-91058  
Erlangen, Germany  
E-mail: rf@kemi.dtu.dk*

There is an increasing global concern about human caused emissions of pollutants like sulfur and nitrogen oxides to the atmosphere leading to e.g. smog and acid rain damaging to the human health and the environment.

Up to now, flue-gas desulphurization (FGD) is one of the most effective techniques to control emission of SO<sub>2</sub> from combustion of fossil fuels, such as coal and oil. A variety of the processes for SO<sub>2</sub> control, such as FGD by wet scrubbing and catalytic sulfuric acid production, have been adopted widely in commercial units. However, the methods need large investments and/or lead to waste problems.

Also NO<sub>x</sub> emissions are of increasing concern in the industrialized countries and stricter regulations of emission limits are envisaged. Emissions from fossil fueled power plants are usually reduced by installation in the gas duct of a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> based heterogeneous catalyst converting NO<sub>x</sub> by NH<sub>3</sub> injection in the flue gas to N<sub>2</sub> and H<sub>2</sub>O. However, this SCR (Selective Catalytic Reduction) catalyst operates around 375°C and it has to be placed in a certain position in the flue gas duct. There is therefore a demand for NO<sub>x</sub> installations more flexible regarding temperature of operation and possible position in the duct e.g. placed after the wet FGD scrubber. Also the increased use of biomass (straw, wood pellets etc.) alone or in combination with fossil fuel has been shown to decrease the life time of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> deNO<sub>x</sub> catalyst dramatically, due to deactivation by especially potassium salts in the biomass fly ash.

We are at present trying to understand the mechanism of biomass deactivation of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst and trying to develop alternative methods to the traditional industrial NO<sub>x</sub> and SO<sub>x</sub> flue gas cleaning processes working at lower temperatures and/or leading to useful products.

In this work we present our latest results regarding flue gas cleaning by heterogeneous catalysis, electrocatalytic membrane separation, ionic liquid reversible absorption and supported ionic liquid phase(SILP) catalysis.

NEW APPROACHES TO H<sub>2</sub> PRODUCTION FOR FUEL CELLS

**Rozovskii A.Ya., Lin G.I., Kipnis M.A., Samokhin P.V., Volnina E.A., Belostotsky I.A.,  
Grafova G.M., Zavalishin I.N.**

*Topchiev Institute of Petrochemical Synthesis RAS, Moscow, Russia*

*E-mail: kipnis@ips.ac.ru*

Methanol steam reforming (MSR) and preferential CO oxidation (PROX) were studied with the view to improve the production of H<sub>2</sub>-rich gas. For MSR, a theoretic kinetic model (based on reaction mechanism for Cu-based catalysts) was established.

During PROX in a “quasi-adiabatic” reactor, ignition and extinction of the catalyst surface and the transition states of the process were observed. The proposed catalyst in combination with the control of the macrokinetic regime of PROX allowed reduction of residual CO content in gaseous mixtures produced by methanol steam reforming down to <15 ppm at GHSV~100 m<sup>3</sup>/(kg<sub>CAT</sub>)/h and O<sub>2</sub>/CO ratio of 1.

Methanol steam reforming (MSR) over Cu-based catalysts occurs as the reaction reverse to methanol synthesis:



It is coupled with the reverse water-gas-shift-reaction (RWGSR):



The results of mechanism studies for these reactions and a simplified kinetic model of methanol synthesis have been presented in our publications [1-3]. Thus, the mechanistic scheme of the MSR can be interpreted as the mechanistic scheme of methanol synthesis “read” in the reverse direction. On this basis, the theoretic kinetic model and correspondingly a computer model of the MSR were developed.

The MSR kinetics was studied using a flow reactor in the pressure range 0.1-3 MPa and in the temperature range 240-460 °C. Water-methanol mixture was fed as a gas with a flow rate within the range 4\*10<sup>3</sup>-6\*10<sup>4</sup> h<sup>-1</sup>, molar water/methanol ratio being in the range 1.3-3.

Various catalysts (Cu-based, as a rule) were tested: commercial catalysts of methanol synthesis; Cu-based laboratory samples with various modifying agents (Zr, Y, Ce, Cr, γ-Al<sub>2</sub>O<sub>3</sub>); also, catalysts on the basis of crystalline intermetallics Zr<sub>1</sub>Cu<sub>1</sub>, Zr<sub>7</sub>Cu<sub>10</sub>. The calculation results were compared with experimental data (not only ours but also adopted from the literature): theoretical kinetic model of MSR described the process satisfactorily in all cases.

It has been shown [3] that low residual CO content could be obtained if the PROX reaction occurred in the macrokinetic mode of catalyst surface ignition (the transition to this

#### OP-III-4

state takes place under the conditions  $dq^+/dT > dq^-/dT$ ,  $q^+$  - the reaction heat emission,  $q^-$  - the reactor heat dissipation).

The feed mixture modeled the products of methanol steam reforming over low-temperature catalysts (51-2, for example) with the  $O_2$ ,  $N_2$  admixture (vol. %: 0.75  $CO$ , 0.75  $O_2$ , 57  $H_2$ , 18  $CO_2$ , 20-21  $H_2O$ , the rest  $N_2$ ). Residual  $CO$  concentration was monitored with IR-analyzer BINOS 100 (sensitivity threshold 1 *ppm*). Two thermocouples (1 mm in diameter) were inserted into the inlet and outlet of the catalyst bed (~12 mm). Residual  $CO$  and temperatures were recorded by a multichannel controller device.

For  $CO$  oxidation, a 0.1%  $Ru/Al_2O_3$  catalyst was selected (among others) together with appropriate process conditions which provided very efficient  $CO$  removal (less than 15 *ppm*) from the gaseous mixture in presence of  $H_2O$  and  $CO_2$  at a feed rate as high as  $\sim 100 \text{ m}^3/\text{kg}_{CAT}/\text{h}$ .

Stability of  $Ru$  catalysts performance was studied in isothermal and adiabatic reactors. It was found that deactivated catalyst can be reactivated by treatment in  $H_2$  atmosphere.

The data obtained can serve as a basis for the development of an efficient one-step process for cleaning the hydrogen-containing gas from  $CO$  impurity, in particular, a gas mixture produced by methanol steam reforming.

This work was carried out with the support of Russian Foundation for Basic Research (grants No. 02-03-32202, 06-03-32848).

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**SUPPORT EFFECT ON SILVER CATALYSTS FOR NO DECOMPOSITION**

**Chien Shu-Hua, Kuo Ming-Chih, Yu Wen-Yueh, Yang Yu-Sheng**

*Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan*

*Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan*

*E-mail: chiensh@gate.sinica.edu.tw*

The decomposition of NO was studied by temperature programmed desorption technique in an ultrahigh vacuum system along with XPS elemental analysis. Titania supported Ag catalyst exhibited the best catalytic activity for NO decomposition among Ag/TiO<sub>2</sub>, Ag/SiO<sub>2</sub>, Ag foil, and TiO<sub>2</sub>. The NO conversion was 90.6 % and the N<sub>2</sub> selectivity was 92.8 %. The high catalytic activity of Ag/TiO<sub>2</sub> was contributed by the synergetic effect of Ag and TiO<sub>2</sub>. Also, Ag/TiO<sub>2</sub> showed a high photocatalytic activity for NO decomposition.

**INTRODUCTION**

Direct catalytic decomposition of nitric oxide into N<sub>2</sub> and O<sub>2</sub> is the most attractive and challenging deNO<sub>x</sub> approach. The adsorption and reaction of NO on single crystals have been extensively studied for understanding the reaction mechanism of the heterogeneous catalysis. However, the adsorption and reaction of NO on the surface of powder catalysts may adapt to understand real mechanism. In the present study, we systematically studied catalytic NO decomposition over various Ag catalysts including Ag/TiO<sub>2</sub>, Ag/SiO<sub>2</sub>, Ag foil and TiO<sub>2</sub>.

**EXPERIMENTAL**

The Ag/TiO<sub>2</sub> and Ag/SiO<sub>2</sub> catalysts used in the present study were prepared by incipient wetness impregnation method with 2 wt% Ag content. For comparison, Ag foil and TiO<sub>2</sub> were also investigated. XPS studies were performed in an Omicron ESCA system with monochromatic Al K<sub>α</sub> X-ray source and hemispherical analyzer. UHV-TPD experiments were carried out in the ESCA system and the desorbed gases were detected by quadrupole mass spectrometer. EPR spectra were taken at 77 K using a Bruker X-band E500CW spectrometer. The g values of EPR signals were measured using DPPH (g = 2.0036) as a reference.

**RESULTS AND DISCUSSION**

The powder catalysts, Ag/TiO<sub>2</sub>, Ag/SiO<sub>2</sub>, and TiO<sub>2</sub>, were pressed as pellets and reduced in H<sub>2</sub> at 573K for 3 h prior to NO adsorption and reaction. For Ag foil, Ar<sup>+</sup> sputtering was performed to obtain clean surface. The XPS spectrum of clean Ag foil showed sharp peaks at 367.6 and 373.7 eV associating with Ag 3d<sub>5/2</sub> and 3d<sub>3/2</sub>, which decreased in intensity significantly after NO adsorption where appeared two N 1s peaks at 406.3 and 399 eV

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corresponding to the molecular adsorption and the dissociative adsorption of NO, respectively. Only molecular NO adsorption was detected on Ag/SiO<sub>2</sub> and TiO<sub>2</sub>, and no N signals on Ag/TiO<sub>2</sub>. However, in the UHV-TPD of NO experiment, the molecular NO desorbed at low temperature between 242 and 372 K along with decomposition products of N<sub>2</sub>, N<sub>2</sub>O, and trace of O<sub>2</sub>. At higher temperature, N<sub>2</sub> appeared to be the major desorbed signal, indicating the nearly complete decomposition of NO. The overall NO conversion of Ag/TiO<sub>2</sub> is 91% with a high N<sub>2</sub> selectivity of 93%. Fig. 1 depicts the TPD profiles of Ag/TiO<sub>2</sub>. Other samples showed similar TPD profiles to Ag/TiO<sub>2</sub> with different catalytic activity as in the order: Ag/TiO<sub>2</sub> > TiO<sub>2</sub> > Ag foil > Ag/SiO<sub>2</sub>. The high catalytic activity of Ag/TiO<sub>2</sub> was attributed to the synergistic interaction between both active components of Ag and TiO<sub>2</sub>. Besides, Ag/TiO<sub>2</sub> also showed a highly photocatalytic activity for NO decomposition as investigated by in-situ EPR experiment (see Fig. 2). After introducing NO in contact with Ag/TiO<sub>2</sub>, an intense EPR signal of adsorbed NO appeared at  $g_{\perp} = 2.0015$  and  $g_{\parallel} = 1.9443$  with a hyperfine constant  $A_{\perp} = 25$  G due to N ( $I = 1$ ). The signal of adsorbed NO decreased gradually with time under UV irradiation and disappeared after 40 min with the products of N<sub>2</sub> and N<sub>2</sub>O as detected by a quadrupole mass spectrometer. In summary, due to the strong metal-support interaction, Ag/TiO<sub>2</sub> is a promising catalyst, as well as a highly active photocatalyst for NO decomposition.

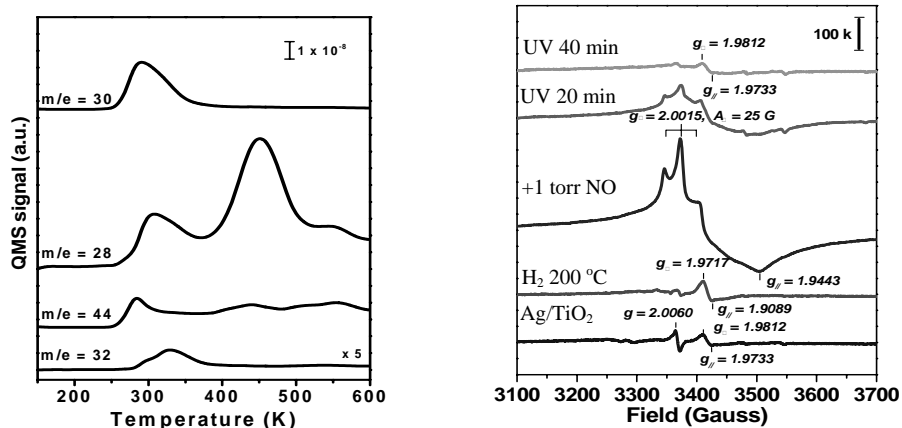


Fig. 1. UHV-TPD profiles of Ag/TiO<sub>2</sub>. Fig. 2. EPR spectra of Ag/TiO<sub>2</sub>



## DEVELOPMENT OF PGM-FREE CATALYSTS FOR AUTOMOTIVE APPLICATIONS (I, II)

**Shigapov A.**

### DEVELOPMENT OF PGM-FREE CATALYSTS FOR SOOT OXIDATION AND NO<sub>x</sub> ACCUMULATION AND REDUCTION (I)

**Shigapov A.<sup>1,2</sup>, Dubkov A.<sup>1</sup>, Ukropec R.<sup>1</sup>, Carberry B.<sup>1</sup>, McCabe R.<sup>2</sup>**

<sup>1</sup>*Ford Forschungszentrum Aachen, Suesterfeldstrasse 200, D-52072 Aachen, Germany;*

<sup>2</sup>*Ford Research and Innovation Center, Dearborn, MI, USA*

*E-mail: achigapo@ford.com*

The activity of Ag-based catalysts in soot oxidation using NO<sub>2</sub> and oxygen as oxidants has been studied using TGA and it was also evaluated under real engine conditions, showing comparative or better activity than commercial Pt-containing catalysts using both low-temperature NO<sub>x</sub>-assisted and high-temperature soot oxidation by oxygen. Some Ag-based compositions revealed good NO<sub>x</sub> storage properties and were quite active in NO oxidation, also providing some passive NO<sub>x</sub> reduction. Such systems are promising for retrofit applications.

The high and steadily increasing prices for Platinum Group Metal (PGM) components of automotive catalysts coupled with limited supply and high demand put a pressure on automakers to reduce and replace costly PGM. PGM free catalytic compositions comprising silver and/or cobalt stabilized ceria facilitating soot oxidation during the regeneration of Diesel particulate filters (DPF), replacing PGM formulations are described [1]. The catalysts have been studied by a TGA method on soot oxidation activity. Among formulations tested, the silver-stabilized ceria and cobalt-stabilized ceria formulations e.g. can oxidize soot at 250-300 °C in the presence of NO<sub>2</sub> and oxygen, while silver-stabilized ceria can slowly oxidize diesel soot even in the presence of only oxygen as the sole oxidizing agent at these temperatures. The composition Ag-La-Mn perovskite was very active in soot oxidation at temperatures above 300 °C. They proved to be particularly useful as washcoat compositions for DPF as part of an automotive aftertreatment system for elimination and/or minimizing of

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exhaust gas emissions, particularly for directly injected fuel engine vehicles. This was shown by testing of full-size coated Diesel particulate filters having Ag-based coating under real engine conditions, revealing comparable or better performance than commercial prototypes, Pt formulations with Pt loading of 100 g/ft<sup>3</sup> (28.32 g Pt/m<sup>3</sup>). The balance point, where the rates of soot deposition and oxidation are equal, was achieved at 250-275 °C with complete soot oxidation at 325 °C using NO<sub>x</sub> emitted from the engine. The levels of CO, NO<sub>x</sub> and HC emissions during regeneration were also comparable.

However; such passive filter regeneration is difficult for passenger cars due to low temperatures and low level of nitrogen oxides, in addition it leads to increased NO<sub>x</sub> emissions. For passenger diesel cars, automakers can rely only on periodical high-temperature regeneration near 600 °C using active engine measures and intake air as an oxidant. For such type of active regeneration, the new catalytic compositions containing very low 5-15 g/ft<sup>3</sup> Pd or Pt-Pd PGM compositions containing base metals and PGM-free Ag-CuO-La<sub>2</sub>O<sub>3</sub> compositions have been developed [2]. Engine testing revealed better or comparable performance combined with lower NO<sub>2</sub> emissions in comparison with commercial prototypes having high Pt loading

We also studied Ag-based catalysts for NO<sub>x</sub> accumulation, NO oxidation, SCR with CO and HC [3]. Those catalysts revealed good NO<sub>x</sub> storage properties comparable with commercial Pt-based lean NO<sub>x</sub> traps (LNT) except high temperatures, and released basically NO<sub>2</sub> in contrast to LNT where NO was the basic product. This NO<sub>2</sub> was emitted at temperature window 300-350 °C, the most favorable for soot oxidation and can be used for soot oxidation. Such systems can accumulate NO<sub>x</sub> for soot oxidation even at low temperatures. The good activity was found for NO oxidation, higher than for LNT but lower than for diesel oxidation catalyst (DOC). Such Ag-based systems provide some moderate passive NO<sub>x</sub> reduction from 10 up to 30 % depending on conditions.

Based on results obtained, such Ag- containing aftertreatment catalysts are the most promising for retrofit automotive applications to provide passive particulate matter (soot) and NO<sub>x</sub> reduction.

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**REVERSIBLE SULFUR TRAPS FOR DIESEL AND LEAN-BURN GASOLINE  
AUTOMOTIVE APPLICATIONS (II)**

**Shigapov A.<sup>1,2</sup>, Dubkov A.<sup>1</sup>, Ukropec R.<sup>1</sup>, Carberry B.<sup>1</sup>, Graham G.<sup>2</sup>, Chun W.<sup>2</sup>, McCabe R.<sup>2</sup>**

<sup>1</sup>*Ford Forschungszentrum Aachen, Suesterfeldstrasse 200, D-52072 Aachen, Germany*

<sup>2</sup>*Ford Research and Innovation Center, Dearborn, MI, USA*

*E-mail: achigapo@ford.com*

Cu-based systems have been tested as catalyst-adsorbent for reversible sulfur trap to protect lean NO<sub>x</sub> trap (LNT) from sulfur poisoning. These formulations have shown good sulfur storage capacity under lean conditions and release only SO<sub>2</sub> during regeneration under rich conditions. Such formulations, especially CuO/SiO<sub>2</sub> were completely regenerated at temperature window of LNT operations, namely below 450°C and are promising as sulfur trap material for automotive applications.

Sulfur oxides (SO<sub>x</sub>) have negative effect on a performance of components of automotive catalysts and traps (noble metals, Ce-Zr oxide, alkaline-earth oxides in NO<sub>x</sub> trap) [1].

In particular, «sulfur» problem is very important for so-called lean NO<sub>x</sub> traps (LNTs). Sulfur dioxide can be relatively easy oxidized on Pt to SO<sub>3</sub>. The last compound reacts with barium and/or other alkaline or alkaline-earth metal component of the NO<sub>x</sub> trap forming stable sulfates [2], which are more thermodynamically stable than nitrates, and so high-temperature desulfation under reductive conditions is required in order to regenerate LNT [3].

One of the possible ways to avoid the sulfur poisoning of NO<sub>x</sub> trap, is to remove SO<sub>x</sub> from gas under lean conditions, and to release SO<sub>2</sub> under rich conditions using so called "sulfur trap". Under rich conditions SO<sub>2</sub> is not considered to be a poison for the NO<sub>x</sub> trap [4, 5]. SO<sub>x</sub> trap should operate in the same temperature range as NO<sub>x</sub> trap, i.e. typically at 250-450 °C. SO<sub>x</sub> trapping properties of Pt, Pd and Rh- oxidation components supported on storage components such as oxides of Ce, Zr and Ba, were investigated in [6].

The present study is dealing with catalytic compositions suitable for reversible entrapping SO<sub>x</sub> [7]. Such catalyst compositions can adsorb SO<sub>x</sub> as metal sulfate under lean conditions and can desorb accumulated SO<sub>x</sub> as SO<sub>2</sub> under rich conditions. Such reversible SO<sub>x</sub> trap material is able to work under typical NO<sub>x</sub> trap operating conditions to prevent sulfur poisoning of NO<sub>x</sub> trap and can be regenerated under rich conditions of NO<sub>x</sub> trap operation at 300-450 °C.

The following criteria have been formulated for efficient SO<sub>x</sub> trap:

- Appropriate SO<sub>x</sub> capacity at low (e.g. 200 °C) and high (e.g. 500 °C) temperatures;
- Appropriate thermal stability of the surface sulfates formed;

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- Low temperature of the reductive regeneration (in H<sub>2</sub>);
- Regeneration with SO<sub>2</sub> formation (not H<sub>2</sub>S);
- Multi-cycle stability

Among different systems tested, Cu and Fe-containing compositions revealed the most desirable properties, especially CuO deposited on SiO<sub>2</sub>, Zr-SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> with high copper oxide loading up to 25 mol%. Such systems can store up to 100 mg S/g. The advantage of such Cu-containing systems is that only SO<sub>2</sub> was emitted under rich conditions while for Pt-containing sulfur traps H<sub>2</sub>S was the basic or sole component during regeneration that is not acceptable for automotive applications. CuO/ SiO<sub>2</sub> have shown the lowest temperature of SO<sub>2</sub> release; nevertheless stored sulfate was stable under lean conditions. Other copper-containing systems mentioned above were also successfully regenerated below 450 °C under rich conditions. Such systems are not active in SO<sub>2</sub> oxidation to SO<sub>3</sub>, but taking into account their installation downstream of Pt-containing Diesel oxidation catalyst (DOC), which is very active in such oxidation, it is not a problem for implementation of Cu-based sulfur traps in automotive applications.

For irreversible SO<sub>x</sub> trap, which can collect SO<sub>x</sub> under lean conditions and can be regenerated only at elevated temperatures in a separate mode of operation, the systems containing praseodymia, zirconia-praseodymia and manganese oxide-yttria have shown to be an effective material for SO<sub>x</sub> removal.

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**DEACTIVATION FEATURES RELATED TO THE MECHANISM OF XYLENE  
TOTAL OXIDATION OVER Pd CATALYSTS**

**Nekrasov N.V., Drjahlov A.S., Kumbilieva K.<sup>1</sup>, Gaidai N.A., Petrov L.<sup>1</sup>, Lapidus A.L.**

*N.D. Zelinsky Institute of Organic Chemistry RUN, Moscow, Russia*

<sup>1</sup>*Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

*E-mail: gaidai@mail.ioc.ac.ru*

The research is focused on the deactivation mechanism of metal-supported Pd catalysts for total xylene oxidation. Experimental observations give evidence that the catalyst deactivation is related to formation of polymer species. The apparent catalyst activity is most appreciable at lower temperature of operation. The mechanism scheme suggested to explain the observed phenomena distinguishes the contribution of surface sites of different adsorption strength to different routes involved in the reaction network.

Catalytic total oxidation of hydrocarbon impurities is an efficient and beneficial method for the purification of waste gases. In view of this, detailed knowledge on the kinetics and evolution of these processes, as well as on the catalyst deactivation mechanism, is of primary importance for optimizing the process performance.

**Experimental observations:** The catalytic system subject to this study is total oxidation of xylene in air excess over two metal-supported Pd catalysts, containing 0.2wt% Pd (sample\_1), and 1wt% Pd (sample\_2); specific catalyst area 0.046m<sup>2</sup>/g-cat. The metallic support is a precaution from deactivation caused by internal diffusion of industrial dust. Operation conditions: atmospheric pressure; temperature interval 225 °C – 400 °C; initial feed concentrations of xylene within the range (0.0037 – 0.105) mmol/l. Accompanying reactions of major importance: (i) formation of polymer species; (ii) destruction of the polymer species. The observed evolution of the process with time on stream showed the following trends: abrupt drop of the main reaction rate when the process was carried out at temperature values T<280 °C; steeper decrease within the temperature interval 290 °C < T< 320 °C, and not a noticeable change at T>330 °C. Special transition response experiments gave evidence that the reaction occurred without propagation into the gas phase.

**Reaction model:** The kinetic equations describing the rate of total oxidation on the fresh catalyst,  $r_0$ , are of the form

$$r_0^A = \frac{k_1^0 \exp(-E_a^A / RT)C}{(1 + k_2 C)^2} \quad (1a) \quad \text{and} \quad r_0^B = \frac{k_1^0 \exp(-E_a^B / RT)C}{(1 + k_2 C)^2} \quad (1b)$$

Superscripts A and B denote the regions in which the observable oxidation rate decreases (A) or keeps constant (B),  $k_2$  is xylene adsorption coefficient; C stands for xylene concentration,  $E_a$  for the apparent activation energy. Evidences are that  $E_a^A$  is much higher than  $E_a^B$ .

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On deriving the detailed scheme of the process, special significance was attached to the fact that Pd catalysts are characterized by inhomogeneous surface properties, non-uniformity of adsorption strength in particular. In view of this, the suggested model distinguishes the contribution of surface sites of different adsorption strength. It was assumed that mobile equilibrium forms of adsorbed oxygen originate on sites of moderate adsorption ability. These intermediates have a key role for the formation of peroxide-type surface species which give rise to the products of total oxidation. The strong adsorption sites generate tightly bound surface formations which may evolve into precursors of the polymer film. The latter is the main cause for the catalyst deactivation, as far as the covered fraction of the active surface is eliminated from the catalyst action. At the same time, there may take place degradation of the polymer formations via their interaction with mobile forms of adsorbed oxygen. Indications are that the rate of the degradation reaction strongly increases with temperature. Accordingly, Eq (2) and (3) describe the current overall output rate  $r_t$  of total oxidation, and the rate  $r^*$  of formation of the polymer film at time  $t$ :

$$r_t = r_0 \cdot \sigma(t) + k_3 \cdot \theta(T) P_{O_2} \varphi(t) \quad (2)$$

The right hand term of this relation considers the oxidation products generated on the expense of the polymer-degradation reaction.

$$r^* = k^* (\lambda)^2 \cdot \sigma(t) - k_3 \theta(T) \cdot P_{O_2} \varphi(t) \quad (3)$$

$\theta(T)$  stands for the impact of sites of moderate adsorption strength;  $\lambda$  for the surface concentration of sites capable to generate tightly adsorbed species.  $\sigma(t)$  and  $\varphi(t)$  denote the fractions of catalyst surface respectively unblocked and covered by polymer film;  $\sigma(t) + \varphi(t) = 1$ . Some of the surface interactions involved in the reaction mechanism result in degradation of the polymer film or prevent its formation. Interactions of this type actually reduce the deactivation effect caused by the polymer film. As far as they are facilitated at higher temperature, the compensation effect increases accordingly. Under operation conditions for which the terms of Eq. (3) satisfy the relation  $k^* (\lambda)^2 \sigma(t) \ll k_3 \theta(T) P_{O_2} \varphi(t)$ , the catalytic system becomes insensitive for the influence of the polymer formations, and the apparent deactivation effects become negligible. On substituting for  $\sigma(t)$  and  $\varphi(t)$  the functions following from the kinetic analysis, and solving the obtained set of equations, we come to explaining the observed behavior of the reaction system within the frames of the suggested model.

In summary, the model derived considers the catalyst deactivation as a constituent part of this process, and points to resources for reducing and/or compensating the deterioration effects.

## CATALYTIC TECHNOLOGY OF NITRATES REDUCTION IN WASTE WATER

**Gavrilenko A., Sulman E., Matveeva V.**

*Tver Technical University, Tver, Russia*

*E-mail: sulman@online.tver.ru*

In this study novel catalysts for waste water denitrification are described. Several types of mono- and bimetallic heterogeneous catalysts were investigated: (i) catalysts on the base of traditional support, (ii) catalytic nanoparticles stabilized in ultra thin polyelectrolyte layers deposited on inert support and (iii) catalysts on the base of polymeric matrix. For the investigated catalysts the optimal conditions of reduction providing the highest nitrates conversion were found. On the base of physical-chemical analysis of the catalysts developed and kinetic data the hypothesis of the reduction mechanism was proposed. The catalysts having high activity and stability provide effective reduction of nitrates to nitrogen. Low content of catalytic active phase (palladium) and mild reaction conditions allow recommending these catalysts for the industrial application.

Nitrates are one of the most dangerous pollutants. Long consumption of drinking water and food-stuffs containing considerable amount of nitrates (25-100 mg/dm<sup>3</sup>) can cause intoxication. The nitrate concentration in ground water, which is the main source for drinking water, is still rising throughout the world. Waste water is the most wide-spread type of the environment pollution resources (Table 1). Thus the technologies for the removal of nitrate from drinking water and waste water will be required in the nearest future.

Several types of mono- and bimetallic heterogeneous catalysts were investigated:

(i) As catalysts on the base of traditional support the following catalysts were developed: Pd/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.5% Pd), Pd-Zn (1:3) /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.5% Pd), Pd-Cu (4:1) /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (4.7% Pd) and Pd-Sn (4:1) /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (4.7% Pd).

(ii) To synthesize the catalyst on the base of palladium nanoparticles stabilized in ultra thin polyelectrolyte layers deposited on the inert support the chitosan was used as a cationic biopolymer which is able to sorbs on the charged surface of alumina. Thus Pd-chitosan /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.37% Pd) was developed.

(iii) As a polymeric matrix for Pd nanoparticles stabilization the hypercrosslinked polystyrene (HPS) was chosen, and the following catalysts we synthesized: Pd-Zn (1:3) / HPS (0.5% Pd) and Pd-Cu (4:1) / HPS (4.7% Pd).

Heterogeneous catalytic reduction of nitrates in a water solution was carried out in a constant-temperature glass reactor with a tube for constant hydrogen supply. NO<sub>3</sub><sup>-</sup> ions concentration has been determined by a potentiometric method using nitrate-selective

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electrode. For all catalysts physical-chemical investigations (XPS, XFA, and BET) were conducted.

As a result of the investigation as the optimal catalytic system providing the most effective nitrates reduction in an aqueous solution Pd-Cu (4:1) /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (4.7% Pd) was chosen. For this catalyst nitrates conversion reached up to 97 % during the first 30 min of the reaction at 14 °C.

According to the experimental results the description of the process of nitrates catalytic reduction to nitrogen by of the method of formal kinetics with the calculation of the numerical values of the parameters of mathematical description equation was suggested.

We sincerely thank to Russian Foundation of Basic Research (grant 04-03-32928) for financial support.



## MODELING OF A RADIAL-FLOW MOVING-BED REACTOR FOR DEHYDROGENATION OF ISOBUTANE

**Moghimpour-Bijani P., Sahebdehfar S.**

*Catalyst Research Group, Petrochemical Research and Technology Company, National  
Petrochemical Company, P.O. Box 14458, Tehran, Iran  
E-mail: s.sahebdehfar@npc-rt.ir*

### Introduction

Dehydrogenation of isobutane is conducted at high temperatures to achieve reasonable commercial yields. Under these conditions, catalyst deactivation is rapid and frequent catalyst regeneration is necessary [1]. In the *Oleflex* process [2], the reaction is carried out in a series of radial-flow moving-bed reactors in the presence of hydrogen as a coke-removing agent and the catalyst is continuously regenerated and recycled.

### Experimental

Commercial bimetallic Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst samples (2.2-2.8 g) were tested in a fixed-bed quartz reactor (ID=15 mm). The operating conditions were selected close to industrial conditions. The reactor effluent was analyzed by an online gas chromatograph, equipped with TCD and FID detectors for C<sub>1</sub>-C<sub>4</sub> hydrocarbons.

### Modeling

According to previous studies reported in the literature [3], the kinetics of dehydrogenation of isobutane (A) to isobutene (B) was considered to be:

$$-r'_A = k_1 a \left( C_A - \frac{C_B C_{H_2}}{K_{eq}} \right) \quad (1)$$

where  $r'_A$  is the rate of disappearance of isobutane per catalyst weight,  $k_1$  is the rate constants of forward reaction,  $a$  is catalyst activity,  $K_{eq}$  is the equilibrium constant and  $C$  concentration of the species. The above kinetics along with a first-order decay law, were applied to the design equations of a fixed-bed, and a radial-flow moving-bed reactor and the resulting equations were solved analytically for isobutene conversion. The former was used to obtain the necessary kinetic parameters from lab-scale test data, and the latter was used to predict the performance of the commercial reactor.

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### Results and Discussion

The external and internal mass transfer limitation effects were found to be negligible. Figure 1 shows verification of the kinetic models based on experimental concentration-time data. The reaction and deactivation rate constants were derived from the intercept and slope, respectively. The conversion in the commercial-scale reactors was found to be a function of a dimensionless decay time; i.e., the ratio of a “catalyst deactivation time constant” to residence time of the catalyst within the reactor. For a large dimensionless decay time (negligible catalyst decay) the performance equation approached to that of a simple packed-bed reactor. Despite assuming isothermal conditions and using single-temperature experimental data, predictions of the model were fair (Table 1).

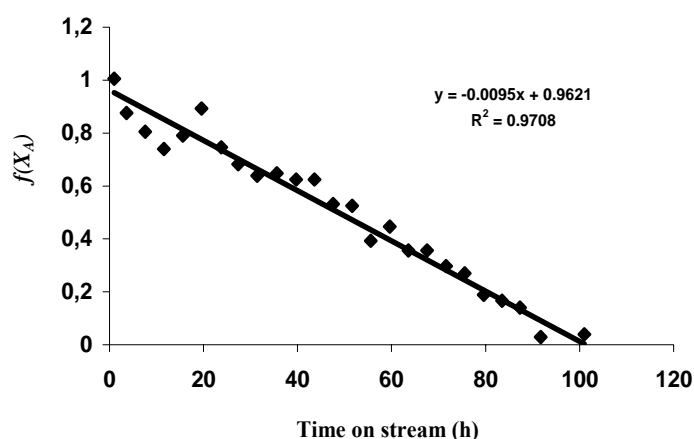


Fig. 1. Testing kinetic models using experimental data ( $T=848\text{ K}$ ,  $\text{WHSV}=2.2\text{ h}^{-1}$ ,  $\text{H}_2/\text{HC}=0.8\text{ mol/mol}$ ).

Table 1. Comparison of the industrial results with model

	Reactor 1	Reactor 2	Reactor 3	All reactors
Predicted conversion (reactor outlet)	0.21	0.20	0.135	0.55
Conversion in industrial reactor (reactor outlet)	0.20	0.165	0.135	0.5
Activity of outlet catalyst	0.65	0.4	0.23	0.23

### Conclusions

The applicability of single-parameter first-order kinetic expressions in describing the dehydrogenation of isobutane was verified. Fair predictions of the commercial-scale moving-bed reactors were obtained.

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**CATALYSIS IN WATER MEDIUM: STATE OF THE ART****Goncharuk V.V., Sychev M.V., Prihod'ko R.V.***Dumanski Institute of Colloid and Water Chemistry, Kiev, Ukraine**E-mail: m.v.sychev@icccw.kiev.ua*

Catalytic processes in water as an environmental application is a subject with great potential in the near future. New catalysts and supports with advanced surface and textural properties have improved catalytic efficiency of these processes. The present review examines the number of catalytic reactions in water phase explored within last years. Oxidation, hydrogenation processes as well as photocatalysis are considered. Following the reviewed references, heterogeneous catalysis related to the water purification is developing rapidly.

Quality problems of groundwater and freshwater along with importance of drinking water have generated many studies dealing with catalytic water purification including oxidation and hydrogenation processes. Many active homogeneous catalysts, such as some metal salts are a potential environmental problem. Therefore, there is a need for heterogeneous catalytic procedures where the catalyst is in different phase.

This review presents the wide scale of heterogeneous reactions in water phase studied mainly within past ten years. Oxidation, hydrogenation as well as photocatalytic processes are included. The chemical aspects of water purification are also reviewed in details. Some new catalysts and catalytic processes recently developed in Dumanski Institute of Colloid and Water Chemistry are considered as well.

It will be demonstrated that heterogeneous catalysis offers a promising novel approach in liquid phase environmental processes. If they are capable to replace other application with higher energy consumption there is a proper place for them. Many of applications presumably will be limited to narrow field of waste streams. For photocatalysis, the most rapid development is expected in engineering related aspects, e.g. specific reactor design and advanced supports. Novel catalysts, among them immobilized organometals, may have potentiality in the future. Some of the more traditional processes are moving towards commercial applications.

**ETHYLENE SELECTIVITY ENHANCEMENT OF OXIDATIVE COUPLING OF METHANE ON Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> CATALYST USING A FLUIDIZED BED REACTOR**

**Salehoun V., Mortazavi Y., Khodadadi A., Talebizadeh A.**

*Catalyst and Reaction Engineering Laboratory, Oil & Gas Center of Excellence, School of Chemical Engineering, University of Tehran, Tehran, Iran*

*E-mail: mortazav@ut.ac.ir*

Performance of Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst in oxidative coupling of methane (OCM) is investigated in a fluidized bed reactor and compared to that in a fixed bed reactor under the same conditions. Feed flow rate, CH<sub>4</sub>/air, and temperature were varied for both reactors. C<sub>2</sub> selectivity in the fluidized bed reactor is higher than that in the fixed bed one in the range of 700-870 °C and WHSV of 4100-41000 ml/g-h and lower CH<sub>4</sub>/air ratios. However, the methane conversion in most cases in the fluidized bed reactor is slightly lower than that for the fixed bed one. High ethylene/ethane ratios up to 3.5 are obtained in the fluidized bed reactor.

### **Introduction**

The main problem in industrialization of oxidative coupling of methane (OCM) process is exothermicity of the reaction, which have various negative effects including run away and unsafe operation with low C<sub>2</sub> selectivity [1, 2]. OCM should be performed in the reactor to cope with the large amount of heat released in this process. Fluidized bed reactor is a suitable choice for controlling a uniform temperature in the reactor. In OCM, Mn-Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst has shown a high stable yield of C<sub>2</sub> for a long time on stream [3]. In this paper, the performance of a fluidized bed reactor in OCM on Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> is investigated under different conditions. The results are compared with the performance of a fixed bed reactor at the same conditions.

### **Experimental procedure**

4%Mn-5%Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst was prepared based on the method reported elsewhere [1]. Magnesium nitrate and Na<sub>2</sub>WO<sub>4</sub> solutions were sequentially impregnated onto SiO<sub>2</sub> and the sample was dried and then calcined at 800 °C for 8 h. A quartz laboratory scale fluidized bed reactor of ID = 30 mm containing about 3.5 g catalyst was used. A porous sintered quartz plate was used to distribute the feed containing pure methane and air with different ratios controlled by individual mass flow controllers. A PID temperature-controlled tubular furnace was used to adjust the reactor temperature. The feed flow in the same reactor under similar conditions was reversed to obtain the OCM performance in the fixed bed reactor. An on-line

multi-valve, multi-column Carl 400AGC gas chromatograph was used to analyze the reactor effluents for CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>.

### Results and discussion

Variations of OCM methane conversion and C<sub>2</sub> selectivity with temperature in both types of reactors are presented in Figure 1a and 1b, respectively. At lower temperatures, methane conversion for the fluidized bed reactor is slightly higher than that for the fixed bed one. For both reactors the C<sub>2</sub> selectivity increases with temperature in the lower ranges and then levels off. At all temperatures examined, the C<sub>2</sub> selectivity in the fluidized bed reactor is significantly higher. At 700 °C the C<sub>2</sub> selectivity in the fluidized bed is enhanced by about 50 %.

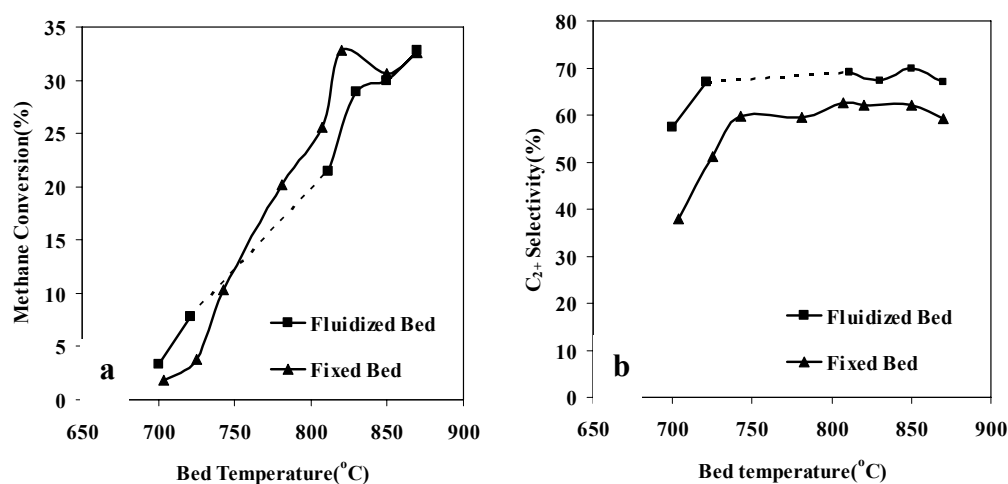


Fig. 1: Comparison of a) methane conversion and b) C<sub>2</sub> selectivity variation with bed temperature in fixed and fluidized bed reactors (Feed flow rate= 487 sccm, CH<sub>4</sub>/Air=1)

Figures 2a and 2b show the effect of contact time on methane conversion and different products of OCM on the Mn/Na<sub>2</sub>WO<sub>4</sub>/SiO<sub>2</sub> catalyst in a fluidized bed reactor at 850 °C. Fig. 2a indicates that the methane conversion in the fluidized bed reactor remains constant up to a contact time of 28700 ml/g-h. The conversion linearly drops at higher flow rates. It seems that complete oxygen conversion limits the methane conversion at lower flow rates. Figure 2b shows that very high ethylene/ethane ratios up to about 3.5 are obtained in the fluidized bed reactor. Generally C<sub>2</sub> selectivity drops with the feed flow rate. Back-mixing of the products may have caused the effect.

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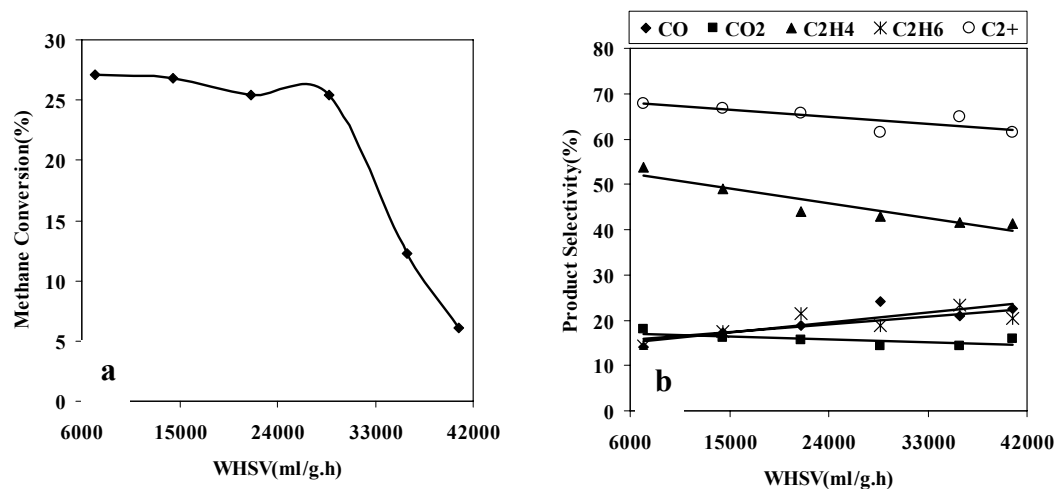


Fig. 2: Variation of a) methane conversion and b) products selectivities with feed flow rate in a fluidized bed reactor at 850 °C and CH<sub>4</sub>/Air of 1.0.

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**SELECTIVE OXIDATION OF METHANE TO SYNGAS IN THE REACTOR WITH  
MONOLYTHIC CATALYST: HEAT AND MASS TRANSFER STUDIES WITH CFD  
MODELING**

**Klenov O.P., Pokrovskaya S.A., Chumakova N.A., Pavlova S.N., Sazonova N.N.,  
Gubanova E.L., Sadykov V.A., Noskov A.S.**

*Borekov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: klen@catalysis.ru*

Hydrodynamics of gas flow in the channels of LaNiPt-monolithic catalyst for methane selective oxidation into syngas was studied on the basis of complete 3D model of a catalytic reactor with the software FLUENT 6.1. Distribution of gas velocity and heat transfer rate along the monolith channel was determined and their effect on methane conversion and product selectivity was investigated varying the catalyst and process parameters. The optimal feed rates and channel lengths were evaluated to achieve high methane conversion and product selectivity.

Structured catalyst systems are promising for development of compact syngas generators from natural gas and/or other hydrocarbons feedstock. To determine the optimal shape and size of monolithic catalysts, reactor design and its operation regimes the detailed data concerning heat and mass transfer effects on the reaction rates are necessary. The use of the boundary-layer models does not always allow to reveal all features of hydrodynamic processes in such catalyst systems, more detailed analysis becomes possible on the basis of CFD modeling [1].

In this work, some results concerning reaction flow hydrodynamics in the reactor with monolithic catalyst at short contact times are presented. 3D model of a catalytic reactor was considered and the complete system of Navier-Stokes equations for multicomponent, catalytically reacting gas flow was solved on the basis of software FLUENT 6.1. The studies were performed for the operation parameters of the methane selective oxidation into syngas on LaNiPtO<sub>x</sub>/CeO<sub>2</sub>-ZrO<sub>2</sub>/α-Al<sub>2</sub>O<sub>3</sub> catalyst in the reactor with one separate unit of monolith with triangular channels. The temperature range was 600-900 °C, the inlet reaction mixture contained 3-7 vol.% CH<sub>4</sub> with required amount of O<sub>2</sub>, the contact times were equal to 4-15 ms.

The velocity distribution of the gas flow was shown to be essentially non-uniform. At the entrance of the catalyst channel, the narrowing of the gas stream induces its alteration. Along the channel, the permanent alteration of the gas velocity distribution exists due to formation and growth of the boundary layers, that narrows the effective cross-section of the channel and

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speeds up the flow in the central part. For studied conditions, stabilization of the flow is not occurred along all the channel length, and the gas velocity distribution is characterized by essential cross-section gradients.

For different channel lengths and gas velocities, the comparison of characteristics of the heat and mass transfer between the gas flow and the catalyst surface was performed. The distribution of the temperature and heat transfer rate over the channel surface as well as the gas velocity distribution is essentially non-uniform. The maximum heat exchange intensity exists near the channel inlet, zones with the minimum heat exchange are located at the channel corners. The profiles of Nusselt number and heat transfer coefficient along the channel were determined, the values of the heat transfer rate in different sections change by 2 orders (Fig.1).

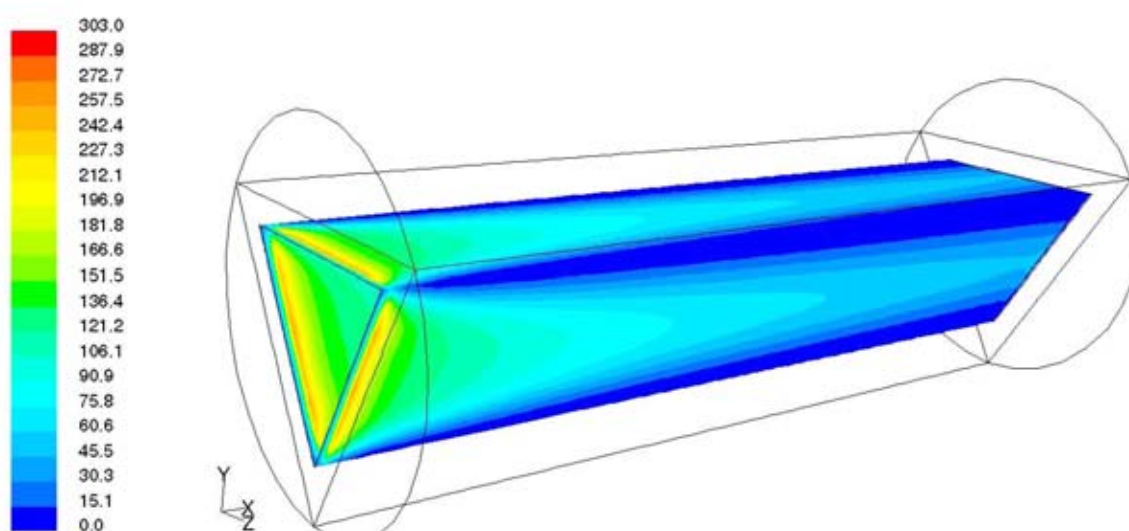


Fig. 1. Contours of surface heat transfer coefficient  $[W/(m^2 \cdot K)]$  on inside channel wall.

The effect of the gas velocity distribution as well as the heat and mass transfer on the process characteristics - methane conversion and product selectivity was determined varying the catalyst and process parameters – channel length, gas velocity, inlet temperature and reagent concentrations. For modeling, the processing of experimental data with nearly isothermal conditions performed in the 4mm ID reactor with one catalyst fragment (triangular channel) allowed to define the main reaction pathways and to estimate their kinetic parameters.

It was shown, that at studied conditions the reaction occurs with mass and heat transfer limitations, especially at the inlet of the catalyst channel where the rates of exothermic reactions of methane oxidation are high. In this part, the catalyst temperature significantly exceeds that of the gas phase and the surface concentrations of reagents (especially, oxygen concentration) are much lower than ones in the gas phase. Along the channel, the difference



between the catalyst and gas temperature decreases and the concentrations of desired products – CO and H<sub>2</sub> rise due to the growth of endothermic reforming reaction rates with the lowering oxygen concentration. The optimal feed rates and channel lengths were evaluated to achieve methane conversion about 95-97 % with a high product selectivity.

This work was carried out in the frames of Associated European Russian-France Laboratory on Catalysis.

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## REACTION KINETICS AND MASS TRANSFER ON FRACTAL CATALYSTS

**Strizhak P.E.***L.V. Pysarzhevsky Institute of Physical Chemistry, NAS of Ukraine, Kiev, Ukraine**E-mail: pstrizhak@hotmail.com*

A new theoretical approach is used for description of reaction kinetics and mass transfer on catalyst, which is characterized by fractal geometry. The approach gives simple extension for the Thiele modulus and activation energy for internal diffusion for fractal catalysts. The obtained theoretical results are confirmed by experiments.

Modern catalysis demands developing of efficient predictive techniques and algorithms for describing simultaneous reaction and diffusion in porous catalysts. A possible approach to solve this problem is based on the fractal geometry emerged in the mid-1970s by Mandelbrot [1]. This approach gives the representation of the apparently complex geometrical structure of catalyst by simple parameter known as fractal dimension ( $D_F$ ). The expression that embodies the whole concept of the fractal structure of an object is very simple:

$$\text{Property} \sim R^{D_F}$$

where “Property” may be any measurable value, for example, the mass of object, and  $R$  is a linear measure of size. Accordingly,  $D_F$  is a measure of the scaling of the catalyst structure. Fractal approach has been already successfully applied for diffusion and reaction in porous catalysts [2-3]. The most of the obtained results are based on a simple rescaling of the surface area or other parameters leading to relationship between the rate of chemical conversion and fractal dimension of a catalyst.

In the present contribution we apply the fractal approach for reaction kinetics and mass transfer on catalyst characterized by fractal geometry. The approach is based on modified “reaction-diffusion” equation in which diffusion term depends on fractal dimension of a catalyst. The modified “reaction-diffusion” equation is derived from the first principles. That allows one to analyze an effect of catalyst irregularity on its catalytic properties. In the simplest case the modified “reaction-diffusion” equation is equivalent to the usual “reaction-diffusion” that corresponds to the Fick’s law. Another cases concern fractional diffusion and anomalous diffusion. Here we present a detailed analysis for the chemical reaction and mass transfer caused by anomalous diffusion (Levy flights).

Analysis of the chemical reaction and anomalous diffusion gives an extension for the Thiele modulus and for the activation energy in the Zeldovich regime (internal diffusion)

taking into account an irregular geometrical structure of a catalyst. We show that for the internal diffusion the activation energy  $E$  is expressed as

$$E = E_k/\gamma \quad (1)$$

where  $E_k$  gives the activation energy of the chemical process measured in kinetic regime, and  $\gamma$  characterizes geometrical irregularity of the catalyst. In general case  $\gamma$  takes values in the range between 1 and 2. For classical case of usual diffusion (Fick's law)  $\gamma=2$ , and Eq.(1) gives the well-known result. We show that in some cases the value of  $\gamma$  depends linearly on the fractal dimension of a catalyst.

Comprehensive experimental verification of the fractal approach described above is presented by the CO oxidation on solids characterized by different fractal dimensions. Our experiments indicate appearance of anomalous diffusion on different silicas,  $\gamma\text{-Al}_2\text{O}_3$  and zeolite NaY. Those solids are characterized by fractal dimension in the range between 2 and 3. Temperature dependencies for the rate of the CO oxidation is in a good agreement with our theoretical results. Moreover, our experiments show a linear relationship between  $\gamma$  and fractal dimension of those solids as shown in Fig.1.

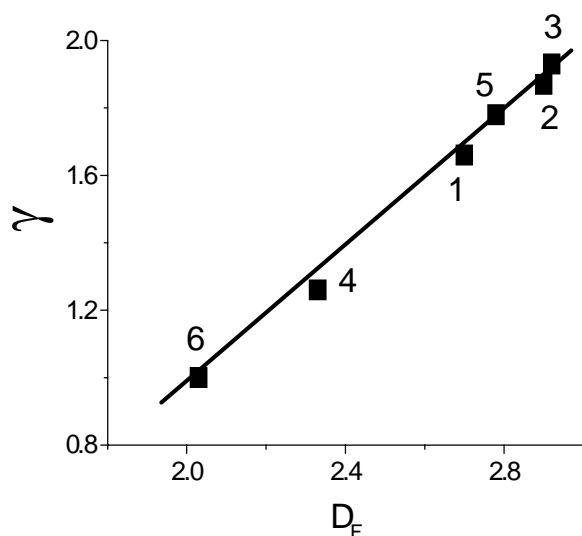


Fig.1 Dependence between  $\gamma$  and fractal dimension for different solids in the CO oxidation: 1- 4 – different silicas, 5 -  $\gamma\text{-Al}_2\text{O}_3$ , 6 – zeolite NaY.

Finally we demonstrate usefulness of the fractal approach for design of catalysts for some industrial process.

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**PRESENT STATE AND PROSPECTS OF BASE OIL MANUFACTURING  
CATALYTIC PROCESSES**

**Tsvetkov O.N., Skolnikov V.M.**

*The All-Russian Scientific and Research Institute of Oil Processing, Moscow, Russia*

*E-mail: paom@rambler.ru*

The main catalytic processes used to produce mineral and poly- $\alpha$ -olefine oils are discussed. The catalyst nature proves to be the dominating characteristics determining the base oil chemical composition and properties in the course of feedstock conversion reactions. For mineral base oil manufacturing hydrocatalytic processes heterogeneous catalysts containing Ni, Mo, W, Pt, Pd, and different zeolites are used. To synthesize poly- $\alpha$ -olefine oils on the stage of  $\alpha$ -olefin oligomerization pseudo-homogeneous catalysts are applied, while on the stage of oligomer hydrogenation heterogeneous Ni – or Pd-containing catalyst are used.

The start of the new century was marked with the realization and scientific substantiation of the inevitability of principle changes in the approaches to the production and application of lubricants. Along with meeting the ever growing technical requirements, the environmental requirements are constantly becoming more stringent. As the world annual production of lubricants exceeds 37 mln.t., the acute problems of reducing the emission of harmful matter formed in the process of production and use of lubricating oils, greases and special fluids are arising on an ever growing scale.

So, the new motor oil requirements regulate the sulfur, phosphorus, sulphate ash content by 1.5-2 times lower compared to the existing ones. The requirements placed upon the automotive vehicles, both with gasoline and diesel engines are becoming stricter in terms of the exhaust gas content of harmful substances. All this is accompanied by increasing the intervals between the maintenance operations, i. e. by raising the motor oil performance.

Strict limitation of the motor oil sulfur eliminates the possibility of using conventional solvent refined base oils. The sulfur content in the lubricating oil will be exclusively determined by the availability of sulfur-containing additives. By the API base oil classification the sulfur content of group II and III base oils should not exceed 0.03%, as in the process of combustion 100 % of the sulfur contained in the base oils are transformed to sulfur oxides. The share of saturated hydrocarbons in the base oils has to be raised to 90 % due to the fact that particularly they exhibit the lowest volatility compared to other hydrocarbons with similar molecular weight and viscosity.

The transition to low-sulfur base oils with a high share of saturated hydrocarbons requires restructure of the base oil production system. Apart from efficient solvent refining technologies and conventional hydrotreating of oils at 5 MPa pressure, mastering technologies of hydroconversion of oil raffinates, hydrocracking vacuum distillates, slack wax and paraffin hydroisomerization. Intensive implementation of synthetic oil technologies are nowadays on the agenda. According to the predictions the share of the highest group oils by API classification will be raised by 2015 to 30 % based on the total base oil production volume, that means a substantial increase in the role of catalytic processes in the lubricating oil production.

The results of the VNIINP research activities in this area permit to principally modernize the shape of the current base oil production. In one of the versions of low-viscosity base oil production technology, emphasis is placed on catalytic hydrocracking of low-viscosity vacuum distillate followed by the rectification, after the diesel fraction stabilization and separation, to recover the transformer oil cut which is subjected to solvent or catalytic dewaxing resulting in a base oil exhibiting a low content of sulfur and unsaturated compounds. Such technology has in particular been implemented in the transformer oil production. The lube oil hydrocracking proves to be the most promising trend in the production of API groups II and III base oils. Due to the fact that all the lube oil refineries possess solvent refining units, it seems to be expedient to implement the raffinate hydroconversion to produce group II base oils. Wherever no paraffin production has not been arranged in parallel with stable production of solvent refined oils, it seems to be reasonable to process slack waxes by means of slack wax hydrotreating to minimize the sulfur and nitrogen content followed by their isomerization to isoparaffinic group III oils – most valuable basestocks for motor oil formulations exhibiting the highest performance characteristics.

For complex segments of base oil application, in particular, for motor oils with enhanced low-temperature rheological characteristics and at the same time exhibiting the highest performance characteristics, such as oils for aviation gas-turbine engines of the recent generations special-purpose hydraulic, industrial, compressor oils and greases, the use of poly- $\alpha$ -olefinic oils ( PAOO) as the basestock proves to be most acceptable. The technology of PAOO synthesizing is primarily based on ion- or ion-coordinating oligomerization of a limited number of  $\alpha$ -olefin fractions. The paramount role in the molecular-mass distribution and in the chemical group composition of the poly- $\alpha$ -olefins is played by catalytic systems on the stage of  $\alpha$ -olefin oligomerization. On the stage of  $\alpha$ -olefin oligomers hydrogenation it is reasonable, due to their high molecular mass, to use heterogeneous catalysts with the location of the hydrogenating components on the external surface of the supports.

**SORPTION-ENHANCED STEAM REFORMING OF HYDROCARBONS WITH  
AUTOTHERMAL SORBENT REGENERATION IN A MOVING HEAT WAVE OF  
CATALYTIC COMBUSTION REACTION**

**Zagoruiko A.N., Okunev A.G.**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: zagor@catalysis.ru*

The presentation is devoted to novel technological concept of sorption-enhanced hydrocarbon steam reforming with autothermal regeneration of the carbon dioxide scavenger in the moving heat wave of the exothermic catalytic combustion reaction performed directly inside the adsorption-catalytic bed. Process modelling and pilot tests results, confirming the capability and high efficiency of proposed technological concept, are presented.

Active development of hydrogen-based energy technologies is in a great extent limited today by availability of efficient and low-cost hydrogen production. The most promising technological way in this direction is application of sorption-enhanced catalytic methane steam reforming. This approach, first formulated even in 19-th century [1], has received a lot of attention in modern practice since 1980-s and now is developing extremely fast by numerous research groups worldwide [2-6].

The sorption-enhanced catalytic methane steam reforming concept except usual methane and carbon monoxide steam conversion catalytic reactions, widely applied in conventional technologies



also includes the adsorption of product  $\text{CO}_2$  by solid sorbent:



leading to favorable equilibrium conditions for reactions (1), (2) and to achievement of high yield of high-purity hydrogen in one conversion stage. After saturation of sorption capacity of the sorbent it is necessary to provide its regeneration according to reaction



Though the research efforts in this area are very intensive and active, the achieved level of process efficiency is still far from ideal. While performance of basic reaction cycle (reactions 1-3) is well studied and more or less optimized, the source of most complications is sorbent regeneration reaction stage (4). The major attention in current developments is concentrated on application of mixed catalyst-sorbent fixed beds with so called “isothermal” sorbent regeneration, meaning external bed heating during regeneration stage. Such heating

approach is characterized with high level of inefficient energy losses. Moreover, efficient and uniform heating of the bed in this case is possible only in reactors with relatively small diameter and this factor limits the scale of approach application or requires unreasonable complication of reformer design.

Much more promising, but much less studied, regeneration method is adiabatic or autothermal regeneration, meaning heating of the catalyst-sorbent bed by exothermic reaction performed directly inside the bed. In this case CO<sub>2</sub>-sorbent regeneration is performed according to reaction (4) with supply of heat, necessary for regeneration, by oxidation of available combustible substances (say, hydrogen or methane) in the air flow directly in the adiabatic sorbent-catalyst bed:



Both process stages may be performed in a periodical “traveling heat wave” regime and in this case it becomes possible to create at each process stage the axial profiles of catalyst temperature, optimal for performance of next stage. Especially efficient operation mode may be realized by application of counter-current (or reverse flow) operation, when methane/steam and air/fuel mixtures are fed into processor bed in opposite directions.

Such approach will provide fast and efficient sorbent regeneration with minimum heat losses to environment. Application of low-cost and available within the process combustible fuels (such as recycled unused hydrogen from fuel cell or methane from initial natural gas) will result in advantageous economic efficiency of the proposed technology in comparison with existing processes. Application of cheap and simple equipment (adiabatic reactors with fixed beds of sorbent-catalyst, absence of external furnaces and heat supply piping etc.) will make the proposed hydrocarbon fuel processor inexpensive and simple in operation.

The presentation discusses process modelling and pilot tests results, confirming the capability and high efficiency of proposed technological concept.

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**STUDY OF CATALYST AND ISOAMYLENES DEHYDROGENATION TO  
ISOPRENE UNDER REDUCED PRESSURE**

**Kotelnikov G.R., Kachalov D.V., Sidnev V.B., Lugovkin S.N., Kuzhin A.V., Bespalov V.P.**

*Joint Stock Company Research Institute “Yarsintez”, Yaroslavl, Russia*

*E-mail: postprof@mail.ru*

The results of new catalyst development for isoamylenes dehydrogenation to isoprene and studies of the process in the presence of the given catalyst under reduced pressure are given. The process parameters and conditions range are determined for implementation in industry.

The paper refers to study of catalyst and isoamylenes dehydrogenation process under reduced pressure to isoprene which is the most important monomer for synthetic rubber production. At present in Russian industry the isoprene is produced by isoamylenes dehydrogenation in the presence of catalysts based on iron oxide. Iron oxide catalysts have the indisputable advantages against the phosphate catalysts used earlier mainly because they are able to work for a long period without regeneration. The use of iron oxide catalysts allowed to decrease the energy consumption of isoprene process and simplify the process operation..

The studies of the process and catalyst developments for isoamylenes dehydration to isoprene have been carried out during some decades at JSC RI “Yarsintez”.

A new effective KDI -2 catalyst for isoamylenes dehydrogenation has been developed as a result of these studies. According to the results of lab testing KDI-2 catalyst is one of the best up-to-date catalyst and has all properties which attract the customer, that is:

- High catalytic activity and selectivity provide the unit productivity, and low feedstock consumption index
- High mechanical strength provide low dust content, low hydraulic resistance of bed and increase catalyst service life
- The catalyst is manufactured of different geometric shape, special patented shape provides high ratio of external surface to weight unit resulted in decrease of diffusion braking and catalyst use efficiency increase, and additional reduction of hydraulic resistance in comparison with cylindrical shape.

It is well known that the temperature increase and pressure reduction contribute into the dehydrogenation reaction course. As the industrial isoamylenes dehydrogenation process is



performed at high enough temperatures 550-630 °C, and further temperature increase leads to a significant selectivity decrease than the most promising way of process efficiency increase is to reduce the reaction pressure.

The data of isopentane-isoamylenes mixtures thermal dynamic calculations shows that the system pressure reduction shifts significantly reaction equilibrium to isoprene.

At pilot unit there were carried out a number of experiments in order to determine the actual pressure effect on the process factors of isoamylenes dehydrogenation. According to the obtained data it should be that the pressure reduction by 0.1 atm leads to isoprene yield increase by 0.6-0.8 %, and selectivity increases by 0.8-1.0 %. It was also observed that at pressure reduction the CO<sub>2</sub> content of dehydrogenation contact gas decreases and interregeneration run increases: the catalyst did not require the regeneration during the whole period of studies (more than 800 hours) at the pilot unit and this give the evidence of self-regeneration conditions improvement.

Thus it was experimentally determined the range of conditions and process parameters of isoamylenes dehydrogenation under pressure below atmospheric one and this allows to use the obtained data for the purposes of industrial designing.

**CATALYST AND PROCESS DEVELOPMENT FOR INDUSTRIAL PRODUCTION  
OF MULTIWALLED CARBON NANOTUBES**

**Wolf A., Buchholz S., Michele V., Mleczko L.**

*Bayer Technology Services GmbH, 51368 Leverkusen*

*E-mail: aurel.wolf@bayertechnology.com*

Carbon Nanotubes are currently synthesized by different methods summarized in table 1. The methods differ largely by the achievable Space-Time-Yield, amorphous carbon content and carbon purity.

Table 1 Synthesis methods for Carbon Nanotubes

Method	Space-Time-Yield	Amorphous carbon	C-purity
Arc discharge	Low	High	High
Laser ablation	Low	High	High
Floating Methods	Medium	Low	Med
CVD, CCVD	High	Low	Med

High space-time-yields can only be achieved by CVD processes. Though usually low contents of amorphous carbon are observed in CVD processes, C-purity is generally decreased due to catalyst residues. Optimized CCVD processes can overcome this drawback. However, the main obstacles for industrial applications of CNT are their still high prices and uneven product properties. Therefore Bayer Technology Services has developed a high-yield process for MWNT (Baytubes<sup>®</sup>) based on a CCVD process starting from light hydrocarbons. As the “micro- and nanoproperties” of MWNT such as diameter, aspect ratio, entanglement, number of defects, surface properties and many more strongly influence the properties of potential applications like for example conductive CNT-polymer composites, a high reproducibility of catalyst and MWNT synthesis is essential. The produced Baytubes<sup>®</sup> are characterized by a small diameter, a narrow diameter distribution, a very high graphite content and an excellent purity (carbon content > 98 wt.%). In order to tailor the nanotubes properties to the needs of particular applications, downstream treatment processes can be applied to remove residual catalyst and/or to attach functional groups to the nanotubes surfaces. Due to their high purity and quality, Baytubes<sup>®</sup> can be employed directly in further processing. The overall process is summarized in figure 1. The CCVD process yields agglomerates of CNT

which can be incorporated e.g. into polymer materials using different methods, depending on the properties required by the respective application.

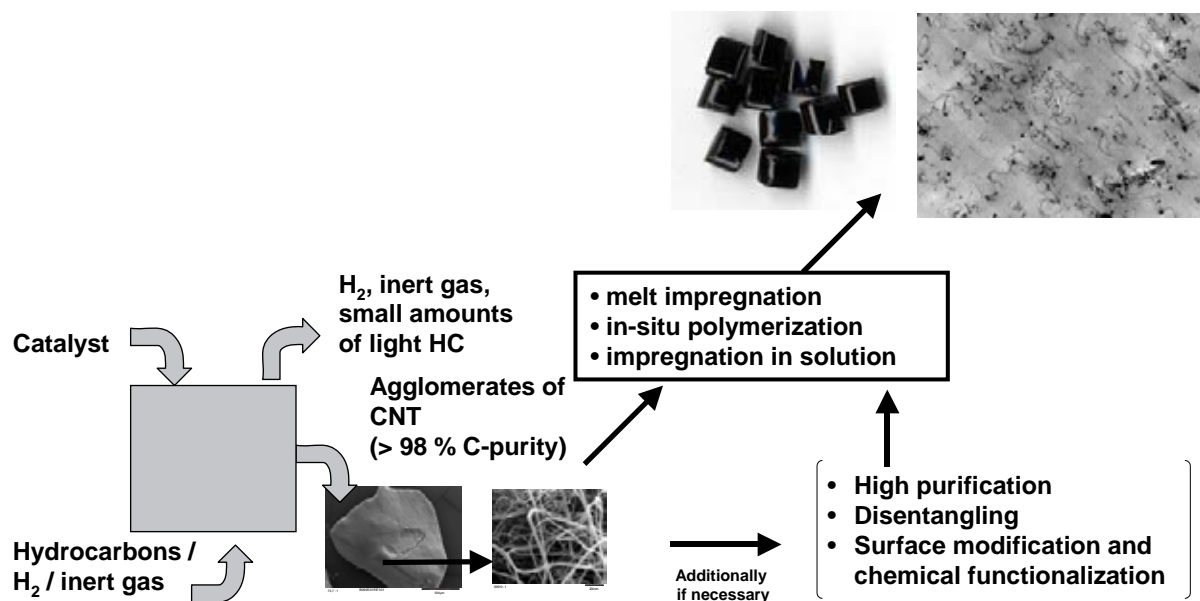


Figure 1: Summary of Bayer Process for the production of MWNT (Baytubes®) and polymer composites

The presentation will give an insight into the development of a highly productive catalyst and the development of a process for the production of MWCNT.

NEW SOLUTIONS IN CATALYTIC AMMONIA OXIDATION PROCESS

**Brushtein E.A., Golovnya E.V., Vanchurin V.I., Grunskiy V.N.<sup>1</sup>**

*NTC ALVIGO-M Ltd, Moscow, Russia*

<sup>1</sup>*Mendeleev University of Chemical Technology of Russia, Moscow, Russia*

*E-mail: alvigom@alvigo.ee, Web: <http://www.alvigo.ee>*

Ammonia oxidation process in practically every Russian domestic nitric acid plant is performed over two-stage catalytic system comprising a stack of platinoid gauzes and blocks of non-precious oxide catalyst made in Boreskov Institute of Catalysis SB RAS, Novosibirsk as the second stage. It is exactly the using of regular-structured block catalyst as both distributive and catalytically active second stage of the system which has led to a considerable improvement in technical and economic indices of the process.

On the other hand, the evident improvements in ammonia oxidation process over platinoid systems have been achieved during last 30 years by means of using noble metal alloy catchment gauzes, e.g. Pd/W, along with catalyst gauzes. The operating experience of such catalytic systems in UKL-7 type nitric acid plants demonstrates the advantages of reduction of specific direct losses of platinoids by 10-28 % and overall decrease of initial costs by 20 30-35 % comparing to conventional systems of 12 catalyst gauzes.

A promising direction in development of ammonia oxidation process can be implementation of a new advanced catalytic system which integrates the advantages of mentioned conventional ones. Obviously, the new system can not be introduced to the market without carrying out comprehensive operation tests under process conditions similar to those in industry.

Various arrangements of catalytic system for ammonia oxidation have been tested at the research facility at JSC ACRON, Velikiy Novgorod, Russia with the participation of NTC ALVIGO-M Ltd. Ammonia conversion rate NO yield reached 95,3 % for the two-stage system of 9 Pt catalyst gauzes placed over the layer of oxide block catalyst, which was on the same level with 95,0 % conversion rate NO yield over conventional system of 12 Pt gauzes. For the systems with number of Pt gauzes varying from 6 to 9, the layer of block catalyst under the stack added the average of 2 % to NO yield ammonia conversion..

It was found that NO yield selectivity of combined systems of 10 gauzes (7 Pt + 3 Pd/W) and 12 gauzes (7 Pt + 5 Pd/W) was slightly lower than that for systems of 10 and 12 Pt gauzes. For instance, the achieved NO yield ammonia conversion rate for the system of 12 Pt

catalyst gauzes amounted to 95,0%, whereas the combined system 7 Pt catalyst + 5 Pd/W catchment gauzes made up 94,2 %. Consequently, replacement of a part of catalyst gauzes in a stack by catchment ones can result in approximately the same NO yield ammonia conversion rate. Like this, the NO yieldselectivity of combined (7 Pt + 3 Pd/W) stack corresponded to that of the (9 Pt) stack. This testifies that catchment gauzes possess the certain catalytic activity in desired ammonia conversion into nitrogen oxide, i.e. operate bifunctionally.

Ammonia slip sharply decreased at increasing the number of Pt catalyst gauzes in a stack from 6 to 9, falling to 0,062 vol. %. The ammonia concentration in a effluent gas of 10 Pt gauzes system was 0,029 vol. %, while for (7 Pt + 5 Pd/W) system ammonia slip fell to 0.012 vol. %. According to our data, in terms of NO yieldselectivity the system of (7 Pt + 5 Pd/W) gauzes is equivalent to 10 Pt catalyst gauzes, therefore the lower ammonia concentration in converted gas at using catchment gauzes could be caused by intensification of undesired reactions, particularly ammonia oxidation into nitrogen.

NO yield Ammonia conversion rate for the system comprising 7 Pt, 3 Pd/W gauzes and a layer of block catalyst reached the maximum value of 95,4 % and ammonia slip was negligibly small. It is possible that more favourable hydrodynamics due to block catalyst layer situated under the gauzes stack allowed to avoid the NO yieldselectivity decrease observed in case of system without block catalyst.

The described new advanced system is considered to be polyfunctional, combining catalytic, absorptive and distributive properties. It is characterized by considerably reduced initial costs and specific losses of platinoids in comparison with well-known catalytic systems, securing similar values of NO yield ammonia conversion rate at the same time.



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## PECULIARITIES OF Cu-Zn METHANOL CATALYST STRUCTURE

**Khassin A.A., Shtertser N.V., Anufrienko V.F., Ruzankin S.F., Minyukova T.P.,**

**Altynnikov A.A., Larina T.V., Zaikovskii V.I., Yurieva T.M., Parmon V.N.**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: aakhassin@catalysis.ru*

Mechanism of methanol synthesis is one of the intriguing topics of catalysis. The nature of the active component and of the key reaction intermediates, mechanisms of CO and hydrogen activation are the questions still debated in literature. Despite Cu<sup>0</sup> surface is believed to be crucial for catalytic activity, the reaction is extremely sensitive to the chemical composition and structure of the precursor compound. Thus, the specific activity (i.e. activity related to the surface of Cu<sup>0</sup>) can differ by 2-3 orders of magnitude and depends on the oxide source of Cu<sup>0</sup>. In spite of similar values of the specific Cu<sup>0</sup> surface area of ca. 80-100 m<sup>2</sup>/g<sub>Cu</sub>, catalysts derived from Cu hydrosilicate, Cu-Zn-hydrosilicate, Cu-Zn-Al oxide (spinel structure) and Cu-Zn-Al oxide (wurtzite structure, WZ) exhibit dramatically different activity in methanol synthesis. The Cu-Zn-containing catalysts with WZ-like structure are manifold more active and selective than any other studied catalyst. The uniqueness of the Cu-Zn-containing catalysts with WZ structure is fascinating. There should be some important peculiarity either in reactant activation or in the intermediate interaction routes over this catalyst. Many hypotheses were published, referring to peculiar metal surface composition, electronic effects, role of metal-oxide interface. Each of them sounds plausible; however none has found direct experimental confirmation. The interesting hypothesis, which we address below, draws the parallel between the heterogeneous C=O bond hydrogenation and the well-known homogeneous catalytic conversion of ketones to alcohols in Brønsted acid solutions at the presence of Cu<sup>0</sup> [1, 2].

Similarity of mechanisms of the quoted above homogeneous reaction and heterogeneous hydrogenation of acetone to isopropanol over copper chromite was proved in [2]. It was shown that the reduction of CuCr<sub>2</sub>O<sub>4</sub> by H<sub>2</sub> is not accompanied with oxygen elimination. Instead, hydrogen donates electrons to Cu<sup>2+</sup> giving protons, which substitute for copper cations in tetrahedral sites of the spinel structure. Copper cations are reduced to form flat epitaxially bonded copper particles at the surface of the chromite substrate, while protons take the released positions and form covalent bonds with the oxygen atoms of the tetrahedron. Removing the protons by their interaction with oxygen or with acetone leads to Cu<sup>0</sup> oxidation and to restoration of the initial CuCr<sub>2</sub>O<sub>4</sub> structure. In catalytic reaction, hydrogenated chromite support acts as the solid Brønsted acid. We have to note, however, that copper chromite exhibits rather poor activity in methanol synthesis.

## OP-YS-1

Copper-zinc oxide catalysts has been shown to exhibit the similar mechanism of copper reduction-reoxidation [3-5]. Initially, the copper cations and anionic admixtures mainly concentrate as nanoclusters in the planar defects of missing basal plane, at that ZnO contains numerous stacking faults, with characteristic distance between them of 2-3 basal layers. The process of the samples reduction leads to the  $\text{Cu}^0$  state. The planar defects of ZnO structure are preserved even after reduction. During the reoxidation, copper atoms return back to the extended stacking faults of ZnO as the clusters of flat-square coordinated  $\text{Cu}^{2+}$ .

UV-Vis DRS of the Cu-Zn oxide catalyst precursor showed, that the edge of the fundamental adsorption by ZnO structure is shifted to the visible range ( $18000\text{-}22000\text{ cm}^{-1}$ ). This means, that either conduction band margin (CBM) is lowered or defect-induced states are formed at 0.8-1.2 eV below the normal CBM level of ZnO. It is noteworthy, that CBM of pure WZ-like ZnO is ca. 0.1 eV lower than Fermi level of hydrogen at standard conditions, which cause electron transfer from hydrogen to ZnO CB and stabilization of protons at the ZnO interstitions (see e.g. [6]). Therefore, hydrogen acts as a shallow electron donor for ZnO.

The presence of stacking faults may cause significant change in energy levels of both: valence band margin and conduction band margin. According to DFT modelling [7], the CBM level can differ by 0.147 eV for ZnO domains with different stacking of basal planes (WZ and zinc blende). Observed in our study decrease in the band gap by almost 1 eV may relate to high concentration of stacking faults and may lead to the dramatic increase in ZnO capacity to accept electrons of hydrogen and, consequently, the significant increase in concentration of protons dissolved in the ZnO support structure. If that is the case, the exceptional performance of Cu-ZnO catalyst is the sequence of extraordinary low CBM level of defective ZnO structure, which transforms under hydrogen-containing medium to solid Broensted acid  $\text{HZnO}$ .

The formulated hypothesis has to be confirmed by physical methods, incl. neutron spectroscopy and ESR as well as thorough measuring elementary reaction steps kinetics.

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## ESTABLISHING SYNTHESIS-STRUCTURE-ACTIVITY RELATIONSHIPS OF CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> CATALYSTS FOR METHANOL SYNTHESIS

**Baltes C., Vukojević S., Schüth F.**

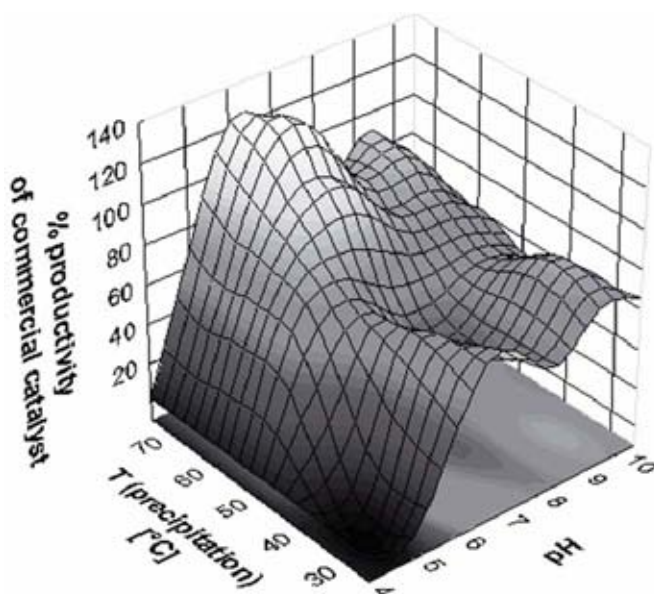
*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany*

*E-mail: baltes@mpi-muelheim-mpg.de*

Ternary Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts were systematically prepared via the co-precipitation route under strict control of parameters such as pH, precipitation temperature and calcination temperature. All catalysts were tested with respect to their methanol activity in a 49-fold multi-tubular high-throughput experimentation setup under conditions similar to the commercial methanol production route, using a syngas mixture of CO, CO<sub>2</sub> and H<sub>2</sub>.

Statistically representative catalysts were chosen for more detailed structure and morphology analysis in order to study correlations between the catalyst “preparation history” and the methanol productivity.

The highest catalyst performance was observed for catalysts obtained in the pH range from 6 to 8 at 70 °C. XRD measurements allowed the “grouping” of catalysts based on their composition. It was found that a group of best-performance catalysts exhibited the characteristic XRD pattern of non-calcined Cu/Zn hydroxycarbonate residues, leading to the assumption that carbonate species in the final catalyst structure may enhance its productivity. Further investigations of these hydroxycarbonate containing catalysts gave more detailed



**Figure 1: Precipitation conditions correlated to catalyst productivity**

insights into the dynamic aging process and its influence on the catalytic performance. Highest methanol activity was observed for catalysts aged between 20 and 60 minutes after an initial phase formation time. The optimum calcination temperature was found to be in the range from 250 to 300 °C. Under these conditions the resulting Cu/Zn/Al hydroxycarbonates remained stable.

Additionally, the syngas feed composition was varied under reaction

## OP-YS-2

conditions and correlated to catalytic activities. Highest methanol productivity over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts was observed for the following gas concentrations; H<sub>2</sub>: 50 –60 %, CO: 30 – 40 % and CO<sub>2</sub>: 5- 10 % at 4.5 MPa and 245 °C.

The CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by co-precipitation from aqueous solutions of Cu(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> using Na<sub>2</sub>CO<sub>3</sub> as precipitation agent under strictly controlled conditions (pH, temperature, duration of precipitation, aging time and flow rate of the solutions). Corresponding to their activity, some representative selected catalyst samples were studied in detail (TEM, XRD, TG-MS, and TPR). *Cu(0) reactive frontal chromatography* was done using a 16 channel parallel flow reactor combined with a multi channel IR cell, equipped for simultaneous N<sub>2</sub>O concentration measurements. TEM photographs of selected catalysts are illustrating the changes in catalyst morphology during the preparation procedure. An example is given in figure 2.

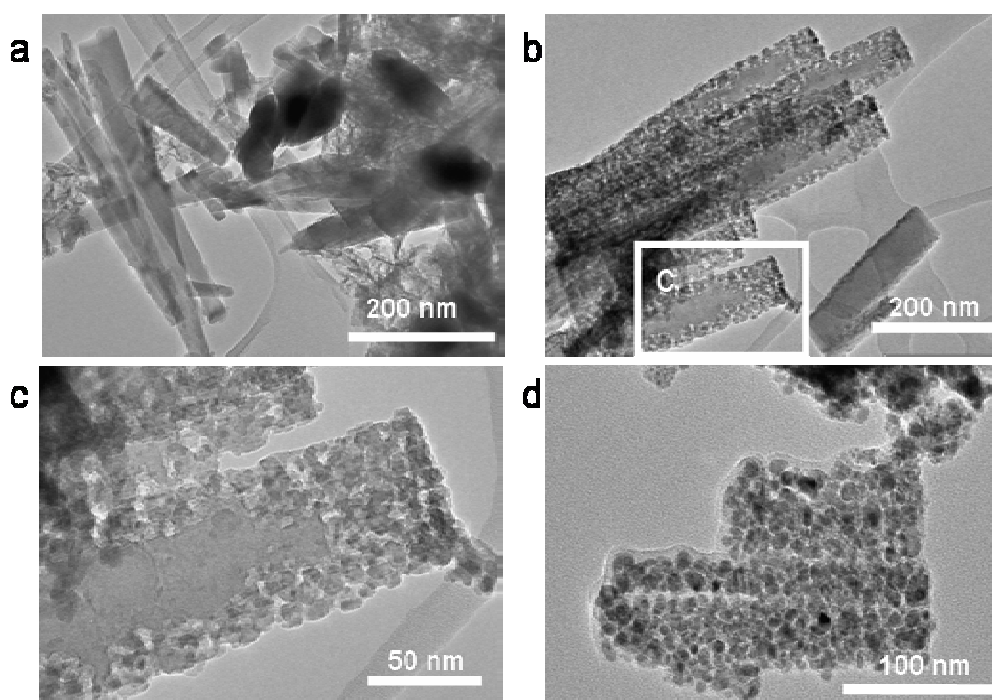


Figure 2: Catalyst morphology in dependence on the preparation conditions (a: catalyst precursor after aging of 1h, b: catalyst after 4 h calcination at 300 °C, c: enlarged picture of the crystallite in picture b, d: catalyst after reduction prior to reaction)

**THE EFFECT OF COPPER GROUP METALS ADDITION ON PHYSICOCHEMICAL  
PROPERTIES OF FeAlO<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub>, Al<sub>3</sub>CrO<sub>6</sub> SUPPORTED CATALYSTS FOR  
METHANOL SYNTHESIS**

**Maniecki T.P., Mierczyński P., Maniukiewicz W., Józwiak W.K.**

*Technical University of Łódź Institute of General and Ecological Chemistry 90-924 Łódź,  
Zeromskiego 116, tel. 048426313125, fax. 048426313128, Poland*

*E-mail: mierzyn@wp.pl*

The physicochemical properties of supported metals: Ag, Au, Ru, Cu on binary oxides FeAlO<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub>, Al<sub>3</sub>CrO<sub>6</sub> were studied. The spinel like type structures were prepared. The promoting effect of noble metal addition on the reducibility of semireducible bi-oxides was proved. The activity tests in methanol synthesis at atmospheric pressure and under high pressure were carried out.

In the past 20 years, there has been considerable interest referring to alcohol synthesis from syngas. Alcohols are important solvents and chemicals, additives to gasoline to enhance the octane number and reduce pollution. In conventional industrial synthesis of a mixture of methanol and higher alcohols the composite catalysts were used Cu-Zn or Cr-Zn with different additives. This work is focused on the physicochemical properties and catalytic activity of supported catalysts for synthesis of alcohols. The addition of metals (Au, Ag, Cu, Ru) on different supports improves catalyst reducibility and generally increase the activity and stability of these catalysts in methanol synthesis.

**Catalysts were prepared** by wet impregnation method. The starting compounds were nitrates of Al, Cu, Fe, Cr and Zn acetate. The ammonia was used for co-precipitation of binary chromium and aluminium hydroxides., zinc and aluminium hydroxides, iron and aluminium hydroxides. They were dried and calcined 3h in air at: 600, 500 and 700 °C, respectively. The obtained supports Al<sub>2</sub>O<sub>3</sub>, Al<sub>3</sub>CrO<sub>6</sub>, ZnAl<sub>2</sub>O<sub>4</sub> and FeAlO<sub>3</sub> were impregnated by appropriate aqueous solutions of metal compounds. The metal loading was 5% Me(Me=Au, Ag, Ru, Cu). **Methods of characterization.** The TPR<sub>H<sub>2</sub></sub> measurements were carried out in automatic TPR system AMI-1 in temperature range 25-900 °C with the linear heating rate 10 °C/min. Specific surface area and porosity were determined with automatic sorptometr Carlo-Erba. Phase composition was studied by XRD diffraction method using PAN analytical X'Pert MPD diffractometr. Activity tests were carried out in a flow reactor system witch GC analysis. **Result and discussion** Results of specific surface area measurements for supports (Al<sub>2</sub>O<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub>, FeAlO<sub>3</sub>, Al<sub>3</sub>CrO<sub>6</sub>) and Me/support catalysts

### OP-YS-3

after their calcination are presented in Table 1, in figure 1 there are shown the XRD patterns and TPR<sub>H2</sub> profiles for catalysts after calcined in air at 400°C and for supports Al<sub>2</sub>O<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub>, FeAlO<sub>3</sub> and Al<sub>3</sub>CrO<sub>6</sub>.

Table 1. Specific surface area of the supports and Me(Au, Ag, Cu, Ru)/FeAlO<sub>3</sub> catalysts.

catalyst/T <sub>calc.</sub> [°C]	Surface area [m <sup>2</sup> /g]	support	Calcination temperature [°C]	Surface area [m <sup>2</sup> /g]
Au/FeAlO <sub>3</sub> / 400	112	Al <sub>2</sub> O <sub>3</sub>	400	237
Ag/FeAlO <sub>3</sub> / 400	150	FeAlO <sub>3</sub>	500	143
Ru/FeAlO <sub>3</sub> / 400	143	ZnAl <sub>2</sub> O <sub>4</sub>	600	87
Cu/FeAlO <sub>3</sub> / 400	144	Al <sub>3</sub> CrO <sub>6</sub>	700	82

One can see that introduction of Fe<sup>3+</sup> ions into alumina network decrease its specific surface area only about 40%. This effect can be connected to the easy formation FeAlO<sub>3</sub> spinel with crystalline network is isostructural with alumina. In the case of both binary supports containing zinc and chromia a significant drop of the surface area was observed. This behaviour probably was caused by different elementary cell of zinc oxide and different size of elementary cell in the case of chromium oxide. The metal introduction in the surface of FeAlO<sub>3</sub> does not change significantly the specific surface area. Only the gold deposition decreases its surface 22 %, this effect is performed by strongly acid gold nitrate solution.

In the figure 1a one can see that all cases only spinels phase were detected. Metal introduction does not change a lot XRD patterns except in the case of gold which metallic phase was identified. The instability of gold oxide and its decomposition leads to metal phase during catalyst pre-treatment at 400 °C.

The TPR profiles for Me/FeAlO<sub>3</sub> catalysts were presented in figure 1c. One can see that metal addition moves the TPR effects toward lower temperature and increase the degree of catalysts reduction (20 %). The activity tests in methanol synthesis were carried out for supported metal catalysts on binary oxide. Generally all supported metal catalysts show comparable relatively high activity.

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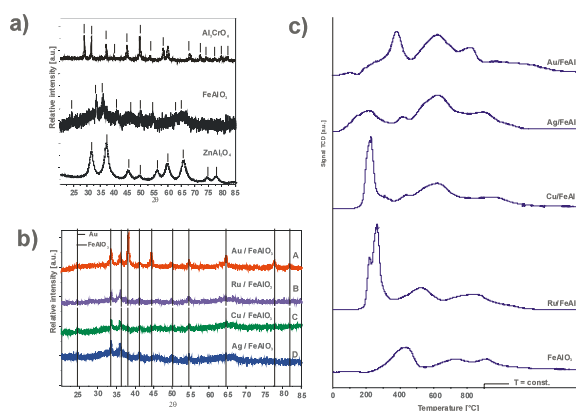


Figure 1 XRD patterns (a,b), and TPR profiles (c) for: a) Al<sub>3</sub>CrO<sub>6</sub>, FeAlO<sub>3</sub>, ZnAl<sub>2</sub>O<sub>4</sub> after their calcination at 600, 500, 700°C respectively. b) supported (Au, Ru, Cu, Ag)/FeAlO<sub>3</sub> catalysts. c) FeAlO<sub>3</sub>, (Ru, Au, Ag, Cu)/FeAlO<sub>3</sub> after their calcination in air for 4h at 400°C.

GENERATION SYNTHESIS GAS BY PARTIAL OXIDATION OF METHANE OVER  
Pt/PrCeZrO AND Pt/GdCeZrO CATALYST

**Gubanova E.L.**<sup>1,2</sup>, Sadykov V.A.<sup>2,3</sup>, Pazhetnov E.<sup>2</sup>, Boronin A.<sup>2</sup>, Mezentseva N.<sup>2</sup>,  
van Veen A.C.<sup>1</sup>, Mirodatos C.<sup>1</sup>

<sup>1</sup>*Institut de Recherches sur la Catalyse – CNRS, 2 avenue Albert Einstein, 69626  
Villeurbanne Cedex, France*

<sup>2</sup>*Borekov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>3</sup>*Novosibirsk State University, Novosibirsk, Russia*

*E-mail: gubanova@catalysis.nsk.su*

Catalytic partial oxidation of methane (POM) over the Pt/PrCeZrO and Pt/GdCeZrO (1.4 wt.% Pt, Ce:Zr=1:1, Gd or Pr content 5-30 at. %) catalysts was investigated using a temporal analysis of products (TAP). Influence of process parameters, state of catalyst (reduced or oxidized), dopants type and content on activity and selectivity of syngas formation was studied. Oxidized catalysts exhibits a lower reactivity towards methane than their thermally reduced state, which is explained by stabilization of oxidic Pt forms by support.

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

This study is focused on using the fast pulsed TAP reactor to investigate mechanistic features of the partial oxidation of methane (POM) over ceria- zirconia based mixed oxides doped with Pr or Gd and promoted with Pt. State of supported Pt was characterized by XPS and FTIRS of adsorbed CO test molecule.

Mixed oxides were prepared via Pechini route, and Pt (1.4 wt.%) was supported by incipient wetness impregnation with H<sub>2</sub>PtCl<sub>6</sub> solution followed by drying and calcination as described elsewhere [1].

## OP-YS-4

A high temperature TAP reactor was charged with 20 mg of the catalyst in a sieve fraction of 100 to 200 microns sandwiched between inert quartz sections. Prior to the experiments the sample was heated to 800 °C and pulses of an O<sub>2</sub>/Ar mixture were introduced to remove residual carbon. The catalytic performance was estimated in the temperature range from 550 to 700 °C using pulses of a mixture of O<sub>2</sub> and Ar and a mixture of CH<sub>4</sub> and Ar in both cases in a ratio of 1:1. Pulse sizes were adjusted to  $1.7 \cdot 10^{14}$  –  $1.3 \cdot 10^{15}$  molecules per pulse for catalytic experiments (Knudsen diffusion was required). To achieve a dynamic saturation of the surface by oxygen before TPD O<sub>2</sub>, bigger ( $3.6 \cdot 10^{14}$  –  $2.4 \cdot 10^{15}$  molecules) pulses of the O<sub>2</sub>/Ar mixture were injected. The detection of the pulse responses and characteristic masses during TPD scanning experiments was accomplished with a quadruple mass-spectrometer.

For Gd -doped sample oxygen starts to desorb from ~ 250 °C, while for Pr -doped sample there is no significant oxygen desorption up to 350 °C. Hence, doping of ceria-zirconia oxide by Gd favors formation of more weakly bound oxygen species being potentially more reactive.

Results of pump-probe experiments revealed higher methane conversions for Gd -doped samples. It is especially noteworthy that the methane conversion is lower for the case of a dynamically oxidized catalyst than for a thermally reduced catalyst. According to XPS and FTIRS data, this is explained by the presence on the surface of oxidized samples mainly oxidic (Pt<sup>2+</sup> and Pt<sup>4+</sup>) cationic species less efficient in methane activation than Pt<sup>0</sup> clusters. More oxidized Pt<sup>4+</sup> species are stabilized only for Pr -doped samples, which explains their lower reactivity along with a higher syngas selectivity.

Comparison experiments over platinum black and Pt/Al<sub>2</sub>O<sub>3</sub> revealed no significant oxygen responses for the TPD experiment and a very low selectivity in syngas production, while the desorption of oxygen on the bare Pr<sub>0.3</sub>Ce<sub>0.35</sub>Zr<sub>0.35</sub>O<sub>x</sub> material proceeded very slowly. The latter observations clearly indicate the synergy between Pt and the active support. Hence, for doped Pt-supported ceria-zirconia samples methane transformation into syngas is the primary process followed by subsequent oxidation of thus formed CO and H<sub>2</sub>. For Gd-doped samples delayed H<sub>2</sub> evolution was observed at 550 °C suggesting participation of strongly bound species (hydroxyls, formates etc) in the step of H<sub>2</sub> generation at this temperature.

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The authors like to acknowledge the joined European laboratory (LEA-313) between France and Russia on catalysis (LFRC) and the financial support of the PhD thesis of E.L. Gubanova. This study was also supported by the RFBR-CNRS 05-03-34761 project.

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## GOLD NANO-PARTICLES STABILIZED IN MESOPOROUS MCM-48 AS ACTIVE CO-OXIDATION CATALYST

**Bandyopadhyay M., Korsak O., van den Berg M., Grünert W., Birkner A., Li W.<sup>1</sup>,  
Schüth F.<sup>1</sup>, Gies H.**

*Ruhr-Universität Bochum, Universitätsstr. 150, D-44780 Bochum, Germany*

<sup>1</sup>*MPI für Kohlenforschung, Kaiser-Wilhelmplatz 1, D-45470 Mülheim, Germany*

*E-mail: hermann.gies@rub.de*

Gold in nano-crystal size is known as highly active catalyst for many important chemical reactions such as CO oxidation, hydrogenation of unsaturated hydrocarbons, reduction of NO<sub>x</sub>, epoxidation of propane, combustion of methane, etc. For all catalytic applications it is important that the small gold particles are highly dispersed on the oxide support. A series of active Au/oxides catalysts were reported in the literature leading to the conclusion that, Au/TiO<sub>2</sub> and Au/CeO<sub>2</sub> are the most active systems. However, a draw back of all nano-dispersed Au on oxide supports is its ready aggregation to larger particles already at moderate temperatures, usually at ~60 °C. The key issue in this problem is to encapsulate gold nano-particles inside the porous matrix and so to provide nano-size confinement inside the pore system. Three dimensional M41S materials are thought to be particularly useful because of on the one hand they possess high thermal and chemical stability and on the other hand their 3D-framework gives an opportunity for the shape selective catalysis. The use of silica-MCM-48 with quantum-sized titania oxide particles inside the porous matrix as a support for Au particles is the main interest of our present study.

Mesoporous titania-modified Si-MCM-48 was prepared by a post-synthetic wet impregnation method using tetrabutylorthotitanate. Three times impregnated TiO<sub>2</sub>/MCM-48 containing ~15 wt.% titania was used for Au loading. Gold has been deposited onto TiO<sub>2</sub>/MCM-48 matrix using the deposition–precipitation technique. After two impregnation runs the final Au content amounted to ~3 wt.%. The whole procedure was carried out in absence of light. Characterization of the catalysts was carried out by PXRD, TEM, EXAFS and XANES-studies.

As a test reaction CO-oxidation was chosen. The freshly prepared catalysts convert CO to CO<sub>2</sub> at 50% level at –20 °C. The encapsulation in mesoporous MCM-48 prevents the gold nano-particles from sintering up to at least 200 °C, a temperature which would lead to the deactivation of the catalyst deposited on a bulk TiO<sub>2</sub> powder. XANES and EXAFS-studies confirm the coexistence of elementary and ionic gold during the catalytic activity. If the Au ions detected are relevant for the CO oxidation activity is subject to ongoing research.

**THE MECHANISM OF CATALYTIC C<sub>3</sub>H<sub>6</sub> OXIDATION ON STEPPED Rh(410)  
AND Pt(410) SURFACES**

**Matveev A.V., Weststrate C.J.<sup>1</sup>, Sametova A.A., Gorodetskii V.V., Nieuwenhuys B.E.<sup>1</sup>**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>1</sup>*Leiden Institute of Chemistry, Leiden, the Netherlands*

*E-mail: matveev@catalysis.ru*

The activity of stepped Rh(410) and Pt(410) surfaces in complete (CO<sub>2</sub>, H<sub>2</sub>O) and partial (CO, H<sub>2</sub>) oxidation of propylene was compared by using the temperature-programmed reaction (TPR) method. The nature of dissociative propylene adsorption on clean and oxygen covered surfaces was studied. Under steady state conditions ( $R=p(\text{O}_2)/p(\text{C}_3\text{H}_6)$ , T), a correlation was found between the surface coverages of intermediates and the reaction selectivity in partial oxidation of propylene.

Catalytic oxidative conversion of light C<sub>3</sub>-C<sub>4</sub> hydrocarbons into synthesis gas is a very important process nowadays. In this work we studied Pt(410) and Rh(410) single-crystal surfaces, consisting of (100) terraces with a width of 4 atoms and monatomic (110) steps. These surfaces are good models for the defective surfaces of real catalysts. The mechanism of dissociative propylene adsorption on clean and oxygen precovered surfaces was studied by TPR, TDS and LEED. Reaction conditions ( $R=p(\text{O}_2)/p(\text{C}_3\text{H}_6)$ , T) for complete (CO<sub>2</sub>, H<sub>2</sub>O) and partial (CO, H<sub>2</sub>) propylene oxidation were found.

*Propylene adsorption.* According to TDS data, C<sub>3</sub>H<sub>6ads</sub> molecules desorb and dissociate on clean Rh(410) and Pt(410) surfaces at T~150-300 K. Observed desorption of hydrogen in reaction  $\text{C}_3\text{H}_{6\text{ads}} \rightarrow \text{C}_3\text{H}_{5\text{ads}} + \text{H}_{\text{ads}}$  at T ~ 230÷290 K corresponds to hydrogen desorption from clean surfaces, which points to formation of separate layers of propylidyne (CCH<sub>2</sub>CH<sub>3ads</sub>) and hydrogen (H<sub>ads</sub>) on the surface. The further dehydrogenation of propylidyne intermediates  $\text{C}_3\text{H}_{5\text{ads}} \rightarrow \text{CCH}_{\text{ads}} + \text{CH}_{\text{ads}} + \text{H}_{\text{ads}}$  is accompanied by hydrogen desorption at T ~ 370÷440 K and by formation of CCH<sub>ads</sub> and CH<sub>ads</sub> species. High-temperature H<sub>2</sub> desorption at T ~ 600 K corresponds to the final process of decomposition of CCH<sub>ads</sub>- and CH<sub>ads</sub>- hydrocarbon species with formation of graphite on the surface.

*Oxygen adsorption.* Dissociative adsorption of oxygen on clean Pt and Rh surfaces was studied. The formation of various adsorbed oxygen states was found: atomic (O<sub>ads</sub>), apparent subsurface (O<sub>sub</sub>) and surface oxide (O<sub>oxi</sub>), depending on the conditions. Reactivity of oxygen species was studied in reaction with CO. The most active is the atomic oxygen O<sub>ads</sub>, the least the surface oxide O<sub>oxi</sub> species.

*Propylene oxidation.* Corresponding to TPR-data, propylene molecules react with oxygen in several consecutive steps. In the beginning, at  $T < 300$  K, interaction of  $O_{\text{ads}}$  atoms with dissociative propylene state ( $C_3H_{6\text{ads}} \rightarrow C_3H_{5\text{ads}} + H_{\text{ads}}$ ) accompanied by a desorption peak of water at 285 K, formed by  $2H_{\text{ads}} + O_{\text{ads}} \rightarrow H_2O_{\text{gas}}$ . At  $T \sim 300 \div 700$  K high-temperature peaks appear:  $H_2O$  (370 K),  $CO$  (500 K),  $CO_2$  (335, 450 K) and  $H_2$  (380, 500, 670 K), suggesting the occurrence of several parallel reactions: (i)  $O_{\text{ads}} + CO_{\text{ads}} \rightarrow CO_{2\text{gas}}$ : -  $CO_{\text{ads}}$  oxidation; (ii)  $CCH_2CH_{3\text{ads}} + O_{\text{ads}} \rightarrow H_2O_{\text{gas}} + CCH_{\text{ads}}$ : -  $CH_x$ -species oxidation; (iii)  $CH_2CH_{3\text{ads}} \rightarrow CCH_{\text{ads}} + H_{2\text{gas}}$ : -  $CH_x$ -species dissociation; (iv)  $CH_{\text{ads}} + O_{\text{ads}} \rightarrow [CHO]_{\text{ads}} \rightarrow CO_{\text{gas}} + H_{2\text{gas}}$ : - conversion; (v)  $CCH_{\text{ads}}, CH_{\text{ads}} \rightarrow H_{2\text{gas}} + CC_{\text{ads}}, C_{\text{ads}}$ : - graphite formation.

Under reaction conditions  $P_{\text{all}} \sim 10^{-7}$  mbar,  $R = p(O_2)/p(C_3H_6) = 30$  in range  $T \sim 400 \div 600$  K TPR shows the complete oxidation of propylene to  $CO_2$  and  $H_2O$ . A change in reaction mechanism takes place at higher temperatures, in the range  $T \sim 700 \div 1000$  K: propylene is then selectively oxidized to synthesis-gas ( $H_2 + CO$ ).

The mechanism of complete and partial propylene oxidation on Rh(410) was found to be very close to the one, observed on Pt(410). The key role of carbon and oxygen accumulation in the selectivity of reaction was demonstrated. It was shown, that the catalytic activity of Pt(410) at  $R < 30$  is higher than that of Rh(410). At  $R > 30$  surface oxide-like structures on Pt and Rh surfaces are formed, which decrease the catalytic activity of Pt in the whole temperature range (300 ÷ 1100 K) and increase the activity of Rh in the  $T$  range  $\sim 300 \div 400$  K.

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**MODIFIED CHROMIA-OXIDE CATALYSTS OF NON-OXIDATIVE  
DEHYDROGENATION OF PROPANE****Barbashova P.S., Derlyukova L.E., Anufrieva T.A., Dobrovolsky Yu.A.***Institute of Problems of Chemical Physics RAS, Chernogolovka**E-mail: barbashova@list.ru*

This work is devoted to the investigation of catalytic properties of  $\text{CrO}_x(\text{Na}_2\text{O})/\text{support}$  and  $\text{CrO}_x/\text{CoAl}_2\text{O}_4/\gamma - \text{Al}_2\text{O}_3$  in the reaction of non-oxidative propane dehydrogenation. Relationship between amount of alkali promoter and properties of coke depositions, accumulated in the process of catalyst's work were investigated by thermal analysis. Optimal composition of catalysts was found. Noted, that the  $\text{CrO}_x/\text{CoAl}_2\text{O}_4/\gamma - \text{Al}_2\text{O}_3$  catalyst, synthesized without alkali promoter, have an equal activity and deactivation resistance with traditional  $\text{CrO}_x(\text{Na}_2\text{O})/\text{support}$  catalysts.

Light olefins (ethylene, propylene, butylenes and isobutylenes) are the valuable feedstock for chemical industry. Traditionally they are received as co-products of steam or catalytic cracking of naphtha. Alternative way is the catalytic dehydrogenation of light paraffines, where olefins can be received as target products. The most popular catalysts of this process are chromia-oxide systems.

Samples of  $\text{CrO}_x(\text{Na}_2\text{O})/\text{support}$  were synthesized by wetness impregnation of supports ( $\gamma\text{-Al}_2\text{O}_3$  and  $\text{CeO}_2$ ) with  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  solution in presence of small amount of Na as a promoter. Catalytic activity of those samples in the reaction of propane dehydrogenation was analyzed.

We found out that ceria-based samples do not have appropriate catalytic activity up to 670 °C. Selectivity to propylene does not exceed the 40 per cent.

The catalytic activity of alumina-based samples is significantly depending of the concentration of active component and promoter.

The combination of 5-10 weight % of Cr and 1,0 weight % of  $\text{Na}_2\text{O}$  found to be optimal and allowed to achieve up to 92-95 % selectivity to dehydrogenation products at 550 °C.

Thermal analysis of deactivated catalysts on the STA 409PC (NETZSCH) indicated that the concentration of alkali promoter have influence on the amount and properties of coke, accumulated in the process of catalyst's work. The increase of amount of  $\text{Na}_2\text{O}$  leads to the decrease of amount of coke; carbon depositions become less resistant to the oxidative treatment. It's indicated by the increase of  $\Delta H$  and  $T_{\text{MAX}}$  of the annealing process (Table 1). It makes the regeneration of the catalyst easier.

Table. 1. Characteristics of the coke annealing process for the samples, containing different amount of Na<sub>2</sub>O, by TG/DSC data

Sample	Conc. Cr, weight.%	Conc. Na <sub>2</sub> O, weight.%	ΔH, J/g	T <sub>MAX</sub> , °C	Δm, %
1	5,0	0,5	2059	379	3,61
2		1,0	1719	368	2,82
3		3,0	557	345	1,82

Also we synthesized CrO<sub>x</sub>/CoAl<sub>2</sub>O<sub>4</sub>/γ – Al<sub>2</sub>O<sub>3</sub> samples without alkali promoter. Their catalytic activity and deactivation resistance is equal to the classic CrO<sub>x</sub>(Na<sub>2</sub>O)/support catalysts.

**THE OXIDATIVE DEHYDROGENATION OF PROPANE TO PROPYLENE ON  
VANADIUM AND MOLYBDENUM OXIDES SUPPORTED ON TITANAEROSILE**

**Redkina A.V., Khomenko K.N., Konovalova N.D**

*Institute of Sorption and Problems Endoecology NASU, Kiev, Ukraine*

*E-mail: toniamail@rambler.ru*

It was investigated ODH of propane on  $V_2O_5$  and  $MoO_3$  supported on superfine pyrogenic titanaerosile (TAS) with the different contents of titanium dioxide. It was shown, that at the contents  $TiO_2$  in TAS, appropriate to isomorphic replacement of ions of silicon with the titan, it is formed active and selective vanadium oxide catalyst. A more amount of titanium dioxide in the support increases efficiency  $MoO_3$ . By method X-ray diffraction analysis it was established, that TAS obstructes with deep reduction of oxides in during reaction. By method TPD of propylene it is shown, that at optimum reduction of a surface of oxides conditions for optimum convertible chemisorption propylene are created.

Oxides of vanadium and the molybdenum, applied on various supports now are widely investigated as the most perspective catalysts for developed process of oxidative dehydrogenation (ODH) of propane to propylene. In the pure state these oxides, having a low specific surface, are poorly effective for this process. But their applying on the developed surfaces of supports and creation of the isolated active sites, preventing inevitable oxidation formed propylene in conditions enough of high temperatures necessary for activation neutral propane, it allows to create catalysts on which the yield of propylene achieves 30-35 mol. % [1, 2]. However, it is not enough for industrial realization of process. It is marked, that supports render essential influence on properties of an active phase.

In this work as supports  $V_2O_5$  and  $MoO_3$ , the superfine powders of pyrogenic titanaerosil with different percentage contents of titanium dioxide, received by joint flaming hydrolysis of chlorides of silicon and the titan, were tested. An active phase oxides in amount 5-10 weight. % it was applied by a method of impregnation of supports by solutions of metavanadate and paramolybdate ammonium with the subsequent drying and calcination of samples. Catalytic activity of the obtained structures and pure oxides was tested in a quartz reactor of flowing type in reaction ODH of propane at temperatures 300-650 °C on a mix containing 5 vol. % of propane in a helium - oxygen mix. X-ray phase analysis of supports and catalysts are carried out before and after reaction ODH of propane. Oxidized and in a different degree reduced surfaces of oxides were investigated by a method programmed thermal desorption (PTD) of propylene adsorbed at room and increased temperatures individually and from mixes with oxygen.

It was shown, that the applying  $V_2O_5$  on TAS in which ions of the titan replace silicon in oxygen tetrahedrons of matrix  $SiO_2$  and do not contain separate phases of titanium dioxide it allows to create highly selective catalyst ODH of propane. It gives at 600 °C, ratio  $C_3H_8:O_2=3:1$  and time of contact - 4 s the yield of propylene from above 50 mol. % while on pure oxide in these conditions it turns out only 18 %  $C_3H_6$ . On the contrary, the presence of separate phases of  $TiO_2$  in structure TAS allows to increase yield of propylene on supported  $MoO_3$  more than twice, in comparison with pure oxide, though the received catalyst is considerably less effective, than structures on a basis supported  $V_2O_5$ .

By method X-ray diffraction analysis it was established, that during reaction  $V_2O_5$ ,  $MoO_3$  and  $TiO_2$  are reduced up to the lowest oxides. At that, on vanadium oxide the degree of transformation of propane begins to be decreased, due to the beginning of return reaction of hydrogenation of propylene, which is catalysed by  $V_2O_3$ . At applying of  $V_2O_5$  on TAS, in process ODH it is reduced at most than up to  $V_2O_4$  and at rise in reaction temperature the conversion of propane grows continuously at preservation of high selectivity on propylene.

One of condition of creation of the effective catalyst of propane dehydrogenation is provision convertible chemisorption formed propylene. By method TPD in work it was established, that on oxidized surface  $V_2O_5$  and  $MoO_3$  the propylene is chemisorbed basically destructively with formation of products of full oxidation. At reduction of oxides the general adsorption of propylene grows considerably and it is chemisorbed mainly convertible. The maximum of this form chemisorption of propylene on  $MoO_3$  falls to 0,2-0,4 monolayers of the removed oxygen. On  $MoO_3$ , reduced it is more than on a monolayer, the propylene is not adsorbed absolutely. Adsorption of  $C_3H_6$  on  $V_2O_5$  is much higher, than on  $MoO_3$  and it grows at increase of depth of reduction. At adsorption of propylene from its mix with oxygen the amount of convertible chemisorbed propylene on  $V_2O_5$  grows over many times and the peak its desorption is displaced in area of high temperatures. The optimal of a ratio between the convertible form chemisorption of propylene and energy of activation its desorption from surface of  $V_2O_5$  it falls to a degree of reduction corresponding to  $V_2O_4$ .

In work it was made supposition about influence of  $Ti^{3+}$  ions in structure TAS on the state of vanadium and molybdenum ions in supported oxides and on the procession of ODH reaction of propane in propylene.

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**DESIGN OF NOVEL HETEROGENEOUS CATALYSTS OF HYDROCARBONS  
DEHYDROGENATION BASED ON Pt-Ru (Re) ALLOYS**

**Efimov M., Karpacheva G., Zemtsov L., Ermilova M., Orekhova N., Efimov O.<sup>1</sup>**

*A.V. Topchiev Institute of Petrochemical Synthesis RAS, Moscow, Russia*

<sup>1</sup>*Institute of Problem of Chemical Physics RAS, Moscow Region, Chernogolovka, Russia*

*E-mail: efimov@ips.ac.ru*

Novel heterogeneous catalysts for hydrocarbon dehydrogenation with alloys Pt-Ru (Re) nanoparticles finely dispersed in a carbon matrix were developed under IR-pyrolysis of a precursor based on PAN, purified coal SKT-6A, PtCl<sub>4</sub>, RuCl<sub>3</sub> (or (NH<sub>4</sub>)<sub>2</sub>ReO<sub>4</sub>). Alloy nanoparticles Pt-Ru and Pt-Re finely dispersed in structure of carbon carriers were firstly obtained directly during the process of catalyst formation. Catalyst 5% Pt-Ru deposited in carbon carrier based on IR-PAN and coal SKT-6A shows high catalytic activity and 100 % selectivity in dehydrogenation of cyclohexane and propane.

Novel heterogeneous catalysts for hydrocarbon dehydrogenation with bimetallic nanoparticles finely dispersed in carbon matrix were developed. IR-pyrolyzed polyacrylonitrile (IR-PAN) with graphite-like structure and carbon-carbon composites based on IR-PAN and multiwalled carbon nanotubes (MCNT) or purified finely dispersed coal SKT-6A were used as carbon carriers. The common solution of PAN (MM=150000), PtCl<sub>4</sub> and RuCl<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>ReO<sub>4</sub> in DMFA (conc.5 mas.%) was employed as a catalyst precursor. On introduction in precursor composition MCNT or coal SKT-6A their one hour ultrasonic dispersion was applied. IR-pyrolysis of precursors was carried out in two stage mode. The first stage is preliminary IR-annealing at 150-200 °C during 15 min in air in the course of which solvent disposal and tentative structuring take place. The main stage is IR-pyrolysis at T=450-800 °C in inert atmosphere during 10-60 s. Carbonization processes growing in these conditions lead to formation of graphite-like layer structure. It is amorphous due to irregular shift of grapheme planes with respect to each other and small sizes of areas of crystallites coherent scattering. The structure ordering of carbon carriers was shown to take place with the increase of IR-irradiation intensity. Interlayer distance changes from 3.71 Å to 3.43 Å and crystallites size rises from 15 up to 32 Å.

During the IR-pyrolysis the effective metal reduction with the participation of hydrogen evolving in dehydrogenation of the main PAN chain in parallel with the formation of ordered carbon structures takes place. In such way metal-carbon catalysts including nanosized



bimetallic particles Pt-Ru or Pt-Re were obtained. On the basis of X-ray diffraction data bimetallic nanoparticles are the Pt-Re or Pt-Ru alloys. They have simple cubic lattice with the parameter  $a=3,888 \text{ \AA}$  for Pt-Re alloy and  $a=3,899 \text{ \AA}$  for Pt-Ru one. Decrease of crystal lattice parameters in compare with value of this parameter for Pt ( $a = 3.993 \text{ \AA}$ ) evidences the obtaining the solid solution of substitution. On the basis of transmission electron microscopy data bimetallic nanoparticles was shown to be finely dispersed in a carbon matrix. Histograms for nanoparticles sizes distribution were done,  $3 < d < 18 \text{ nm}$ .

Nanoparticles of Pt-Ru and Pt-Re alloys finely dispersed in structure of carbon carriers were firstly obtained directly during the process of catalyst formation. It is a significant advantage of developed method of catalyst preparation. In common conditions the alloy preparation is separated and nonordinary stage of technological process. The method of catalyst preparation was applied for inserting nanosized particles of catalitically active metals in structure of carbon carrier "in situ" while the IR-pyrolysis of precursor composition occurs. It is another advantage of developed method in compare with known ones which include stages of pre-starting procedures, precursor solution impregnation with following hydrogen calcinations at high temperature during quite long time.

Catalysts based on 5% Pt-Ru dispersed in different carbon carriers were chosen for testing their catalytic activity in relation to dehydrogenation of cyclohexane. The catalyst with IR-PAN as a carrier was shown to offer the lowest catalytic activity due to minimal specific surface. At the same time the use of Pt-Ru catalyst deposited on carbon-carbon composites on the basis of IR-PAN (10 mas.%) and coal SKT-6A (90 mas.%) shows high catalytic activity and selectivity in dehydrogenation of cyclohexane. 100 % conversion is obtained at  $T > 450 \text{ }^\circ\text{C}$ . In all temperature range the selectivity for benzene is 100 %. Catalysts prepared were tested in dehydrogenation of propane with the obtaining of propylene. Propylene yield is equaled to 16 % with 100 % selectivity. That is the content of 10 mas.% PAN in precursor proved to be sufficient for the full reduction of metals and homogeneous distribution the active centers in the structure of carbon-carbon carrier.

Developed by us method of preparation of catalysts of dehydrogenation may be applied for the formation of other catalytic systems including different metal nanoparticles on different nature carbon carriers

## CARBON FIBERS CONTAINING TUNGSTEN NANOPARTICLES AS A CATALYST FOR HYDROCARBON CONVERSION

**Tumanyan P.B., Trusova E.A., Skryleva E.A.<sup>1</sup>, Pisarev S.A.<sup>2</sup>**

*A.V. Topchiev Institute of Petrochemical Synthesis RAS, Moscow, Russia*

<sup>1</sup>*Moscow Steel and Alloys Institute, Moscow, Russia*

<sup>2</sup>*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia*

*E-mail: trusova@ips.ac.ru*

The texture and catalytic activity of carbon fibers in the conversion of a light C<sub>5</sub>-C<sub>6</sub> distillate fraction have been investigated. The catalyst was synthesized by encapsulating nanostructured tungsten into carbon fibers. It has been shown that tungsten (0-VI) finely dispersed in the carbon matrix may affect catalytic activity in the enrichment of C<sub>5</sub>-C<sub>6</sub> fraction by isoaliphatic, (poly)alkyl-aromatic and (poly)alkyl-alicyclic HC at the temperature of 60 °C and pressure 1 atm.

Due to the porous structure in which the share of mesopores is dominating the carbon fibers (CF) proves to be promising as an object to be used in catalysis as a support. Previously [1] we had reported about the synthesis of a catalyst on the basis of CF in the pores of which tungsten nanoparticles had been encapsulated by the template method, as well as about the peculiarities of hexane isomerization (in gas and liquid phases) while being present under various conditions (60-250 °C, 1atm) The method developed by us permits to encapsulate metal/oxide in nanostructured state into the mesopores: in form of 0D particles or 2D coatings, thereby maintaining sufficient space for the penetration of the reacting ingredients of the reaction mixture.

In this report we have also presented the findings of the study of the W-catalyst based on the broad CF fraction obtained using an organic template. The catalyst contained 33.7wt.% of tungsten (calculated on WO<sub>3</sub>) the state of which was tested by the ESCA (PH1 5500 ESCA, Perkin Elmer) additionally using ionic staining (Ar<sup>+</sup>, Ei=2keV), as well as PC ACCESS ESCA v 7.2c software for the computation of the element atomic concentration. The W/CF microphotographs had been obtained by means of TEM Philips EM-301. Testing of the catalyst had been performed in conversion of the C<sub>5</sub>-C<sub>6</sub> hydrocarbon fraction in liquid phase (60 °C, 1 atm). It is known that this process has drawn particular interest of developers in the last few years due to the fact that it is a potential source for the production of additional high-octane gasoline amounts.

It has been shown by the ESCA method that tungsten is non-uniformly distributed through the C-cross-section: on the surface its concentration amounts to 2.3-2.6 at.%, while at the depth of 40 nm from the CF surface the tungsten concentration is increased by 1.5 times.

It has also been found that the deeper from the surface the lower the tungsten oxidation degree dropping from 6+ down to  $\ll 1+$  whereas the existence of not only W-O, but also W-C bonds at the depth of 40 nm may be assumed to a high probability, therewith the share of tungsten with a low degree of oxidation amounts to 43 %.

By the microphotographs shown in Figs 1a and 1b obtained by the TEM method it is possible to assess the CF diameter, amounting, 40-90 nm. In this case tungsten is not observed in form of separate particles, and is apparently completely distributed in the CF bulk, thus testifying its high dispersity and deep penetration into CF. The latter is fully coinciding with the above discussed ESCA results.

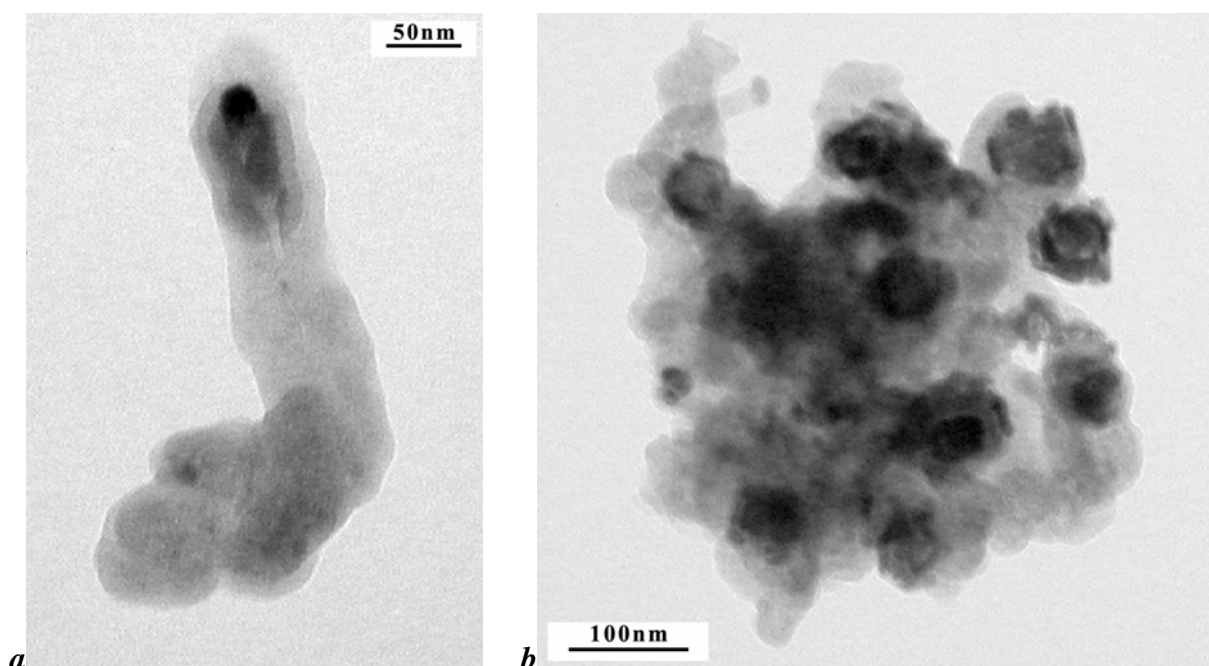


Fig. 1. TEM image of the obtained W/CF catalyst

The catalyst testing in converting the light  $C_5$ - $C_6$  fraction (GLC data) has shown that substantial decrease in the  $C_4$ -components (93-94%), as well practically complete conversion of  $n$ - $C_6$ ,  $-C_7$  and benzene are occurring in the process. At the same time an increase by 2-30 times of  $i$ - $C_7$ - $C_9$  and also (poly)alkyl-aromatic and (poly)alkyl-alicyclic components contents (alkyl =  $C_1$ ,  $C_2$ ,  $n$ - or  $i$ - $C_3$ ) are observed.

In conclusion, we have shown that the tungsten encapsulating into CF by the template method allows for obtaining a catalyst with an intricate morphology, which contain a finely dispersed metal in the bulk of carbon matrix. As-obtained W/CF catalyst exhibits high activity in conversion of the light  $C_5$ - $C_6$  fraction even at the temperature 60 °C and 1 atm. pressure, resulting in the fraction enrichment with  $i$ -HC and (poly)alkyl benzenes.

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**CREATING MULTIPLE SLURRIES FOR EFFECTIVE Pt-CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> SECONDARY  
LAYERS OF BLOCK CATALYSTS**

**Drobakha G.S., Drobakha E.A., Solntsev K.A.**

*Institute of Physical and Chemical Problems of Ceramic Materials RAS, Moscow, Russia*

*E-mail: greg\_flash@mail.ru*

The compositions of slurries based on boehmite (AlOOH) were studied under pH of the liquid phase from 1,5 to 9,4. It was found the means to stabilize slurries and to coat slurries on the block cordierite carrier (BCC). Obtained Pt-CeO<sub>2</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/BCC catalysts calcined at the temperatures in the range of 550 to 1000 °C were studied using XRD, BET, SEM technique and the catalytic activity analysis. Calcined at 800 °C catalysts with the mole ratio  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> 1:1 in the secondary layer showed an increase in the catalytic activity in comparison with the catalysts calcined at 550 °C. The work is in the progress.

The problem of creating effective block catalysts for purification of exhaust fumes of internal combustion engines and industrial plants is still remains important today as environment protection requirements increase. The existing methods of creating block catalysts are usually multistage, power-hungry and labour-consuming, the secondary layers having quickly insufficient adhesiveness (adhesion) with block carrier surface and demand heavy expenses of materials.

In our work multiple slurries have been elaborated. They include both alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), ceria which have thermal-stabilizing influence upon  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and active component compounds.

The compositions of slurries based on boehmite (AlOOH) were studied under pH of the liquid phase from 1,5 to 9,4. It was found means to prevent sedimentation in slurries and to coat slurries on the block cordierite carrier (BCC). The application of the multiple slurries makes it possible to combine the calcination of coating with catalyst reduction.

Obtained samples of the Pt-CeO<sub>2</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/BCC catalysts containing about 1,5 g/dm<sup>3</sup> of Pt were tested by using flowing gas-plant with "OPTOGAS 500.2" gas analyzer through the oxidizing reaction of CO with O<sub>2</sub> in a gas flow, in which the volume component concentrations were CO - 0,3%, O<sub>2</sub> - 1,0% and N<sub>2</sub> - 98,7%. The gas volume rate was either 10000 or 20000 h<sup>-1</sup>. Produced by elaborated procedure, Pt-CeO<sub>2</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/BCC catalysts with the mole ratio of CeO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> was 1:1 showed high catalytic activities which compare well with industrial catalysts. The mass content of the secondary layer was reduced 2-4 times in these catalysts.

Calcined at the temperatures in the range of 550 to 1000 °C, coated secondary layers and catalysts were studied using the X-ray diffraction (XRD) technique, the BET surface area analyzer, the scanning electron microscope and the catalyst activity analysis. The XRD analysis showed that only  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> phases in different stages of their crystallization and Pt in highly dispersed state are present in the secondary layer. XRD plots of the samples after heat treatment at 800 and 1000 °C show contraction of peaks and increase of their intensity which indicates partial amorphous to crystalline phase transmission of the secondary layer components. Normally this heat treatment results in the decrease of catalyst activity.

The results of catalytic activity and BET surface area analysis after various heat treatments are shown in table 1. Catalyst activity (the results reported in table 1) decreased after heat treatment at 1000 °C. However, we observed an increase in activity for the catalyst calcined at 800 °C, i.e. thermal activation effect, although its BET surface area decreased 1,5 times. This effect is of interest and may have practical significance. The work in this field is in the progress.

**Table 1.** The results of activity analysis of catalysts Pt/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>/BCC synthesized with 1:1 CeO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> mole ratio and containing about 1,5 g/dm<sup>3</sup> of Pt.

Sample number	Catalyst type	Heat treatment temperature, °C	BET surface area, m <sup>2</sup> /g	Temperature of CO conversion rate, °C		
				20%	50%	80%
1	Pt/CeO <sub>2</sub> /γ-Al <sub>2</sub> O <sub>3</sub> /BCC	550	120-150	140	170	180
2	Pt/CeO <sub>2</sub> /γ-Al <sub>2</sub> O <sub>3</sub> /BCC	800	65-90	75	95	110
3	Pt/CeO <sub>2</sub> /γ-Al <sub>2</sub> O <sub>3</sub> /BCC	1000	20-30	235	260	270

The elaborated method of making secondary layers from multiple slurries will permit to simplify block catalyst production and to decrease their prime cost thus getting effective catalysts for environment protection.

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## NANOSIZED COMBUSTION-SYNTHESIZED CATALYSTS WITH SPINEL STRUCTURE FOR ALKANE OXIDATION

**Zavyalova U., Scholz P., Ondruschka B.**

*Department of Technical Chemistry and Environmental Chemistry, Friedrich Schiller*

*University Jena, Lessingstr.12, D-07743 Jena, Germany*

*E-mail: u.zavyalova@uni-jena.de*

Nanosized Co-Cu oxide catalysts covered on various supports were prepared by combination of impregnation and combustion synthesis in self-propagating mode. Influence of a support and initial precursors' mixtures on the physicochemical properties of the catalysts was studied by XRD, BET, TGA-DTA, IR-spectroscopy, and TEM methods. Activity of obtained catalysts was tested in the reactions of total oxidation of methane and propane. It was shown that higher catalytic activity of combustion synthesized catalysts in comparison with activity of catalysts produced by conventional impregnation and co-precipitation methods is related to small particle size (5 – 20 nm) of obtained Co-Cu oxide dispersed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub>.

### **Introduction**

Catalytic combustion of hydrocarbons is of great importance for applications such as gas turbines, boilers, domestic heaters, automotive exhaust catalysts and VOC removal from industrial effluents. Strict environmental laws make it essential to eliminate the light hydrocarbons emission, as methane has the greenhouse effect more than an order of magnitude greater than CO<sub>2</sub>. Transition metal-oxides were found perspective catalytic systems for exhaust gases purification due to their high activity, relative low costs and also their capability to suppress NO<sub>x</sub> formation from N-containing fuel [1]. Early we reported about the synergistic effect over complex CuCo<sub>2</sub>O<sub>4</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, synthesized by combustion method in self-propagating mode first proposed by Tsyrlunikov at al. [2], in the reaction of total oxidation of methane [3]. In this presentation we study the influence of supports (γ-Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub>) and initial precursors' mixtures on the physicochemical properties and activity of Co-Cu oxide catalysts for catalytic combustion of hydrocarbons.

### **Experimental**

For catalysts preparation Al<sub>2</sub>O<sub>3</sub> (Merck), TiO<sub>2</sub> (Degussa), ZrO<sub>2</sub> (Aldrich), and CeO<sub>2</sub> (Aldrich) were used as supports. The active components were introduced by impregnation of supports with various redox mixtures of cobalt acetate and copper nitrate solutions and fuels such as urea, citric acid, and glycine. Details of the combustion method for synthesis of oxide

supported catalysts were described in previous publication [3]. For comparison Co-Cu oxide supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by conventional methods: dry impregnation of support with cobalt and copper nitrates and following calcinations at 500 °C during 4 h; and co-precipitation method of cobalt, copper, and aluminum nitrates with sodium carbonate and following calcinations at 500 °C during 4 h. Obtained catalysts were characterized by XRD, BET, TGA-DTA, IR-spectroscopy, and TEM methods. Catalytic activity was tested in the reaction of total oxidation of methane and propane using a fixed bed flow reactor. The analysis of the feed composition was carried out by GC with a Poraplot Q column, TCD. In each experiment 1,0 g of catalyst was tested in the temperature range 100 – 600 °C at space velocity 12000 h<sup>-1</sup> and the initial gas mixture containing 1,0 vol. % hydrocarbon in air.

### Results and discussion

According to XRD data, combustion synthesis in self-propagating mode results in the partial formation of CuCo<sub>2</sub>O<sub>4+ $\delta$</sub>  and Co<sub>3</sub>O<sub>4</sub> oxides with spinel structure. At that, interaction of active components with a supports was not found in all cases. Surface area of obtained catalysts was in the range of 150-165 m<sup>2</sup>/g for catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 120-140 m<sup>2</sup>/g in the case of ZrO<sub>2</sub> and CeO<sub>2</sub> supports, and 50 m<sup>2</sup>/g – for TiO<sub>2</sub>. The dried redox mixtures of Co-Cu precursors covered on various supports and as-burnt catalysts were examined by DTA-TGA to compare the heat efficiency of various precursors' decomposition and by IR-spectroscopy to investigate a completeness of catalysts synthesis. TEM data shown that, the size of the combustion synthesized crystallites is in the range of 5 – 20 nm, which is in a good agreement with the crystallite size evaluated by the Scherrer equation from the XRD experiments. Since process can be finished in very short time, the particle size of the synthesized oxide can remain small.

The highest activity in the studied reactions was achieved over the Co-Cu oxide catalysts covered on CeO<sub>2</sub> from redox mixture of cobalt and copper nitrate and glycine. In this case

100 % conversion of methane was observed at 410 °C and 100 % conversion of propane - at 350 °C. In comparison with catalysts produced by conventional impregnation and co-precipitation methods mostly combustion synthesized catalysts showed essentially higher activity in the reactions of total oxidation of methane and propane. Apparently, high activity of combustion synthesized catalysts is related to a small particle size, as the high synthesis rate allows to avoid oxide particles' agglomeration, and also to formation of non-equilibrium phases and structural defects, which can occur in the process of self-propagating combustion.

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### Conclusions

Therefore, support and initial precursors' mixture have a significant influence on the particle size, morphology, and activity of combustion synthesized Co-Cu oxide catalysts. Proposed approach, based on low-temperature combustion of redox precursors' mixture covered on support, allows to achieve the desired crystal lattice and simultaneously to prevent agglomeration of particles and interaction of active component with a support resulting to nanosized catalysts with high activity in the reactions of hydrocarbons oxidation.

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## DESIGN OF NITROGEN-CONTAINING CARBON NANOFIBERS VIA CHOICE OF APPROPRIATE CARBON SOURCE

**Shalagina A.E., Podyacheva O.Yu., Shmakov A.N., Ushakov V.A., Boronin A.I.,  
Ismagilov Z.R.**

*Boriskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: shalagin@catalysis.ru*

Synthesis of nitrogen-containing carbon nanofibers (N-CNFs) by the catalytic decomposition of hydrocarbon and ammonia mixture was studied. Influence of hydrocarbon nature on the structure and texture of N-CNFs as well as nitrogen content in the material was thoroughly investigated with 65Ni-25Cu-10Al<sub>2</sub>O<sub>3</sub> catalyst as it proved to be the most effective for production of N-CNFs. It was found that carbon source in mixture with ammonia has an effect on morphology of N-CNFs, textural features and nitrogen incorporation in N-CNFs. Evolution of 65Ni-25Cu-10Al<sub>2</sub>O<sub>3</sub> catalyst in the course of N-CNF growth was studied.

Carbon nanofibers (CNFs) because of their exceptional structural and textural properties are of great interest for many applications including heterogeneous catalysis [1, 2]. Introduction of nitrogen atoms into graphite lattice of CNFs results in functionalization of inert carbon surface and favours high dispersity of active component of supported catalysts [3]. It is well known that carbon source used for CNF preparation has an influence on the structural and textural properties of non-doped carbon nanofibers [2]. However, there are no similar definite correlations between the nature of N-CNF precursor and their physicochemical characteristics.

The present study is focused on the investigation of influence of hydrocarbon precursor in the mixture with ammonia on structure, texture and nitrogen content in N-CNFs. In this work methane, ethane and ethylene were compared as representatives of different hydrocarbons. Catalyst 65Ni-25Cu-10Al<sub>2</sub>O<sub>3</sub> (wt. %) was chosen for the detailed analysis as it demonstrated the highest activity in N-CNF production. Ammonia concentration in reaction mixture was varied from 0 to 75 vol. %, and temperature ranged within the interval of 450 – 675 °C. The synthesized N-CNF materials were characterized by the use of elemental analysis, XPS, XRD, electron microscopy and N<sub>2</sub> adsorption methods. It was found that the yield of CNFs, their structural and textural properties, as well as nitrogen content in CNFs are strongly dependent on the synthesis conditions, i.e. carbon precursor, ammonia concentration, temperature and process duration. The optimum synthesis conditions were established to get the high nitrogen content in N-CNFs as well as high surface area of material. TEM studies

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revealed that the nanofiber morphology is greatly affected by precursor composition. According to XPS data, the nitrogen incorporation in N-CNF structure leads to the formation of two main types of nitrogen coordination: pyridinic and quaternary, and their abundance depends on the reaction conditions. N-CNF porous structure is represented primarily by mesopores with average pore size of 5 – 19 nm. Specific surface area ( $S_{\text{BET}}$ ) depends on the synthesis conditions and can be varied from 30 to 350 m<sup>2</sup>/g.

The genesis of 65Ni-25Cu-10Al<sub>2</sub>O<sub>3</sub> catalyst during the N-CNF growth was studied by XRD analysis and X-ray diffraction using anomalous scattering effect. Increase of the lattice parameter of Ni-based alloy from 3.537 to 3.615 – 3.634 Å was found during the ethylene decomposition, while the parameter of Cu-based phase changed slightly as compared with the initial catalyst. It was assumed that dissolution of carbon in the bulk of nickel crystals may cause the increase of Ni lattice parameter.

The more experimental results on investigation of the influence of carbon source on characteristics of N-CNFs produced by catalytic decomposition of hydrocarbon and ammonia mixture and study of the evolution of 65Ni-25Cu-10Al<sub>2</sub>O<sub>3</sub> catalyst during the formation of CNFs from different precursors will be presented.

### Acknowledgements

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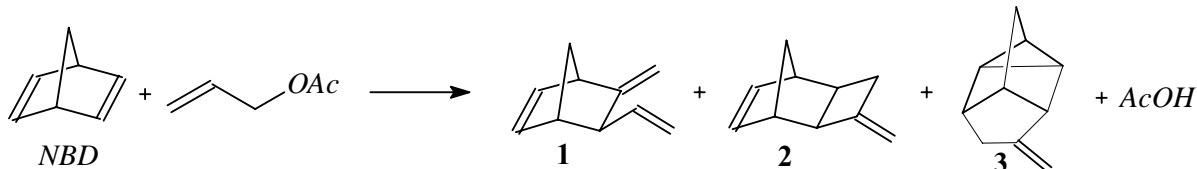
**THE ROLE OF CARBON DIOXIDE IN CATALYTIC NORBORNADIENE  
ALLYLATION**

Flid V., Dmitriev D., Efros I., Evstigneeva E.

*Physical Chemistry Department, Lomonosov Moscow State Academy of Fine Chemical  
Technology, Moscow, Russia  
E-mail: ilya-efros@yandex.ru*

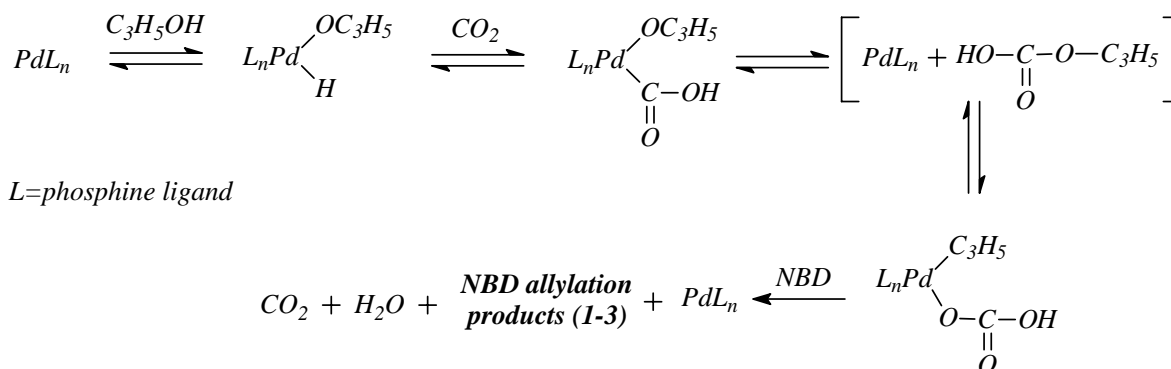
The utilization of carbon dioxide as a reagent is very important for the synthesis of complex organic compounds. But CO<sub>2</sub> applications in catalytic reactions are very seldom. The norbornadiene (NBD) allylation is one of such examples. Usually allylic esters or allyl complexes of transition metals can be used as allylation reagents in this reaction [1-3].

Unconventional mechanism of allylation is connected with the structure of adducts. As a result of [2+2]- or [2+4]-cycloaddition to NBD allylic fragment undergoes C-C bond cleavage and gives methylene-vinyl derivative (1) or incorporates in methylenecyclobutane (2) or methylenecyclohexane (3). In all cases allylic group lose hydrogen, which leaves with carboxylic acid.



Systems based on complexes of nickel and palladium stabilized with organophosphorus ligands are capable catalyze this reaction. Attempts to utilize another allylating reagents in this reaction were ineffective.

We found that in carbon dioxide atmosphere and at presence Pd - phosphine catalytic systems NBD allylates with allylic alcohol. The formation of allylpalladium complex, which is the key intermediate of the reaction is stimulated by carbon dioxide. After addition of C<sub>3</sub>H<sub>4</sub> to NBD and subsequent hydride-transfer, forming carbonic acid decomposes on water and CO<sub>2</sub>.



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Thus carbon dioxide doesn't waste in the resulting reaction, so it can be considered as co-catalyst. The reaction proceeds at a pressure of one atm CO<sub>2</sub>, but its rate increases when the pressure increases. The turn over numbers of 100 can be achieved in this reaction and it seems its limitation. The mechanism of carbon dioxide activation by allylpalladium complexes will be discussed in details at presentation.

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**INFLUENCE OF CONTAMINANTS IN HYDROXYLATION OF AROMATIC  
COMPOUND USING Fe/ZSM-5**

**Sayyar M.H., Wakeman R.J.**

*Department of Chemical Engineering, Loughborough University, Loughborough, LE11 3TU,  
United Kingdom*

*E-mail: m.h.sayyar@lboro.ac.uk*

The performance of the Fe/ZSM-5 catalyst in the hydroxylation of benzene by nitrous oxide was affected by the amount of Fe loaded into the catalyst, the nature and concentration of surface acid sites, and steam pre-treatment. However, the deactivation of catalyst was observed mainly due to coke deposition on the mouth of pores, blocking them and followed by a decrease in the number of active sites. It was shown that isolated and binuclear Fe sites are active centers for both decomposition of N<sub>2</sub>O and hydroxylation of benzene. However, the isolated Fe sites are more effective in the hydroxylation reaction. In the present research, the influence of different contaminants and diluents was investigated. The off-gas stream from the adipic acid or the ammonia oxidation plants must be treated to remove NO<sub>x</sub> and oxygen. NO<sub>x</sub> acts as a poison to the Fe/ZSM-5 and oxygen must also be limited in order to avoid the complete oxidation of benzene to CO<sub>2</sub> and H<sub>2</sub>O. It was shown that NO<sub>x</sub> and oxygen must be removed to less than 50 ppm and 0.01 wt%, respectively. It was also observed that CO accelerates the removal of atomic oxygen from the catalyst surface, resulting in the decreased operation temperature to 100 °C.

The present work was conducted to examine the catalytic stability of Fe/ZSM-5 by adding H<sub>2</sub>O, O<sub>2</sub>, CO, and CO<sub>2</sub> to the feed reactants. It was concluded that H<sub>2</sub>O exerts a promoting effect on prolonged activity of the catalyst and values for catalyst half-life improved by 3 days when concentrations of CO<sub>x</sub> and H<sub>2</sub>O were controlled at less than 3 wt% and 1 wt%, respectively.

**INFLUENCE OF THE INTERACTION BETWEEN H<sub>2</sub>PtCl<sub>6</sub> AND CARBON  
SUPPORT ON THE DISPERSION OF Pt/C CATALYSTS**

**Kholodovich A., Simonov P., Romanenko A.**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail:spa@catalysis.nsk.su*

Regularities of the adsorption of H<sub>2</sub>PtCl<sub>6</sub> onto carbon supports as a stage of Pt/C catalysts preparation were investigated. The nature of the adsorbed Pt compounds was studied using X-ray photoelectron spectroscopy, X-ray diffraction, eluent and element analyses. The correlation between the state of the adsorbed Pt precursors and the state of the active component in Pt/C catalysts (platinum dispersion, its distribution throughout the support grain) was revealed.

Pt/C catalysts were prepared by the excess solution impregnation of carbon with aqueous H<sub>2</sub>PtCl<sub>6</sub> solutions followed by drying in vacuo and the reduction of the supported platinum species with hydrogen at 250 °C. The first stage of the catalysts synthesis, H<sub>2</sub>PtCl<sub>6</sub> adsorption by carbon surface, was found to be a complex chemical process. It doesn't lead to a significant change of pH of the solution within broad platinum loading limits and, contrary to the traditional opinion, doesn't induce the carbon surface oxidation to yield oxygen-containing groups, but it is accompanied by chlorination of the surface.

Among the adsorbed platinum compounds, Pt<sup>0</sup> particles,  $\pi$ -complexes of Pt<sup>II</sup> with C=C fragments of carbon surface and Pt<sup>II</sup> and Pt<sup>IV</sup> chloride anionic complexes were detected. The ratio between the aforementioned compounds depends on platinum loading ( $A_{Pt}$ ) and the nature of carbon support (Fig. 1).

When platinum loadings changing from 0.25 to 0.5  $\mu\text{mol(Pt)/m}^2(S_{BET})$ , the adsorption of H<sub>2</sub>PtCl<sub>6</sub> on highly disordered carbons, namely, active carbons and carbon blacks, results mainly in accumulating chloride anions of Pt<sup>II</sup> and Pt<sup>IV</sup> as the catalyst precursors, while  $\pi$ -complexes of Pt<sup>II</sup> and chloride anions of Pt<sup>II</sup> dominate on carbons with more perfect crystal structure (Sibunit-type carbons). Pt<sup>0</sup> particles are the only surface species for all studied carbons at Pt loadings varying between 0.01 and 0.05  $\mu\text{mol(Pt)/m}^2(S_{BET})$ .

The interaction of H<sub>2</sub>PtCl<sub>6</sub> with carbon supports can be described in terms of the electrochemical theory of adsorption of electrolytes put forward by A.N. Frumkin. The adsorption mechanism proposed by us combines 1) reduction of Pt<sup>IV</sup> to Pt<sup>II</sup> chloride complexes and Pt<sup>0</sup> particles, which is accompanied by chemisorption of Cl<sup>-</sup> ions through C-Cl bonding; 2) formation of Pt<sup>II</sup> chloride  $\pi$ -complexes with C $_{\pi}$ -sites of carbon surface;

3) formation of salt-like compounds between  $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$  or  $[\text{Pt}^{\text{II}}\text{Cl}_4]^{2-}$  and  $\text{C}^{\oplus}$  surface sites (positive holes) via ion exchange. The reduction process starts at the periphery of carbon grains, so that C–Cl species and  $\text{Pt}^0$  particles are concentrated there.

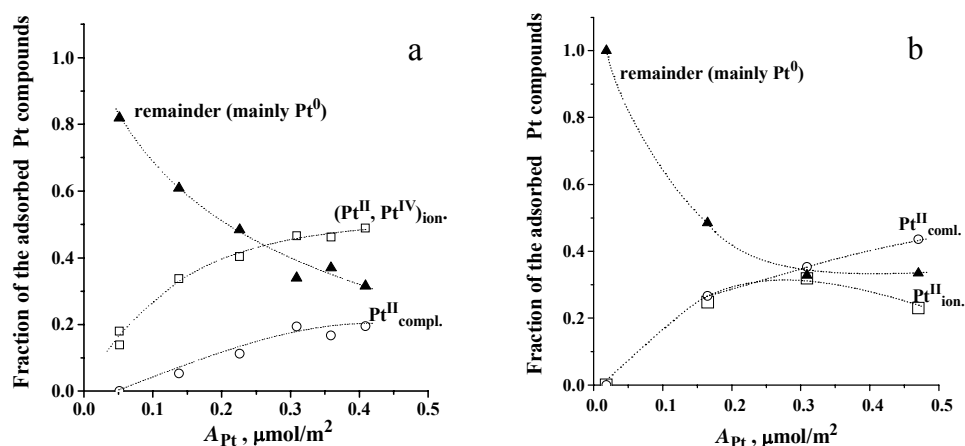


Fig. 1. Experimental data of eluent analysis of the adsorbed Pt compounds: active carbons and carbon blacks (a); carbons of the Sibunit family (b).

The experimental data on platinum dispersion in Pt/C catalysts with different platinum loading allow us to conclude that there is a certain effect of the nature of the adsorbed Pt precursors on the properties of Pt/C catalysts. Most of platinum species adsorbed ( $\text{Pt}^0$  clusters,  $\pi$ -complexes of  $\text{Pt}^{\text{II}}$  chloride, ionic  $[\text{Pt}^{\text{II}}\text{Cl}_4]^{2-}$  compounds) can give birth to small metal particles, 1-1.5 nm in size, if the adsorption of  $\text{H}_2\text{PtCl}_6$  was performed at ambient temperature. Rough dispersion of the catalysts, especially, at platinum loading between 0.01 and  $0.05 \mu\text{mol}(\text{Pt})/\text{m}^2(S_{\text{BET}})$  in the case of active carbons, is explained by negative influence of the C–Cl species which accelerate sintering of  $\text{Pt}^0$  clusters. In its turn, a decrease in the metal dispersion for the catalysts with platinum loading ranged from 0.25 to  $0.5 \mu\text{mol}(\text{Pt})/\text{m}^2(S_{\text{BET}})$  may be caused by accumulation of the adsorbed ionic  $[\text{Pt}^{\text{IV}}\text{Cl}_6]^{2-}$  compounds.

The results of our research allow us forecasting the adsorptive properties of carbon supports with regard to  $\text{H}_2\text{PtCl}_6$  and the state of the active component in the final Pt/C catalysts on the basis of knowledge of the physicochemical characteristics of the supports and the catalyst preparation conditions.

**THE INFLUENCE OF SUPPORT NATURE ON THE PROPERTIES OF  
Pd CONTAINING CATALYSTS IN TRICHLOROBENZENE  
HYDRODECHLORINATION**

**Golubina E.V., Kachevsky S.A., Korotkov A.V., Lokteva E.S.,  
Turakulova A.O., Lunin V.V.**

*Department of chemistry, M.V. Lomonosov Moscow State University, Moscow, Russia*

*E-mail: golubina@kge.msu.ru*

In a process of active sites formation important role plays the metal-support interaction and the texture of support. In this work influence of the nature of oxide and carbon support on the activity of Pd containing catalyst in hydrodechlorination was studied. Zirconia stabilized by  $Y_2O_3$ ,  $Ga_2O_2$  and  $Al_2O_3$  was used as oxide support. Catalysts were prepared by deposition-precipitation technique that allows to form Pd-Zr-O compound on the catalysts surface. The presence of both  $Pd^0$  and  $Pd^{\delta+}$  was confirmed by TPR and IR of adsorbed CO. Using of ultradispersed diamond as support allows to stabilize active Pd particles. Mesoporous structure of ultradispersed diamond provides accessibility of most part of Pd particles.

Interaction between metal and support plays an important role in the formation of catalysts properties. Even the small changes in the electronic state of supported metal could lead to difference in catalytic activity. For example, use of oxides which could chemically interact with supported metal helps to achieve such changes in electronic state. Among carbon supports ultradispersed diamond (UDD) seems to be the most promising. Small diamond particles (about 4 nm) with regulate structure combined by amorphous carbon to aggregates (average size about 20 nm) makes UDD very attractive to application as support.

In this work Pd containing catalysts (2% Pd) on UDD,  $ZrO_2$ ,  $Y_2O_3$ ,  $Ga_2O_2$  and  $ZrO_2-M_2O_3$  (M – Al, Y, Ga) were prepared. In modified zirconia the content of second oxide was 1; 5 and 10 %. Catalytic activity was tested in the multiphase hydrodechlorination of 1,3,5-trichlorobenzene (TCB) at 50 °C

In a series of Pd supported on oxides catalysts with second oxide content of 1 and 5 % were the most active. Complete trichlorobenzene dechlorination was achieved within 20 min. Moreover, catalysts on modified zirconia were more stable than catalysts on individual oxides. Total converted amount of trichlorobenzene was 500 mol per 1 mol of Pd.

According to TPR and IR of adsorbed CO data both  $Pd^0$  and  $Pd^{\delta+}$  are presented on the catalysts surface.  $Pd^{\delta+}$  most likely to be a part of compounds like Pd-Zr-O.



Pd catalysts supported on UDD were highly active in trichlorobenzene hydrodechlorination as well. Complete TCB dechlorination was achieved within about 40 min. During the same time period TCB conversion in the presence of 5%Pd/C was only 9 %.

According TEM micrograms UDD consists of small parts of diamond (average size 4 nm) which combined by amorphous carbon in aggregates. Average size of aggregates is 20 nm. This type of UDD structure favors stabilization of active Pd particles, size about 5-7 nm. Consequently, active surface of catalyst increases.

Texture characteristics were measured for 5% Pd/UDD and 5% Pd/C. Catalysts on UDD have mesoporous structure with pore size 13 nm. Part of micropores is less than 1 %. At the same time activated carbon has microporous structure with average pore size 2 nm. Probably, some parts of Pd particles could be blocked in micropores of activated carbon. This fact was confirmed by TPR analysis. Mesoporous structure of ultradispersed diamond provides accessibility of most part of Pd particles. Consequently, Pd/UDD is more active in hydrodechlorination.

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INFLUENCE OF ELECTRON BEAM IRRADIATION ON THE STRUCTURE AND  
CATALYTIC PERFORMANCE OF 1%Pt/HZSM-5

**Markov P., Pribitkov. A., Mishin. I., Tolkachev N., Stakheev A., Kustov L.,  
Golubeva V.<sup>1</sup>, Tel'nov A.<sup>1</sup>**

*N.D. Zelinsky Institute of Organic Chemistry, Moscow, Russia*

<sup>2</sup>*Russian Federal Nuclear Center, All-Russia Scientific Research Institute of Experimental  
Physics (RFNC-VNIEF), Sarov, Nizhni Novgorod region, Russia*

*E-mail: markovp@mail.ru*

Influence of the electron beam (EB) irradiation on structure and catalytic properties of 1%Pt/HZSM-5 catalyst was studied. Comparative study of the catalyst samples before and after EB treatment were carried out. Several physico-chemical investigation methods like XRD, DRIFT, and low temperature nitrogen adsorption were applied. The effect of EB treatment on catalytic properties in the gas-phase toluene hydrogenation was investigated. It was found that EB treatment can lead to significant increase in catalytic activity. Observed increase in the hydrogenation activity was attributed to the decrease in Pt particles size. Analysis of the data obtained by the physico-chemical methods allows us to conclude that significant reduction of Pt-species occurs on EB treatment as well.

1%Pt/HZSM-5 catalyst was treated by electron beam irradiation of linear resonance accelerator in argon flow. Average energy of electrons was 7.7 MeV. Irradiation dose was varied from 120 to 900 Mrad by the time of the EB treatment.

The effect of EB treatment on catalytic performance of 1%Pt/HZSM-5 catalyst was investigated in the model reaction of gas-phase toluene hydrogenation. It was found that EB pretreatment can lead to a significant increase in activity (1.5-2 times) of irradiated catalyst (fig. 1).

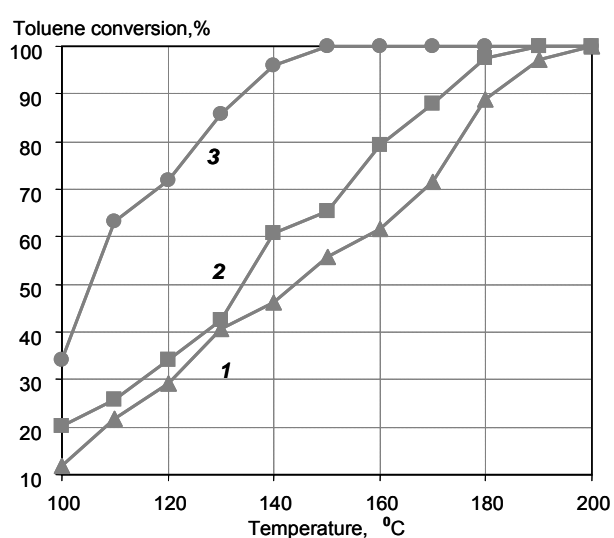
According to data obtained by XRD and N<sub>2</sub> low-temperature adsorption it can be concluded that EB pretreatment does not lead to a noticeable destruction of the zeolite crystal structure. Analysis of DRIFT spectra of Brønsted acid sites does not reveal pronounced changes. Only a minor decrease in intensity of bridge OH group was observed. Hence it was concluded that EB pretreatment has minor effect on the carrier and the catalytic effect is related to changes in Pt-species state.

Information on changes of Pt species upon EB treatment was found by analysis of XRD (fig. 2) and DRIFT data. XRD signal corresponding to bulky Pt<sup>0</sup> particles was observed in XRD pattern of untreated Pt/ZSM-5. Electron beam treatment leads to disappearance of bulky Pt particles. This observation evidences that EB treatment leads to a decomposition of bulky

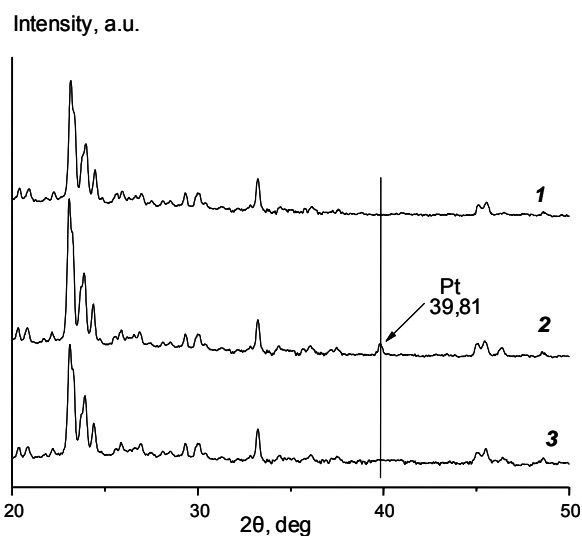
Pt-particles with formation of smaller one. Analysis of the DRIFT spectra of CO adsorbed on EB treated Pt/ZSM-5 catalyst provides us with information that EB treatment can lead to a significant reduction of  $\text{Pt}^{2+}$  species to  $\text{Pt}^0$ .

The data obtained allow us to conclude that following processes can take place in Pt/ZSM-5 catalyst upon EB treatment:

- 1)  $\text{Pt}^{2+}$  species can be reduced to  $\text{Pt}^0$  state by electron beam irradiation
- 2) Redispersion of bulky  $\text{Pt}^0$  species upon electron beam irradiation can take place.
- 3) Redispersion of  $\text{Pt}^0$  species results in an enhancement of the catalytic activity of Pt/HZSM-5 in toluene hydrogenation.



**Fig. 1.** Effect of electron radiation dose on the activity of 1%Pt/H-ZSM-5 in toluene hydrogenation: 1 - untreated Pt/H-ZSM-5; 2 - treated by 120 Mrad; 3 - treated by 900 Mrad



**Fig. 2.** XRD spectra of: parent H-ZSM-5 (1); untreated Pt/H-ZSM-5 (2); Pt/H-ZSM-5 treated by 900 Mrad (3)

THE STUDY OF STRUCTURED CATALYSTS ACIDITY

**Glazneva T.S., Paukshtis E.A., Ismagilov Z.R., Bal'zhinimaev B.S., Goncharov V.B.,  
Rebrov E.V.<sup>1</sup>, Schouten J.C.<sup>1</sup>**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>1</sup>*Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, the Netherlands*

*E-mail: glazn@catalysis.ru*

The catalysts in new geometrical forms, such as fiberglass (FG) materials and mesoporous thin films for (micro-)reactor technology are implemented to catalysis area.

Mesoporous silica thin films (MCM-41 and MCM-48 like) supported on different substrates were prepared by Evaporation Induced Self-Assembly method using tetraethyl orthosilicate as silica source and different ionic and non-ionic surfactants as a structure-directing agent. The acidity of films was investigated by DRIFT spectroscopy of adsorbed CO using a special vacuum cell. The feature of the given cell is the opportunity to work with a sample without destruction in a wide interval of temperatures ranging from 77 K to 273 K.

For samples of mesoporous silica on a glass plate support the spectrum of a glass was found to be overlapped with the spectrum of the covering thin silicalite. However, the sensitivity of a method is sufficient to detect the small amount of mesoporous silica phase even in the presence of bulk silicate. Characteristic peaks at around  $3740\text{ cm}^{-1}$  corresponding to Si-OH groups of mesoporous silica supported on a glass plate were observed. After the CO adsorption this band shifted to low frequency region. For samples of mesoporous silica on a titanium substrate, it was revealed by DRIFT spectroscopy that titanium atoms were inserted into the mesoporous silica channels (the band of CO-Ti complex at  $2176\text{ cm}^{-1}$ ). These complexes could form at the film deposition stage or at the stage of surfactant removal. Basing on DRIFT data, the effective technique for measurement the thickness of the deposited mesoporous silica films was developed. The thickness of films on titanium was found to be in the range of 500-900 nm.

As to acidity study of FG materials, it is of great importance since these materials serve as catalysts in a number of reactions. The traditional method of sampling for FTIR study can not be applied to FG materials because the active sites are located in the bulk of fibers.

The characterization of acid properties of FG materials was carried out using the adsorption of ammonia and reaction of isopropanol dehydration because its rate is

proportional to the Brønsted acid sites (BAS) concentration. The DRIFT study of adsorbed  $\text{NH}_3$  showed that for all the samples the  $\text{NH}_4^+$  ions formation (absorption bands at  $1480\text{-}1490\text{ cm}^{-1}$ ) characterizing BAS were observed. It was found that for FG materials with increasing the Al content the concentration of BAS increased in 3-5 times.

An attempt was made to compare the activity of FG materials in the isopropanol dehydration reaction with the concentration of acid sites. The activity of samples increased with amount of Al. The reaction rate referred to BAS number was constant within one order of accuracy. It was shown that the activity of FG materials referred to the catalyst weight was comparable with that of HZSM-5 zeolite, but the activity referred to the surface area was more than by two order of magnitude higher. On the other hand, the dehydration rate of isopropanol referred to BAS number was less than in case of zeolite, i.e. the catalytic reaction took place in a thin subsurface layers of fibers and not all the sites measured by  $\text{NH}_3$  adsorption were involved into reaction.

Consequently, the acidity of FG materials can be measured by DRIFT spectroscopy but there are no suitable probe molecules. It was suggested to apply the deuterium-hydrogen exchange method for characterization of FG acidity. The obtained results were compared with those of  $\text{NH}_3$  adsorption and isopropanol dehydration reaction. For FG materials modified by zirconium sulphate the rate of H-D exchange correlated well with their acidity.

## NMR IMAGING AS A TECHNIQUE TO STUDY THE SUPPORTED CATALYST PREPARATION

**Lysova A.A., Bergwerff J.A.<sup>1</sup>, Koptug I.V., Espinosa Alonso L.<sup>1</sup>, Weckhuysen B.M.<sup>1</sup>,  
Sagdeev R.Z., Parmon V.N.<sup>2</sup>**

*International Tomography Center SB RAS, Novosibirsk, Russia*

<sup>1</sup>*Inorganic Chemistry and Catalysis, Utrecht University, the Netherlands*

<sup>2</sup>*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: lysova@tomo.nsc.ru*

Several NMR imaging techniques are presented to monitor in a non-invasive manner the processes taking place inside the porous pellets after impregnation of support extrudates with solutions containing the precursors of the active components and various additives/ligands. <sup>1</sup>H NMR imaging has been applied to monitor the transport of the precursors of the active components (Mo(VI) and Co(II) complexes) in the support pellet during the hydrotreating (Co)Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst preparation, as well as to study the distribution of the active components in the catalyst pellets after the drying stage. The influence of various conditions of the pellet impregnation procedure (pH, concentrations, presence of additives in the impregnation solution) on the distribution of the active component inside the pellet has been studied. Multinuclear NMR imaging has been employed to study the distribution of additives in the catalyst pellets before and after the drying stage in an indirect fashion.

Supported catalyst are generally prepared by impregnation of a porous support using a solution of a metal precursor, with subsequent drying and further processing to convert the precursor into the desired active phase [1]. The efficiency of the final catalytic system is strongly dependent on the nature and distribution of the active component [2]. Both properties in their turn are influenced by the conditions of the impregnation procedure and the drying stage. Therefore, control of the preparation process becomes to be essential. The most of the characterizations of the physical-chemical processes during the preparation of the supported catalysts have been done by analysis of bisected catalyst bodies at different stages of the preparation [4], after interruption of the impregnation process. The technique capable of providing the characterization of the impregnation process in a non-invasive manner is required. One of the promising techniques for the *in situ* study the supported catalyst preparation seems to be NMR imaging [5]. This technique is non-invasive, non-destructive, chemically specific, and can provide the information about molecular composition, structure and processes with the spatial resolution on the order of tens or hundreds of microns.

In this work <sup>1</sup>H NMR imaging has been applied to monitor the transport of the precursors of the active components (Mo(IV) and Co(II) complexes) in the support pellet during the hydrotreating (Co)Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst preparation. The paramagnetic influence of Co<sup>2+</sup> ions and

the diamagnetic influence of  $\text{Mo}_7\text{O}_{24}^{4-}$  ions on the relaxation times of water protons were used to study the transport of these species into the support pellet during its dry impregnation. Citric acid was added to the impregnation solution to control the transport rate of metal complexes inside the extrudates and the distribution of the active component after drying. On the basis of the data obtained by NMR imaging and UV-VIS micro spectroscopy, the differences in the transport properties of cobalt species at various pH were explained.

The same approach based on the influence of paramagnetic and diamagnetic complexes on the relaxation times of solvent protons has been used to study the distribution of the active components (Co, Mo) inside the catalyst pellet after the drying stage.

The possibility to detect the NMR signal of nuclei other than proton allowed us to perform a direct *in situ* visualization of the supported catalyst preparation [7].  $^{31}\text{P}$  NMR signal of phosphates and the  $^{13}\text{C}$  NMR-signal of  $^{13}\text{C}$  labeled citrate which are added to the impregnation solution used for the preparation of (Co)Mo/ $\gamma$ - $\text{Al}_2\text{O}_3$  hydrotreating catalysts were detected during the impregnation of the support pellets in order to follow the transport of these additives.  $^{31}\text{P}$  NMR imaging has also been used to study the distribution of phosphates in the catalyst pellets after the drying stage.

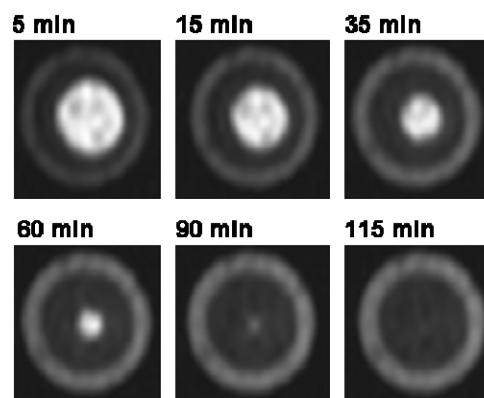
The presented NMR imaging techniques can be readily applied to study the preparation of other catalytic systems, e.g., Pt, Ni, Cu-containing catalysts.

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*Fig. 1.*  $^1\text{H}$  images recorded on  $\text{Al}_2\text{O}_3$  pellets after impregnation with a 0.2 M  $\text{Co}(\text{NO}_3)_2$ , 0.4 M citric acid solution. A dark area in these images represents the presence of  $\text{Co}^{2+}$  ions. SR =  $(139 \times 231) \mu\text{m}^2$ .

**THE MECHANISM OF REDUCTION OF NO WITH H<sub>2</sub> IN STRONGLY OXIDIZING  
CONDITIONS (H<sub>2</sub>-SCR) ON A NOVEL Pt/MgO-CeO<sub>2</sub> CATALYST: EFFECTS OF  
REACTION TEMPERATURE**

**Savva P.G., Costa C.N., Efstathiou A.M.**

*Chemistry Department, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus*

*E-mail: efstath@ucy.ac.cy*

The mechanism of the selective catalytic reduction of NO with H<sub>2</sub> towards N<sub>2</sub> in the presence of strongly oxidizing conditions (H<sub>2</sub>-SCR) has been investigated over a novel 0.1 wt% Pt/MgO-CeO<sub>2</sub> catalyst for which patents were granted [1]. The investigated reaction system has a significant technological interest in the area of NO<sub>x</sub> control emissions from stationary sources (e.g., power plants, combustion processes of fossil fuels, waste incinerators) at low-temperatures ( $T < 200$  °C), where the current NH<sub>3</sub>-SCR technology faces various problems [2]. The support of this novel catalytic system was prepared by the sol-gel method or it was a mechanical mixture of MgO (50 wt%) and CeO<sub>2</sub> (50 wt%) crystals [1, 3].

The most accurate mechanistic information about a given catalytic reaction is obtained when *in situ* studies are performed which do not disturb the on-going catalysis. It has long been appreciated that transient experiments with the use of stable isotopes coupled with mass spectrometry and FTIR detectors provide important mechanistic information, such as the chemical structure and surface coverage of *active* and *inactive* (spectator) adsorbed reaction intermediate species, the nature (reversible or irreversible) of a given elementary reaction step, the rate-determining step of the reaction network, and the intrinsic reactivity (*k*) of a given species in the elementary step [4].

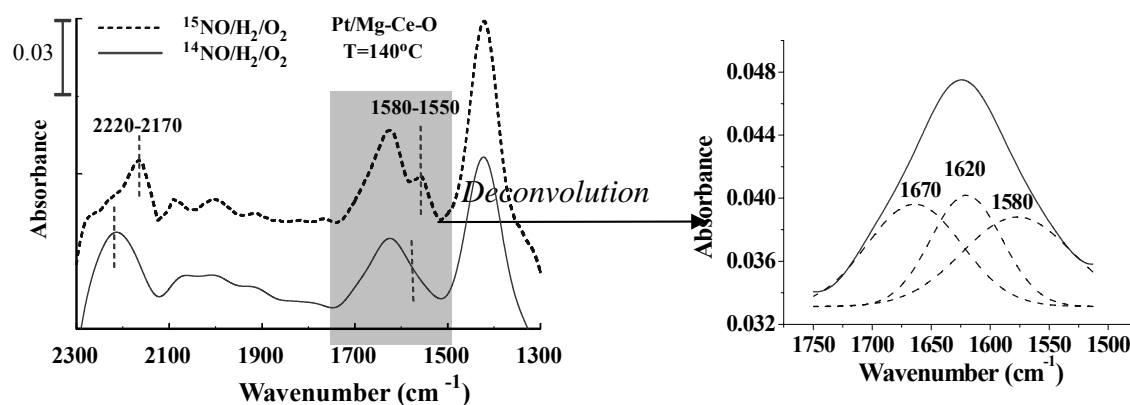
In the present work, steady-state isotopic transient kinetic analysis (SSITKA) experiments following the switch  $^{14}\text{NO}/\text{H}_2/\text{O}_2 \rightarrow ^{15}\text{NO}/\text{H}_2/\text{O}_2$  or  $\text{NO}/\text{H}_2/^{16}\text{O}_2 \rightarrow \text{NO}/\text{H}_2/^{18}\text{O}_2$  at various reaction temperatures (120-400 °C) have been conducted over the 0.1 wt% Pt/MgO-CeO<sub>2</sub> catalyst using *on line* mass spectrometry and *in situ* DRIFTS. The chemical structure of the *active* NO<sub>x</sub> adsorbed intermediate species that eventually lead to N<sub>2</sub> (N-reaction path), and the oxygen participation in the N<sub>2</sub>O formation route (O-reaction path) were found to strongly depend on catalyst support composition [5]. Figure 1 shows *in situ* DRIFTS spectra recorded at 140°C over the 0.1 wt% Pt/MgO-CeO<sub>2</sub> catalyst after 30 min of  $^{14}\text{NO}/\text{H}_2/\text{O}_2/\text{Ar}$  reaction (—), and after 30 min following the isotopic switch  $^{14}\text{NO}/\text{H}_2/\text{O}_2/\text{Ar} \rightarrow ^{15}\text{NO}/\text{H}_2/\text{O}_2/\text{Ar}$  (---). As shown in Fig. 1, only two NO<sub>x</sub> adsorbed species, namely nitrosyl on a support metal cation associated with an adjacent NO<sub>2</sub><sup>-</sup> species (IR band at 2210 cm<sup>-1</sup>),



and bidentate nitrate *on the support* ( $1580\text{ cm}^{-1}$ ) give the isotopic shift corresponding to the N-O stretching vibrational mode. These species were found to be *the active NO<sub>x</sub> species* of the present H<sub>2</sub>-SCR reaction. Based on H<sub>2</sub> TPSR experiments, following reaction and a switch to <sup>15</sup>NO/He gas mixture, it was found that N<sub>2</sub> formation over the Pt/MgO-CeO<sub>2</sub> catalyst invokes the coupling of *two different in structure NO<sub>x</sub> species*, the first one interacting irreversibly and the second one reversibly (exchangeable with <sup>15</sup>NO(g)) with the catalyst surface. A *hydrogen spillover mechanism from Pt metal to the support (oxygen species)* is invoked to explain the reduction steps of the active NO<sub>x</sub> species.

SSITKA experiments with <sup>15</sup>NO coupled with mass spectrometry allowed the *quantification of active NO<sub>x</sub> species* in the present H<sub>2</sub>-SCR reaction. At 140 °C, it was found that three equivalent monolayers (based on Pt<sub>s</sub>) of active NO<sub>x</sub> are formed. This result is in harmony with the DRIFTS-SSITKA studies (Fig. 1), where it was probed that the active NO<sub>x</sub> species are found on the support (vicinity to the Pt nano-particles).

Similar experiments to those described above were performed at other reaction temperatures, where the *nature and amount of active NO<sub>x</sub> species* were found to strongly depend on reaction T for the present H<sub>2</sub>-SCR of NO reaction. These results can explain very well the *volcano type* behavior of the conversion of NO vs. T profile observed [3].



**Fig. 1:** *In situ* DRIFTS spectra recorded on the 0.1 wt% Pt/MgO-CeO<sub>2</sub> catalyst after 30 min of <sup>14</sup>NO/H<sub>2</sub>/O<sub>2</sub>/Ar reaction (—) at 140 °C, and after 30 min following the isotopic switch <sup>14</sup>NO/H<sub>2</sub>/O<sub>2</sub>/Ar → <sup>15</sup>NO/H<sub>2</sub>/O<sub>2</sub>/Ar (---). Feed composition: H<sub>2</sub>=1.0%, NO=0.25%, O<sub>2</sub>=5%.

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**MECHANISMS OF CATALYTIC REDUCTION AND OXIDATION IN THE  
PRESENCE OF METAL-POLYMERIC NANOCOMPOSITES**

**Sulman E., Matveeva V., Demidenko G., Nikoshvili L., Doluda V.**

*Tver Technical University, Tver, Russia*

*E-mail:sulman@online.tver.ru*

Catalytic properties of nanocomposites on the base of amphiphilic block-copolymers, ultra thin polyelectrolyte layers and polymeric matrices were investigated. Physical and chemical investigations showed the possibility of polymer-stabilized metal nanoparticles formation with mean diameter of 1-2 nm and low size distribution. The second modifying metal addition to the cluster containing the main catalytically active component was found to lead to the change of electron density and surface geometry. The kinetics investigation and the data of physical-chemical analyses showed the possibility of the interaction of the catalyst active component with solvent, support, modifier and substrate. So the oxidation and reduction reactions were established to run through a polyligand reaction complex. The substrate activation was due to the electron density transfer from the catalyst active component. The mathematical models and the hypotheses the reactions were proposed.

Catalysts on the base of metal nanoparticles allowing effectively utilizing noble metals are widely used to replace traditional catalysts. To stabilize metal nanoparticles and to overcome its aggregation various polymers are applied. In addition to stabilizing and protecting the particles, polymers offer unique possibilities for modifying both the environment around catalytic sites and access to these sites. Besides, polymers, which contain complexes or metal nanoparticles, combine the advantages both of homogeneous and heterogeneous catalysts.

Several catalysts of different nature were investigated in hydrogenation and oxidation of various substrates.

Nanoparticles were stabilized by the following methods: (i) in micelles of amphiphilic block-copolymers; (ii) in cavities of polymer matrices; (iii) in ultra thin polyelectrolyte layers.

As amphiphilic block-copolymers the polyethylene-polyvinyl pyridine and polystyrene-polyvinyl pyridine were chosen. It is necessary to mention that bimetallic colloids (Pd-Au, Pd-Pt and Pd-Zn) stabilized into the micelle cores of PS-b-P4VP were also investigated to determine the influence of the second metal. The choice of second metal was based on its electronic properties.

Formation of metal nanoparticles in ultra thin polyelectrolyte systems was carried out using polydiallyldimethyl ammonium chloride (PDADMAC).

The hypercrosslinked polystyrene (HPS) allowing controlling the nucleation and growth of the particles by the existence of nanosized voids with the high degree of monodispersion was chosen as a polymeric matrix.

As an example of the reduction reaction, selective hydrogenation of dehydrolinalool (DHL) was chosen. The kinetic investigations and the data on catalytic systems and substrates physico-chemical analyses have shown that the catalytic active components interact with solvent, the carrier and the modifier. The hypothesis on hydrogenation mechanism was proposed. For all catalysts (Pd-PS-b-P4VP, PdPt-PS-b-P4VP and PdZn-PS-b-P4VP), except PdAu-PS-b-P4VP, hydrogen, presumably, is activated on “metallic” centre, and then diffuses along the surface to substrate molecules adsorbed on “organometallic” centres, which might be formed due to coordination of metal with polymer ligands in the micelle core.

For PdAu catalyst the existence of active centres of only one type and probably competitive coordination of substrate and hydrogen on these centres was assumed. According to these hypotheses the mathematical models for hydrogenation rate by the integral method using cubic spline and combined gradient method of Levenberg-Marquardt was constructed. According to the results of this computation, for all the catalysts the kinetic models were chosen which describe well the hydrogenation kinetics.

Another trend of this work was the study of polymeric catalyst in oxidation reactions. L-sorbose direct oxidation to 2-keto-L-gulonic acid, which is the main intermediate in the production of vitamin C, was carried out. The catalysts on the base of amphiphilic-block-copolymers had very low activity and selectivity. So the catalysts derived from microporous and mesoporous HPS containing Pt nanoparticles were used. The hypothesis on oxydation mechanism was also proposed. The incorporation of THF solution containing platinumic acid into microporous HPS was found to results in partial reduction of the Pt(IV) species and the formation of Pt(II) complexes wherein ligands are the product of THF oxidation. The application of the mentioned explicit integral method permitted to develop the mathematical model for L-sorbose oxidation.

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**La<sub>1-x</sub>A<sub>x</sub>BO<sub>3</sub> (A=Ca, Sr; B=Fe, Co, Mn) SUBSTITUTED PEROVSKITES :  
OXYGEN FORMS AND THEIR REACTIVITY**

**Yakovleva I.S., Isupova L.A., Rogov V.A.**

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

*E-mail: irga@cataysis.ru*

Oxygen species and their reactivity in perovskites La<sub>1-x</sub>A<sub>x</sub>BO<sub>3</sub> (A=Ca, Sr; B=Fe, Co, Mn) prepared by ceramic and mechanical activation routes were studied by temperature-programmed reduction by hydrogen (TPR-H<sub>2</sub>). An increase of Ca or Sr content promotes the diversity and reactivity of oxygen forms. The experimental data were compared with data on the catalytic activity in CO oxidation. It was found that the rates of CO oxidation on the perovskites correlated with the amount of reactive oxygen species that were removed by TPR with hydrogen in low-temperature region depending from perovskite composition, especially from transition metal nature and dopant content as well. The influence of preparation conditions on oxygen species and their reactivity was studied also.

Complex perovskites systems including those substituted by the alkaline-earth cations are known to possess a high activity in catalytic oxidation reactions, including CO oxidation, methane combustion etc. [1]. They are also promising as cathodes for high-temperature fuel cells, membranes for air separation and syngas generation [2-4]. Optimization of their performance by tuning the chemical composition and methods of synthesis requires knowledge of factors determining diversity of oxygen forms in substituted perovskites and their reactivity. This work deals with elucidating of oxygen forms and their reactivity by H<sub>2</sub>-TPR in perovskites La<sub>1-x</sub>A<sub>x</sub>BO<sub>3</sub> (A=Ca, Sr; B=Fe, Co, Mn) prepared by the various solidstate methods of the synthesis such as traditional ceramic and mechanical activation routes. The results thus obtained were analyzed with due regard for the real structure, phase composition and surface composition of the samples.

For the purpose of the presented paper, La<sub>1-x</sub>Ca<sub>x</sub>FeO<sub>3-y</sub>, La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3-y</sub>, La<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3+y</sub>, La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-y</sub> systems were selected. The basic features of the real/defect structure of these samples have been presented earlier in a number of publications [5-10]. In this work their prominent role in the forming the variety of oxygen forms in perovskite systems mentioned above will be discussed.

In according to TPR data, an increase of Ca or Sr content promotes the diversity and reactivity of oxygen forms in chosen perovskites systems. In the regions of low and moderate temperatures of TPR surface and subsurface processes of reduction are carried out. At high temperature region, the processes of bulk reduction are carried out, but reduction degree is

different for ferrites, manganites and cobaltites. On the whole, substitution increases reduction degree of these perovskites, and results to the shifts of maximums sets ( $T_{max}$ ) of the peaks of TPR- $H_2$  curves in the region of lower temperatures. The influence of preparation conditions on oxygen species and their reactivity was studied also. Increase of the calcinations temperature leads to the decrease of relative oxygen amounts removed in the course of TPR in corresponding peaks and results to the shifts of temperature maximums sets of the peaks in higher temperature region. Observed specificities are supposed to be concerned with especial microstructures and compositions of surface/subsurface layers of the samples prepared by mechanochemical synthesis characterized by elements segregation in subsurface layer, according to [5, 8, 9].

Catalytic properties of investigated perovskites studied in CO oxidation process in [5, 7-9], were discussed taking into account the real structure/microstructure of the samples. On one hand, maximums of specific catalytic activity were assigned to formation of the microdomain structure for  $La_{1-x}Sr_xCoO_{3-y}$  systems [9] and interphase boundaries for  $La_{1-x}Ca_xFeO_{3-y}$  systems [10]. On another hand, SCA values in CO catalytic oxidation, was found to correlate with the amount of reactive oxygen forms easily removed by TPR- $H_2$  at temperatures up to 150 °C (for cobaltites) and up to 420 °C (for ferrites). There is no correlation between lattice oxygen amounts removed at high temperatures of  $H_2$ -TPR processes and catalytic activity values. So, for the deep oxidation processes, reactivity and mobility of oxygen is connected with presence of microdomain / interphase boundaries.

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## SYNTHESIS AND INVESTIGATION OF POWDERED Pd/SIBUNIT CATALYSTS FOR PARTIAL HYDROGENATION OF VEGETABLE OIL

**Simakova O.A.<sup>1,2</sup>, Simonov P.A.<sup>1</sup>, Romanenko A.V.<sup>1</sup>**

<sup>1</sup>*Boreshkov Institute of Catalysis SB RAS, Novosibirsk, Russia*

<sup>2</sup>*Novosibirsk State University, Novosibirsk, Russia*

*E-mail: oasimak@catalysis.ru*

This work considers the preparation and investigation of Pd/Sibunit catalysts for partial hydrogenation of vegetable oil. Thereto samples of 1%(wt) Pd/Sibunit powdered catalysts with different metal distribution throughout the catalyst grain have been prepared by three different methods based on the  $H_2PdCl_4$  hydrolysis and palladium hydroxide deposition onto a carbon surface at pH 9-11. Samples of 1%(wt) Pd/Sibunit were tested in model reaction of cyclohexene hydrogenation (286 K,  $P_{H_2}=1$  atm, static reactor) and in partial hydrogenation of rapeseed oil. Isomeric products of hydrogenation of rapeseed oil were analyzed by IR-spectroscopy.

In the fats and oils industry the main goals are partial or total saturation of the C=C bonds in molecules of vegetable oils. To achieve one or the other of them, hydrogenation catalysts with certain distribution of the active component throughout the support grain are needed. In this work an attempt was made to prepare a set of samples of 1%(wt) Pd/Sibunit powdered catalysts with different metal distribution throughout the catalyst grain and to investigate their physicochemical properties for hydrogenation of C-C double bonds of rapeseed oil. 1% (wt) Pd/C catalysts were prepared by palladium hydroxide deposition onto a carbon surface at  $pH \geq 9$  of carbonaceous material Sibunit ( $S_{BET} = 450$  m<sup>2</sup>/g, grain size 0.07-0.09 mm). The catalyst synthesis was realized by three ways:

*Method 1:* solution of an alkali was dropped to aqueous  $H_2PdCl_4$  to adjust pH value of 9-11 followed by the addition to carbon slurry without preliminary aging ( $\tau=0$ ) of the catalyst precursor solution.

*Method 2:*  $H_2PdCl_4$  solution was directly introduced into the suspension of carbon in alkali solution.

*Method 3:* the precursor solution was prepared similarly to *method 1* but it was aged for a period of  $\tau = 0.25$  h before the contact with carbon slurry.

For comparison, Pd/C catalysts were prepared by traditional method based on hydrolysis of  $H_2PdCl_4$  at pH 5-6 to yield so-called polynuclear hydroxocomplexes of palladium [1] followed by their adsorption on carbon and increasing of pH slurry up to Na/Pd ratio 1:5 -1:21 (*method 4*).

In all cases  $\text{Na}_2\text{CO}_3$  was used as the alkali agent and the Pd/Na ratio was varied from 1:5 to 1:21 (*methods 1-3*) or from 1:1 to 1:1.5 (*method 4*). Catalyst samples were washed with water, dried at 343 K and reduced by hydrogen at 423 K. Dispersion of Pd was determined by the pulse CO chemisorption method and found to be 0.05-0.54. Catalytic activity and efficiency of the catalyst grain was estimated in liquid-phase hydrogenation of cyclohexene (286 K,  $P_{\text{H}_2}=1$  atm, static reactor), which is known as a structure-insensitive reaction, as well as in hydrogenation of rapeseed oil (370 K,  $P_{\text{H}_2}=6$  atm, static reactor). Isomeric products of hydrogenation of rapeseed oil were analyzed by IR-spectroscopy.

An increase of the aging time ( $\tau$ ) of  $\text{H}_2\text{PdCl}_4+\text{Na}_2\text{CO}_3$  mixture was found to decrease the dispersion of the supported palladium. While  $\tau=0.25$  h, the increase of the Pd/Na ratio from 1:5 to 1:9 gives a rise of catalyst dispersion from 0.05 to 0.30, but further growth of the Pd/Na ratio doesn't affect the dispersion of Pd/C catalysts. *Method 2* provides higher dispersion of palladium at the Pd/Na ratio 1:21. Among the Pd/C catalysts prepared by *methods 1-3*, the efficiencies of the catalyst grain in cyclohexene hydrogenation are higher for the catalysts prepared by *methods 2* and *3*. This means that the latter provide egg-shell distribution of Pd throughout the support grain that is in accordance with XPS data on local metal concentration on carbon surface.

It was observed that the rates of reaction of hydrogenation of rapeseed oil with catalysts produced by *method 2* are close to the rates of process of hydrogenation of rapeseed oil catalyzed by samples prepared according *method 4*. Content of *trans*-isomers in products of hydrogenation of rapeseed oil was shown to be lower for catalysts prepared by *methods 1* and *2*.

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