ANNUAL REVIEW 2009

BORESKOV INSTITUTE OF CATALYSIS

SIBERIAN BRANCH OF THE RUSSIAN ACADEMY OF SCIENCES

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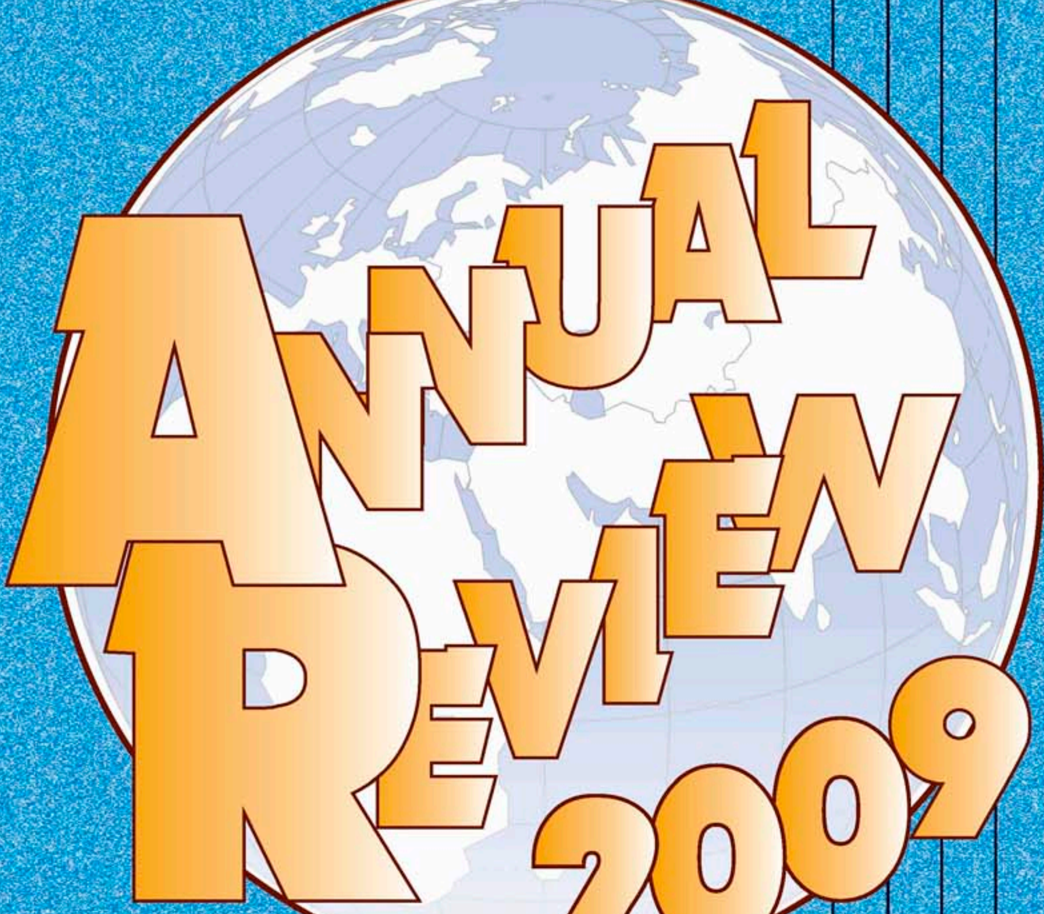

ANNUAL REVIEW 2009

http://catalysis.ru

ANNUAL REVIEW
of Activities in Basic Research Areas
2008

BORESKOV INSTITUTE OF CATALYSIS
SIBERIAN BRANCH OF THE RUSSIAN ACADEMY OF SCIENCES

Novosibirsk

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Dear Colleagues,

As usually, this issue of the Annual Review of the Boreskov Institute of Catalysis concerns the main fields of its academic and R&D activities and covers the year 2008.

The Boreskov Institute of Catalysis, or BIC, appears to be now the world largest research institute in the area of catalysis and is well known to experts in both academic and industrial catalysis not only in Russia and the fSU countries, but also in many western and oriental countries too. Since 1960's, it has remained the largest Russian chemical research institution in the Asian part of Russia and had many deep and stable traditions in providing basic and applied research in nearly all fields of catalysis. The interests of BIC spread from the very sophisticated areas of purely academic research to the real applied problems, including development of commercial catalysts and catalytic technologies.

The current features of BIC reflect entering the Russia into the market economy. Formally, BIC belongs to the Siberian Branch of the Russian Academy of Sciences (SB RAS) and, thus, its main goal is to work in basic areas of scienific research. However, according to realities of Russia, a lot deal of the BIC activity is devoted to numerous industrially oriented topics. The intensity and quality of the research and engineering activity at the Institute became at the new period of the Russian history even higher as before. Fortunately, the Institute gained in research in catalysis fundamentals, thus continuing the old traditions originated from the beginning of the Institute due to a very powerful starting impulse of its creator and first director Academician Georgii K. Boreskov, as well as the master ideas of the second director Academician Kirill I. Zamaraev. Hope, the readers will feel that themselves, when comparing the materials of this and previous issues of the Annual Review.

The year 2008, the same as all previous years, was very important for the life of BIC in many aspects. First of all, this year was the year of the 50th anniversary of the Institute. Thus, it was possible to summarize the results of the BIC activity for half a century and to look around in order to approve or disapprove the strategy of the Institute operation and development.

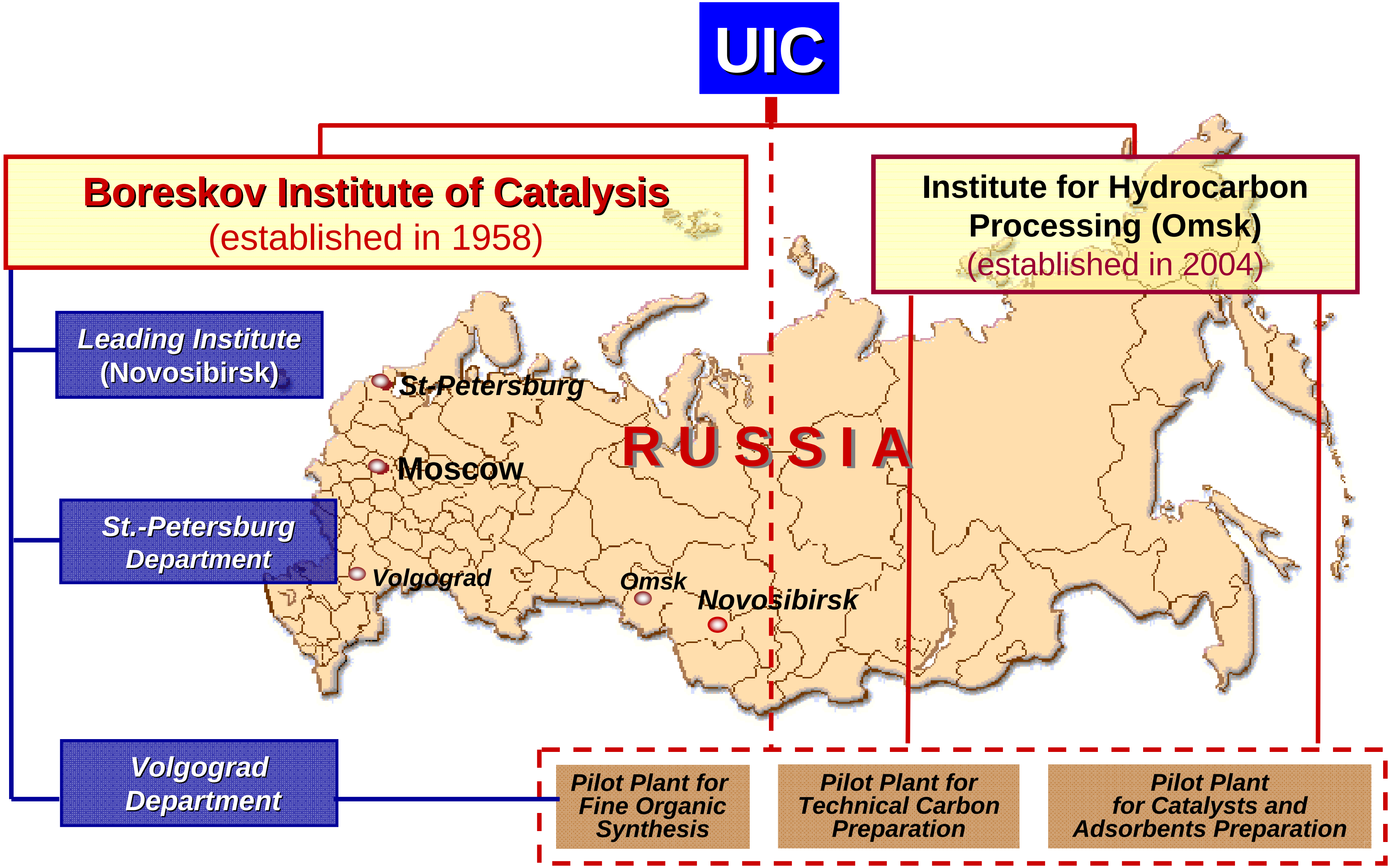
Also, in year 2008 there were several important achievements of the Institute in both academic and applied areas. As to academic research, one of the most interesting breaks through was a very correct observation and study of the size-dependent effect for the supported metal catalysts associated with the successful quantitative description of those effects with the help of a simple and consecutive thermodynamic approach. In the area of advanced and applied research, the BIC has largest enhanced its activity and received few positive results in new directions of the catalytic biomass conversion as well as of heavy oil upgrading. Also, there were many interesting results in numerous directions of regular catalytic study. In 2008, the Institute for the third time has supported to be the leader of the Russian chemical institutions from the point of view of citations. Indeed, this is a real honor for the R&D institutions. Also, the very important feature of the scientific activity of the Boreskov Institute was strenghthening of the strategic collaboration with the Russian and Western industries.

Since 1998, the Institute has been united with few other R&D chemical institutions of the Siberian Branch of the Russian Academy of Sciences in the frame of a R&D association which was called the United Institute of Catalysis (UIC). According to the UIC bylaw, the director of the Boreskov Institute of Catalysis has to be simultaneously the general director of the UIC. In 2004 there were some rearrangements in the UIC structure, since the Omsk Division of the BIC has separated from BIC as a new legal entity, the Institute of Hydrocarbons Processing (IHP), and the Volgograd Scientific center with large flexible pilot facilities for fine organic synthesis has joined BIC as its Volgograd Division. Thus, now UIC consists of two large legal entities: BIC and IHP. The facilities of the UIC include three flexible and powerful semi-industrial plants capable of manufacturing the first industrial batches of various catalysts and specialty chemicals. Thus, BIC together with UIC is now one of the most powerful Russian specialized R&D organizations in the industry-oriented chemistry with unique facilities for scaling up numerous innovations for that industry. Indeed, the current management of the Institute realizes the existing problems of the large R&D structure operation and tries to take care of the maintenance of high R&D activity and productivity of BIC and UIC in both fundamental and applied areas as the goal of the highest priority.

The main trend of the nowadays activity of the BIC management is step-by-step movement in improving its pilot facilities in order to be able to scale up its new catalytic technologies and demonstrate them to prospective industrial customers.

Hope, the current issue of the Annual Review of the Boreskov Institute of Catalysis will succeed in exhibiting many sides of the Institute potentialities in basic research on catalysis, catalysts and catalytic technologies. As to the activity of the Institute in the applied areas, which is now much more active than ever in the past, we publish special leaflets. Also, we are inviting the readers to visit the Bick's website **www.catalysis.ru**.

Valentin N. Parmon



UIC

Boreskov Institute of Catalysis
(established in 1958)

Institute for Hydrocarbon Processing (Omsk)
(established in 2004)

Leading Institute (Novosibirsk)

St.-Petersburg Department

Volgograd Department

Pilot Plant for Fine Organic Synthesis

Pilot Plant for Technical Carbon Preparation

Pilot Plant for Catalysts and Adsorbents Preparation

THE BORESKOV INSTITUTE OF CATALYSIS OF THE SIBERIAN BRANCH OF THE RUSSIAN ACADEMY OF SCIENCES

In 2008 the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences, the largest institution of the Russian Academy of Sciences in chemistry, celebrates 50 years of existence. The 50-year-long history of the Institute is a glowing example of fruitful interaction between fundamental science and industry and of the profound realization that solving scientific problems should be aimed at some practical result. The accomplishments of the Institute embody its original conception, which includes studies at the atomic/molecular level and commercialization of the results. It is due to this approach that the Institute has made a significant contribution to the material and technical basis necessary for the rapid development of the Russian chemical industry and became one of the world's most prominent research centers in chemical catalysis.

The Institute was founded in the summer of 1958 as a part of the Siberian Branch of the USSR Academy of Sciences. Initiator of the Institute and its permanent director up to 1984 was Academician Georgii K. Boreskov (1907-1984), an eminent scientist with international recognition, an outstanding physical chemist and chemical technologist. In 1992 the Institute of Catalysis was named after Academician G.K. Boreskov.

In 1969 the Institute of Catalysis was awarded The Red Banner of labor for the contribution to development of chemical science and for training high-skilled personnel.

In 1976 Professor Kirill I. Zamaraev has been invited by Academician G.K. Boreskov to join the Institute of Catalysis as a Deputy Director. Kirill Ilyich has come to Novosibirsk at early 1977 together with a large team of young chemical physicists, thus largely widening the studies of elementary catalytic reactions on molecular-atomic level through application of modern physical and kinetic instrumental methods of investigation.

In 1984 Professor Zamaraev became the Director of the Institute of Catalysis, and since that time he was the real leader of all research and development activity of this huge Institute. K.I. Zamaraev, the former President of the International Union of Pure and Applied Chemistry, Foreign Fellow of the Indian National Science Academy and of the Korean Academy of Science and Technology, holder of the Silver Medal of the Royal Chemical Society of Great Britain as a centenary lecture, has passed away in the prime of his brilliant scientific career on 26 June 1996.

In 1995 Professor Valentin N. Parmon, prominent specialist in the field of catalysis, chemical kinetics and photocatalysis, headed the third generation of the directorate of the Institute.

Since 1998 the Institute has been united with some other R&D chemical institutions of the Siberian Branch of the Russian Academy of Sciences in the frame of a new R&D association: the United Institute of Catalysis headed by the director of the Boreskov Institute of Catalysis. Now the United Institute of Catalysis (UIC) affiliates the Boreskov Institute of Catalysis with its St. Petersburg and Volgograd Departments, the Institute of Hydrocarbons Processing in Omsk and three pilot plants.

The scope of the Institute’s activities is extremely wide, ranging from solving fundamental problems of catalysis to creating new catalytic technologies and organizing commercial scale production of catalysts.

The high level of the fundamental research carried out by the Institute is reflected by numerous monographs, as well as articles published in prestigious international journals and collections of works. The Institute publishes more than 300 works per year in peer-reviewed journals. According to the interdisciplinary server www.scientific.ru, the Institute has the highest total citation index among the Russian chemical institutions over the last 7 years. The average citation index of one article is above 6 and is high on the citation index list of articles from chemical instructions of the Siberian Branch of the Russian Academy of Sciences.

The Institute patents over 40 discoveries and maintains more than 30 foreign patents annually. The Institute is the avowed intellectual property protection leader among the Russian academic institutions.

The Institute is designing new generations of catalysts and technologies to meet the present-day global trends. Throughout its 50-year-long history, the Institute has been among the leaders in developing new technologies for the chemical and petrochemical industries, power engineering, and environmental protection.

The numerous exploratory and prospective studies of the Institute in the field of catalytic technologies include advancement of a large complex of environmental and energy-saving technologies, use of nontraditional feedstocks in the production of various motor fuels and oil processing products, fine synthesis of medicines and plant protection chemicals, etc.

The Institute designed original devices for studying the properties of catalysts and has organized small-scale production of automated devices and installations for investigation and control of the physicochemical properties of various substances and materials. The novel, high-efficiency catalysts and technologies developed by the Institute satisfy the present-day requirements and are in demand in Russian markets and around the world.

The Institute is widely known abroad for its achievements and is a partner of many Russian and foreign companies.

STRUCTURE OF THE INSTITUTE

The Boreskov Institute of Catalysis (BIC) unites more than 1000 employees, among its 400 researchers being 1 academician, 3 Corresponding Members RAS, about 70 Drs. Sci. and 200 PhD's. The Institute is a unique association of specialists in various fields of science and technology that are capable of solving any catalytic problems from fundamentals to design of industrial catalysts and processes.

The Institute structure comprises **9 research departments**.

The Center for Catalyst Characterization and Testing has a bank of catalyst samples, supports and adsorbents, a set of State Standard Samples to calibrate and certify instruments for measurements of specific surface areas of various dispersed and porous materials.

The main directions of its activity are:

- Complex investigation and characterization of the catalysts by a set of modern physicochemical methods.
- Joint scientific projects with foreign firms and organizations on studying certain catalytic processes and catalysts for the purpose of their improvement.
- Development of modern standard experimental methods and equipment for catalyst studies and tests. Design of catalysts and materials with certificated properties.

The successful research activities are based on the overall access to the latest and reliable scientific data. There is the **Information and Library Center** in the Institute, and the library is one of the best scientific libraries in Siberia.

The **Scientific Organization Department** deals with scientific events such as conferences, seminars, schools, meetings, presentations of various companies and equipment producers, discussions. There is a museum where the information on catalytic science is collected.

Advertising and Exhibits Department of the Institute is active in competence, perfect service in the field of organization of exhibitions of the new inventions and successive achievements of the Institute.

The activities of the **Group of Science, Engineering and Innovation Programs** are aimed at the participation of the Institute in State priority competitive programs for creation of technologies and materials to make Russia an economically independent country.

The **Publishing Department** concentrates its activities on supporting the R&D process inside the Institute, as well as on public information about the BIC’s advances. Among the published items are Annual Reports, Proceedings of conferences organized by the Institute, information bulletins, manuals, etc.

Production Departments provide engineering and technical support of the research activities, exploitation and modernization of the available facilities.

STRUCTURE OF THE INSTITUTE

Directorate:
V.N. Novikov, S.E. Glaznev,
I.A. Kamolkin, A.A. Vedyagin
A.S. Noskov, V.N. Parmon,
V.I. Bukhtiyarov, B.S. Bal'zhinimaev

DIRECTOR

Directorate

Scientific Council

Research Departments

DEPARTMENT OF PHYSICOCHEMICAL METHODS FOR CATALYST INVESTIGATION
Head: Prof. Valerii I. Bukhtiyarov

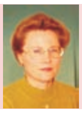
DEPARTMENT OF NONTRADITIONAL CATALYTIC PROCESSES AND TECHNOLOGIES
Head: Acad. Valentin N. Parmon

DEPARTMENT OF HETEROGENEOUS CATALYSIS
Head: Prof. Aleksandr A. Khassin

DEPARTMENT OF EXPLORATORY AND APPLIED INVESTIGATIONS
Center for Catalyst Characterization and Testing
Head: Prof. Bair S. Bal'zhinimaev

DEPARTMENT OF CATALYTIC PROCESS ENGINEERING
Head: Prof. Alexander S. Noskov

DEPARTMENT OF CATALYTIC PROCESSES OF FINE ORGANIC AND BIOORGANIC SYNTHESIS
Head: Prof. Zinaida P. Pai



SCIENTIFIC AND TECHNICAL DEPARTMENT OF APPLIED CATALYSIS
Head: Prof. Lubov A. ISUPOVA

St. PETERSBURG DEPARTMENT OF THE BORESKOV INSTITUTE OF CATALYSIS
Head: Prof. Sergey S. Ivanchev

VOLGOGRAD DEPARTMENT OF THE BORESKOV INSTITUTE OF CATALYSIS
Executive Director Dr. Andrey P. Kovalenko

Scientific-Supportive Units

Manufacturing Facilities

Administration and Services

DEPARTMENT OF PHYSICOCHEMICAL METHODS FOR CATALYSTS INVESTIGATION

Head of the Department Prof. Valerii I. Bukhtiyarov

Surface Science Laboratory
Head: Prof. Valerii I. Bukhtiyarov

Laboratory of Analytical Chemistry
Head: Prof. Vladimir N. Sidelnikov

Laboratory of Investigation of the Mechanisms of Catalytic Reactions
Head: Prof. Eugenii P. Talsi

Laboratory of Catalyst Texture Studies
Head: Dr. Maxim S. Melgunov

Laboratory of Quantum Chemistry
Head: Dr. Igor L. Zilberberg

Laboratory of Spectral Methods
Head: Prof. Dimitrii I. Kochubey

Laboratory of Structural Methods
Head: Prof. Sergey V. Tsybulya

Group of Low Temperature Catalysis by Metals
Head: Prof. Vladimir V. Gorodetsky

Group of Solid-State NMR Spectroscopy
Head: Prof. Olga B. Lapina

Group of Surface Compounds Synthesis
Head: Dr. Vladimir L. Kuznetsov

Group of NMR Spectroscopy for Catalytic Hydrocarbon Conversion
Head: Prof. Alexander G. Stepanov

Group of Nanostructural Analysis
Head: Prof. Fedor V. Tuzikov

DEPARTMENT OF NONTRADITIONAL CATALYTIC PROCESSES

HEAD OF THE DEPARTMENT ACADEMICIAN VALENTIN N. PARMON

Laboratory of Catalytic Methods of Solar Energy Conversion
Head: Academician Valentin N. Parmon

Laboratory of Adsorption
Head: Prof. Oleg N. Martyanov

Laboratory of Hydride Compounds Studying
Head: Prof. Valentina I. Simagina

Laboratory of Catalytic Processes for Desulfurization
Head: Dr. Olga N. Kovalenko

Laboratory of Energy Accumulating Processes and Materials
Head: Prof. Yuriy I. Aristov

Group of Adsorption-Catalytic Processes for Fuel Cells
Head: Dr. Alexey G. Okunev

Group of Aerosol Catalysis
Head: Dr. Valerii N. Snytnikov

Group of Biocatalysis
Head: Prof. Galina A. Kovalenko

Group of Catalysts on Carbon Supports
Head: Dr. Irina L. Simakova

Group of Metal Complex Catalysis

Head: Prof. Nina I. Kuznetsova

Group of Sulfide Catalysts

Head: Prof. Anatolii N. Startsev

Group of Photocatalysis on Semiconductors

Head: Prof. Alexandr V. Vorontsov

Group of Energy-Chemical Processes and Technologies

Head: Prof. Vladimir I. Anikeev

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HEAD OF THE DEPARTMENT PROF. ALEKSANDR A. KHASSIN

Laboratory of Catalytic Processes in Fuel Cells
Head: Prof. Vladimir A. Sobyanin

Laboratory of Heterogeneous Selective Oxidation
Head: Dr. Vladimir I. Sobolev

Laboratory of Dehydrogenation
Head: Prof. Victor V. Molchanov

Laboratory of Catalysts for Deep Oxidation
Head: Prof. Vladislav A. Sadykov

Laboratory of Oxidative Catalysis over Zeolites
Head: Prof. Gennadii I. Panov

Laboratory of Catalysts Preparation
Head: Prof. Aleksandra S. Ivanova

Laboratory of Ecological Catalysis
Head: Prof. Zinfer R. Ismagilov

Laboratory of Catalytic Conversion of Carbon Oxides
Head: Prof. Aleksandr A. Khassin

Group of Noble Metal Based Heterogeneous Catalysts
Head: Prof. Anatolii V. Romanenko

Group of Reactions of Oxidation on Metals
Head: Prof. Aleksandr V. Khasin

DEPARTMENT OF CATALYTIC PROCESS ENGINEERING

HEAD OF THE DEPARTMENT PROF. ALEKSANDR S. NOSKOV

Laboratory of Unsteady-State Catalytic Methods for Gas Purification
Head: Prof. Aleksandr S. Noskov

Laboratory of Multiphase Processes Modeling
Head: Prof. Valerii A. Kirillov

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Head: Prof. Gennadii V. Echevsky

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Head: Prof. Vladimir A. Zakharov

Laboratory for Catalytic Processing of Renewable Sources
Head: Dr. Vadim A. Yakovlev

Sector of Complex Engineering Projects
Head: Dr. Victor A. Chumachenko

Group of Dynamics of Catalytic Processes
Head: Prof. Andrey N. Zagoruiko

Group of Kinetics of Catalytic Processes
Head: Prof. Sergei I. Reshetnikov

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Head: Dr. Natalia A. Chumakova

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Head: Dr. Vitalii N. Kashkin

Group of Hydrogenation Processes
Head: Dr. Galina A. Bukhtiyarova

Group of Processes in Fixed Catalyst Layer
Head: Dr. Ilya A. Zolotarsky

Group of Membrane Catalytic Processes
Head: Dr. Ilya V. Mishakov

DEPARTMENT OF EXPLORATORY AND APPLIED INVESTIGATIONS

HEAD OF THE DEPARTMENT PROF. BAIR S. BAL'ZHINIMAEV

Center for Catalysts Characterization and Testing
Head: Prof. Bair S. Bal'zhinimaev

Laboratory of Acid Base Catalysis
Head: Prof. Eugenii A. Paukshtis

Laboratory of Catalysts Activity Testing
Head: Dr. Nikolai N. Bobrov

Group of Catalytic Conversion of Sulfur-Containing Compounds
Head: Prof. Anna V. Mashkina

DEPARTMENT OF CATALYTIC PROCESSES OF FINE ORGANIC AND BIOORGANIC SYNTHESIS

HEAD OF THE DEPARTMENT PROF. ZINAIDA P. PAI

Group of Liquid-Phase Catalytic Oxidation of Organic Compounds
Head: Prof. Zinaida P. Pai

Group of Catalysts and Processes Based on Heteropoly Acids
Head: Prof. Elena G. Zhizhina

Group of Heterogeneous Catalysts for Selective Liquid-Phase Oxidation
Head: Prof. Oxana A. Kholdeeva

SCIENTIFIC AND TECHNICAL DEPARTMENT OF APPLIED CATALYSIS

HEAD OF THE DEPARTMENT PROF. LYUBOV A. ISUPOVA

Group of Catalysts and Supports for High Temperature Processes
Head: Prof. Lyubov A. Isupova

Group of Aerogel Materials
Head: Dr. Alexander F. Danilyuk

Assurance Group
Head: Sergey A. Lopatin

Group of Catalysts Preparation
Head: Vasilii Yu. Kruglyakov

Group of Catalysts Testing
Head: Alexander S. Bobrin

Group of Pilot Plants and High Pressure
Head: Victor N. Korotkikh

Group of Preparative Synthesis
Head: Dr. Yurii I. Amosov

ST. PETERSBURG DEPARTMENT OF THE BORESKOV INSTITUTE OF CATALYSIS

DIRECTOR AND SCIENTIFIC MANAGER
PROF. SERGEY S. IVANCHEV

VICE-DIRECTOR DR. VALERY P. TULMANKOV

Laboratory of Micellar Catalysis, Emulsion Polymerization and Processes for Obtaining Polymeric Composites
Head: Prof. Valery N. Pavlyuchenko

Laboratory of Novel Catalytic Systems for Olefin Polymerization and Copolymerization
Head: Prof. Sergey S. Ivanchev

VOLGOGRAD DEPARTMENT OF THE BORESKOV INSTITUTE OF CATALYSIS

EXECUTIVE DIRECTOR DR. ANDREY P. KOVALENKO

SCIENTIFIC DIRECTOR DR. ALEKSANDR M. BESKOPYLNYI

SCHOOLS OF THE BORESKOV INSTITUTE OF CATALYSIS

The successful development of the Institute has been possible only due to the existence of scientific schools headed by the Institute's leading scientists in a variety of important research areas.

Academician G.K. Boreskov

Theory of heterogeneous catalysis. The nature of the interaction between the reactants and the catalyst. The effect of the reactant–catalyst bonding energy on the catalytic activity and selectivity. The concepts of stepwise and associative mechanisms of redox catalytic reactions. Unsteady-state catalysis. Development of industrial catalysts.

Academician K.I. Zamaraev

Theory of tunneling transfer of electrons in solids. The coordination chemistry of metal complex solutions. Studies of stepwise mechanisms of homogeneous and heterogeneous catalytic reactions, active site structure at the atomic/molecular level. Search for novel areas in catalysis.

Academician V.N. Parmon

Catalysis and photocatalysis in renewable and non-traditional energetics. Photochemical and thermochemical methods of solar energy conversion. Radiation and thermal catalysis. The role of photocatalysis in the global chemistry of the terrestrial atmosphere. Abiogenic catalysis in the nature. Synthesis of nanomaterials. New types of chemical reactors.

M.G. Slin'ko, Corresponding Member of RAS

Methods of mathematical modeling of catalytic processes and reactors based on hierarchical models. Optimization and modeling of processes in fixed and fluidized beds; liquid-phase, multiphase, and unsteady-state processes. Design of industrial reactors.

R.A. Buyanov, Corresponding Member of RAS

Scientific basis of catalyst preparation and technology. Enhancing the reactivity of solid phases. Mechanochemistry in catalysis. Catalyst deactivation. Theoretical basis of the synthesis of carbon–mineral composites. Theory of nonbranched-chain free-radical catalytic reactions. Development of industrial catalysts.

V.A. Likholobov, Corresponding Member of RAS

Molecular design of catalytic compositions for organic syntheses. "Tailoring" of active sites of metal complex catalysts. Synthesis of porous supports with the desired textural and surface properties.

Professor Yu.I. Yermakov

Targeted synthesis of supported catalysts with the desired composition and dispersion using immobilized organometallic compounds. Catalytic polymerization of olefins. Development of industrial catalysts.

Professor V.A. Dzis'ko

Formation of oxide catalysts of complex composition. Control of the chemical and phase compositions, acid–base surface properties, textural and strength characteristics, and thermal stability of the catalysts. Development of industrial catalysts and supports.

Professor G.M. Zhidomirov

Heterogeneous catalysis theory. Principles of the IR spectroscopy of the surface. Quantum chemical modeling of catalytic systems. Calculation of the electronic structure and properties of the acid and redox sites of zeolite, oxide, and metal catalysts.

R&D ACTIVITY OF THE INSTITUTE

Basic research

- ♦ *Determination of general regularities of catalysis*
- ♦ *Development of the scientific basis for molecular design the catalysts and materials*
- ♦ *Development of the theoretical basis to design the catalytic processes*
- ♦ *In-situ methods to study catalyst and mechanism of important catalytic reactions*
- ♦ *Methods and algorithms to predict the catalytic action*
- ♦ *Methods and facilities for the catalysts testing*
- ♦ *Nanotechnological approach to design the catalysts with predictable properties*

Applied catalysis

- *Design of highly efficient catalysts for production of key chemicals; oil & gas processing*
- *Design of the catalytic composites and technologies for applied purposes*
- *Catalysts and catalytic technologies for polymers production with specified properties*
- *Design of sorbents, catalysts and technologies for detoxication of hazardous man-caused wastes*
- *Selective oxidation of light* C_1-C_4 *paraffins by molecular oxygen*
- *Gas-phase propylene epoxidation by molecular oxygen*
- *Reactors and new processes based on membrane catalysts. Microchannel catalytic reactors*
- *Catalysts and processes related to hydrogen energy technologies*
- *Catalysis concerned to the environmental and energy problems*
- *New directions and opportunities of catalysis in utilization of renewable natural resources*

Some catalytic technologies owned by BIC

- **Reverse process** for catalytic gas purification
- **Zeoforming processes** for synthesis of gasoline
- **Alphox technology** for the one step phenol form benzene production
- **Adsoroption-catalytic purification** of industrial wastewaters

Catalytic Processes from Molecular Level to Industrial Plants

2008 Catalyst for diesel deep desulfunization (EURO-5 standards)

2007 Ultrahigh molecular weight polyethylene (UHMWPE)

2005 Cracking catalyst LUKS and reforming catalyst PR-71

2004 Reburning of Klaus tail gases

2002 Selective water sorbents

2000 New technology of loading the reactors with catalysts

1998 One-step technology for production of nicotinic acid
Licensed to European company, 1999, Degussa, Germany

1997 Non-platinum catalyst for production of nitric acid
Developed in cooperation with Solutia, USA

1996 Alphox technology (benzene + $[N_2O]$ → phenol)

1995 Catalyst for FCC (oil cracking)

1993 Carbonaceous material SIBUNIT
Sibunit for phosgene synthesis, DuPont, 1994, USA

1992 ZEOFORMING process for synthesis of high-octane gasoline
Lurgi, 1997, Germany

1988 Catalysts for propylene polymerization
DSM, 1995, the Netherlands

1982 REVERS-Process
Monsanto Enviro Chem. Systems, 1992, USA

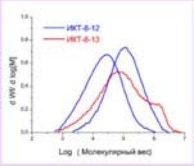
1978 Vanadium catalysts for sulfuric acid production

1958

- **Nitric acid** production with the use of honeycomb catalysts
- **One-step** technology for the **nicotinic acid** production
- New technology of **loading the reactors** with catalysts
- **BIMT technology** for production of gasoline and diesel fuel without preliminary rectifying the hydrocarbon feedstock
- Reburning of Klaus **tail gases**
- The **BICYCLAR** technology for production of aromatic hydrocarbons with methane involvement
- Direct catalytic **oxidation of H_2S** to elemental sulfur
- Treating of mixed **radioactive organic wastes**
- Liquid-phase oxidative **treating of industrial wastewater**
- Technology for **formaldehyde** production
- Technology for **one step formic acid** production
- Technology for **reducing atmospheres** production
- Technique for preparation of **emulsifiers and water-bitumen emulsions**

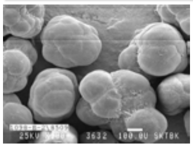
Some industrial catalysts by BIC

Vanadium pentoxide catalysts for sulfuric acid production

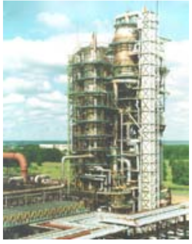


Supported catalysts ICT-8-12 and ICT-8-13 for polyethylene production

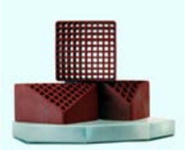
Catalyst ICT-8-20 for production of ultrahigh molecular weight polyethylene



Supported Ti-Mg catalyst IC-8-21 for polypropylene production

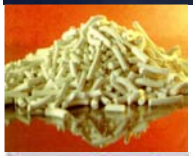


Microspherical zeolite-containing cracking catalysts



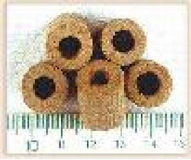
Non-platinum catalyst IC-42-1 for nitrogen acid production

Gasoline reforming catalysts of PR series



High silica zeolite catalysts

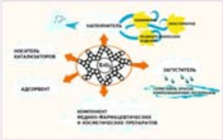
Hydrogenation catalysts of for manufacture of medical products and edible fats



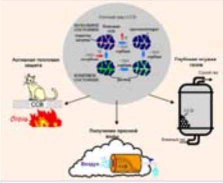
Thermostable catalyst ICT-12-40 for gas purification

Catalyst for hydropurification of terephthalic acid

Some catalyst supports by BIC



Superfine silica gels IC-01-2



Composite selective water sorbents SWS

Mesoporous carbonaceous material SIBUNIT

INSTRUMENTATION FACILITIES

The Institute engages the leading position in the world in the improvement and design of new physicochemical methods for catalyst study. The Boreskov Institute of Catalysis has specialized groups united into Department of Physicochemical Methods for Catalyst Investigation oriented at analytical and scientific studies. At the Department there are many specialists of high qualification specializing in the investigation of catalysts and nanomaterials.

Modern and, in some cases, unique physicochemical methods provide a basis for fundamental studies at the atomic-molecular level.

The types of analytical and research studies performed at the Institute and methods used for them are listed below.

Analytical (composition of catalysts and catalytic reaction products)

Bulk composition

Atomic emission spectrometry
Atomic absorption spectroscopy
X-Ray fluorescence analysis of macro- and microprobes

Phase analysis

X-Ray diffraction, including *in situ* diffraction
Differential dissolution
Thermally programmed reduction, oxidation, desorption
X-Ray diffusion scattering
EXAFS spectroscopy (for amorphous materials)

Morphology

Transmission electron microscopy
High resolution transmission electron microscopy (HRTEM)
Scanning electron microscopy
Scanning tunneling microscopy
X-Ray small-angle scattering

Surface

X-Ray photoelectron spectroscopy (XPS)
Secondary ion mass-spectrometry (SIMS)
Determination of the surface acidity using IR spectroscopy of probe molecules

Molecular composition of individual compounds and their mixtures

Gas, gas-liquid and liquid chromatography on packed, capillary and polycapillary columns
Superrapid chromatography
Mass-spectrometry

Adsorptive (specific surface area, pore structure, adsorption heat)

Porosimetry
Calorimetry

Kinetic

Gradientless and integral differential reactors
Fast relaxation technique
Stop flow technique
Radiochemical and isotopic methods
Mass-spectrometric detection of free radicals.

Spectral methods

NMR spectroscopy on different nuclei, including high-temperature and *in situ*
ESR spectroscopy, including *in situ*
FMR spectroscopy, including *in situ*
VUV electron spectroscopy
UV-VIS electron spectroscopy
Vibrational spectroscopies (IR, including *in situ,* and RAMAN)
HREELS
LEED
X-Ray and NMR tomography

INTERNATIONAL COOPERATION

The scientific cooperation of the Boreskov Institute of Catalysis with the catalytic communities from various countries is effected in accordance with various forms of cooperation: conducting joint seminars on catalysis, exchanging the information and appropriate materials, exchanging research fellows, visiting scientific centers, and participating in congresses and symposia on theoretical and applied catalysis.

According to research programs, projects and grants, the fundamentals of catalysis are studied jointly with researchers from various universities, institutions, research laboratories and companies. BIC collaborates fruitfully on a commercial basis with the leading companies from more than 20 countries, sells licenses, know-how and performs research projects according to client requests.

Academician Valentin N. Parmon is the Russian representative in the European Federation of Catalytic Societies (EFCATS), Member of the International Association of the Catalysis Societies (IACS).

Visits of the specialists from the Boreskov Institute of Catalysis to foreign institutions in 2008

Australia	1	Greece	2	Netherlands	9
Austria	4	Hungary	1	Poland	5
Belarus	8	India	4	Republic of Korea	16
Belgium	11	Ireland	1	Slovenia	1
Bulgaria	7	Israel	4	Spain	4
Canada	2	Italy	16	Switzerland	2
China	25	Japan	12	Sweden	1
Czechia	1	Kazakhstan	3	Taiwan	1
Denmark	1	Lithuania	2	Thailand	1
Egypt	2	Malta	50	Tunisia	1
Finland	8	Mexico	1	Ukraine	6
France	19	Mongolia	1	UK	5
Germany	33	Montenegro	1	USA	8

Visits of foreign specialists to the Boreskov Institute of Catalysis in 2008

Belarus	2	Hungary	1	Serbia and Montenegro	2
Bulgaria	1	India	3	Spain	1
China	7	Japan	4	Republic of Korea	6
Czechia	1	Kazakhstan	1	Ukraine	3
France	11	Netherlands	6	UK	3
Germany	5	Saudi Arabia	1	USA	14

SCIENTIFIC COOPERATION
WITHIN THE FRAMEWORK OF CONTRACTS AND AGREEMENTS
WITH FOREIGN ORGANIZATION

ITALY

The cooperation in the frame of the agreement between **Russian Academy of Sciences** (RAS) and **National Council on the Scientific Research** of Italy with *The Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano"* (CNR Institute of Advanced Energy Technologies "Nicola Giordano"), Messina on the *Project* ***"Materials with Enhanced Properties for Energy Conversion"***. Coordinators: **Prof. Yu. Aristov** (*BIC*) and **Prof. G. Restuccia** (*Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano"*).

FRANCE

According to the agreement between **RAS** and **CNRS** BIC collaborates with the *Institute de Recherches sur la Catalyse* (Research Institute on Catalysis), Villeurbanne in the frame of the Russian-French European associated Laboratory on Catalysis headed by Acad. V. Parmon and Dr. M. Lacroix. The Laboratory was established by an agreement signed December 6, 2004 in Moscow by RAS and CNRS. Four areas of research were identified:

- ***Catalysis and Energy: Production of Syngas and Hydrogen***
- ***Catalysis and Environment: Treatment of Waste Waters***
- ***Catalysis and Fine Chemistry: Selective Oxidation with Hydrogen Peroxide***
- ***Advanced Spectroscopic Methods: Mobility of Species in Porous Medium.***

INDIA

In the frame of Indo-Russian Integrated Long Term Programme of cooperation in science and technology (ILTP) BIC collaborates with:

➢ *Indian Institute of Chemical Technology*, Hyderabad, on the Project ***"Study and Development of Heterogeneous Photocatalytic Removal of Hazardous Compounds from Air and Water"***. Coordinators: **Prof. A. Vorontsov** (*BIC*) and **Dr. M. Sabramaniam** (*Indian Institute of Chemical Technology*).

➢ *National Chemical Laboratory,* Pune on the Project ***"Design of Bifunctional Supported Non-Iron Catalysts for Low Temperature Ammonia Synthesis"***. Coordinators: **Dr. B. Moroz** (*BIC*) and **Dr. S.B. Halligudi** (*National Chemical Laboratory*).

Coordinators on the Program "Catalysis" are Acad. V. Parmon and Dr. S. Sivaram.

GERMANY

The cooperation in the frame of the agreement between **RAS** and **German Scientific Research Society** (GSRS) with *Fritz-Haber-Institut der Max-Planck-Gesellschaft*, Berlin on the

Project ***"Development of in situ Methods for Study of Solid Surfaces"***. Coordinators: **Prof. V. Bukhtiyarov** (*BIC*) and **Prof. R. Schlögl** (*Fritz-Haber-Institut der MPG*).

JAPAN

Bilateral agreement *BIC - Research Laboratory for Nuclear Reactors*, Tokyo Institute of Technology, on the Project "***Adsorption and Chemical Reactions for Heat Transformation***". Coordinators: **Prof. Yu. Aristov** (*BIC*), **Prof. Y. Kato** (*Research Laboratory for Nuclear Reactors*)

CHINA

The cooperation in the frame of *Associated Research Laboratory* which was established by an agreement signed December 4, 2004 by the Boreskov Institute of Catalysis and Heilongjiang University, Harbin. Chief Executive officers of Laboratory are: **Prof. V. Bukhtiyarov** (*BIC*) and **Fu Hong-Gang** *(Heilongjiang University*). Project ***"Synthesis and Modification of ZSM-12 Zeolites. Zeolite ZSM-12 in Reaction of Naphthalene Alkylation with Methanol"***. Coordinators: **Prof. Wu Wei** *(Heilongjiang University)*, **Prof. G. Echevsky** (*BIC*).

KOREA

In the frame of the agreement between **RAS** and **Korea Science and Engineering Foundation** (KOSEF) *BIC* cooperates with *Korea Institute of Science and Technology*, Seoul, Korea.

COOPERATION IN THE FRAME OF PROJECTS FINANCED BY INTERNATIONAL FOUNDATIONS

INTAS - SB RAS Supported Project

Electromagnetic Response Properties of Carbon Onions and Carbon Onion-Based Composites

Project Coordinator:

Dr. Ph. Lambin, *Facultes Universitaires Notre-Dame de la Paix*, Namur, Belgium

Participants:

Belarus State University, Minsk, Belarus; *University of Joensuu*, Finland; *Institute for Technical Physics and Materials Science*, Budapest, Hungary; *The Boreskov Institute of Catalysis*, Novosibirsk, Russia (**Dr. V. Kuznetsov)**, *Nikolaev Institute of Inorganic Chemistry*, Novosibirsk, Russia.

CRDF Project

Carbon Nanoreactor for Solid-State Synthesis of Novel Nanoscale Materials Based on Nanocrystalline Oxides

Project Coordinators:

Prof. A. Volodin, *The Boreskov Institute of Catalysis*, Novosibirsk, Russia

Prof. K.J. Klabunde, *Kansas State University,* Manhattan, Kansas, USA.

EUROPEAN COMMUNITY SIXTH FRAMEWORK PROGRAM

I. International Partnership for a Hydrogen Economy for Generation of New Ionomer Membranes

Coordinator: **Dr. R. Mallant**, *Energy Research Centre of The Netherlands*, Petten, The Netherlands

Partners:

Daimler Chrysler; *FuMA-Tech GmbH*; *CNRS Montpellier*; *Dohgyue Chenzhou New Materials Company*; *Shanghai Jiao Tong University*, Shanghai, China; *The Boreskov Institute of Catalysis*, Novosibirsk, Russia (**Prof. V. Bukhtiyarov**).

II. Co-Processing of Upgraded Bio-Liquids in Standard Refinery Units

Coordinator: **Dr. Y. Solantausta**, *VTT Processes*, Espoo, Finland

Partners:

Rijksuniversiteit Groningen, The Netherlands; *The Boreskov Institute of Catalysis*, Novosibirsk, Russia (**Prof. V. Kirillov**); *Uhde Hochdrucktechnik GmbH*, Germany; *BTG Biomass Technology Group BV*, The Netherlands; *University of Twente*, The Netherlands; *STFI-PACKFORSK AG*, Sweden; *Institute of Wood Chemistry*, Hamburg, Germany; *Slovenian Institute of Chemistry*, Slovenia; *Arkema SA*, France; *Helsinki University of Technology*, Finland; *ALMA Consulting Group SAS*, France; *Centre National de la Recherche Scientifique*, France; *Chimar Hellas SA*, Greece; *Albermarle Catalysts Company BV*, The Netherlands; *Metabolic Explorer*, France; *Shell Global Solutions International*, The Netherlands.

III. Non-Noble Catalysts for Proton Exchange Membrane Fuel Cell Anodes

Coordinator:

Dr. G. Tsotridis, *Institute for Energy, Joint Research Centre*, Petten, The Netherlands

Partners:

Technical University of Denmark, Lyngby, Denmark; *The Boreskov Institute of Catalysis*, Novosibirsk, Russia (**Acad. V. Parmon, Dr. O. Pestunova)**; *Southampton University*, UK; *Technical University of Munich*, Germany; *Bavarian Center for Applied Energy Research*; *Umicore, AG & Co KG*, Germany.

IV. *Novel Materials for Silicate-Based Fuel Cells*

Coordinator: **Dr. Ch. Arguirusis**, *Technische Universität Clausthal*, Clausthal, Germany

Partners:

University of Aveiro, Aveiro, Portugal; *Foundation of Research and Technology Hellas*, Greece; *Katholieke University of Leuven*, Belgium; *Max-Plank Institute of Colloids and Interfaces*, Munchen, Germany; *The Boreskov Institute of Catalysis*, Novosibirsk, Russia (**Prof. V. Sadykov**); *Ceramics and Refractories Technological Development Company*, Greece; *Ceramiques Techniques et Industrielles*, France.

EUROPEAN COMMUNITY SEVENTH FRAMEWORK PROGRAM

Reforming of Crude Glycerine in Supercritical Water to Produce Methanol for Re-Use in Biodiesel Plants

Coordinator: **J. Vos**, *BTG BiomassTechnology Group BV,* The Netherlands

Partners:

Acciona Servicios Urbanos, Spain; *The Boreskov Institute of Catalysis,* Novosibirsk, Russia (**Prof. V. Kirillov**); *Rijksuniversiteit Groningen*, The Netherlands; *University of Maribor*, Slovenia; *UHDE High Pressure Technologies GmbH*, Germany; *SPARQLE International BV*, The Netherlands.

NATO PROGRAMME: SCIENCE FOR PEACE

I. Solid Oxide Fuel Cells for Energy Security

NATO Country Project Director:

Prof. N. Orlovskaya, *Drexel University*, Philadelphia, USA

Partner Country Project Director:

Prof. O. Vasiliev, *Frantcevych Institute for Problems of Material Science*, Kiev, Ukraine

Project Co-Directors:

Prof. V. Sadykov, *The Boreskov Institute of Catalysis*, Novosibirsk, Russia

Prof. J. Irvine, *University of St. Andrews*, St. Andrews, UK|

Prof. N. Sammes, *University of Connecticut*, Storrs, USA

Prof. R. Hasanov, *Azerbaijan State Oil Academy*, Baku, Azerbaijan

Dr. A. Schokin, *State Committee for Energy Saving of Ukraine*, Kiev, Ukraine

Prof. John Kilner, *Imperial College*, London, UK.

II. Mixed Conducting Membranes for Partial Oxidation of Natural Gas to Synthesis Gas

NATO Country Project Director:

Prof. J. Frade, *Departamento de Engenharia Cerâmica e do Vidro*, *Universidade de Aveiro*, Aveiro, Portugal

Partner Country Project Director:

Dr. V. Kharton, *Institute of Physicochemical Problems*, *Belarus State University*, Minsk, Belarus

Project Co-Directors:

Dr. J. Irvine, *School of Chemistry*, *University of St. Andreas*, Scotland, UK

Dr. T. Norby, SMN, *Universitetet i Oslo*, Oslo, Norway

Dr. J. Jurado, *Instituto de Cerámica y Vidrio*, CSIC, Madrid, Spain

Prof. V. Sobyanin, *The Boreskov Institute of Catalysis*, Novosibirsk, Russia

Prof. V. Kozhevnikov, *Institute of Solid State Chemistry*, Yekaterinburg, Russia

Dr. L. Boginsky, *Institute for Personal Development and Staff Retraining in New Areas of Techniques, Technologies and Economics of the Belarus Ministry of Education*, Minsk, Belarus.

III. Development of Electromagnetic Wave Absorbing Coatings Based on Carbon Onions

NATO Country Project Director:

Prof. Ph. Lambin, *Facultés Universitaires Notre-Dame de la Paix*, Namur, Belgium

Partner Country Project Director:

Dr. O. Shenderova, *International Technology Center Raleigh*, USA

Project Co-Directors:

Dr. V. Kuznetsov, *The Boreskov Institute of Catalysis*, Novosibirsk, Russia

Dr. I. Larionova, *Real-Dzerzhinsk Ltd.*, Dzerzhinsk, Russia

Dr. S. Maksimenko, *Belarus State University*, Minsk, Belarus

Prof. A. Okotrub, *Nikolaev Institute of Inorganic Chemistry*, Novosibirsk, Russia

NATO PROGRAMME: SCIENCE FOR PEACE AND SECURITY

Capture and Decontamination of Chemical & Biological Agents by Novel Catalysts and Millisecond Jet Reactors

Project Coordinator from a NATO Country:

Prof. P. Smirniotis, *University of Cincinnaty*, Cincinnaty, USA

Project Coordinator from a Partner Country:

Prof. A. Vorontsov, *The Boreskov Institute of Catalysis*, Novosibirsk, Russia.

INTERNATIONAL SCIENCE AND TECHNOLOGY CENTER (ISTC)

I. Development of Catalysts and Reactors for Syn-Gas Production from Diesel Fuel and for Selective NO_x Reduction with Syn-Gas in Diesel Exhausts

Project Manager from BIC **Prof. V. Kirillov**.

II. Development of High-Performance Oxygen-Containing Membranes and Compact Syn-Gas Generators on Their Base

Project Manager from BIC **Prof. V. Sadykov**.

III. Synthesis and Investigation of the Metal Oxide Catalysts for Photocatalytic Degradation of Harmful Gases Resulted from Terrorist Acts and Man-Caused Catastrophes

Project Manager from BIC **Prof. A. Vorontsov**.

IV. Catalytic Production of SO_3 for Conditioning of Electrostatic Precipitators Using in Russia and the Newly Independent States (NIS)

Project Manager from BIC **Prof. A. Zagoruiko**.

V. Development of an Integrated Separator for Direct Reforming of Hydrocarbons in High-Temperature Fuel Cells

Project Manager from BIC **Prof. Z. Ismagilov**.

VI. Synthesis, Formation and Modification of (In)Organic Nanoparticles in Supercritical Fundamentals and Applications

Project Manager from BIC **Prof. V. Anikeev.**

CONFERENCE AND EXHIBITION ACTIVITIES

The advertising and information activities are universal marketing tools for establishing professional contacts. Again, this is a necessary part of the market examination to be settled in the world. Each year, achievements of the Boreskov Institute of Catalysis are demonstrated at the very prestigious exhibitions in Russia and abroad. The goal is to strengthen collaboration with the present partners and to attract attention of potential customers.

In 2008, the most important BIC's achievements in the area of applied Catalysis were presented at the Exhibitions:

- ***VIII Moscow International Innovations' and Investments' Show***, March 3-6, Moscow, Russia

Golden Medal and Diploma for:

1. "Tseflar®. The Compact Reactor for Rapid Thermal Treatment of Powdered Materials"
2. "Catalysts *IC-GO-1* for Deep Hydropurification of Diesel Fuels"

Silver Medal and Diploma for:

1. "Single-Stage Gas Desulfurization Processes for the Enterprises of Oil-Gas-Chemical Complex"
2. "Catalytic Gas Generators for Autonomous Heat Supply".

- ***Exhibition devoted to 50th Anniversary of the Soviet District of Novosibirsk***, March 26, Novosibirsk, Russia
- ***Exhibition devoted to 50th Anniversary of the Boreskov Institute of Catalysis***, May 14-15, Russian Center of Science and Culture in Brussels, Belgium
- ***"High Technologies of XXI Century"***, September 30-October 10, The State Joint–Stock Company "All-Russian Exhibition Centre", Moscow, Russia

Golden Medal and Diploma for "Vehicle Syn-Gas Generator"

- ***Exhibition "Alternative Energy Sources for Cities"***, October 23-24, Moscow, Russia
- ***Exhibition "Science of Siberia-2008"***, October 28-31, Novosibirsk, Russia

Golden Medal and Diploma for "Vehicle Syn-Gas Generator"

- ***Russian National Exhibition "Russian Science Today"***, November 20-December 1, New Delhi, India

Solution of many specific problems requires joint efforts in order to promote its fastest accomplishing. International congresses, symposia, conferences, and seminars are the most productive to familiarize scientists with innovations outside their own research and to disseminate the information about the results achieved to a wider audience. One of the directions of the scientific-organizational work carried out in the Institute is aimed on conducting conferences and seminars with the participation not only of Russian scientists and researchers from NIS, but foreign participants as well.

PRESENTATION OF THE BORESKOV INSTITUTE OF CATALYSIS OF THE SIBERIAN BRANCH OF THE RUSSIAN ACADEMY OF SCIENSES

May 13-14, Russian Center of Science and Culture, Brussels, Belgium

The Russian Centre of Science and Culture in Brussels invited the Boreskov Institute of Catalysis for the presentation of scientific products of the Institute devoted to the BIC's 50th anniversary. The focus of the presentation was made both on the accomplished developments that were employed by a number of companies and on recent scientific discoveries which may be the basis for cooperation with universities, large and medium companies.

The scope of the presentation covered the following topics:

- Ecological catalysis: methods for treatment of waste gas and water. Catalysis is capable of answering the question how we can make our world more sound
- Catalytic technologies for synthesis of biofuel. What shall we do when oil deposits are exhausted?
- Future of hydrogen vehicles
- Catalysis for human life – catalysis in your home.

Lectures were given by:

- Academician **Valentin Parmon**, Director of the Boreskov Institute of Catalysis -
  50 YEARS OF THE CATALYSIS SCIENCE IN SIBERIA
- Professor **Valery Bukhtiyarov**, Vice-Director of the Boreskov Institute of Catalysis -
  NANOSIZE EFFECTS IN CATALYSIS
- **Dr. Vadim Yakovlev**, group leader of the Boreskov Institute of Catalysis -
  CATALYSIS AND RENEWABLE FEEDSTOCK
- Professor **Alexander Noskov**, Vice-Director of the Boreskov Institute of Catalysis -
  ENVIRONMENTAL CATALYSIS
- Professor **Vladimir Sobyanin**, lab leader of the Boreskov Institute of Catalysis, rector of Novosibirsk State University -
  HYDROGEN AND TRANSPORT-IN-FUTURE
- Professor **Zinfer Ismagilov**, lab leader of the Boreskov Institute of Catalysis -
  CATALYSIS IN YOUR HOUSE

The BIC's products were exhibited during the event at the Exhibition presentation: *"The Boreskov Institute of Catalysis Today"*.

“INTERNATIONAL PARTNERSHIP FOR A HYDROGEN ECONOMY FOR GENERATION OF NEW IONOMER MEMBRANES” - IPHE-GENIE

May 23-24, Novosibirsk, Russia

IPHE-GENIE project is aimed at promoting strategically important international cooperation of research institutes, universities and industry from Russia, China, Holland, Germany and France. The technical barrier that IPHE-GENIE addresses is that of the too low operating temperature of the PEMFC and the need for high humidity of the reactants.

The 4th Meeting on IPHE-GENIE was organized by the Boreskov Institute of Catalysis. The aim of the Meeting was to discuss the results obtained during the first half-year of 2008, to sum up the results of joint works on the third stage of the investigations and to refine plan of the further cooperation in the frames of IPHE-GENIE project on the second half-year of 2008.

MODERN TRENDS IN CATALYSIS. FROM MOLECULAR TO INDUSTRIAL LEVEL

June 5, Novosibirsk, Russia

The Conference was devoted to 50th anniversary of the Boreskov Institute of Catalysis. More than 200 scientists took part in the Conference.

The lectures of the specialists in the field of catalysis were presented by:

- **Valentin Parmon** (*The Boreskov Institute of Catalysis, Novosibirsk, Russia*) - MODERN PROBLEMS OF CHEMICAL CATALYSIS
- **Valerii Lunin** (*Lomonosov Moscow State University, Moscow, Russia*) - CHEMICAL EDUCATION IN RUSSIA
- **Sergey Tsyb** (*Ministry of the Industrial Energetics, Moscow, Russia*) - STRATEGY OF THE DEVELOPMENT OF THE CHEMICAL AND PETROCHEMICAL INDUSTRY IN RUSSIA
- **Vladimir Likholobov** (*Institute of Hydrocarbons Processing, Omsk, Russia*) - INSTITUTE OF HYDROCARBONS PROCESSING SB RAS: SCIENCE AND PRACTICE OF THE NEW TECHNOLOGIES OF THE HYDROCARBON MATERIALS PROCESSING
- **Dmitry Murzin** (*Åbo Akademi University, Turky, Finland*) - ROLE OF CATALYSIS IN ORGANIC CHEMISTRY
- **Nail Gilmutdinov** (*JSC Nizhnekamskneftekhim, Nizhnekamsk, Russia*) - PRIMARY TASKS OF PETROCHEMICAL INDUSTRY BY THE EXAMPLE OF *JSC NIZHNEKAMSKNEFTEKHIM*

INTERNATIONAL CONGRESS “MAGNETIC RESONANCE FOR FUTURE” (EUROMAR-2008)

July 6-11, St. Petersburg, Russia

EUROMAR is a major undertaking of the European Magnetic Resonance community that is merging under one this name three formerly separate international conference series: AMPERE congress, the European Experimental NMR conference (EENC) and the UK RSC NMR Discussion Group.

Versatility of magnetic resonance in its many fields of application generates continuous demand for a variety of new more advanced techniques. This demand fuels rapid evolution of magnetic resonance into apparently diverging branches. However, a common physical basis and a common language turn this diversity into a powerful force for new discoveries.

EUROMAR's mission is to become a converging place for magnetic resonance research in Europe and world-wide and to actively contribute to its evolution. The main purpose of this conference was to identify new frontiers and areas of application of magnetic resonance, to promote innovative ideas and techniques among a large community dispersed both geographically and by specialization, and to encourage interdisciplinary exchange.

EUROMAR is supported by the European Science Foundation (ESF) for a five-year Research Networking Program (2007-2011) including training and discovery activities with the participation of European National Societies of Nuclear Magnetic Resonance and Electronic Paramagnetic Resonances.

EUROMAR responsibility is organization of annual congresses. 650 leading specialists on magnetic resonance from universities and scientific centers of 43 countries, including 183 participants from Russia took part in the Congress EUROMAR-2008.

Organizers:

The Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
St. Petersburg State University, Russia
St. Petersburg Scientific Center, Russia

EUROMAR 2008 covered all aspects of magnetic resonance (NMR and EPR) in liquid and solid state, including methodological and applied aspects in different fields: biology, chemistry, physics, material sciences, computation and medical applications:

- Bio-Macromolecules in Liquids
- Drug Discovery
- Relaxation

- Frontiers
- Molecular Dynamics and other Computational Aspects
- Applications in Catalysis
- Imaging
- Enhanced Magnetic Resonance
- Spin Dynamics in Solids
- Biosolids
- Methods for Biosolids
- ESR Methods and Paramagnetic Systems
- ESR-Applications
- Solid-State Physics and Polymers

Plenary lectures:

- **Bernhard Blümich** (*Macromolecular Chemistry, RWTH Aachen University, Germany*) - ADVANCES IN MOBILE NMR: MAGNETS, VIOLINS, AND BUBBLES
- **Jacques Fraissard** (*UPMC and ESPCI, Paris, France*) - NMR OF PHYSISORBED ^{129}Xe USED AS A PROBE TO INVESTIGATE POROUS SOLIDS
- **Lucio Frydman** (*Department of Chemical Physics, Weizmann Institute of Science, Israel*) - PROGRESS IN SINGLE-SCAN MULTIDIMENSIONAL NMR
- **Gunnar Jeschke** (*Physical Chemistry University Konstanz, Germany*) - MEMBRANE PROTEIN STRUCTURE AND FOLDING - WHAT CAN EPR CONTRIBUTE?
- **Wolfgang Lubitz** (*Max-Planck-Institut fuer Bioanorganische Chemie, Germany*) - MAGNETIC RESONANCE STUDIES TO ELUCIDATE STRUCTURE AND FUNCTION OF THE WATER SPLITTING COMPLEX IN PHOTOSYNTHESIS
- **Chris J. Pickard** (*School of Physics & Astronomy, University of St. Andrews, North Haugh Scotland, UK*) - A SOLID STATE PHYSICS THEORY OF SOLID STATE NMR
- **Klaas P. Pruessmann** (*Institute for Biomedical Engineering ETH Zurich, Switzerland*) - ULTRA-HIGH-FIELD MAGNETIC RESONANCE IN HUMANS
- **Daniel Rugar** (*IBM Almaden Research Center Mailstop, Harry Rd. USA*) - NANOMETER-SCALE MAGNETIC RESONANCE IMAGING
- **Hans Wolfgang Spiess** (*Polymer Spectroscopy Group, Max Planck Institute for Polymer Research, Germany*) - SOLID-STATE NMR METHODS OF FUNCTIONAL MACROMOLECULAR AND SUPRAMOLECULAR SYSTEMS
- **Gerhard Wagner** (*Department of Biological Chemistry and Molecular Pharmacology, Harvard Medical School, USA*) - NON-STANDARD ACQUISITION AND PROCESSING METHODS – APPLICATION TO STUDIES OF LARGE PROTEINS, PROTEIN COMPLEXES AND METABOLITE MIXTURES

Alexander Pines became **the winner of the Russell Varian Prize 2008.**

The Raymond Andrew Prize 2008 was awarded to **Boaz Shapira** for his outstanding Ph.D. Thesis: "SPATIAL ENCODING IN NMR SPECTROSCOPY".

The MRC Wiley Prize Winners - **Eugenio Daviso, Kirill Kovtunov**, **and Giuseppe Sicoli -** were selected by the EUROMAR Chairman with the help of the Program Committee -2008 on the base of the submitted abstracts of the young scientists' presentations.

The winners of the Zamaraev Foundation Prize became **Sergei Arzumanov** (*The Boreskov Institute of Catalysis*), **Kirill Kovtunov**, **Vladimir Zhivonitko.** They were selected on the base of the traditional procedure by the reviewing the papers submitted to the Foundation a half a year before the Congress.

The Euromar-2008 prize established by the Programme Committee was awarded to **Maria Concistrè**

Saint Petersburg State University continues Annual International Symposium and Summer School **"Nuclear Magnetic Resonance in Condensed Matter",** "**NMRCM**". The fifth meeting was opened on July 4, 2008.

The goal of the meeting was to provide a platform to scientists and students for use of all aspects of nuclear magnetic resonance methods and techniques as well as computational and theoretical approaches to the various problems in life sciences.

210 young scientists from 25 countries took part in the event.

VI RUSSIAN CONFERENCE “SCIENTIFIC FUNDAMENTALS OF CATALYSTS PREPARATION AND TECHNOLOGY” AND V RUSSIAN CONFERENCE “PROBLEMS OF CATALYSTS DEACTIVATION” with participation of NIS countries

September 4-9, Tuapse, Russia

The Organizers:

- The Boreskov Institute of Catalysis, Novosibirsk, Russia
- The Institute for Hydrocarbons Processing, Omsk, Russia
- Scientific Council on Catalysis RAS
- Russian Foundation for Basic Research, Moscow, Russia
- Novosibirsk State University, Novosibirsk, Russia

169 specialists from Russia, Ukraine, Azerbaijan, Kazakhstan, Belarus, Germany and Uzbekistan participated in the Conferences.

Scientific program of the Conferences included 5 invited plenary lectures, 8 key, 64 oral, 41 poster presentations and also 12 oral presentations of young scientists on the following topics:

- Scientific Foundations for Catalyst Preparation and Technology
- Commercial Catalysts: Production and Operation
- Problems of Catalyst Deactivation

Plenary lectures:

- **V.I. Petkov**, M.V. Sukhanov, M.M. Ermilova*, N.V. Orekhova*, G.F. Tereschenko* (*Nizhnii Novgorod State University, Nizhnii Novgorod, Russia; *Topchiev Institute of Petrochemical Synthesis, Moscow, Russia*) - DESIGN AND PRODUCTION OF COMPOSITE MEMBRANE CATALYSTS BASED ON FRAMEWORK PHOSPHATES AND MOLYBDATES

- **K.D. Dosumov** (*D.V. Sokolskii Institute of Organic Catalysis and Electrochemistry, Almaty, Republic of Kazakhstan*) -
OXIDATION CATALYST DEACTIVATION AND REGENERATION
- **V.V. Molchanov**, M.N. Schuchkin*, N.A. Zaitseva (*The Boreskov Institute of Catalysis, Novosibirsk, Russia; *FSUE RFNC-VNIIEF, Sarov, Russia*) -
CARBON XEROGELS: PREPARATION, PROPERTIES, APPLICATION IN CATALYSIS
- **A.S. Ivanova** (*The Boreskov Institute of Catalysis, Novosibirsk, Russia*) -
PHYSICOCHEMICAL AND CATALYTIC PROPERTIES OF THE CeO_2 BASED SYSTEMS
- **B.N. Kuznetsov** (*Institute of Chemistry and Chemical Technology, Krasnoyarsk, Russia*) –
SCIENTIFIC BASES FOR SELECTION OF CATALYSTS FOR DEEP SOLID FOSSIL FUELS AND RENEWABLE ORGANIC MATERIALS CONVERSION

Two Round Tables on the subjects "*Catalysts Industry of Russia: State-of-the-Art and Prospects*" and "*Innovation-Oriented RFBR Contests: Results and Prospects*" were organized in the framework of the Conferences and appeared to be quite representative.

XVIII International Conference on Chemical Reactors
CHEMREACTOR-18

September 29 - October 3, Malta

The Conference was held in the Oracle Conference Centre of the New Dolmen hotel. It is situated in the seaside resort part of Malta (Qawra-Bugibba) and beautifully located at the water's edge with panoramic view of St. Paul's Bay.

240 participants (among them 120 western participants) took part in the Conference.

The Organizers:

- The Boreskov Institute of Catalysis, Novosibirsk, Russia
- Russian Scientific and Cultural Center in Valletta, Malta
- Russian Center of International Scientific and Cultural Cooperation under RF Government
- Ministry of Education and Science of the Russian Federation
- European Federation on Chemical Engineering
- Scientific Council on Theoretical Fundamentals of Chemical Technology RAS
- Scientific Council on Catalysis RAS

The Conference was traditionally devoted to the fundamental aspects and practical application of the catalytic processes and chemical reactors, as well as to the development of the novel modern technologies. The event was directed at presenting the latest achievements and understandings in the field of Chemical Engineering science and providing a venue for the fruitful interaction and exchange of ideas.

Four-day scientific program comprised 5 plenary invited lectures, 6 key-note presentations, 80 oral presentations and 100 posters on the following topics:

- Kinetics of catalytic reactions. The Section was dedicated to the *100th anniversary of Professor M.I. Temkin*, the outstanding specialist in the field of physical chemistry and chemical kinetics
- Physico-chemical and mathematical fundamentals of the processes in chemical reactors
- Catalytic processes development and reactors design: modeling, optimization, new catalyst application
- Catalytic technologies in fuel and energy production
  - production of hydrogen
  - production of environmental friendly fuels
  - environmentally friendly engineering
- Catalytic processing of renewable sources: fuel, energy, chemicals

Plenary lectures:

- **Guy Marin**, J. Wieme, M.-F. Reyniers (*Ghent University, Belgium*) - SUSPENSION POLYMERIZATION REACTIONS AND REACTORS
- R.H. Venderbosch, S.R.A. Kersten, **Wolter Prins** (*University of Twente, The Netherlands*) - THE ROLE OF CATALYSIS IN FAST PYROLYSIS
- **Jesus Santamaria** (*University of Zaragoza, Spain*) - DEVELOPMENT OF ZEOLITE-COATED MICROREACTORS
- **Olaf Deutschmann** (*University of Karlsruhe, Germany*) - CATALYTIC CONVERSION OF HYDROCARBON FUELS: FROM MOLECULAR MODELING TO REACTOR OPTIMIZATION
- **Pio Forzatti** (*Technical University of Milan, Italy*) - CATALYTIC PARTIAL OXIDATION OF METHANE TO SYNGAS

Key-Note Presentations

- **Dmitrii Murzin** (*Åbo Akademi University, Turku, Finland*) - 100 ANNIVERSARY OF PROFESSOR M.I. TEMKIN

- **Grigorii Yablonsky***'**, J.T. Gleaves**, X. Zheng **, B. Feres** (**Saint Louis University, USA; **Washington University in St. Louis, USA*) - GETTING TO THE POINT: NEW TRENDS IN NON-STEADY-STATE CATALYTIC KINETICS
- **Nikolai Kulov** (*Kurnakov Institute of General and Inorganic Chemistry, Russia*) - CATALYTIC DISTILLATION: PROSPECTS AND PROBLEMS

- **Bair Bal'zhinimaev**, E.M. Sadovskaya, A.P. Suknev (*The Boreskov Institute of Catalysis, Russia*) -
  ISOTOPIC TRANSIENT KINETICS STUDY TO IDENTIFY REACTION MECHANISMS
- **Andrey Zagoruiko** (*The Boreskov Institute of Catalysis, Russia*) -
  CATALYTIC TECHNOLOGIES APPLYING ARTIFICIALLY CREATED CATALYST NONSTATIONARITY AND SORPTION-CATALYTIC PROCESSES

SPECIALIST TRAINING SCHOOL "SYNCHROTRON RADIATION FOR MODERN TECHNOLOGIES"

October 6-13, Novosibirsk, Russia

The Organizers:

- The Boreskov Institute of Catalysis, Novosibirsk, Russia
- Budker Institute of Nuclear Physics, Novosibirsk, Russia
- Novosibirsk State University, Novosibirsk, Russia

The School program included 16 plenary lectures of leading specialists in the field of synchrotron radiation, practical training in computer center of the Boreskov Institute of Catalysis, investigation of the samples at the stations of Siberian SR Center.

EDUCATIONAL ACTIVITIES

With that deep belief that people are a decisive factor and that the best way to educate is to teach others, many researchers of the Institute participate in the training of specialists in chemistry and, particularly, in catalysis, ensuring closest and time-tested links of the Institute with the main sources of researchers – Novosibirsk State University (NSU), Novosibirsk State Technical University (NSTU), Tomsk State University (TSU), Tomsk Polytechnical University (TPU). Students studying at the following chairs realize their graduate works within the Boreskov Institute of Catalysis:

- Catalysis and Adsorption, Department of Natural Sciences, NSU
- Physical Chemistry, Department of Natural Sciences, NSU
- General Chemistry, Department of Natural Sciences, NSU
- Environmental Chemistry, Department of Natural Sciences, NSU
- Chemical and Biological Physics, Department of Physics, NSU
- Differential Equations, Department of Mathematics and Mechanics, NSU
- Environmental Engineering, Aircraft Department, NSTU
- Technological Processes and Apparatuses, Department of Mechanics and Technology, NSTU
- Physical and Colloid Chemistry, Chemical Department, TSU
- Fuel Chemical Technology and Chemical Cybernetics, Chemical-Technological Depaertment, TPU.

About 70 scientists combine teaching and their job at the Research Institute. They present lectures, give seminars and practical classes; participate in the organization and renovation of the educational process.

From the first years, the strategy of the training of students was built up by leading scientists of BIC and harmonically combines two aspects: on the one hand, curricula provide the students with deep theoretical and practical knowledge in catalysis, i.e. theory of the prevision of the catalytic action of substances, kinetics of catalytic reactions, scientific bases of the preparation of catalysts, bases of the technology of catalytic processes, application of modern physical and mathematical methods for investigation of catalysts and catalysis; on the other hand, the educational process arrangement allows to wide significantly the sphere of the postgraduate activity of the students. They can work as technologists, production managers, researchers at various research organizations, teach at universities.

All these features allow students to prepare their diploma at the highest scientific level and become widely informed specialists in chemistry and catalysis. The graduates of the chair of adsorption and catalysis are the principal source of recruitment of the personnel of the Institute.

BIC – NSU

Novosibirsk State University was established as an essential part of the Siberian Branch of the Academy of Sciences; it embodies the idea of the close integration of education and science.

The chief mission of the University is to train professionals for scientific institutions of the country.

From its earliest age, the University pursues *three fundamental principles.* The *first* one is that the teachers are experts engaged in the real science. The intellectual basis of the University is more than 5000 scientists of 30 research institutes of the Siberian Branch. The *second* principle is a thorough mathematical background provided to students of all the departments. And the *third* principle means that the students master theoretical disciplines during their first three years and do their practical research in academic institutes of the Siberian Branch during the last years.

The Boreskov Institute of Catalysis is a key element in the training of specialists in chemistry at NSU. Graduation works of the students are conducted at the laboratories of the Institute and are supervised by experienced researchers. Their results are usually published in scientific journals and form the basis of their future Ph.D. theses.

The *Chair of Catalysis and Adsorption* is of special importance for the Institute. It is only 5 years younger than Novosibirsk State University itself. The organization of the chair was initiated in 1964 by Academician G.K. Boreskov – the founder and first director of the Boreskov Institute of Catalysis SB RAS. The chair is located at the Institute, which provides it with everything required for efficient training of students specializing in catalysis and technology of catalytic processes.

Courses of lectures:

- Catalysis
- Adsorption and Porous Structure
- Scientific Bases for Catalysts Preparation
- Kinetics of Heterogeneous Catalytic Reactions
- Engineering Chemistry of Catalytic Processes
- Catalysis, Environment and Sustainable Development of Civilization
- Molecular Design of Catalysts
- Modern Technique of Catalytic Experiments
- Analytical Methods
- Quantum-Chemical Methods in Catalysis
- Magnetic Resonance Spectroscopy
- Optical Spectroscopy
- X-Ray Technique
- Thermodynamics of Working Catalyst
- Physical Methods in Catalysis
- Computer Application for Catalytic Studies

The *Chair of Physical Chemistry* prepares highly skilled specialists in the field of chemical kinetics and thermodynamics, application of physical methods for catalysis.

Courses of lectures:

- Physical Chemistry
- Chemical Thermodynamics
- Chemical Kinetics
- Nonequilibrium Thermodynamics
- Matter Structure
- Terminal System: Computer Modeling of Processes and Physical-Chemical Phenomena
- NMR and ESR Spectroscopy for Catalysis

BIC – NSTU

Novosibirsk State Technical University is one of the largest research and educational centers in Russia. The University trains and retrains qualified specialists for research and industrial complex of Siberia and the Far East. Joint training of specialists at NSTU and institutes of the Siberian Branch of RAS in the field of technology of catalytic processes is of special importance for practical application of fundamental knowledge in the field of catalysis. The basic training is conducted by the *Chair of Environmental Engineering* founded at the Boreskov Institute of Catalysis.

Courses of lectures:

- Technology Bases for Environmental Protection
- Processes and Apparatuses for Environmental Protection
- Catalytic Methods for Environment Protection
- Methods and Devices for Environmental Control, Ecological Monitoring
- Mathematical Modeling of Chemical Processes and Reactors
- Organic Chemistry
- Industrial Ecology
- Technologies for Utilization of Industrial Wastes
- Oil-Gas Branch
- Analytic Chemistry and Physical-Chemical Methods of Analysis

Chemical engineering is a science-intensive industry. The engineers will be able to successfully work in the priority investment areas. The close co-operation of the *Chair of Technological Processes and Apparatuses* with research institutes of the Siberian Branch of Russian Academy of Science is the key to train high-skilled specialists.

Joint Educational Scientific Centers and Laboratories

***Educational Scientific Centers* (*ESC*)** were established according to the Government concept for the education modernization. Educational, scientific and innovational complexes give the possibility to increase quality of professional education by providing the unity of educational, scientific and technical innovational activity at every stage of training specialists.

The Educational Scientific Center on *Adsorption and Catalytic Technologies* was made on the basis of Chair of Catalysis and Adsorption and BIC's laboratories. It includes educational, scientific and innovational constituents.

The Educational Scientific Center *on Photochemistry* was made on the basis of Chair of Physical Chemistry, laboratories of the Institute of Chemical Kinetics and Combustion and BIC. It gives the opportunities to train specialists in the field of physical chemistry, photochemistry and photocatalysis.

The Educational Scientific Center *"Chemical Technologies and Catalysis"* was made on the bases of Kemerovo State University.

The Educational Scientific Center with MIFI branch in Seversk.

The Educational Scientific Center "*Chemical Material Science and Prospect Technologies*" at Tomsk State University.

4 Joint Laboratories were created with the purpose of integration of high education and fundamental science to increase the efficiency of joint efforts aimed to the training of high skilled specialists.

Joint Laboratory for Catalytic Processing of Light Hydrocarbons of the *Boreskov Institute of Catalysis* (Novosibirsk) and *Institute of Petroleum Chemistry* (Tomsk), created in 2000. Scientific Coordinators are **Prof. Aleksandr S. Noskov** (The Boreskov Institute of Catalysis) and **Dr. Aleksandr V. Vosmerikov** (Institute of Petroleum Chemistry).

Main areas of scientific research of the Laboratory are:

- Development of the Scientific Basis for the Technology for Light Hydrocarbons Catalytic Processing
- Engineering Elaboration of Catalytic Processes and Devices for Light Hydrocarbons Processing
- Study of Combined Catalytic Processes for Oil and Natural Gas Processing.

Laboratory acts in close contact with Institution of Higher Education of Tomsk.

Joint Laboratory of Catalytic Processes and Apparatuses of the *Boreskov Institute of Catalysis* and *Novosibirsk State Technical University,* created in 2002. Scientific Coordinators are **Prof. Aleksandr S. Noskov** (The Boreskov Institute of Catalysis) and **Prof. Gennadii G. Kuvshinov** (Novosibirsk State Technical University).

Main areas of scientific research of the Laboratory are:

- Mass and Thermo Transport Processes in Apparatuses for Chemical Engineering
- Design and Development of New Processes and Apparatuses for Energy- and Resource-Saving Chemical Technologies
- Development of the Scientific Basis for the Technology of Nanofilament Carbon Synthesis
- Simulation of Apparatuses with Moving Bed.

Joint Laboratory of Sorption and Catalytic Processes of the *Boreskov Institute of Catalysis* (Novosibirsk) and *Butlerov Institute of Chemistry*, *Kazan State University* (Kazan) created in 2003. Scientific Coordinators are **Prof. Aleksandr S. Noskov** (The Boreskov Institute of Catalysis) and **Prof. Aleksandr A. Lamberov** (Kazan State University).

Main areas of scientific research of the Laboratory are:

- Design of the Catalysts and Sorbents for Petrochemistry and Oil Refinery in Russia
- Scientific Basis of the Support Texture Formation - Industrial Synthesis and Working-Off
- Comparative Testing of Supports, Sorbents and Catalysts
- Development of New Highly Efficient Energy- and Resource-Saving Technologies for Petrochemistry and Oil Processing.

Joint Laboratory Engineering Chemistry of the *Volgograd Department of the Boreskov Institute of Catalysis* (Volgograd) and *Volgograd State Technical University* (Volgograd), created in 2004. Scientific Coordinators are **Dr. Alexandr M. Beskopylnyi** (Volgograd Department of the Boreskov Institute of Catalysis) and **Prof. Yurii V. Popov** (Volgograd State Technical University).

Main areas of scientific research of the Laboratory are:

- Development of New Highly Efficient Energy- and Resource-Saving Chemical Technologies
- Fundamentals and Technologies for Synthesis of Physiologically Active Substances for Chemical-Pharmaceutical Industry, Agriculture and Health Service
- Fundamentals of Heterogeneous Catalytic Process Technologies for Chemicals Production
- Development and Investigation of Additives for Fuels and Oils.

Dissertation Council Activities

Besides teaching of the students in many Russian universities, researchers of the Institute participate in the training of young scientists of the highest qualification capable to provide original basic and applied research in the field of catalysis. Their training has priority importance for the Institute and is directly related to its development and well being. The Institute solves these problems through the postgraduate school of SB RAS and postgraduate school of NSU. Annually 20-30 postgraduates are trained at the graduate school working at the Institute. Supervised by the researchers of the Institute, postgraduate students conduct their Ph.D. studies in chemical kinetics and catalysis, physical chemistry, chemical engineering in the BIC laboratories.

Dissertation Council D 003.012.01 was confirmed by Supreme Certifying Commission (SCC) of Russia on December 8, 2000. Dissertation Council is allowed to uphold a thesis to receive an academic degree Doctor of Science on specialties: 02.00.15 “Catalysis” within chemical and technical sciences and 02.00.04 “Physical Chemistry” within chemical sciences. Head of the Dissertation Council is the director of the Institute – Academician V. Parmon.

Dissertation Council К 003.012.01 was confirmed by SCC on December 8, 2000. Dissertation Council is allowed to uphold a thesis to receive an academic degree on specialties 02.00.15 “Catalysis” within chemical sciences and 05.17.08 “Processes and Apparatuses in Chemical Technology” within technical sciences. Head of the Dissertation Council deputy director of the Institute Prof. Vladimir A. Sobyanin.

2 Doctoral thesis and 17 Ph.D. theses have been defended in 2008.

Doctoral theses:

Konstantin P. Brylyakov – “*Key Intermediates and Mechanism of Homogeneous Catalytic Asymmetric Oxidation and Polymerization: Magnetic-Resonance Spectroscopy Study*”

Sergey I. Reshetnikov – “*The Use of the* Nonstationary State *of a* Catalyst *for Reaction Rate and Selectivity Control*”

Ph.D. theses:

Natalia A. Baronskaya – “*Single-Stage Steam Carbon Monoxide Conversion: Catalysts and Catalytic Bed Arrangement*”

Yuliya N. Bespalko – “*Synthesis and Studying of Composite Supports and Catalysts Based on Ni(Cr), FeZr Alloys and Their Hydrides in Alumina Matrix*”

Tatiana S. Glazneva – “*Acid Properties of Fiberglass and Silica Thin Films Catalysts*”

Anna G. Gentsler – “*Development and Investigation of Bimetallic Catalysts for Liquid Phase Hydrogenolysis of Chloroaromatic Compounds*”

Alesya N. Kholodovich – “*Effect of the Nature of* H_2PtCl_6 *Interaction with the Surface of Carbon Supports on the Formation of Pt/C Catalysts*”

Mikhail K. Kovalev – “*Adsorption and Textural Properties of Mesoporous Mesophase Silica-Based Films*”

Ekaterina A. Kozlova – “*Photocatalytic Decomposition of Fluorinated and Sulphur Organic Compounds for Environmental Protection and Hydrogen Production*”

Kirill V. Kovtunov – “*Parahydrogen-Induced Nuclear Spins Polarization in Heterogeneous Hydrogenation*”

Eugenia V. Kulko – “*Physico-Chemical Properties of Alumina, Prepared from a Hydrated Product of Centrifugal Thermal Activation of Hydrargillite, and Catalysts for Deep Hydrodesulfurization of Diesel Fuels*”

Pavel E. Mikenin – “*Supercritical Solvent Effects on Decomposition and Synthesis of Organic Compounds*”

Alexey L. Nuzhdin – “*Resolution of Chiral Sulfoxides by Enantioselective Sorption over Homochiral Porous Coordination Polymers*

Vera P. Pakharukova – “*Structural Peculiarities of Oxide Copper-Cerium-Zirconium Oxide Catalysts*”

Anna A. Sametova – "*Mutual Effect and Reactivity of Adsorbed Atoms and Molecules in* $CO + O_2$, $H_2 + O_2$, $NO + H_2$ *Reactions over Pd(110) and Pt(111) Monocrystals*"

Anastasiya E. Shalagina – "*Catalytic Synthesis and Studying of Nitrogen-Containing Carbon Nanofibers*"

Alexey A. Shutilov – "*Synthesis and Characterization of* TiO_2*-Based Nanostructures for CO Oxidation over Supported Platinum Catalysts*"

Tatiana A. Trubitsyna – "*Ti- and Zr-Substituted Polyoxometallates as Molecular Models for Studying Mechanisms of Selective Oxidation with Hydrogen Peroxide*"

Vladimir V. Zhivonitko – "^{1}*H NMR Study of the Effect of Reactive Media Transfer on the Dynamics of Chemical Waves Propagation*"

There is a great demand for specialists in catalysis trained at the Boreskov Institute of Catalysis. Many of them apply their knowledge in these fields at various research centers, universities and manufacturing companies.

SCIENTIFIC SOCIAL LIFE

The Agreement for Cooperation between Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology and the Boreskov Institute of Catalysis was concluded on 23 January, 2008 with signatures of Prof. Parmon, Director of BIC and Prof. Aritomi, Director of RLNR. The signed document was passed to Prof. Aritomi from Prof. Aristov, Visiting Professor of Tokyo Tech, BIC, on 8 February, 2008.

The paper "*Selective Oxidation of Carbon Monoxide in Excess Hydrogen over Pt-, Ru- and Pd-Supported Catalysts*" by **P.V. Snytnikov, V.A. Sobyanin, V.D. Belyaev, P.G. Tsyrulnikov, N.B. Shitova, D.A. Shlyapin** (Applied Catalysis A: General, vol. 239, Issue 1-2, 2003, Pages 149-156) has been recognized in the "Top-50 most cited articles" as published in Elsevier's Catalysis journals 2003-2007.

Prof. Gennadii I. Panov was given the rank of "*Honored Chemist of Russian Federation*" by the decree of the President of the Russian Federation, dated 11 January, 2008, for an important contribution to Academic science in Siberia.

On **August, 4, 1997 Zamaraev International Charitable Scientific Foundation** has been organized in the memory and honor of Professor Kirill I. Zamaraev.

The main Founders of the Foundation from the Russian side are:

- The Boreskov Institute of Catalysis, Novosibirsk
- Institute of Semiconductors Physics, Novosibirsk
- Russian D.I. Mendeleev Chemical Society, Moscow
- Scientific-Industrial Company "Altay", Byisk
- "Ecogeochem Ltd.", Moscow
- Association "Russian House for International Scientific and Technological Cooperation"
- Other scientific, commercial and financial institutions.

The Foundation is supported by IUPAC and some Russian sponsors.

Zamaraev Foundation is grateful to all sponsors for their contribution and invites Russian and foreign organizations (as well as wealthy persons) to become the honorary participants of the campaign.

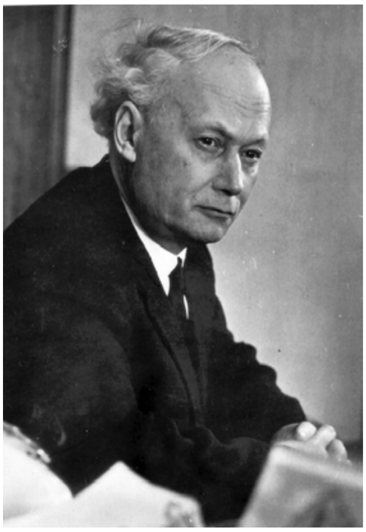
The main aim of the Foundation is to support gifted Russian scientific youth working in the field of chemical catalysis, physical methods of its research and chemical physics.

Major part of Foundation means is spent on Zamaraev post-graduate scholarships, prizes and grants. Foundation plans to support the international cooperation of scientific youth in the field of chemical catalysis and chemical physics, i.e., their participation in international scientific conferences and seminars. In 2008 **T. Kardash** and **O. Lyakin** have got the post-graduate scholarship**; S. Prikhodko, L. Kibis** and **A. Gabrienko** - incentive post-graduate scholarships.

● **Council of Scientific Youth** unites young scientific people in the Institute, helps them to achieve their professional purposes and to resolve important social problems. The Council initiates competitive programs and seminars for young researchers, arranges fellowship in foreign research centers, preparation for PhD examinations in order to promote their carrier growth. Much arttention is paid to the social program for young scientists.

Memorial Rooms of Academician Georgii K. Boreskov and Academician Kirill I. Zamaraev

The **Memorial Room of Academician Georgii K. Boreskov**, the founder and first director of the Institute of Catalysis, was opened in June 1987, on the occasion of his 80th anniversary. Georgii Konstantinovich always emphasized that the foundation of the Institute was the most important cause of his life. In 1991, the Institute of Catalysis was named after Georgii K. Boreskov.



There is a small exhibition based on the documents, awards, books, Boreskov's belongings in one of the rooms of Laboratory of Oxidation, which was headed by Georgii Konstantinovich.

A series of photos dated 1930's through 1960's tell about an extremely intense and fruitful activity of G.K. Boreskov in the fields of research and science management. He headed the Laboratory of Catalysis at the Chemicoradiological Institute (Odessa) in 1932 through 1937 (the laboratory registry dated 1931 with records by Georgii Konstantinovich concerning the preparation and characterization of vanadium catalysts was kept); the Laboratory of Catalysis at the Research Institute for Fertilizers and Insecto-Fungicides (Moscow) in 1937 through 1946, the Laboratory of Technological Catalysis at the Karpov Institute of Physical Chemistry (Moscow), and in 1958 became the Director of the Institute of Catalysis (Novosibirsk).

For his contribution to the Russian science, distinguished scientific, educational, managing and social activities, his great role in establishing the Siberian Branch of the USSR Academy of Sciences, Georgii Boreskov was awarded the Badge of Honor, three Orders of Lenin, Order of the Red Banner of Labor, Golden Medal of Hammer and Sickle, he was twice USSR State Prize winner, Ukrainian SSR State Prize winner, he was awarded the title of a Hero of Socialist Labor. Among the others, these decorations are exhibited in the Museum.

Boreskov's activity in the area of catalysis was recognized worldwide. He was a foreign member of the National Academy of Sciences of German Democratic Republic, honorary member of the New York Academy of Sciences, Doctor HONORIS CAUSA of the Wroclaw Polytechnic Institu te (Poland) and of the Poitiers University (France). Government of Bulgarian Republic awarded the Order of Kirill and Mephodium to G.K. Boreskov. Visitors can see an unusual exposition displaying the full attributes of ceremonies of awarding the HONORIS CAUSA titles to Georgii Boreskov in Wroclaw in 1976 and in Poitiers in 1981, these are black mantles and caps, an ermine scarf and leather tubules for storing the Diplomas.

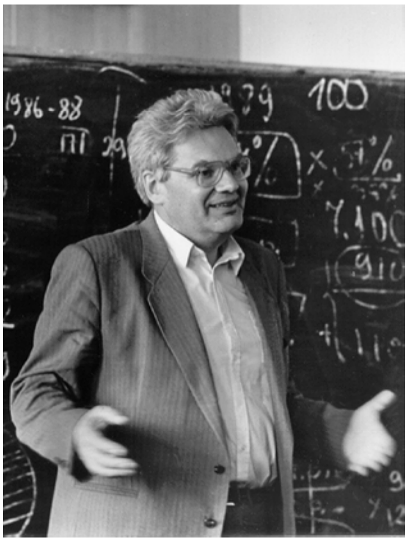
Of particular interest among the exhibit is the personal book collection of Georgii Konstantinovich including more than 1000 scientific volumes and 15 sets of Russian and foreign scientific journals. There are especially memorable copies with dedicatory inscriptions by the authors and the rarities published in the end of XIX and beginning of XX century in the collection. The books capable of telling about Boreskov's educatory activity are displayed in one of the showcases, these are course descriptions and lecture summaries, books used for preparing the lectures, and the like.

There is his writing table, case, bureau and an old push-button typewriter.

Albums, arranged by the colleagues and friends in different periods of time and presented by foreign colleagues, tell about numerous scientific events, where Boreskov presented lectures, about his keenness to winter fishing and to summer “mushroom hunting”, as well as about many other interesting events.

We see the same Georgii Konstantinovich in the portraits and photos, as he was – an intellectual and charming individual.

The **Memorial Room of Academician Kirill I. Zamaraev**, the Director of the Institute of Catalysis from 1984 through 1995, was opened on the 20th of May 1999, the day of 60th anniversary of K. Zamaraev. Establishment of the Memorial Room was promoted by the International Charitable Zamaraev Foundation and directly participated by Kirill Ilyich’s widow, Lyudmila Aleksandrovna Zamaraeva. This small museum exposition relates to the life and activities of Academician Kirill Ilyich Zamaraev, who was a hereditary scientist.



Diplomas, awards, photo archives and belongings of Kirill Ilyich are displayed in showcases. A unique scientific book collection gathered by him is also available here.

Kirill demonstrated his brilliant potentialities in sciences as early as his school years. He finished school as the Golden Medal winner; the medal is also stored in the Museum. He continued his education in the Mendeleev Institute of Chemical Technology in Moscow, but after the third year moved to the Moscow Physical and Technological Institute (MPhTI) in order to get a strong background in chemical physics. In the Museum, there are laboratory registries of post-graduate student Kirill Zamaraev and EPR spectra recorded by him during his post-graduate years.

The Moscow period (1956-1976) of his life and work is illustrated by the photo expositions: here is Kirill Zamaraev as a junior, then senior researcher at the Institute of Chemical Physics of the USSR Academy of Sciences; he heads a laboratory and, at the same time, he is an assistant professor in MPhTI.

Early in 1977 Kirill Ilyich was invited by Academician G.K.Boreskov; with his family and a team of young MPhTI graduates, he moved to Novosibirsk. Owing to the activity of Kirill Zamaraev and his colleagues, investigations of mechanisms of catalytic reactions at the atomic and molecular levels were considerably extended and intensified in the Institute of Catalysis.

He combined his vast research and management activity with teaching in the Novosibirsk State University.

The decade from mid-1980’s to mid-1990’s was the time of international recognition of his scientific achievements. The exhibition demonstrates his state awards, honorary medals of the USSR Academy of Sciences, as well as the certificate of full member of the USSR Academy of Sciences. He became a foreign member of Indian and Korean Academies of Sciences, awarded the Silver Medal by the Royal Chemical Society as an “Outstanding Lecturer of the Century”, and was elected a member of Academy of Europe. In 1994 K.I. Zamaraev became a President of IUPAC, International Union of Pure and Applied Chemistry, and in 1995 was honored with the German prestigious Karpinski Award for Russian Scientists. There are diplomas and medals, as well as a number of photos of that time in the Museum.

Everyone, who knew personally Kirill Ilyich, remember his exceptional ability not to loose courage at any, even very severe, circumstances. He had a really iron character, and it was not without vain that the sport he went in for was mountaineering.

A smiling, talented, brilliant and courageous man appears before visitors to the Memorial Room.

RESEARCH ACTIVITY

Quantum-Chemical Investigations

CLUSTER MODEL DFT STUDY OF CO ADSORPTION TO GALLIUM IONS IN Ga/HZSM-5

G.M. Zhidomirov, A.A. Shubin, M.A. Milov, V.B. Kazansky*, R.A. van Santen, E.J.M. Hensen**** (**Zelinsky Institute of Organic Chemistry, Moscow, Russia; **Eindhoven University of Technology, Eindhoven, The Netherlands*)

J. Phys. Chem. C,
112(9) (2008) pp. 3321-3326.

Cluster model DFT calculations of CO adsorption on various possible forms of gallium in Ga/HZSM-5 zeolites have been performed. CO was found to only weakly interact with Ga^+, $(GaO)^+$, and $(Ga(OH)_{2-n}H_n)^+$ (n = 1, 2) cationic clusters. The resulting shifts of the CO stretching frequency ($\Delta\nu_{CO}$) are only very small. On the other hand, CO coordination to small mononuclear and binuclear Ga^{3+} hydride/hydroxide/oxide species results in positive shifts in the stretching frequency in the range $\Delta\nu_{CO} = 20–40$ cm^{-1}. Larger shifts ($\Delta\nu_{CO} = 70–90$ cm^{-1}) are associated with CO coordination to Ga ions at the corners of small three-dimensional Ga–oxide clusters. The experimentally observed changes in the infrared spectrum of adsorbed CO over Ga/HZSM-5 zeolites upon reductive and oxidative treatments are interpreted with these insights. Possibilities for the formation of such polynuclear oxide species in the zeolite micropore space are discussed. On the basis of recent literature insights, it is suggested that large shifts derive from CO coordination to oligomeric Ga cationic complexes stabilized by the negative zeolite charge.

NON-LOCALIZED CHARGE COMPENSATION IN ZEOLITES: A PERIODIC DFT STUDY OF CATIONIC GALLIUM-OXIDE CLUSTERS IN MORDENITE

E.A. Pidko*, E.J.M. Hensen*, G.M. Zhidomirov, R.A. van Santen* (**Eindhoven University of Technology, Eindhoven, The Netherlands*)

J. Catal.,
255(2) (2008) pp. 139-143.

Periodic DFT calculations show that stability of binuclear cationic gallium–oxo clusters in high-silica zeolites is mainly controlled by the favorable geometrical environment of the Ga^{3+} ions, whereas the effect of the direct interaction with the charge-compensating framework anionic sites is less important. Extraframework cyclic $Ga_2O^{2+}_2$ cations are shown to be active for light alkane dehydrogenation.

ADSORPTION PROPERTIES OF OXIDIZED GALLIUM-MODIFIED ZEOLITE ZSM-5 FROM DIFFUSE-REFLECTANCE IR-SPECTROSCOPIC AND QUANTUM-CHEMICAL DATA: II. INTERACTION WITH CARBON MONOXIDE AND WATER

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Kinet. Catal., 49(1) (2008) pp. 149-155.

Diffuse-reflectance IR spectroscopy was used to study the adsorption and subsequent high-temperature transformations of water and carbon monoxide molecules on the oxidation-treated gallium-modified zeolite Ga/HZSM-5. The results were correlated with the corresponding quantum-chemical calculation data. Usually, it is thought that the oxo ions $[Ga{=}O]^+$ are formed in the oxidation of Ga/HZSM-5. Based on the experimental and calculated data, the possible reactions of the gallium oxo ions with the above molecules are considered. The oxo ions were found highly reactive, and it is likely that polynuclear gallium oxide nanoclusters were formed in the oxidation of the gallium-substituted zeolite Ga/HZSM-5. The Ga^+ ions, which appeared in the course of Ga/HZSM-5 reduction, were partially oxidized by water at 573 K; in turn, this could initiate the formation of polynuclear nanoclusters. It was found that ~25% of the Ga^+ ions were oxidized in the interaction with water to liberate molecular hydrogen. The thermal reduction of a nitrous oxide–preoxidized Ga/HZSM-5 sample with carbon monoxide was studied, and a conclusion on dissimilar states of oxygen bound to gallium was drawn.

A THEORETICAL INVESTIGATION OF THE ADSORPTION SURFACE SITES OF THE ACTIVATED $MgCl_2$

D.A. Trubitsyn, V.A. Zakharov, I.I. Zakharov

J. Mol. Catal. A: *Chem.*,
270(1-2) (2007) pp. 164-170.

The adsorption of carbon monoxide on activated $MgCl_2$ has been investigated within DFT using different models of the $MgCl_2$ surface. All the models were Mg_6Cl_{10} clusters with two saturating OH groups. It has been found that the adsorption sites within the models based on the geometry of the ideal $MgCl_2$ crystal are stronger than they are in the experiment. It has also been found that relaxed clusters based on the geometry of the relaxed $MgCl_2$ surface present more accurate models of the $MgCl_2$ surface and account the relaxation effects properly. IR spectra of carbon monoxide bounded to three different adsorption sites calculated within relaxed clusters approximation is in excellent agreement with the experimental data. Such an agreement allows to conclude that adsorption sites of the activated $MgCl_2$ surface in general are 3-, 4- and 5-fold Mg atoms and the structure of these sites follows the structure of corresponded relaxed $MgCl_2$ crystallographic faces.

SIZE-DEPENDENCE OF ADSORPTION PROPERTIES OF METAL NANOPARTICLES: A DENSITY FUNCTIONAL STUDY ON Pd NANOCLUSTERS

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J. Phys. Chem. C,
112(51) (2008) pp. 20269–20275.

Interatomic distances in metal nanoparticles are reduced from their values in the bulk. It was studied computationally how this size-dependent geometry change (from the bulk) relates to the size-dependence of other properties of large metal clusters, including their reactivity. For this purpose, using an all-electron scalar-relativistic density-functional approach, structures and binding energies for the example of CO adsorption on 3-fold hollow sites at the center of (111) facets of cuboctahedral nanoscale clusters Pd_n ($n = 55-260$) were calculated. The average nearest-neighbor Pd−Pd distance of optimized structures is 4−7 pm (2−3%) shorter than the extrapolated limit of the lateral distance within an infinite (111) surface. In consequence, the energy of CO adsorption on a cluster of ~100 atoms is ~15 kJ mol^{-1} smaller than the extrapolated limit. On the basis of these results, a strategy was suggested for modeling particles of larger size, e.g. of 1000 atoms and more, with the help of smaller model particles of up to ~300 atoms where one keeps the core of a model cluster fixed at the bulk structure and restricts the structure optimization to the outermost shell of cluster atoms.

HOW THE C-O BOND BREAKS DURING METHANOL DECOMPOSITION ON NANOCRYSTALLITES OF PALLADIUM CATALYSTS

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J. Amer. Chem. Soc.,
130(29) (2008) pp. 9342-9352.

Experimental findings imply that edge sites (and other defects) on Pd nanocrystallites exposing mainly (111) facets in supported model catalysts are crucial for catalyst modification via deposition of CH_x (x=0-3) byproducts of methanol decomposition. To explore this problem computationally, the authors applied recently developed approach to model realistically metal catalyst particles as moderately large three-dimensional crystallites. The first results of this advanced approach are presented here where the authors comprehensively quantify the reactivity of a metal catalyst in an important chemical process. In particular, to unravel the mechanism of how CH_x species are formed, density functional calculations of C-O bond scission in methanol and various dehydrogenated intermediates (CH_3O, CH_2OH, CH_2O, CHO, CO), deposited on the cuboctahedron model particle Pd_{79}, were carried out. The lowest activation barriers, ~130 kJ mol^{-1}, of C-O bond breaking and the most favorable thermodynamics for the adsorbed species CH_3O and CH_2OH which feature a C-O single bond were calculated. In contrast, dissociation of adsorbed CO was characterized as negligibly slow. From the computational result that the decomposition products CH_3 and CH_2 preferentially adsorb at edge sites of nanoparticles, the authors rationalize experimental data on catalyst poisoning.

HYDROGEN ACTIVATION ON SILVER: A COMPUTATIONAL STUDY ON SURFACE AND SUBSURFACE OXYGEN SPECIES

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J. Phys. Chem. C,
112(5) (2008) pp. 1628-1635.

Clean silver is known to be inert toward H_2 dissociation. Nevertheless, silver catalysts recently have been found to exhibit a noteworthy selectivity in the hydrogenation of unsaturated aldehydes to unsaturated alcohols. Experimental studies indicate that pretreatment in oxygen atmosphere activates the catalyst. To examine the role of oxygen in activation of hydrogenation catalysts, a density functional study on periodic slab models of H_2 dissociation at various oxygen species on silver surfaces, including subsurface oxygen, were carried out. According to calculations all oxygen forms under scrutiny promote dissociation of molecular hydrogen. With hydrogenation reactions in mind, the authors discuss a mechanism according to which an oxygen species, before it desorbs as a water molecule, produces one or two active hydrogen atoms on a metal terrace.

SPIN STATES OF IRON-NITROSYL ADSORPTION COMPLEXES FORMED IN Fe-ZSM5 ZEOLITES

S.E. Malykhin, A.M. Volodin, G.M. Zhidomirov

Appl. Magnet. Resonance,
33(1-2) (2008) pp. 153-166.

The capability of extra-framework monoiron sites to adsorb up to three NO molecules has been proven by quantum chemical calculations. Spin states of iron-nitrosyl adsorption complexes formed in Fe-ZSM5 zeolites have been found. For an initial iron site with $S = 2$, successive adsorption of one, two and three NO molecules changes S to 3/2, 1 and 1/2, respectively. Thus, the electron paramagnetic resonance (EPR) $S = 1/2$ signal observed after NO adsorption on the Fe-ZSM5 catalyst may be assigned to the $Fe^{2+}(NO)_3$ species. Some peculiarities of the $S = 1/2$ EPR spectra obtained for iron-nitrosyl species in zeolites are discussed.

ESEEM MEASUREMENTS OF LOCAL WATER CONCENTRATION IN D_2O-CONTAINING SPIN-LABELED SYSTEMS

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Appl. Magn. Reson.,
35 (2008) pp. 73-94.

To calibrate electron spin echo envelope modulation (ESEEM) amplitudes with the respect to the deuterium water content in spin-labeled biological systems, ESEEM of nitroxide TEMPO has been studied in frozen glassy D_2O-dimethylsulfoxide mixtures of different composition. The interaction between the unpaired electron of nitroxide and the deuterium nuclei manifests itself in a cosine Fourier transform spectrum as the sum of a narrow line with the doublet quadrupole splitting and of a broad one. The narrow line arises from interaction with distant deuterium nuclei, the broad one arises from interaction with nearby nuclei belonging to nitroxide-water molecule complexes. The dependence on water concentration was found to be nonlinear for the intensity of the narrow line and close to linear for the intensity of the quadrupole doublet. Therefore, the intensity of the quadrupole doublet is suggested as a measure of concentration of free water around a spin label in biological objects. Fourier transform line shape was theoretically simulated for different model distributions of water molecules around the spin label. Simulations confirm the linear dependence of the quadrupole doublet intensity on water concentration seen in the experiment. The suggested approach was applied to analyze data for spin-labeled dipalmitoylphosphatidylcholine (DPPC) and DPPC-cholesterol D_2O-hydrated model membranes. The concentration of free water near the spin-labeled fourth carbon atom along the lipid chain was estimated as 5.2 and 7.2 M for DPPC and DPPC-cholesterol membranes, respectively.

ELECTRONIC STRUCTURE AND CHARGE TRANSPORT PROPERTIES OF AMORPHOUS Ta_2O_5 FILMS

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J. Non-Cryst. Solids,
354(26) (2008) pp. 3025-3033.

Amorphous Ta_2O_5 films were deposited by sputtering Ta onto silicon substrates with reactive ion beam. Electron energy loss spectroscopy measurements on the film found that the plasma oscillation energy is 23.1 eV. The refractive index and the extinction coefficient were measured with spectroscopic ellipsometry over the spectral range of 1.9-4.9 eV. The optical band gap is found to be 4.2±0.05 eV. The valence band consists of three bands separated by ionic gaps. The values of electron effective masses were estimated with *ab initio* quantum chemical calculation. Experiments on injection of minority carriers from silicon into oxide were also conducted and the authors found that the electron component of conduction current governed by the electron current in the amorphous Ta_2O_5.

ON THE MECHANISM OF MECHANOCHEMICAL DIMERIZATION OF ANTHRACENE. QUANTUM-CHEMICAL CALCULATION OF THE ELECTRONIC STRUCTURE OF ANTHRACENE AND ITS DIMER

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J. Struct. Chem.,
49(4) (2008) pp. 581-586.

The electronic structure of anthracene, its dimer, and intermediate structures composed of two anthracene molecules were calculated in the density functional theory. The calculated potential barrier to anthracene dimerization is ~55 kcal/mol; the dissociation barrier is ~45 kcal/mol. The pressure required for the reaction to reach the transition state and acting on the anthracene crystal is ~60 kbar. Lower pressures, ~10 kbar, are required for molecules to approach each other to distances of ~3 Å, at which tunnel dimerization is possible for photoexcited molecules.

NEW APPROACH TO THE CORRELATION PROBLEM: ELECTRON INTERACTION POTENTIAL AS A VARIABLE IN SOLVING THE MANY-PARTICLE SCHRÖDINGER EQUATION

V.M. Tapilin

J. Struct. Chem.,
49(3) (2008) pp. 387-394.

The many-electron wave function is represented as the product of the wave function of the independent particles and the function that depends only on the value of the interelectron interaction potential. The function defines the electron correlation effects; a standard linear differential equation was derived to define the function. The equation depends on the functions of independent particles; a generalization of the Hartree-Fock equations including electron correlation was obtained for these functions. The total energy calculation of two-electron ions shows that even solving an ordinary differential equation for the function of independent particles represented by the functions of noninteracting electrons leads to higher accuracy than the one achieved in the Hartree-Fock theory.

Monte-Carlo Simulation to Study Physicochemical Processes

ORIGINAL MONTE CARLO METHOD FOR ANALYSIS OF OXYGEN MOBILITY IN COMPLEX OXIDES BY SIMULATION OF OXYGEN ISOTOPE EXCHANGE DATA

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Solid State Ionics,
179(21) (2008) pp. 847-850.

The kinetics of $^{16}O/^{18}O$ isotope exchange over CeO_2–ZrO_2 and CeO_2–ZrO_2-La_2O_3 were investigated at T=923 K and P=760 Torr by original Monte Carlo method simulating these processes in the time mode of real transient kinetic experiments. The rate constants of the elementary stages of isotope exchange giving excellent agreement between calculated and experimental isotope transient curves were found. Preliminary results for modeling isotopic exchange over Pt/CeO_2–ZrO_2 and Pt/CeO_2–ZrO_2–La_2O_3 were also obtained and discussed.

DEPOSITION AT GLANCING ANGLE, SURFACE ROUGHNESS, AND PROTEIN ADSORPTION: MONTE CARLO SIMULATIONS

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J. Phys. Chem. B,
112(24) (2008) pp 7267-7272.

To generate rough surfaces in Monte Carlo simulations, the 2+1 solid-on-solid model of deposition with rapid transient diffusion of newly arrived atoms supplied at glancing angle was used. The surfaces generated are employed to scrutinize the effect of surface roughness on adsorption of globular and anisotropic rodlike proteins. The obtained results are compared with the available experimental data for Ta deposition at glancing angle and for the bovine serum albumin and fibrinogen uptake on the corresponding Ta films.

STERIC CONSTRAINTS ON ADSORPTION IN HETEROGENEOUS CATALYTIC REACTIONS

V.P. Zhdanov

Catal. Commun.,
9(14) (2008) pp. 2319-2322.

The kinetics of heterogeneous catalytic reactions with participation of large molecules can be influenced by steric constraints on their adsorption. Using a generic model of alkane hydrogenolysis, the author presents Monte Carlo simulations explicitly illustrating that this effect may dramatically change the apparent reaction order in alkane. The predictions drawn are in good agreement with the results of numerous experimental studies performed on various metals.

CABRERA-MOTT KINETICS OF OXIDATION OF nm-SIZED METAL PARTICLES

V.P. Zhdanov, B. Kasemo* (**Chalmers University of Technology, Göteborg, Sweden*)

Chem. Phys. Lett.,
452(4-6) (2008) pp. 285-288.

The conventional Cabrera–Mott model for describing the kinetics of growth of thin oxide films on metal crystals is based on the assumption that the process is limited by the field-facilitated activated jumps of metal ions on the flat metal-oxide interface. The authors modify this model in order to apply it to nm-sized metal particles. Analysis indicates that due to the difference in the distribution of the electric field the kinetics of oxidation of nm-sized particles may be much faster compared to those of macroscopic samples.

AVRAMI-KOLMOGOROV-JOHNSON-MEHL KINETICS FOR NANOPARTICLES

V.P. Zhdanov

Surf. Rev. Lett.,
15(5) (2008) pp. 605-612.

In the conventional Avrami-Kolmogorov-Johnson-Mehl model, the reaction or phase transition occurring in the 2D or 3D infinite medium is considered to start and proceed around randomly distributed and/or appearing nucleation centers. The radius of the regions transformed is assumed to linearly increase with time. The Monte Carlo simulations presented, illustrate what may happen if the transformation takes place in nanoparticles. The attention is focused on nucleation on the regular surface, edge and corner sites, and on the dependence of the activation energy for elementary reaction events on the local state of the sites.

KINETICS OF THE FORMATION OF A NEW PHASE IN NANOPARTICLES

V.P. Zhdanov, B. Kasemo* (**Chalmers University of Technology, Göteborg, Sweden*)

Chem. Phys. Lett.,
460(1-3) (2008) pp. 158-161.

Monte Carlo simulations of the formation of a new phase (e.g., hydride in metal) during uptake of atoms by a nanoparticle are presented. The corresponding kinetics exhibit a short initial stage, which is sensitive to the specification of the subsurface layers, and a more universal long stage with the time scale proportional to L^z, where L is the lattice size, and $2.3 \leq z \leq 3$ is the exponent dependent on the diffusion dynamics. For realistic diffusion dynamics, the model also predicts the third late stage when the growth of a new phase becomes very slow compared to that observed during the former stages.

KINETICS OF MIGRATION AND COALESCENCE OF SUPPORTED nm-SIZED METAL PARTICLES

V.P. Zhdanov

Surf. Rev. Lett.,
15(3) (2008) pp. 217-220.

Monte Carlo simulations of the kinetics of migration and coalescence of nm-sized metal particles on a uniform surface and a surface with traps in the physically reasonable case when the diffusion coefficient of particles varies inversely as the fourth power of the particle size are presented. The Monte Carlo kinetics are demonstrated to be in good agreement with the mean-field results. The size distribution of particles is found to be nearly symmetrical with respect to the average value.

KINETICS OF OXIDATION OF nm-SIZED SOOT SPHERULES

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Chem. Phys. Lett.,
454(5-6) (2008) pp. 341-344.

The non-catalytic soot oxidation kinetics predicted by four models implying, respectively, (i) monosized uniform spherically shaped soot spherules, (ii) monosized disk-like spherules formed of carbon sheets, (iii) spherically shaped spherules with a realistic size distribution, and (iv) disk-like spherules with a realistic size distribution was analysed. In all the cases, the reaction front is considered to move from the periphery to the center. The effect of the spherule size distribution on the oxidation kinetics is found to be appreciable and accordingly should be taken into account in interpretations of the corresponding experiments. The latter is illustrated by scrutinizing relevant experimental data and illustrating that model (iv) appears to be preferable.

KINETICS OF ELECTROCHEMICAL REACTIONS ON MODEL SUPPORTED CATALYSTS: READSORPTION AND MASS TRANSPORT

V.P. Zhdanov, B. Kasemo* (**Chalmers University of Technology, Göteborg, Sweden*)

Surf. Rev. Lett.,
15(6) (2008) pp. 745-751.

To bridge the structure gap, electrochemical reactions can be studied in flow cells with nm-sized catalyst particles deposited or fabricated on the cell walls. The understanding of the role of mass transport in such cells is now limited. To clarify the likely effects in this field, the authors analyze the simplest reaction scheme including intermediate desorption, readsorption, and subsequent reaction and show how the net rate of the formation of intermediate can be influenced by its diffusion in the liquid phase. With certain approximations, the authors derive analytical results describing reaction and diffusion near catalyst particles and in more remote regions in the simplest 1D case and more complex 2D and 3D situations.

SIMULATION OF PROLIFERATION AND DIFFERENTIATION OF CELLS IN A STEM-CELL NICHE

V.P. Zhdanov

Physica A,
387(24) (2008) pp. 6126-6136.

Stem-cell niches represent microscopic compartments formed of environmental cells that nurture stem cells and enable them to maintain tissue homeostasis. The spatio temporal kinetics of proliferation and differentiation of cells in such niches depend on the specifics of the niche structure and on adhesion and communication between cells and may also be influenced by spatial constraints on cell division. The authors propose a generic lattice model, taking all these factors into account, and systematically illustrate their role. The model is motivated by the experimental data available for the niches located in the subventricular zone of adult mammalian brain. The general conclusions drawn from Monte Carlo simulations are applicable to other niches as well. One of the authors main findings is that the kinetics under consideration are highly stochastic due to a relatively small number of cells proliferating and differentiating in a niche and the autocatalytic character of the symmetric cell division. In particular, the kinetics exhibit huge stochastic bursts especially if the adhesion between cells is taken into account. In addition, the results obtained show that despite the small number of cells present in stem-cell niches, their arrangement can be predetermined to appreciable extent provided that the adhesion of different cells is different so that they tend to segregate.

KINETIC OSCILLATIONS IN THE EXPRESSION OF MESSENGER RNA, REGULATORY PROTEIN, AND NONPROTEIN CODING RNA

V.P. Zhdanov

Chem. Phys. Lett.,
458(4-6) (2008) pp. 359-362.

The interplay of messenger RNA (mRNA), protein, produced via translation of this RNA, and nonprotein coding RNA (ncRNA) may include regulation of the ncRNA production by protein and (i) ncRNA-mRNA association or (ii) ncRNA-protein association resulting in degradation of the corresponding complex. The kinetic models, describing these two scenarios and taking into account that the association of ncRNA with a target occurs after ncRNA conversion from the initial form to the final form (e.g., from a long RNA to microRNA), are found to predict oscillations provided that the rate of ncRNA formation increases with increasing protein population.

BIFURCATIONS IN THE INTERPLAY OF MESSENGER RNA, PROTEIN AND NONPROTEIN CODING RNA

V.P. Zhdanov

J. Phys. A: Math. Theor.,
41(28) (2008) 285101 (8 pp.).

The interplay of messenger RNA (mRNA), protein, produced via translation of this RNA, and nonprotein coding RNA (ncRNA) may include regulation of the ncRNA production by protein and (i) ncRNA–protein association resulting in suppression of the protein regulatory activity or (ii) ncRNA–mRNA association resulting in degradation of the miRNA–mRNA complex. The kinetic models describing these two scenarios are found to predict bistability provided that protein suppresses the ncRNA formation.

INTERPLAY OF MASTER REGULATORY PROTEINS AND mRNA IN GENE EXPRESSION: 3D MONTE CARLO SIMULATIONS

V.P. Zhdanov

Chem. Phys. Lett.,
456(4-6) (2008) pp. 247-252.

3D spatio-temporal Monte Carlo simulations of gene expression for a generic model with negative feedback between the mRNA and regulatory-protein production are presented. The attention is focused on the role of mRNA diffusion between the nucleus and cytoplasm. For rapid diffusion, the model predicts that the fluctuations of the mRNA and protein numbers are comparable to those corresponding to the Poissonian distribution. With decreasing diffusion rate, the fluctuations become much larger. Specifically, the time dependence of the mRNA and protein numbers exhibits huge bursts.

STOCHASTIC MODEL OF THE FORMATION OF CANCER METASTASES VIA CANCER STEM CELLS

V.P. Zhdanov

Eur. Biophys. J. Biophys. Lett.,
37(8) (2008) pp. 1329-1334.

The author presents Monte Carlo simulations of the temporal kinetics of the formation of cancer metastases with emphasis on cancer stem cells. The model used implies the existence of premetastatic niches. The population of cancer stem cells located outside tumors and inducing the formation of new tumors in niches is considered to be heterogeneous. If the niches are equivalent with respect to the formation of metastases, the kinetics are predicted to exhibit an induction period and then rapid growth of the number of metastases. If the niches are heterogeneous, the kinetics are found to be more gradual.

AMPLIFICATION OF KINETIC OSCILLATIONS IN GENE EXPRESSION

V.P. Zhdanov

JETP Lett.,
88(4) (2008) pp. 281-285.

Because of the feedbacks between the DNA transcription and mRNA translation, the gene expression in cells may exhibit bistability and oscillations. The deterministic and stochastic calculations presented illustrate how the bistable kinetics of expression of one gene in a cell can be influenced by kinetic oscillations in expression of another gene. Due to stability of the states of the bistable kinetics of gene 1 and relatively small difference between the maximum and minimum protein amounts during oscillations of gene 2, the induced oscillations of gene 1 are found to typically be related either to the low- or high-reactive state of this gene. The quality of the induced oscillations may be appreciably better than that of inducing oscillations. This means that gene 1 can serve as an amplifier of kinetic oscillations of gene 2.

SWITCHES IN GENE EXPRESSION INCLUDING microRNA AND A LARGE NUMBER OF DISTINCT mRNAS

V.P. Zhdanov

JETP Lett.,,
88(7) (2008) pp. 539-542.

In eukaryotic cells, the kinetics of gene expression depend on the interplay of messenger RNAs (mRNAs), proteins, and nonprotein coding RNAs, or, more specifically, microRNAs. Some of microRNAs may target hundreds of mRNAs. To describe this case, the author proposes a kinetic model implying that the microRNA synthesis is suppressed by protein produced via translation of one of the target mRNAs. With physically reasonable model parameters, the model predicts bistability or, in other words, switches in expression of hundreds of genes.

REACTION DYNAMICS AND KINETICS: TST, NON-EQUILIBRIUM AND NON-ADIABATIC EFFECTS, LATERAL INTERACTIONS, etc.

V.P. Zhdanov

In *"Handbook of Surface Science"*, vol. 3,
"Dynamics", Eds. E. Hasselbrink, B.I. Lundqvist,
ch. 7, 2008, pp. 231-267.

As a rule, the dynamics and kinetics of elementary steps of chemical reactions occurring on solid surfaces are complex due to the specifics of the adsorbate–substrate interaction, adsorbate–adsorbate lateral interactions, surface heterogeneity, spontaneous and adsorbate-induced changes in a surface, and/or limited mobility of reactants. In the present chapter, the main concepts of the rate theory of such reactions are illustrated by using the results obtained during the past decade. The goal of the presentation is to show new trends and opportunities in this interdisciplinary field of research.

STEREOSELECTIVE HYDROGENATION OF ACETYLENE ON COPPER CATALYSTS: A QUANTUM-CHEMICAL STUDY

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Kinet. Catal.,
49(4) (2008) pp. 527-530.

The structure of the alkyne adsorption complex on the copper surface is favorable for the stereoselective formation of *cis* isomers in the hydrogenation reaction. The pathway of dissociative hydrogen adsorption on copper is reported. It is assumed that the electron-donating promoter acts to reduce the electron work function of the copper catalyst by partially covering or “decorating” the surface of the copper particles.

Studying of Active Sites, Mechanism and Reaction Kinetics

KINETICS OF THE β-PICOLINE OXIDATION TO NICOTINIC ACID OVER VANADIA-TITANIA CATALYST:

II. EFFECT OF DIOXYGEN AND β-PICOLINE

E.V. Ovchinnikova, T.V. Andrushkevich

React. Kinet. Catal. Lett,
93(2) (2008) pp. 203-210.

The effect of the dioxygen and β-picoline concentrations on the oxidation of β-picoline to nicotinic acid was studied at 270°C over a 20% V_2O_5-80% TiO_2 (wt %) catalyst. The study was performed in a differential reactor at constant concentrations of water and nicotinic acid. A considerable excess of dioxygen was shown to be necessary for the formation of nicotinic acid. It was found that the rates of β-picoline transformation into nicotinic acid, pyridine-3-carbaldehyde, pyridine-3-nitrile, pyridine and carbon oxides as well as selectivities to products and the catalyst state depend strongly on the ratio of dioxygen to β-picoline concentrations. The minimum admissible ratio of these concentrations under industrial conditions was determined.

KINETICS OF β-PICOLINE OXIDATION TO NICOTINIC ACID OVER VANADIA-TITANIA CATALYSTS: III. THE OXIDATION OF NICOTINIC ACID

V.M. Bondareva, E.V. Ovchinnikova, T.V. Andrushkevich

React. Kinet. Catal. Lett.,
94(2) (2008) pp. 327-336.

Over vanadia-titania catalysts, the oxidation of β-picoline into nicotinic acid proceeds under a parallel-consecutive network. Nicotinic acid is formed both directly from picoline and through pyridine-3-carbaldehyde as anintermediate. Products of total oxidation and nitrile are formed on a parallel path from picoline, and on a consecutive path via overoxidation of partial oxidation products. Introduction of water into the reaction mixture raises selectivity and activity due to an acceleration of the formation of carbaldehyde and nicotinic acid and not due to repressing the reactions of total oxidation.

AN INTERPRETATION OF THE KINETICS OF ETHYLENE OXIDATION OVER SILVER BASED ON SEPARATE STUDIES OF KINETICS OF THE REACTION STEPS

A.V. Khasin

React. Kinet. Catal. Lett.,
95(2) (2008) pp. 345-353.

The kinetics of the separate reaction steps, corresponding to the stepwise redox mechanism of ethylene oxidation over silver, was studied. The results are used for the interpretation of the kinetics of overall catalytic reactions by taking into account an influence of the adsorption of oxygen on the surface properties of silver.

Zn-PROMOTED HYDROGEN EXCHANGE FOR METHANE AND ETHANE ON Zn/H-BEA ZEOLITE. *IN SITU* ^{1}H MAS NMR KINETIC STUDY

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J. Catal.,
253(1) (2008) pp. 11-21.

Hydrogen (H/D) exchange between Brønsted acid sites of both the acidic form of zeolite beta (H-BEA) and Zn-loaded zeolite beta (Zn/H-BEA) and small alkanes (methane and ethane) has been studied by monitoring the kinetics of the exchange *in situ* with ^{1}H MAS NMR spectroscopy within the temperature range of 433–563 K. On Zn/H-BEA, the exchange has been found to be more than two orders of magnitude faster compared to that on H-BEA. The decrease of reaction temperature and activation energy of the exchange on Zn/H-BEA (86–88 kJ mol^{-1}) compared to the acidic form of zeolite H-BEA (138 kJ mol^{-1}) has been rationalized by the promoting effect of zinc. It is proposed that the mechanism of the H/D exchange on Zn/H-BEA involves Zn-alkyl species as intermediates.

KINETICS OF H/D EXCHANGE FOR n-BUTANE ON ZEOLITE H-ZSM-5 STUDIED WITH ^{1}H MAS NMR *IN SITU*

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J. Phys. Chem. C,
112(31) (2008) pp. 11869-11874.

Kinetics of hydrogen (H/D) exchange between Brønsted acid sites of zeolite H-ZSM-5 and deuterated n-butanes (n-butane-d_{10} and n-butane-1,1,1,4,4,4-d_6) has been monitored by ^{1}H MAS NMR spectroscopy *in situ* within the temperature range of 423-448 K. The initial part of the kinetics is defined mainly by the hydrogen exchange, whereas the final part is strongly influenced by the chemical transformation of the alkane. Analysis of the initial part has been performed on the basis of consecutive, parallel and cyclic kinetic schemes of the H/D exchange. It has been found that both the methyl and methylene groups of n-butane are directly involved in the exchange with acidic SiOHAl groups of the zeolite. No intramolecular hydrogen exchange between the methyl and the methylene groups of the adsorbed n-butane has been detected. Similar rates of the direct exchange of either the methyl or methylene group with acidic SiOHAl groups and the apparent activation energy of 108 kJ mol^{-1} are rationalized in terms of carbonium ion mechanism of the exchange with involvement of penta-coordinated carbon atom in a transition state.

SIGNIFICANT INFLUENCE OF Zn ON ACTIVATION OF THE C–H BONDS OF SMALL ALKANES BY BRØNSTED ACID SITES OF ZEOLITE

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ChemPhysChem.,
9(17) (2008) pp. 2559-2563.

Herein, earlier obtained and new data about peculiarities of the H/D hydrogen exchange of small C(1)-n-C(4) alkanes on Zn-modified high-silica zeolites ZSM-5 and BEA in comparison with the exchange for corresponding purely acidic forms of these zeolites are analyzed. This allows to identify an evident promoting effect of Zn on the activation of C-H bonds of alkanes by zeolite Brønsted sites. The effect of Zn is demonstrated by observing the regioselectivity of the H/D exchange for propane and n-butane as well as by the increase in the rate and a decrease in the apparent activation energy of the exchange for all C(1)-n-C(4) alkanes upon modification of zeolites with Zn. The influence of Zn on alkane activation has been rationalized by dissociative adsorption of alkanes on Zn oxide species inside zeolite pores, which precedes the interaction of alkane with Brønsted acid sites.

UNDERSTANDING METHANE AROMATIZATION ON A Zn-MODIFIED HIGH-SILICA ZEOLITE

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Angew. Chem. Int. Ed.,
47(24) (2008) pp. 4559-4562.

In summary, by using isotope-tracing experiments with ^{13}C-labeled methane it have been demonstrated a high level of involvement of methane in the aromatization of higher alkanes on Zn-modified zeolites. The mechanism of the aromatization has been established and consists of the alkylation of aromatic compounds, which form exclusively from the higher alkanes. The methoxy species formed by dissociative adsorption of methane on ZnO species is responsible for the alkylation. Further embedding of the ^{13}C-labeled atoms from the methyl groups of methyl-substituted benzene derivatives into their aromatic rings occurs through a ring-expansion/contraction mechanism.

KINETICS OF CO OXIDATION ON A Pd-CONTAINING GLASS-FIBER CATALYST

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Catal. Ind.,
1 (2008) pp. 5-9.

A process of CO oxidation on a non-conventional silica glass-fiber Pd-containing catalyst (0.01 mass percent of Pd) is investigated. A kinetic model describing the rate of reaction by an equation of Langmuir-Hinshelwood type is proposed.

Kinetic constants and their temperature dependencies are determined. It is shown that the constants calculated on the basis of experimental data are statistically reliable in kinetic area and can be used in modeling of mass-transfer processes by glass-fiber catalysts. This is of practical importance for many industrial chemical-engineering processes.

IRON(II) SULFATE OXIDATION WITH OXYGEN ON A Pt/C CATALYST: A KINETIC STUDY

L.B. Okhlopkova, N.I. Kuznetsova

Kinet. Catal.,
49(1) (2008) pp. 34-42.

The kinetics of iron(II) sulfate oxidation with molecular oxygen on the 2% Pt/Sibunit catalyst was studied by a volumetric method at atmospheric pressure, T = 303 K, pH 0.33–2.4, $[FeSO_4]$ = 0.06–0.48 mol/l, and $[Fe_2(SO_4)_3]$ = 0–0.36 mol/l in the absence of diffusion limitations. Relationships were established between the reaction rate and the concentrations of Fe^{2+}, Fe^{3+}, H^+, and Cl^- ions in the reaction solution. The kinetic isotope effect caused by the replacement of H_2O with D_2O and of H^+ with D^+ was measured. The dependence of Fe^{2+} and Fe^{3+} adsorption on the catalyst pretreatment conditions was studied. A reaction scheme is suggested, which includes oxygen adsorption, the formation of a Fe(II) complex with surface oxygen, and the one-electron reduction of oxygen. The last step can proceed via two pathways, namely, electron transfer with H^+ addition and hydrogen atom transfer from the coordination sphere of the iron(II) aqua complex. A kinetic equation providing a satisfactory fit to experimental data is set up. Numerical values are determined for the rate constants of the individual steps of the scheme suggested.

INFLUENCE OF THE MOBILITY OF OXYGEN IN A COMPLEX OXIDE CARRIER ON THE MECHANISM OF PARTIAL OXIDATION OF METHANE

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Russ. J. General Chem.,
78(11) (2008) pp. 2191-2202.

The catalytic partial oxidation of methane was studied over single channels of monolith catalysts $Pt/PrCeZrO/\alpha\text{-}Al_2O_3$ and $Pt/GdCeZrO/\alpha\text{-}Al_2O_3$ using the temporal analysis of products (TAP) and kinetic transients. Effects of catalyst composition, oxidation state, time offset between O_2 and CH_4 pulses on activity, selectivity and dynamics of product formation were elucidated. Realization of the direct pyrolysis–CH_4 partial oxidation route was reliably established. This route is favored by optimum lattice/surface oxygen mobility and reactivity controlled by the dopant type (Gd, Pr) and oxidation state of the complex cerium/zirconium oxide.

NEW REACTION OF ANION RADICALS O^- WITH WATER ON THE SURFACE OF FeZSM-5

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J. Catal.,
254(1) (2008) pp. 110-120.

Complexes of bivalent iron stabilized in the FeZSM-5 zeolite matrix (α-sites) are known to be able to decompose nitrous oxide stoichiometrically to form oxygen anion radicals O^- bound to the iron (α-oxygen):

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

Similarly to O^- radicals on V and Mo oxides, α-oxygen is highly reactive in respect to CO, H_2, methane and other hydrocarbons. It participates in catalytic oxidation of benzene to phenol by nitrous oxide, providing the selectivity close to 100%.

In this work, adsorption measurements, IR spectroscopy, TPD and isotopic methods are used to describe an earlier unknown reaction of O^- species with water, which proceeds in the temperature range of 5–200°C via the hydrogen abstraction mechanism according to the equation:

$$2(Fe^{III}\text{–}O^-)_\alpha + H_2O \rightarrow 2(Fe^{III}\text{–}OH^-)_\alpha + ½\, O_2$$

The reaction leads to the hydroxyl groups formed on α-sites, and equivalent amount of O_2 evolved into the gas phase from water. Desorption of the hydroxyl groups occurs at above 400°C via their recombination into water and dioxygen, resulting in the reactivation of α-sites:

$$2(Fe^{III}\text{–}OH^-)_\alpha \rightarrow 2(Fe^{II})_\alpha + H_2O + ½\, O_2$$

High sensitivity of α-oxygen to water admixtures may be an important factor explaining some contradictory results reported in the literature on the behavior of α-oxygen.

Since α-oxygen is a typical representative of anion radicals O^-, the discovered reaction may be important not only for conventional oxidation catalysis over zeolites and metal oxides, but also for the photocatalytic processes, including photooxidation of both hydrocarbons and water.

KINETICS AND THERMODYNAMICS OF LIQUID PHASE ISOMERIZATION OF α- AND β-PINENE OVER Pd/C CATALYST

I.V. Deliy, I.L. Simakova

React. Kinet. Catal. Lett.,
95(1) (2008) pp. 161-174.

Kinetics of α- and β-pinene hydrogenation and isomerisation over Pd/C, Ru/C, Rh/C, Pt/C and Ir/C in temperature regime 20÷100°C and hydrogen pressure 0.5÷11 bar are studied. Thermodynamic parameters were calculated. The scheme of the mechanism of α- and β-pinene hydrogenation and isomerisation over Pd/C was proposed.

PERCHLOROETHYLENE HYDROFLUORINATION IN THE PRESENCE OF A CHROMIUM-MAGNESIUM CATALYST

A.A. Zirka, S.I. Reshetnikov

Kinet. Catal.,
49(5) (2008) pp. 663-666.

The gas-phase hydrofluorination of perchloroethylene into pentafluoroethane (R-125) at $T = 330$-$390°C$ and $P = 0.4$ MPa in the presence of a chromium–magnesium catalyst is reported. The reaction rate under these conditions is described by a first-order equation. A hydrofluorination scheme including main product and by-product formation routes is deduced from the observed dependences of particular product selectivities on the total perchloroethylene conversion.

TRANSITION METAL CATALYZED ASYMMETRIC OXIDATION OF SULFIDES

K.P. Brylyakov, E.P. Talsi

Curr. Org. Chem.,
12 (2008) pp. 386-404.

In the past two decades, chiral sulfoxides have been finding increasing use, reflecting growing interest both in convenient auxiliaries in asymmetric synthesis and products with biological properties containing a chiral sulfinyl group. In 1984, groups of Kagan and Modena discovered that titanium(IV) isopropoxide-diethyltartrate based systems (also known as “modified Katsuki-Sharpless reagents”) are capable of asymmetric oxidizing of prochiral sulfides by alkylhydroperoxides. Later, catalytic versions of the titanium tartrate systems were developed (with up to 90 % yield and 90 % ee for certain sulfides) that remain the most applied systems for asymmetric sulfoxidations. However, the low turnover numbers (5-20), complexity and expensiveness of such systems stimulated the search for other transition metal based catalytic systems. This review will cover the progress in transition metal catalyzed asymmetric sulfides oxidations achieved since the discoveries of early 1980s to the present days.

TITANIUM-SALAN-CATALYZED ASYMMETRIC OXIDATION OF SULFIDES AND KINETIC RESOLUTION OF SULFOXIDES WITH H_2O_2 AS THE OXIDANT

K.P. Brylyakov, E.P. Talsi

Eur. J. Org. Chem.,
19 (2008) pp. 3369-3376.

Asymmetric oxidation of sufides to sulfoxides by aqueous hydrogen peroxide with catalysis by titanium-salan complexes is presented. Optically active sulfoxides have been obtained with good to high enantioselectivities (up to 97 % *ee*) by a tandem enantioselective oxidation and kinetic resolution procedure, the catalyst performing over 500 turnovers with no loss of enantioselectivity.

THE NATURE OF ACTIVE SPECIES IN CATALYTIC SYSTEMS BASED ON NON-HEME IRON COMPLEXES, HYDROGEN PEROXIDE, AND ACETIC ACID FOR SELECTIVE OLEFIN EPOXIDATION

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Kinet. Catal.,
49(3) (2008) pp. 379-385.

The catalytic systems $[(BPMEN)Fe^{II}(CH_3CN)_2](ClO_4)_2/H_2O_2/CH_3OOH$ and $[(TPA)Fe^{II}(CH_3CN)_2](ClO_4)_2/H_2O_2/CH_3OOH$, where BPMEN = *N*,*N'*-dimethyl-*N*,*N'*-bis(2-pyridylmethyl)-1,2-diaminoethane and TPA = tris(2-pyridylmethyl)amine, provide selective olefin epoxidation. Proton NMR studies showed that the mononuclear iron(IV) oxo complexes $[(L)Fe^{IV}{=}O]^{2+}$, with L = BPMEN or TPA, are present in the cited catalytic systems. These intermediates are the decomposition products of the acylperoxo complexes $[(L)Fe^{III}\text{-}O_3CCH_3]^{2+}$. Such a complex was observed by the ^2H NMR technique at low temperatures. The $[(L)Fe^{IV}{=}O]^{2+}$ and $[(L)Fe^{V}{=}O]^{3+}$ oxo complexes are possible active species in the studied catalytic systems.

FORMATION AND STRUCTURES OF HAFNOCENE COMPLEXES IN MAO- AND AlBu$^{i}_{3}$/CPh$_3$[B(C$_6$F$_5$)$_4$]-ACTIVATED SYSTEMS

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Organomet.,
27(23) (2008) pp. 6333-6342.

The formation of cationic species relevant to olefin polymerization based on (SBI)HfCl$_2$, Me$_2$C(C$_5$H$_4$)(Flu)HfCl$_2$, Ph$_2$C(C$_5$H$_4$)(Flu)HfCl$_2$, and L′HfCl$_2$ activated by MAO, AlMe$_3$/CPh$_3$[B(C$_6$F$_5$)$_4$], and AlBu$^{i}_{3}$/CPh$_3$[B(C$_6$F$_5$)$_4$] (SBI = *rac*-Me$_2$Si(Ind)$_2$; L′ = C$_2$H$_4$(Flu)(5,6-C$_3$H$_6$-2-MeInd)) was studied by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. Thermally stable heterobinuclear intermediates of the type [LHf(μ-Me)$_2$AlMe$_2$]$^+$[MeMAO]$^-$ and [LHf(μ-Me)$_2$AlMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ were identified when using MAO and AlMe$_3$/CPh$_3$[B(C$_6$F$_5$)$_4$] as activators, respectively. The stability of these species explains the low productivity of hafnocene catalysts in the presence of AlMe$_3$-containing activators, compared to zirconocenes. By contrast, in the ternary systems LHfCl$_2$/AlBu$^{i}_{3}$/CPh$_3$[B(C$_6$F$_5$)$_4$] hydride species were detected that must be responsible for the formation of the highly active sites in olefin polymerization. The ionic hydrido species differ significantly in stability. The formation of the mixed-alkyl complex L′Hf(Me)CH$_2$SiMe$_3$ proceeds with surprisingly high diastereoselectivity; the sterically more hindered isomer is produced preferentially. It reacts with CPh$_3$[B(C$_6$F$_5$)$_4$] to afford the ion pair [L′Hf-CH$_2$SiMe$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ as two diastereomers that exist in dynamic equilibrium. The rates of site epimerization of this ion pair indicate only small energy differences between the two isomers.

ACTIVE SITES OF THE METHANE DEHYDROAROMATIZATION CATALYST W-ZSM-5: AN HRTEM STUDY

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Kinet. Catal.,
49(1) (2008) pp. 110-114.

Nonoxidative methane conversion into aromatic hydrocarbons on a zeolite modified with nanosized tungsten powder has been studied. The highest methane conversion and the maximum yield of aromatic hydrocarbons are attained on the catalyst containing 8.0 wt % W. The nature and the distribution of the active phases in the W-containing zeolite were investigated by high resolution transmission electron microscopy and energy dispersive X-ray spectroscopy. The deactivation of the W–HZSM-5 catalyst was studied at different stages of methane conversion. The distribution of coke deposits on the surface of the W–HZSM-5 catalyst was determined.

CONVERSION OF NATURAL GAS INTO LIQUID PRODUCTS ON BIMETALLIC ZEOLITE CATALYSTS

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Theor. Found. Chem. Eng.,
42(5) (2008) pp. 622-626.

The joint promotion effect of molybdenum with zinc and gallium on the catalytic properties of the zeolite ZSM-5 in the process of conversion of natural gas into liquid hydrocarbons were studied. It was shown that the addition of zinc and gallium cations to the Mo-containing zeolite enhances catalytic activity and selectivity in the formation of aromatic hydrocarbons from the components of natural gas. It was established that the maximal amount of aromatic compounds is formed in the presence of zeolite catalysts containing simultaneously 4.0% Mo and 0.5% Zn or 4.0% Mo and 1.0% Ga.

MECHANISTIC FEATURES OF REDUCTION OF COPPER CHROMITE AND STATE OF ABSORBED HYDROGEN IN THE STRUCTURE OF REDUCED COPPER CHROMITE

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Yu.A. Chesalov, V.I. Zaikovsky, A.V. Khasin,
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Russ. J. General Chem.,
78(11) (2008) pp. 2203-2213.

The review discusses the experimental data on the unusual mechanism of the reduction of copper cations from the copper chromite, CuCr$_2$O$_4$, structure. Treatment of copper chromite in hydrogen at 180-370°C is not accompanied by water formation but leads to absorption of hydrogen by the oxide structure with simultaneous formation of metallic copper as small flat particles which are epitaxially bound to the oxide. This process is due to the redox reaction $Cu^{2+} + H_2 \rightarrow Cu^0 + 2H^+$; the protons are stabilized in the oxide phase, which is confirmed by neutron diffraction studies. The reduced copper chromite which contains absorbed hydrogen in its oxidized state and the metallic copper particles epitaxially bound to the oxide phase structure exhibit catalytic activity in hydrogenation reactions.

EFFECT OF THE STRUCTURE OF Ti-Sb-O CATALYSTS ON THEIR ACID-BASE PROPERTIES, SURFACE OXYGEN BINDING ENERGY, AND CATALYTIC PROPERTIES IN PROPYLENE AMMOXIDATION

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Kinet. Catal.,
49(1) (2008) pp. 127-132.

The structure of Ti–Sb–O catalysts, namely, a solid solution of antimony ions in rutile-type TiO_2 and the titanium antimonate $TiSb_2O_6$, is characterized by X-ray diffraction, high-resolution electron microscopy, calorimetry, and IR spectroscopy. The structure effects on the acid–base properties and the surface oxygen binding energy are considered, as well as the correlation of these characteristics with the catalytic properties of the Ti–Sb–O system in propylene ammoxidation. The solid solution has a regular crystal structure. As a consequence, the surface has high concentrations of strong aprotic acid and strong basic sites and is characterized by a high surface oxygen binding energy. In the titanium antimonate structure, extended crystallographic shear defects cause a marked enrichment of the surface with antimony and, accordingly, an increase in the relative concentration of weak aprotic acid sites and a decrease in the surface oxygen binding energy. The changes of the structure and acid–base properties of the surface in passing from the solid solution to $TiSb_2O_6$ result in an increase in the acrylonitrile selectivity.

COPPER CATALYSTS BASED ON FIBERGLASS SUPPORTS FOR HYDROCARBON OXIDATION REACTIONS WITH THE PARTICIPATION OF HYDROGEN PEROXIDE

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Kinet. Catal.,
49(4) (2008) pp. 499-505.

Copper-containing catalysts were prepared by the adsorption of the ammonia complexes of Cu(II) on the surface of a silicate fiberglass material followed by the thermal and oxidative treatment of the samples. The states of copper after the adsorption of ammonia complexes and in the prepared samples were characterized using electronic diffuse reflectance spectroscopy. The catalytic activity of the samples in hydrogen peroxide decomposition and cyclohexane oxidation reactions was studied. It was found that molecular oxygen can be involved in the radical process of hydrogen peroxide oxidation. Based on spectroscopic data, it was hypothesized that partially reduced Cu(I)–Cu(0) compounds are active species in the catalysts of this type.

FORMS OF OXYGEN IN $La_{1-x}Ca_xMnO_{3+\delta}$ (x = 0-1) PEROVSKITES AND THEIR REACTIVITIES IN OXIDATION REACTIONS

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Kinet. Catal.,
49(2) (2008) pp. 261-170.

The effects of substitution in the cationic sublattice and of the synthesis procedure on the reactivity of different forms of oxygen in $La_{1-x}Ca_xMnO_{3+\delta}$ perovskites synthesized by mechanochemical and ceramic processing was studied by temperature-programmed reduction (TPR) with hydrogen. As the calcium content of the perovskite is raised, the maxima of the TPR peaks shift to lower temperatures and the extent of reduction of the perovskite increase, implying an increase in the reactivity of the system. Conversely, raising the calcination temperature or extending the calcination time shifts the maxima of the peaks to higher temperatures and diminishes the extent of reduction of the sample. TPR data for the intermediate-composition samples can be explained in terms of the dependence of microstructure on the synthesis procedure (near-surface calcium segregation in the mechanochemically synthesized samples and the microheterogeneous structure of the ceramic samples). The reduction process $Mn^{4+} \rightarrow Mn^{2+}$ takes place in the low- and medium-temperature regions. According to the literature, the bulk reduction process $Mn^{3+} \rightarrow Mn^{2+}$ occurs at high temperatures. The activity of the system in CO oxidation is correlated with the amount of the most reactive surface oxygen, which is eliminated in hydrogen TPR runs below 250–300°C.

EFFECT OF THE MICROSTRUCTURE OF Pt/CeO_2-TiO_2 CATALYSTS ON THEIR CATALYTIC PROPERTIES IN CO OXIDATION

A.A. Shutilov, G.A. Zenkovets, G.N. Kryukova, V.Yu. Gavrilov, E.A. Paukshtis, A.I. Boronin, S.V. Koscheev, S.V. Tsybulya

Kinet. Catal.,
49(2) (2008) pp. 271-278.

The microstructure of 2% Pt/CeO_2–TiO_2 catalysts has an effect on their catalytic properties in CO oxidation. The nanostructured catalysts as platinum clusters 0.3–0.5 nm in size are the most active. These clusters are stabilized at crystal boundaries formed by irregularly intergrown anatase particles. The catalyst containing platinum particles 2–5 nm in size is less active because of the decrease in the extent of dispersion of platinum and the change of its electron state.

ACTIVITY OF Rh/TiO_2 CATALYSTS IN $NaBH_4$ HYDROLYSIS: THE EFFECT OF THE INTERACTION BETWEEN $RhCl_3$ AND THE ANATASE SURFACE DURING HEAT TREATMENT

V.I. Simagina, O.V. Netskina, O.V. Komova, G.V. Odegova, D.I. Kochubey, A.V. Ischenko

Kinet. Catal.,
49(4) (2008) pp. 568-573.

The reaction properties of Rh/TiO_2 sodium tetrahydroborate hydrolysis catalysts reduced directly in the reaction medium depend on the temperature at which they were calcined. Raising the calcination temperature to 300°C enhances the activity of the Rh/TiO_2 catalysts. Using diffuse reflectance electronic spectroscopy, photoacoustic IR spectroscopy, and chemical and thermal analyses, it is demonstrated that, as $RhCl_3$ is supported on TiO_2 (anatase), the active-component precursor interacts strongly with the support surface. The degree of this interaction increases as the calcination temperature is raised. TEM, EXAFS, and XANES data have demonstrated that the composition and structure of the rhodium complexes that form on the titanium dioxide surface during different heat treatments later determine the state of the supported rhodium particles forming in the sodium tetrahydroborate reaction medium.

ACTIVE SURFACE FORMATION AND CATALYTIC ACTIVITY OF PHOSPHOROUS-PROMOTED ELECTROLYTIC SILVER IN THE SELECTIVE OXIDATION OF ETHYLENE GLYCOL TO GLYOXAL

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Appl. Catal, *A*,
344(1-2) (2008) pp. 142-149.

Unpromoted and phosphorus-promoted electrolytic silver catalysts have been investigated in the partial oxidation of ethylene glycol. It was shown that the addition of the phosphorus-containing promoter on the surface of electrolytic Ag catalyst led to 15-20% increase in glyoxal yield. The formation mechanism of the active P-containing surfaces of silver catalyst as well as polycrystalline Ag foil has been studied by means of X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD) and scanning electron microscopy (SEM) methods. It was shown that silver clusters located nearby the P-containing Ag surface participate in the ethylene glycol oxidation into glyoxal. The rise of glyoxal selectivity is explained by the absence of low temperature peak at 250°C in TPD spectra of both P-promoted Ag foil and electrolytic Ag catalysts. This peak was assigned to the decomposition of surface oxide-like species ((Ag_2O)-O-s) responsible for deep oxidation of ethylene glycol.

Application of Physicochemical Methods for Characterization of Catalysts, Supports, Synthesized Substances and Materials

THE STATE OF THE COMPONENTS IN Cu-CeO_2-ZrO_2 CATALYSTS FOR SELECTIVE OXIDATION OF CO

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Bull. Russ. Acad. Sci.: Phys.,
72(8) (2008) pp. 1098-1103.

Cu–CeO_2 catalysts deposited on a commercial ZrO_2 support have been investigated. The catalyst composition has been optimized: the optimum copper content was found to be 5–10 wt % at a cerium oxide content of 23 wt %. The catalysts were investigated by X-ray diffraction analysis and X-ray photoelectron spectroscopy. According to the X-ray diffraction data, the support consists of the monoclinic ZrO_2 phase and cubic CeO_2 phase with an enlarged lattice parameter, while the catalysts contain CuO. The X-ray photoelectron data indicate the presence of a highly dispersed CuO_2 phase interacting with cerium oxide and zirconia on the surface of the catalyst having the optimum copper content.

ACTIVITY AND STABILITY OF Ni/Al_2O_3 CATALYSTS IN CARBON DIOXIDE CONVERSION OF METHANE AS INFLUENCED BY ALKALI METAL OXIDE ADDITIVES (K_2O, Na_2O, Li_2O)

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Russ. J. Appl. Chem.,
80(11) (2007) pp. 1883-1887.

Properties of Ni/Al_2O_3 composites supported by synthetic cordierite ceramic block matrices of honeycomb structure in carbon dioxide conversion of methane in the presence of alkali metal oxides (K_2O, Na_2O, Li_2O) were studied in comparison with those of GIAP-18 granulated catalyst.

THE PRODUCT OF THERMOBARIC TREATMENT OF $Pt_{0.25}Os_{0.75}$

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J. Struct. Chem.,
49(2) (2008) pp. 382-385.

The products obtained from the $Pt_{0.25}Os_{0.75}$ nonequilibrium solid solution treated by the thermobaric procedure (1.5–2 GPa, 2000°C, 3 min) were investigated by X-ray powder diffraction. The phase compositions were evaluated from quantitative X-ray phase analysis, energy dispersion spectroscopy, and crystal-chemical analysis data for known Pt_xOs_{1-x} phases.

STRUCTURE OF NANOCRYSTALLINE PARTICLES OF METALLIC COBALT FORMED DURING THE REDUCTION OF Co_3O_4 OXIDE

S.V. Cherepanova, O.A. Bulavchenko,
S.V. Tsybulya

J. Struct. Chem.,
49(3) (2008) pp. 512-516.

X-ray diffraction is applied to investigate metallic cobalt obtained by the reduction of nanocrystalline particles of Co_3O_4. The particles of metallic cobalt have a high concentration of stacking faults, i.e., violations of the layer packing sequence *ABABAB*..., which is seen in X-ray diffraction patterns as anisotropic broadening of diffraction peaks. Simulation of the diffraction patterns of α-Co with a different concentration of stacking faults is carried out.

NANOCOMPOSITES INTERMETALLICS/OXIDES, PRODUCED BY MA SHS

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T.L. Talako*, A.P. Barinova*, I.A. Vorsina*,
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Rev. Adv. Mater. Sci.,
18(4) (2008) pp. 326-328.

MA SHS was used for preparation of oxide/intermetallics nanocomposites. Mechanochemical reduction of Fe_2O_3 was investigated in conditions of high dilution by iron and aluminium. It shows that excess of Al content significantly alters the process. Mechanical activation of mixture 60.9 wt % Fe + 26.6 wt % Al + 12.5 wt % Fe_2O_3 leads to formation of nanocomposite Al_2O_3/Fe/Al, and following SHS creates nanocomposite Al_2O_3/FeAl.

XRD-patterns were obtained with URD-63 diffractometer. Microstructure was studied by scanning electron microscopy (a Camscan scanning electron microscope with a Link Analytical AN10000 energy dispersive X-ray analyzer, Link ZAF4-FLS software was used for quantitative analysis), and transmission electron microscopy (a JEM 1000x microscope).

VACANCIES ORDERING IN $La^{3+}_{1-x}Ba^{2+}_{x}FeO_{3-\delta}$ PEROVSKITES

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Z. Kristallogr. Suppl.,
26 (2007) pp. 381-386.

Using powder X-ray diffraction the $La^{3+}_{1-x}Ba^{2+}_{x}FeO_{3-\delta}$ perovskite related solid solutions were investigated. A morphotropic phase transition from orthorhombic to cubic was shown for the sample with x ~0.3. High temperature XRD patterns of $La_{0.2}Ba_{0.8}FeO_{3-\delta}$ obtained under air and vacuum revealed new diffraction peaks related to local ordering of the oxygen vacancies. Such ordering remained at room temperature only after cooling in vacuum.

WEAKLY BOUND OXYGEN AND ITS ROLE IN STABILITY OF SOLID SOLUTIONS $La_{1-x}Sr_{x}FeO_{3-\delta}$

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J. Struct. Chem.,
49(6) (2008) pp. 1077-1083.

In the present study high-temperature X-ray diffraction, thermal analysis, and mass-spectrometry have been employed for investigation of samples in the $La_{1-x}Sr_{x}FeO_{3-\delta}$ family ($0 \le x \le 1$), the materials being solid solutions having perovskite structure. It has been shown that the loss of oxygen by the samples on heating to 1200°C in air ($0 \le x \le 1$) or in vacuum ($x < 0.75$) does not result in structural rearrangement of the solid solutions, but causes an increase in the lattice parameters. Heating of the compositions with $x \ge 0.75$ in vacuum affords phases with ordered vacancies. The observed structural evolutions (growth of the unit cell parameter and vacancy ordering) are reversible, and on re-oxidation (on cooling in air or additional heating of the "vacuum" samples in air atmosphere) the original parameters of the oxides are recovered. The amount of oxygen evolved on heating increases in vacuum or in helium atmosphere, as compared to air, and also grows with rising strontium content, but under experimental conditions does not reach the maximum possible value ($\delta = x/2$).

NANOCRYSTALLINE TRANSITION ALUMINAS: NANOSTRUCTURE AND FEATURES OF X-RAY DIFFRACTION PATTERNS OF LOW-TEMPERATURE Al_2O_3 POLYMORPHS

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Phys. Rev. B: Condens. Matter,
77(2) (2008) 024112-024125.

Low-temperature γ-, η-, and χ-Al_2O_3 polymorphs were studied by high resolution transmission electron microscopy and X-ray powder diffraction along with computer simulation of the diffraction patterns. Planar defects lying on the {111}, {110}, and {100} planes, which are the origin of the broadening of X-ray diffraction peaks in different forms of aluminium oxide, were revealed. In addition to providing strong experimental support for the imperfect character of the specimen structures, these results demonstrate the possibility of using nanosized crystalline domains with a spinel-type arrangement, which are regularly shaped and have a specified, developed face and bounding surfaces, for the description of the nanostructure of a whole variety of low-temperature Al_2O_3 derivatives. It was found that different ways of domain packing in the oxide particles with a subsequent formation of planar defects contribute to specific kinds of line-shape broadening observed in the X-ray diffraction patterns of these materials. The mechanism of the vacancy generation upon propagation of the shear-type defect in the {110} plane of the spinel structure, which changes the Al_3O_4 stoichiometry to Al_2O_3, is also discussed.

SYNTHESIS AND STUDY OF THE THERMAL STABILITY OF $SrFe_{1-x}M_xO_{3-z}$ (M=Mo, W) PEROVSKITES

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Solid State Ionics,
179(21-26) (2008) pp. 1076-1079.

In the present work, solid solutions of the composition $SrFe_{1-x}M_{x}O_{3-z}$, where M = Mo, W and $0 < x < 0.5$, are synthesized. The structure of the new materials depending on the composition and on oxygen stoichiometry is studied; the results of high-temperature X-ray diffraction measurements, thermal stability and phase transformations in various environments are presented.

SOFT ACTIVATION OF THE C-S BOND: X-RAY DIFFRACTION AND SPECTROSCOPIC STUDY OF THE CLUSTER $Ru_4(\mu_4\text{-}S)(\mu,\eta^3\text{-}C_3H_5)_2(CO)_{12}$

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J. Struct. Chem.,
49(4) (2008) pp. 719-723.

The complex $Ru_4(\mu_4\text{-}S)(\mu,\eta^3\text{-}C_3H_5)_2(CO)_{12}$ is prepared and examined by IR and NMR spectroscopy; its crystal structure is determined (an automatic Bruker-Nonius X8 Apex four-circle diffractometer equipped with a 2-D CCD-detector, 100 K, graphite-monochromated molybdenum source, $\lambda = 0.71073$ Å). The crystal belongs to the orthorhombic crystal system with unit cell parameters $a = 19.3781(9)$ Å, $b = 12.2898(7)$ Å, $c = 10.1726(4)$ Å, $V = 2422.6(2)$ Å^3, space group *Pnma*, $Z = 4$, composition $C_{18}H_{10}O_{12}Ru_4S$, $d_x = 2.343$ g/cm^3. The molecule of point symmetry C_1 is situated on the mirror plane of the space group *Pnma*, two carbonyl groups at Ru2 and Ru3 atoms overlapping with the allylic ligand with a weight of 50% so that carbon atoms coincide. Thus, one has a racemic structure with two overlapping enantiomers of the molecule of $Ru_4(\mu_4\text{-}S)(\mu,\eta^3\text{-}C_3H_5)_2(CO)_{12}$.

X-RAY PHOTOELECTRON STUDY OF THE INTERACTION OF H_2 AND H_2+O_2 MIXTURES ON THE Pt/MoO_3 MODEL CATALYST

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J. Struct. Chem.,
49(2) (2008) pp. 255-260.

The effects of H_2 and $H_2 + O_2$ gas mixtures of varying composition on the state of the surface of the Pt/MoO_3 model catalyst prepared by vacuum deposition of platinum on oxidized molybdenum foil were investigated by X-ray photoelectron spectroscopy (XPS) at room temperature and a pressure of 5–150 Torr. For samples with a large Pt/Mo ratio, the XP spectrum of large platinum particles showed that the effect of hydrogen-containing mixtures on the catalyst was accompanied by the reduction of molybdenum oxide. This effect results from the activation of molecular hydrogen due to the dissociation on platinum particles and subsequent spillover of hydrogen atoms on the support. The effect was not observed at low platinum contents in the model catalyst (i.e., for small Pt particles). It is assumed for the catalyst that the loss of its hydrogen-activating ability is a consequence of the formation of platinum hydride. Possible participation of platinum hydride as intermediate in hydrogen oxidation to H_2O_2 is discussed.

USE OF THE DIFFERENTIAL CHARGING EFFECT IN XPS TO DETERMINE THE NATURE OF SURFACE COMPOUNDS RESULTING FROM THE INTERACTION OF A $Pt/BaCO_3/Al_2O_3$ MODEL CATALYST WITH NO_x

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Kinet. Catal.,
49(6) (2008) pp. 831-839.

A $Pt/BaCO_3/Al_2O_3$ model NO_x storage–reduction catalyst, which was prepared as a thin film (~100 Å) on the surface of tantalum foil, was studied by X-ray photoelectron spectroscopy (XPS). It was found that the $Pt/BaCO_3$ and Pt/Al_2O_3 catalyst constituents acquired different surface charges in the course of photoelectron emission; that is, differential charging occurred. An analysis of this effect allowed to determine the nature of the products formed in the interaction of the catalyst with a mixture of NO (260 Pa) +O_2 (2600 Pa) + H_2O (525 Pa) at 250°C followed by reduction with a mixture of CO (2100 Pa) + H_2O (525 Pa) at 450°C. It was found that barium carbonate was converted into barium nitrate as a result of reaction with NO_x on the surface of $BaCO_3$. Simultaneously, platinum supported on both $BaCO_3$ and Al_2O_3 was oxidized. The reduction of the catalyst treated with a mixture containing NO resulted in nitrate decomposition and regeneration of a carbonate coating on the surface of $BaCO_3$; this is accompanied by the reduction of oxidized platinum particles to platinum metal.

COMPARATIVE STUDY OF RUBIDIUM AND CESIUM AS PROMOTERS IN CARBON-SUPPORTED RUTHENIUM CATALYSTS FOR AMMONIA SYNTHESIS

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Catal. Lett.,
120(3-4) (2008) pp. 204-209.

Sibunit-supported Ru-catalysts promoted with cesium or rubidium compounds have been comparatively studied with XPS. The cesium promoter interacts both with support and with active component. The absence of the promoter-support interaction in the case of rubidium provides a stronger interaction between promoter and active component compared to the cesium-based catalysts. These differences in the promoter-support and promoter-metal interactions are exhibited when a sequence of ruthenium and alkali introduction are changed.

NEW OPPORTUNITIES FOR THE IDENTIFICATION OF OXIDE CLUSTERS IN SUPPORTED Ru/MgO CATALYSTS

Yu.V. Larichev, S.E. Malykhin

Kinet. Catal.,
49(4) (2008) pp. 581-586.

The Ru/MgO systems were studied using XPS, transmission electron microscopy, and X-ray diffraction analysis. It was found that from 25 to 75% of the supported metal can occur in an X-ray amorphous form with a particle size of smaller than 3 nm. The insertion of supported metal ions into the support structure was absent. A comparison between the valence band XPS spectra and the corresponding densities of states calculated by quantum-chemical methods indicated that the X-ray amorphous portion of the metal can occur as both metal and oxide clusters depending on the precursor of ruthenium.

PHOTOELECTRON STUDIES OF ADSORPTION AND CATALYSIS ON THE SURFACE OF METAL SINGLE CRYSTALS AND POLYCRYSTALS

A.I. Boronin

J. Struct. Chem.,
49 (Supplement) (2008) pp. 138-158.

The potential of photoelectron spectroscopy (XPS) and its use in studies of the state of the surface and adsorption processes on bulk metal samples (disk single crystals, polycrystalline foil and plates) are discussed. Methods for determining the electronic state of the surface layer and geometrical localization of adsorbed atoms on the metal surface using angle-resolved photoelectron spectroscopy are described. The spectrokinetic use of the dynamic mode of XPS with high accuracy and time resolution for kinetic studies of fast processes on the surface (adsorption-desorption, reconstruction, reaction, diffusion-segregation) is considered in detail.

XPS, UPS, AND STM STUDIES OF NANOSTRUCTURED CuO FILMS

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J. Struct. Chem.,
49(2) (2008) pp. 341-347.

A $Cu_1O_{1.7}$ oxide film containing a large amount of superstoichiometric oxygen was obtained by low-temperature oxidation of metallic copper in the oxygen plasma. An STM study of the film structure showed that ~10 nm planar copper oxide nanocrystallites are formed with particles packed parallel to the starting metal surface. In an XPS study, the spectral characteristics of the Cu2*p* and O1*s* lines indicated that particles with a CuO lattice formed ($E_{bnd}(Cu2p_{3/2})$ = 933.3 eV and the presence of a shake-up satellite, $E_{bnd}(O1s)$ = 529.3 eV). The additional superstoichiometric oxygen is localized at the sites of contact of nanoparticles in the interunit space and is characterized by a state with the binding energy $E_{bnd}(O1s)$ = 531.2 eV. Due to the formation of a nanostructure in the films during low-temperature plasma oxidation, the resulting copper oxide has a much lower thermal stability than crystalline oxide CuO.

CHEMICAL VAPOR DEPOSITION AND CHARACTERIZATION OF HAFNIUM OXIDE FILMS

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J. Phys. Chem. Solids,
69(2-3) (2008) pp. 685-687.

HfO_2 layers were grown on silicon by metalorganic chemical vapor deposition using $(C_5H_5)_2Hf(CH_3)_2$, $(C_5H_5)_2Hf(N(C_2H_5)_2)_2$ and $Hf(dpm)_4$ as volatile precursors and were characterized by IR, XP, ED-spectroscopy, X-ray diffraction, ellipsometry and electrophysical methods. The films were shown to consist of monoclinic HfO_2 and to contain hafnium silicide and silicate at the HfO_2/Si interface. The presence of hafnium silicide was attributed to oxygen deficiency induced by argon ion sputtering of the film during XPS analysis. Hafnium silicate was formed as a result of the reaction between hafnia and silicon oxides during annealing. Current-voltage and capacitance-voltage measurements on Al/HfO_2/Si test structures were used to determine the dielectric permittivity and electrical resistivity of the films: k = 15-20, p = $10^{15}\Omega$ cm.

COMPOSITION AND STRUCTURE OF HAFNIA FILMS ON SILICON

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Inorg. Mater.,
44(9) (2008) pp. 965-970.

Ellipsometry, electron microscopy, and X-ray photoelectron spectroscopy data indicate that, during HfO_2 deposition onto silicon, the native oxide reacts with the HfO_2 deposit to form an amorphous intermediate layer which differs in refractive index (≅1.6) from both HfO_2 (1.9–2.0) and SiO_2 (1.46). Thermodynamic analysis of the $Si–SiO_2–HfO_2–Hf$ system shows that Si is in equilibrium with Si/HfO_{2-y} only at low oxygen pressures. Starting at a certain oxygen pressure (equivalent to the formation of a native oxide layer), the equilibrium phase assemblage is $Si/HfSiO_4/HfO_{2-y}$.

PLASMA-CHEMICAL DEPOSITION OF SiCN FILMS FROM VOLATILE N-BROMHEXAMETHYLDISILAZANE

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Inorg. Mater.,
44(12) (2008) pp. 1312-1318.

Process of silicon-carbonitride (SiCN) film production from a new volatile organosilicon, N-bromhexamethyldisilazane, is developed. The use of this chemical comprising the relatively week N–Br bond makes it possible to increase the film growth velocity in the plasma-chemical process with remote plasma in comparison with the processes in which hexamethyldisilazane and hexamethylcyclotrisilazane are used. The chemical composition of the films is determined using a complex of spectroscopic methods. It is found that inorganic SiCN films containing Si–N, Si–C, and C–N bonds are deposited at temperatures 570–870 K. The C–N bonds are formed already at a temperature of about 470 K. It is shown that the use of this volatile organosilicon material makes it possible to synthesize silicon carbonitrides with various ratios of the Si–N, Si–C, and C–N bonds. This enriches the possibilities of producing films and coatings with various functional parameters. The nanohardness of 100-nm films prepared at $T > 770$ K is 17 GPa.

PHOTOLUMINESCENCE STUDY OF THE ELECTRONIC STRUCTURE OF HfO₂ FILMS

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J. Struct. Chem.,
49(1) (2008) pp. 21-30.

A method was developed for investigating hafnium dioxide films; this procedure uses a hydrogen-deuterium lamp as a source of photoluminescence (PL) excitation. Photoluminescence in HfO_2 films was investigated. An analysis of the PL spectra of the films showed that they coincided with the spectra described in the literature and recorded using more powerful sources (synchrotron radiation or ArF laser). A comparison of obtained results with the literature data confirmed that the PL spectra of the films weakly depended on the type of the substrate used for the synthesis. The PL band intensity depends on the synthetic conditions and the annealing temperature. The authors analyzed the PL and excitation spectra and revealed an emission band at an energy $E \sim 4$ eV with a narrow excitation maximum at $E_{\max} \cong 4.25$ eV, which was assigned to the vibronic resonance transition $A\ ^2\Sigma^+ \leftrightarrow X\ ^2\Pi_i$ in the OH•* excited radical. Water was detected in the PL spectra of the HfO_2 films; it is trapped as an impurity after thermal decomposition of $Hf(dpm)_4$ in the course of film growth. The detection of water in the PL spectra of these films provides new insight into the problem of the effect of this impurity on the leakage currents and the importance of control over its content in the films.

LUMINESCENCE OF THE INTRINSIC AND EXTRINSIC DEFECTS IN HAFNIA FILMS

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Phys. Rev. B: Condens. Matter,
B76(23) (2007) pp. 235315-1-23515-6.

Both intrinsic and extrinsic defects of hafnium oxide films are investigated based on photoluminescence (PL) and cathodoluminescence

(CL) measurements. Instead of using the high-power synchrotron radiation or ArF excimer laser sources, a hydrogen-deuterium lamp (HDL) was used for the PL measurements to avoid the possible generation of active oxygen and hydroxyl ions. Results show that the HDL PL spectra generally agree with those registered using the conventional high-power excitation sources. CL spectra also agree with the PL ones. Narrow emission band at peak energy of 4.0 eV, which is ascribed to the vibronic transition of excited $OH\cdot^*$ radical, was found using photoluminescence excitation and at energy of 4.25 eV.

LUMINESCENCE OF HAFNIUM DIOXIDE FILMS PRODUCED FROM HAFNIUM DIPIVALOYLMETHANATE

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Russ. Phys. J.,
50(4) (2007) pp. 374-378.

A technique is developed for measuring luminescence spectra of hafnium dioxide using a hydrogen lamp as an excitation source. The luminescence spectra of the as-grown and annealed hafnium dioxide films prepared by chemical deposition from volatile hafnium dipivaloylmethanate on the Si(111) substrates are measured at room temperature. Intense luminescence at $\lambda \sim 280$ nm is characteristic of nanocrystallites of monoclinic modification. The band gap width is found to be ~ 5.76 eV. It is shown that the film composition significantly deviates from the stoichiometric one.

EXAFS STUDY OF THE LOCAL STRUCTURE AND CATION DISTRIBUTION IN V-Mo-Nb OXIDE

T.Yu. Kardash, D.I. Kochubey, L.M. Plyasova, V.M. Bondareva

J. Struct. Chem.,
49(Supplement) (2008) pp. 116-123.

The local structure and cation distribution in Mo-Nb and V-Mo-Nb oxides with M_5O_{14} type structures, which are active in the oxidative transformations of ethane, were studied by EXAFS spectroscopy. In the amorphous (or nanocrystalline) state, the oxides have fragments of the M_5O_{14} structure in the form of stars of pentagonal MO_7 bipyramids connected with MO_6 octahedra along edges and arranged in a disordered matrix of octahedra. Possible crystallographic positions occupied by vanadium cations were revealed.

REFINEMENT OF THE CATION DISTRIBUTION IN Nb-Mo DOUBLE OXIDE

T.Yu. Kardash, L.M. Plyasova, V.M. Bondareva, A.N. Shmakov

J. Struct. Chem.,
49(4) (2008) pp. 701-707.

The structure of $Nb_2Mo_3O_{14}$ double oxide is refined from powder data using synchrotron radiation and the anomalous scattering effect; space group $P\bar{4}2_1m$ is found for the material. It is demonstrated that in the tetragonal unit cell with parameters $a = 23.173$ Å, $c = 4.0027$ Å Nb^{5+} and Mo^{6+} ions are stochastically distributed in MO_6 octahedra and MO_7 pentagonal bipyramids of the polygonal network structure of the Mo_5O_{14} type.

GENESIS OF THE ACTIVE-COMPONENT PRECURSOR IN THE SYNTHESIS OF Pt/Al_2O_3 CATALYSTS: I. TRANSFORMATION OF THE $[PtCl_6]^{2-}$ COMPLEX IN THE INTERACTION BETWEEN CHLOROPLATINIC ACID AND THE γ-Al_2O_3 SURFACE

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Kinet. Catal.,
49(5) (2008) pp. 729-736.

Gradient elution experiments have revealed the difference between platinum complexes in terms of the strength of their interaction with the alumina surface. A considerable part (30–40%) of the supported platinum is nondesorbable via competitive ion exchange reactions or upon changes in the charge state of the support surface. The surface platinum complexes can be divided into ion-exchangeable and coordinatively fixed species according to the nature of their bonding with aluminum oxide. Combining desorption and spectroscopic methods (EXAFS and diffuse reflectance spectroscopy) has made it possible to characterize the surface complexes. The strongest metal–support interaction takes place in the fixation of hydrolyzed platinum species.

INVESTIGATION OF POLYCRYSTALLINE COPPER(II) CHLORIDE–1.5-DIMETHYLTETRAZOLE COMPLEX COMPOUND WITH X-RAY ABSORPTION SPECTROSCOPY

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J. Surf. Invest. X-Ray, Synchrotron Neutron Tech., 2(4) (2008) pp. 641–645.

The polycrystalline copper(II) chloride–1.5-dimethyltetrazole ($CuCl_2L$, where L is 1.5-dimethyltetrazole) complex compound is investigated with the methods of extended X-Ray absorption fine-structure (EXAFS) and X-Ray absorption near-edge structure (XANES) spectroscopy at the *K* absorption edge. The data on the complex structure are compared to the results of X-Ray diffraction study.

THE STRUCTURE STUDY OF AMORPHOUS NANOCRYSTALLINE NANOCOMPOSITE FILMS OF GERMANIUM BY AFM AND EXAFS METHODS

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Surf. Interface Anal., 40(3-4) (2008) pp. 547-551.

Nanocomposites based on nanocrystallites in amorphous matrix of semiconductor material involved increasing interest. Such structures allow not only to avoid charge transfer between separate quantum dots by means of spatial division of elements, but also to protect nanostructures from external influences. Moreover using of an amorphous matrix enables greatly raise a quantum yield of a luminescence of nanocomposites in case of their application in light-emitting devices as formation of "environment" of the amorphous semiconductor with the large width of the band gap around nanocrystalline core. It allows to avoid non-radiating recombination of excitons on a crystallite surface. One of the main aspects of technological application of materials on the basis of semiconductor nanocomposites, is their use as new generation of nanoelectronic devices (diodes, switches) because the phenomena occurring on the amorphous semiconductor – nanocrystalline semiconductor border has undressed in many respects are similar to effects of system metal-semiconductor.

In the given work researches of structure of amorphously-nanocrystaline composite germanium films by methods of X-Ray Diffraction and EXAFS-spectroscopy are carried out. Films were obtained by a method of thermal evaporation of a material in ultrahigh vacuum. It is shown, that the nanocrystallites sizes in an amorphous matrix essentially vary depending on obtaining conditions (according to XRD-data), their percentage vary from 10 up to 90 % (according to EXAFS).

LOCAL ATOMIC STRUCTURE OF ZINC SELENIDE FILMS: EXAFS DATA

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J. Struct. Chem., 49(Supplement) (2008) pp. 124-128.

This paper presents the results of the study of the structural state and local atomic structure of zinc selenide films obtained by thermal evaporation in supervacuum at condensation temperatures of −150°C, 0, and 150°C. Structure-sensitive methods such as X-ray diffraction, atomic force microscopy, and EXAFS spectroscopy were used. The parameters of the local atomic environment (interatomic distances, coordination numbers) of zinc and selenium atoms were obtained by Fourier transformation.

INFLUENCE OF THE NUCLEARITY OF COPPER(II) CHLORIDE COMPLEXES ON THEIR ACTIVITY IN CATALYTIC C-Cl BOND METATHESIS

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Kinet. Catal., 49(5) (2008) pp. 737-742.

Catalytic systems containing mainly mononuclear ($CuCl_4^{2-}$) or dinuclear ($Cu_2Cl_6^{2-}$) tributyl-benzylammonium chlorocuprates are prepared by adsorption on silicar surfaces of different structures

(Aerosil and Silokhrom). Using ESR, XANES, and electronic spectroscopy, the $CuCl_4^{2-}$ ions are shown to be reduced rapidly under conditions of C–Cl bond metathesis, whereas the dinuclear chlorocuprates are relatively stable. A correlation between the number of copper ions in the chlorocuprate anion and its catalytic activity is established: the mononuclear complexes are several times more active than their dinuclear counterparts.

NMR STUDIES OF INTERACTIONS IN SOLUTIONS DURING THE SYNTHESIS OF MoVTeNb OXIDE CATALYSTS

R.I. Maksimovskaya, V.M. Bondareva,
G.I. Aleshina

Eur. J. Inorg. Chem.,
11(31) (2008) pp. 4906-4914.

Aqueous solutions used for the synthesis of MoVTeNb oxide catalysts have been studied using ^{125}Te, ^{95}Mo, ^{51}V and ^{17}O NMR. Polyoxometalate (POM) anion $V_9TeO_{28}^{5-}$ (**I**) of the decavanadate structure, containing Te^{6+} in one of its two central positions, has been for the first time identified in V^{V}-Te^{VI} solutions. In ternary Mo^{VI}-V^{V}-Te^{VI} solutions, the following POMs were observed: $TeMo_6O_{24}^{6-}$ (**II**) (pH ~7.8–2), previously unknown complexes of proposed compositions $TeV_3Mo_3O_{24}^{9-}$ (**III**) (pH ~ 8–5) and $TeMo_3V_5O_{27}^{5-}$ (**IV**) (pH ~ 6–1). In addition to the above complexes, VO_2^+ and MoO_2^{2+} oxalates form in the presence of oxalic acid. Upon adding niobium oxalate, Nb_2O_5 gel forms without any Nb containing species in solution.

PRACTICAL ASPECTS OF ^{51}V AND ^{93}Nb SOLID-STATE NMR SPECTROSCOPY AND APPLICATIONS TO OXIDE MATERIALS

O.B. Lapina, D.F. Khabibulin, A.A. Shubin,
V.V. Terskikh

Progr. NMR Spectr.,
53(3) (2008) pp. 128-191.

Advantages and restrictions of various solid-state NMR techniques as applied to vanadium and niobium are discussed with illustrations from a variety of vanadium and niobium containing oxide materials, including individual highly-crystalline compounds, solid solutions, glasses and catalysts. The main purpose of this work is to provide readers with the latest comprehensive compilation of ^{51}V and ^{93}Nb NMR data in oxide materials, and to demonstrate the great potential of ^{51}V and ^{93}Nb NMR in solid-state chemistry.

RADIATION-CHEMICAL SYNTHESIS OF PHOSPHORUS- AND SULFUR-CONTAINING POLYMERS

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Theor. Found. Chem. Eng.,
42(5) (2008) pp. 657-661.

Phosphorus- and sulfur-containing polymers were obtained by radiation-chemical synthesis from elementary phosphorus and sulfur in benzene. The structure and composition of the products were studied by solid-phase ^{31}P NMR spectroscopy, MALDI mass spectroscopy, and other physicochemical analytical methods. The reactivity ratios of inorganic monomers, phosphorus and sulfur, were determined.

STRUCTURAL AND REACTIVE RELEVANCE OF V+Nb COVERAGE ON ALUMINA OF V–Nb–O/Al_2O_3 CATALYTIC SYSTEMS

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J. Catal.,
255(1) (2008) pp. 94-103.

Vanadium and niobium species (together and separately) were loaded on γ-alumina, and the resulting catalysts were run in the methanol conversion. This reaction was studied by both GC analysis and FTIR study in the flow system. The catalytic properties are discussed based on the combined FTIR and ^{27}Al, ^{51}V and ^{1}H MAS NMR studies. The NMR studies revealed a different mechanism of interaction between Nb and Al_2O_3 than that between V and Al_2O_3. This predetermines the structure of vanadium sites in bimetallic VNb/Al samples. The effect of coverage was considered for various metal loadings ranging from below to above monolayer. One of the most interesting findings is that the surface Nb oxide species exhibited a redox character below monolayer but were acidic above monolayer. ^{27}Al MAS NMR revealed a strong alumina-Nb interaction that may account for its redox performance. Moreover, the role of sulfate from vanadium precursor is evidenced.

^{129}Xe NMR SPECTROSCOPY OF ADSORBED XENON: POSSIBILITES FOR EXPLORATION OF MICROPOROUS CARBON MATERIALS

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Russ. J. General Chem.,
78(11) (2008) pp. 2171-2181.

Despite the extensive use of ^{129}Xe NMR for characterization of high surface-to-volume porous solids, particularly zeolites, this method has not been widely used to explore the properties of microporous carbon materials. In this study, commercial amorphous carbons of different origin (produced from different precursors) and a series of activated carbons obtained by successive cyclic air oxidation/pyrolysis treatments of a single precursor were examined. Models of ^{129}Xe chemical shift as a function of local Xe density, mean pore size, and temperature are discussed. The virial coefficient arising from binary xenon collisions, δXe–Xe, varied linearly with the mean pore size given by N_2 adsorption analysis; δXe–Xe appeared to be a better probe of the mean pore size than the chemical shift extrapolated to zero pressure, δS.

MULTINUCLEAR MRI OF SOLIDS: FROM STRUCTURE TO TRANSPORT

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Appl. Magn. Reson.,
32(3) (2007) pp. 1-11.

Direct multinuclear imaging of rigid solids has been performed using the conventional two-pulse spin-echo pulse sequence and liquids magnetic resonance imaging (MRI) hardware. Two-dimensional ^{27}Al and ^{51}V images of an Al_2O_3-V_2O_5-glass composite sample and ^{11}B, ^{23}Na, ^{27}Al and ^{29}Si images of glass have been detected, extending the range of nuclei and solid materials that can be studied by this approach. For a spinning cylinder packed with Al_2O_3 powder, quantitative velocity maps have been obtained by directly detecting the ^{27}Al nuclear magnetic resonance signal of the solid phase. The two velocity components in the imaging plane transverse to the rotation axis have been mapped using the three-pulse stimulated echo sequence. Some possibilities to improve sensitivity in the MRI experiments on rigid solids have been considered. In particular, inversion of the satellite transitions by a double frequency sweep adiabatic passage has led to a signal enhancement by a factor of two in ^{27}Al MRI of a glass sample despite a short repetition time (0.5 s) of the imaging pulse sequence.

MONITORING TRANSPORT PHENOMENA OF PARAMAGNETIC METAL-ION COMPLEXES INSIDE CATALYST BODIES WITH MAGNETIC RESONANCE IMAGING: TUNING THE COBALT DISTRIBUTION FROM EGG-SHELL OVER EGG-WHITE AND EGG-YOLK TO UNIFORM BY THE ADDITION OF CITRATE

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Chem. Eur. J.,
14 (2008) pp. 2363-2374.

An indirect magnetic resonance imaging (MRI) method has been developed to determine in a noninvasive manner the distribution of paramagnetic Co^{2+} complexes inside Co/Al_2O_3 catalyst extrudates after impregnation with Co^{2+}/citrate solutions of different pH and citrate concentrations. UV/Vis/NIR microspectroscopic measurements were carried out simultaneously to obtain complementary information on the nature of the Co^{2+} complexes. In this way, it could be confirmed that the actual distribution of Co^{2+} inside the extrudates could be derived from the MRI images. By combining these space- and time-resolved techniques, information was obtained on both the strength and the mode of interaction between $[Co(H_2O)_6]^{2+}$ and different Co^{2+} citrate complexes with the Al_2O_3 support. Complexation of Co^{2+} by citrate was found to lead to a stronger interaction of Co with the support surface and formation of an eggshell distribution of Co^{2+} complexes after impregnation. By addition of free citrate and by changing the pH of the impregnation solution, it was possible to obtain the rather uncommon egg-yolk and egg-white distributions of Co^{2+} inside the extrudates after impregnation. In other words, by carefully altering the chemical composition and pH of the impregnation solution, the macrodistribution of Co^{2+} complexes inside catalyst extrudates could be fine-tuned from eggshell over egg white and egg yolk to uniform.

BIOPOLYMER AND WATER DYNAMICS IN MICROBIAL BIOFILM EXTRACELLULAR POLYMER SUBSTANCE

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Biomacromol.,
9(9) (2008) pp. 2322-2328.

Nuclear magnetic resonance (NMR) is a noninvasive and nondestructive tool able to access several observable quantities in biofilms such as chemical composition, diffusion, and macroscale structure and transport. Pulsed gradient spin echo (PGSE) NMR techniques were used to measure spectrally resolved biomacromolecular diffusion in biofilm biomass, extending previous research on spectrally resolved diffusion in biofilms. The dominant free water signal was nulled using an inversion recovery modification of the traditional PGSE technique in which the signal from free water is minimized in order to view the spectra of components such as the rotationally mobile carbohydrates, DNA, and proteins. Diffusion data for the major constituents obtained from each of these spectral peaks demonstrate that the biomass of the biofilm contains both a fast and slow diffusion component. The dependence of diffusion on antimicrobial and environmental challenges suggests the polymer molecular dynamics measured by NMR are a sensitive indicator of biofilm function.

THE FIRST (^{31}P, ^{17}O, AND ^{103}Rh) NMR OBSERVATION COMPLEX FORMATION OF RHODIUM(III) WITH PHOSPHORIC ACID

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Russ. J. Inorg. Chem.,
53(5) (2008) pp. 761-764.

^{31}P, ^{17}O, and ^{103}Rh NMR spectroscopy shows that rhodium(III) reacts with phosphoric acid to generate polynuclear aquaphosphate complexes in which phosphate ions mostly have a bridging function. Assignment of ^{103}Rh NMR signals in dominant rhodium complexes is suggested.

THE STATE OF Al(III) IN ALCOHOL SOLUTIONS OF ALUMINUM ALKOXIDE AS PROBED BY ^{27}Al AND ^{13}C NMR AND SMALL-ANGLE X-RAY SCATTERING

M.A. Fedotov, V.V. Molchanov, R.N. Zotov, F.V. Tuzikov

Russ. J. Inorg. Chem.,
53(10) (2008) pp. 1621-1627.

Solutions of aluminum alkoxides obtained by interaction of aluminum metal with methyl, ethyl, and isopropyl alcohols were studied by ^{27}Al and ^{13}C NMR and small-angle X-ray scattering. Alkoxides with a tetrahedral environment of aluminum prevail in methanol solutions, and those with an octahedral environment of aluminum predominate in ethanol solutions. In isopropyl alcohol at 293 K, polynuclear alkoxides with tetrahedral, octahedral, and pentacoordinated aluminum environments coexist. The structure of polynuclear complexes was refined by comparison of their calculated dimensions with small-angle X-ray scattering data.

EFFECT OF TEMPERATURE ON THE STRUCTURAL CHARACTERISTICS OF ZIRCONIUM DIOXIDE NANOPARTICLES PRODUCED UNDER CONDITIONS OF MICROWAVE TREATMENT

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Theor. Exp. Chem.,
44(3) (2008) pp. 144-149.

The effect of the sintering temperature on the structural characteristics of nanosized zirconium dioxide particles treated by microwave radiation during the drying process was investigated by small-angle X-ray scattering and the BET method. It was shown that the specific surface area, particle size, polydispersivity index, and surface and mass fractal dimensionality of zirconium dioxide depend on its heat treatment conditions.

A STUDY OF SOLID-STATE RHODIUM(III) SULFATES

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Russ. J. Coord. Chem.,
34(12) (2008) pp. 917-923.

Solid-state rhodium(III) sulfates and their aqueous solutions were examined by IR and electronic absorption spectroscopy, thermogravimetry, X-ray powder diffraction analysis, and ^{103}Rh and ^{17}O NMR spectroscopy. A study of the spontaneous aquation of freshly prepared solutions showed that this process results in an equilibrium between the subsystems of monomeric and oligomeric complexes. It was found that solid-state rhodium(III) sulfates vary in phase composition, basically consisting of dimeric and trimeric complexes.

WATER DYNAMICS IN BULK AND DISPERSED IN SILICA $CaCl_2$ HYDRATES STUDIED BY ^{2}H NMR

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J. Phys. Chem. C,
112(33) (2008) pp. 12853-12860.

The mobility of water in deuterated analogues of $CaCl_2 \times nH_2O$ (n = 2, 4, 6) hydrates has been studied by solid-state ^{2}H NMR spectroscopy. The dynamics of water molecules in the hydrates dispersed in the mesopores of silica are compared with the bulk state. Analysis of the ^{2}H NMR line shape and T_1 and T_2 relaxation times allowed to characterize the dynamics of water in a wide temperature range (120-493 K). In both crystalline and melted hydrates, the mobility of water molecules is governed by O-*D...Cl* hydrogen bonding. Both the bulk and dispersed hydrates have been found to exhibit three types of molecular motion. Two of them represent fast internal and local motions performed on a time scale of 10^{-10}-10^{-11} s. The third slow isotropic reorientation occurs on a time of 10^{-6}-10^{-7} s. The dispersed hydrates become involved in the slow isotropic motion at a temperature 50-130 K lower than the corresponding bulk hydrates. The temperature T_{NMR} at which the dispersed hydrates is involved in isotropic motion represents the melting point of the hydrates located in the silica pores. The decrease of the melting point for the dispersed hydrates is in a good accordance with Gibbs-Thompson effect for dispersed materials. In the dispersed hydrates, the water molecules reorient isotropically one order of magnitude faster in the temperature range 230-490 K, that is water is more mobile in the dispersed hydrates. The slow isotropic reorientation of water molecules is influenced by both the quantity of water in the hydrate and the dispersibility of the hydrates. In the case of the hydrate with n = 4, the activation energy of this motion decreases by *ca*. 3 times when the hydrate becomes dispersed in the silica pores.

^{1}H NMR SIGNAL BROADENING IN SPECTRA OF ALKANE MOLECULES ADSORBED ON MFI-TYPE ZEOLITES

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Solid State NMR,
33(4) (2008) pp. 65-71.

The anisotropic behavior of C_1–C_6 alkane molecules adsorbed in MFI zeolite was studied by ^{1}H nuclear magnetic resonance (NMR) using single-pulse excitation, Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence, Hahn echo (HE) pulse sequence, and magic-angle spinning. The molecular order parameter was obtained by both static ^{2}H NMR spectroscopy and molecular simulations. This yields an order parameter in the range of 0.28–0.42 for linear alkanes in MFI zeolite, whereas the parameter equals zero for FAU zeolite with a cubic symmetry. Thus, in the case of a zeolite with a non-cubic symmetry like MFI, the mobility of the molecules in one crystallite cannot fully average the dipolar interaction. As a consequence, transverse nuclear magnetization as revealed in the echo attenuation notably deviates from a mono-exponential decay. This information is of particular relevance for the performance of pulsed field gradient (PFG) NMR diffusion experiments, since the occurrence of non-exponential magnetization attenuation could be taken as an indication of the existence of different molecules or of molecules in different states of mobility.

OBSERVATION OF PARAHYDROGEN-INDUCED POLARIZATION IN HETEROGENEOUS HYDROGENATION ON SUPPORTED METAL CATALYSTS

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Angew. Chem. Int. Ed.,
47(8) (2008) pp. 1492–1495.

It was demonstrated for the first time that heterogeneous hydrogenation of an alkene (propylene) with supported metal catalysts (Pt/Al_2O_3, Pd/Al_2O_3) leads to an observation of enhanced signals in the ^{1}H NMR spectra of the reaction product (propane) when hydrogen enriched in the para-H_2 spin isomer is used in the reaction. This observation indicates that hydrogen addition occurs pairwise to a measurable extent.

TEMPERATURE EFFECTS ON THE IR SPECTRA OF CRYSTALLINE AMINO ACIDS, DIPEPTIDES, AND POLYAMINO ACIDS:
II. L-AND DL-SERINES

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J. Struct. Chem.,
49(4) (2008) pp. 627-638.

The IR spectra of L-and DL-serines H_3^+-CH(CH$_2$OH)-COO$^-$ (without diluents) were investigated in the temperature range 93–413 K; the changes in the IR spectra due to temperature variations were correlated with previously obtained diffraction data on anisotropic compression of structure and changes in the geometrical parameters of the hydrogen bonds.

STUDY OF THE TEMPERATURE EFFECT ON IR SPECTRA OF CRYSTALLINE AMINO ACIDS, DIPEPTIDS, AND POLYAMINO ACIDS:
III. α-GLYCYLGLYCINE

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J. Strut. Chem.,
49(6) (2008) pp. 1012-1021.

The IR spectra of α-glycylglycine (H_3^+N-CH$_2$-CO-NH-CH$_2$-COO$^-$) are studied in the temperature range of 93 to 413 K. Changes in the spectra due to temperature variation are correlated with the previously obtained X-ray diffraction data on anisotropic compression of the structure and changes in the parameters of hydrogen bonding. Changes in the vibrational frequencies of NH_3^+ and COO groups in the IR spectrum of α-glycylglycine are compared to changes in the vibrational frequencies of the same groups in the IR spectra of polymorphs of glycine, L- and DL-serine.

STUDY OF THE TEMPERATURE EFFECT ON IR SPECTRA OF CRYSTALLINE AMINO ACIDS, DIPEPTIDES, AND POLYAMINO ACIDS: IV. L-CYSTEINE AND DL-CYSTEINE

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E.V. Boldyreva*,** (**Novosibirsk State University, Novosibirsk, Russia; **Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia*)

J. Struct. Chem.,
49(6) (2008) pp. 1022-1034.

A study of the IR spectra of L- and DL-cysteine is carried out in a range of frequencies from 4000 cm^{-1} to 600 cm^{-1} and temperatures from 333 K to 83 K. Changes in the spectra of L- and DL-cysteine (NH_3^+CH(CH$_2$SH)-COO$^-$) on cooling are analyzed in comparison with the spectra of L- and DL-serine (NH_3^+CH(CH$_2$OH)-COO$^-$) and three polymorphs of glycine (NH_3^+CH$_2$-COO$^-$) previously studied under temperature variation. Changes in the IR spectra at variable temperatures are correlated with previously obtained diffraction data on anisotropic compression of the structure and changes in the geometric parameters of hydrogen bonds. Special attention is paid to temperature regions in which anomalies were detected by vibrational spectroscopy, X-ray diffraction, and calorimetry.

FT-IR AND FT-RAMAN SPECTRA OF FIVE POLYMORPHS OF CHLORPROPAMIDE. EXPERIMENTAL STUDY AND *ab initio* CALCULATIONS

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N.V. Chukanov, V.A. Drebushchak***** (**Institute of Solid State Chemistry, Novosibirsk, Russia; **Novosibirsk Institute of Organic Chemistry, Novosibirsk, Russia; ***Institute of Geology and Mineralogy, Novosibirsk, Russia*)

J. Mol. Struct.,
891(1-3) (2008) pp. 75-86.

IR- and Raman spectra were studied for five polymorphs of chlorpropamide (α, β, γ, δ and ε) (phase purity proved by DSC, X-ray single-crystal and powder diffraction). The equilibrium geometry and the vibrational spectra for different molecular conformations were calculated *ab initio* (DFT, B3LYP approximation). The assignment of the vibrational bands was made on the basis of the theoretical calculations and a comparison of the experimentally measured spectra for the crystalline polymorphs and the melt. The differences in the experimental vibrational spectra of the five chlorpropamide polymorphs were correlated with the X-ray structural data, and shown to be mainly due to the intermolecular interactions effect, and only to a smaller extent – to the conformational changes.

PHOTOCATALYTIC OXIDATION OF TABUN SIMULANT-DIETHYL CYANOPHOSPHATE: FTIR *IN SITU* INVESTIGATION

P.A. Kolinko, D.V. Kozlov

Environ. Sci. Technol.,
42(12) (2008) pp. 4350-4355.

Gas phase photocatalytic oxidation of diethyl cyanophosphate vapor in a static reactor using TiO$_2$

and modified TiO_2 as the photocatalyst was studied with the FTIR *in situ* method. The transition metals Pt, Au, and Ag were used for TiO_2 modification by the chemical and photochemical deposition methods as well as the mechanical mixture of TiO_2 with manganese oxide to improve its adsorption and catalytic activity. Photocatalytic oxidation of diethyl cyanophosphate in a static reactor results in its complete mineralization with carbon dioxide, phosphoric and nitric acids, and water as the major final products. HCN was demonstrated to be the only toxic gaseous intermediate of diethyl cyanophosphate photocatalytic oxidation, formed as a result of diethyl cyanophosphate hydrolysis. Diethylphosphate and acetic and formic acids were registered as the surface intermediates. It was found that cyanhydric acid is oxidized slowly with the use of unmodified TiO_2. The formation of surface cyanide complexes with Ag and Au ions could be responsible for the fast removal of HCN from the gas phase and its further photooxidation in the case of using TiO_2 with deposited Au and Ag.

ISOPROPANOL DIFFUSION AND DEHYDRATION IN ZEOLITE HZSM-5. SPECTROKINETIC STUDY

T.S. Glazneva, V.P. Shmachkova, E.A. Paukshtis

React. Kinet. Catal. Lett.,
94(1) (2008) pp. 11-20.

The isopropanol diffusion and dehydration in zeolite HZSM-5 were studied by FTIR spectroscopy. The alcohol dehydration was shown to start at the temperature above 60°C. It was found that at temperatures above 350°C, the isopropanol dehydration was limited by diffusion in the mesopores of zeolite. The method developed allows studying the kinetics of interactions of the reagent molecules with the OH-groups at the external surface of the zeolite and inside its channels.

BRØNSTED ACIDITY OF GLASS FIBER MATERIALS

T.S. Glazneva, E.A. Paukshtis

Chem. Sustain. Devel.,
16(4) (2008) pp. 473-478.

The results of investigation of acid properties of glass fiber materials by IR spectroscopy using the adsorption of ammonia, H/D exchange and isopropanol dehydration, are given. It is shown that the catalysts contain a large amount of Brönsted acid sites (BAS) with the strength comparable with that of BAS of zeolite HZSM-5. Number of BAS is proportional to Al content in the glass fiber. It is revealed that BAS are located in the bulk of the glass fiber. The centers located at up to 100 nm depth of a glass fiber are accessible for the reagent molecules of isopropanol.

SURFACE ACIDITY AND BASICITY OF OXIDE CATALYSTS: FROM AQUEOUS SUSPENSIONS TO *IN SITU* MEASUREMENTS

T.S. Glazneva, N.S. Kotsarenko, E.A. Paukshtis

Kinet. Catal.,
49(6) (2008) pp. 859–867.

The review covers the achievements of recent decades in the investigation of the acid–base properties of oxide catalyst surfaces. Both conventional and new investigation techniques are reviewed, including SSITKA for H/D exchange.

REVERSIBLE MODIFICATION OF MAGNETIC PROPERTIES OF Fe_3C NANOPARTICLES BY CHEMISORPTION OF CO

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Appl. Magn. Reson.,
33(3) (2008) pp. 285-291.

The paper is devoted to the electron spin resonance and magnetic measurements of Fe_3C nanoparticles covered by a carbon structure. There is a reversible modification of the magnetic properties by the chemisorption of CO and O_2. The CO chemisorption results in the transition of the majority of the Fe_3C nanoparticles from the ferromagnetic to the superparamagnetic state. The O_2 chemisorption results in the backward transition.

FORMATION OF DISPERSE FERROMAGNETIC NANOPARTICLES IN ZEOLITES IN THE COURSE OF THERMAL ACTIVATION IN OXYGEN

O.N. Martyanov, V.F. Yudanov

J. Struct. Chem.,
49(3) (2008) pp. 421-426.

Samples of synthetic high-silica zeolites after high-temperature activation in oxygen are studied by ferromagnetic resonance. Observation of the fine structure of ferromagnetic resonance (FMR FS) indicates the formation of magnetic iron oxide nanoparticles in the course of thermal treatment of zeolites in oxygen. Features of the formation of a dispersed ferromagnetic phase in zeolites, geometric and magnetic characteristics of constituent nanoparticles are discussed.

STEPWISE MAGNETIZATION OF DISPERSED FERROMAGNETS DUE TO MAGNETIC INTERPARTICLE INTERACTIONS

S.N. Trukhan, O.N. Martyanov, V.F. Yudanov

Phys. Solid State,
50(3) (2008) pp. 456-462.

The main features of stepwise magnetization of dispersed ferromagnets caused by magnetic interparticle interactions are studied using a two-particle model. The ranges of values of the magnetic anisotropy constants of particles and of the dipole–dipole interaction between them are determined over which a reproducible jumpwise change in the magnetization of the system occurs in an external positive magnetic field. The proposed model is shown to explain the main specific features of the fine structure of the ferromagnetic resonance spectra.

FMR FINE STRUCTURE OF DISPERSED MAGNETS. PHYSICAL ORIGIN AND APPLICATIONS

O.N. Martyanov, S.N. Trukhan, V.F. Yudanov

Appl. Magnet. Resonance,
33 (2008) pp. 57-71.

An original approach is proposed to study the dipole-dipole interparticle interactions in dispersed magnets. This is the registration and analysis of the noise-like ferromagnetic resonance fine structure (FMR FS), which is caused by the magnetic dipole-dipole interaction between magnetic domains. The peculiarities of fine structure formation are discussed. The experimental examples of the possible FS method applications are summarized.

INFLUENCE OF Pd CODEPOSITION ON THE MAGNETIC PROPERTIES OF Co PARTICLES ON ALUMINA/NiAl(110)

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J. Phys. Chem. B,
129(11) (2008) pp. 104705-104712.

Changes of the magnetic properties of ferromagnetic Co particles deposited at room temperature on a thin alumina film grown on a NiAl(110) substrate were investigated as a function of Pd coverage by subsequent deposition of Pd onto deposited Co particles. From previous X-ray photoelectron spectroscopy, IR, and temperature programmed desorption experiments it was concluded that Pd forms a shell on top of Co particles. However, the current experiments indicate that Pd does induce structural rearrangements within the Co particles which may also involve the intermixing of small amounts of Pd into the Co particles. The latter is inferred from a change in the □-value for small particles. The impact of a larger intermixture of Co and Pd on the magnetic properties will be emphasized by a reversed deposition order where Pd particles were deposited first and subsequently covered by Co. The reversal of the deposition order increases the magnetic anisotropy of the particles considerably.

PREPARATION, MICROSTRUCTURE, MAGNETIC AND TRANSPORT PROPERTIES OF BULK TEXTURED $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$ AND $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x$+Ag CERAMICS

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A.A. Dubrovskii*, S.I. Popkov*, A.D. Vasiliev*,
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Supercond. Sci. Technol.,
21(10) (2008) 105019.

A new method of preparation of bulk textured Bi2223 ceramics and Bi2223+Ag composites, based on room temperature pressing of foamed precursor (Bi2223, Bi2223+Ag) in a liquid medium, is proposed. SEM and XRD data prove a high degree of texture of the bulk samples obtained. Magnetic measurements performed in directions H || C–axis and H || a-b-planes of Bi2223 crystallites demonstrates anisotropy of magnetization confirming the texture of the ceramics. The materials obtained possess large diamagnetic response in the direction H || a-b-planes of Bi2223 crystallites at both 77.4 and 4.2 K.

FORMATION OF HOLLOW SPHERES UPON OXIDATION OF SUPPORTED COBALT NANOPARTICLES

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J. Phys. Chem. C,
112(26) (2008) pp. 9573-9578.

Oxidation of cobalt nanoparticles supported on montmorillonite was studied using transmission electron microscopy and temperature programmed reduction of the oxide particles. It has been shown that hollow shells of cobalt oxide were formed in this process, consisting of the mixture of CoO and Co_3O_4 oxides. A linear relationship between the thickness of shells and the initial particles size was established which suggests that both diffusion of cobalt ions through the oxide layer and diffusion of the oxygen into cobalt occur, but particles sintering is negligible compared with the reverse diffusion of cobalt. The lower critical diameter of cobalt particles was estimated, above which formation of hollow shells occurred. The hollow shells formation is suggested to be the reason for cobalt redispersion upon oxidation–reduction cycling of supported heterogeneous catalysts.

FORMATION OF SPHERICAL VOIDS IN THE OXIDATION OF Co NANOPARTICLES

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Russ. J. Phys. Chem. A,
82(4) (2008) pp. 690-693.

A high-resolution transmission microscopy study showed that the oxidation of Co nanoparticles deposited on montmorillonite resulted in the formation of nanoshells consisting of cobalt oxides and containing spherical voids. A linear dependence was found between the initial diameter of Co particles and the oxide shell thickness.

FORMATION OF MAGNETIC NANOCRYSTALS IN GERMANATE GLASSES DOPED WITH Fe AND Dy

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Nanotech. Russ.,
3(11-12) (2008) pp. 722-728.

Magnetic nanocomposites were synthesized from germanate glasses doped with iron and dysprosium oxides at low concentrations. The formation of nanoparticles (~5–20 nm in size) in glasses subjected to heat treatment under different conditions was observed using high-resolution electron microscopy. Nanoparticles had a well-resolved crystal structure. X-ray fluorescence microprobe analysis showed that iron and dysprosium are concentrated in particles. The examination of the field dependences of the magneto-optical effect revealed magnetic ordering in particles. A comparison of the interplanar distances obtained using electron microdiffraction with those of the known iron oxide compounds did not lead to unambiguous results. Almost all specific features in the magnetic circular dichroism spectra of the glasses corresponded to the features previously observed in the spectra of garnet ferrites. On this basis, it was assumed that the particles formed in the germanate glasses have a distorted garnet structure.

STABILIZATION OF COPPER NANOPARTICLES IN Cu-ZSM-5

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Stud. Surf. Sci. Catal.,
174A (2008) pp. 177-180.

The copper nanoparticles formed during reduction of Cu-ZSM-5 in hydrogen at temperature 150 – 400°C were studied by UV-Vis spectroscopy and HRTEM. The plasmon resonance (PR) absorption at 16000-17500 cm^{-1} was used for copper nanoparticles identification. It was shown that the chain-like and square-plain copper-oxide clusters stabilized in Cu-ZSM-5 during its preparation are the precursors of copper nanoparticles 2-10 nm.

FORMATION AND EVOLUTION OF MAGNETIC NANOPARTICLES IN BORATE GLASS SIMULTANEOUSLY DOPED WITH Fe AND Mn OXIDES

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J. Appl. Phys.,
104(10) (2008) 103917 (11 pp.).

Evolution of the phase state of paramagnetic additions at various stages of synthesis and subsequent thermal treatment of glasses of the system Al_2O_3–K_2O–B_2O_3 simultaneously doped with Fe_2O_3 and MnO is studied by means of a combination of experimental techniques: Faraday rotation (FR), electron magnetic resonance (EMR), transmission electron microscopy (TEM), Mössbauer spectroscopy, and magnetic measurements. Both FR and EMR show that magnetically ordered clusters occur already at the first stage of the glass preparation. In particular, for the ratio of the Fe and Mn oxides in the charge close to 3:2, fine magnetic nanoparticles are formed with characteristics similar to those of manganese ferrite. By computer simulating the EMR spectra at variable temperatures, a superparamagnetic nature of these nanoparticles is confirmed and their mean diameter is estimated as approximately 3.2 nm. In the thermally treated glasses larger magnetic nanoparticles are formed, giving rise to FR spectra, characteristic of magnetically ordered systems, and the EMR spectra different from those in as-prepared glasses but also showing superparamagnetic narrowing. The Mössbauer spectroscopy corroborates the manganese ferrite structure of the nanoparticles and indicates their coexistence in the ferrimagnetic and superparamagnetic states. The TEM shows the presence of polydisperse nanoparticles on the background of the glass matrix, and electron diffraction of a selected region containing larger particles indicates a crystal structure close to that of $MnFe_2O_4$. Energy-dispersive atomic X-ray spectra confirm that the major part of Fe and Mn introduced to the glass composition is gathered in the particles, with the concentration ratio close to 2:1, characteristic of bulk $MnFe_2O_4$. Magnetic hysteresis loops of samples subjected to an additional thermal treatment demonstrate a strong increase in the coercive force, remnant magnetization, and high-field magnetic susceptibility with temperature decrease. The consistent results obtained using various techniques demonstrate that the formation of nanoparticles with characteristics close to those of $MnFe_2O_4$ confers to these glasses magnetic and magneto-optical properties typical of substances possessing magnetic order.

STRUCTURE OF HETEROGENEOUS STATES IN NANOCRYSTALLINE CoPd FILMS

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Bull. Russ. Academy Sci.: Phys.,
72(10) (2008) pp. 1330-1332.

Thin films of equiatomic alloy CoPd have been produced by condensation at high substrate temperatures. The films obtained are characterized by microdiffraction patterns in the form of diffuse halo in the initial state. This is polymorphic martensitic transient state, formed during martensitic transformation of the low-temperature hcp phase to the high-temperature fcc phase. The metastable crystal structures arising in these alloy films are identified.

STRUCTURE OF GLASS SURFACES TREATED WITH THE NEW GLASS FROSTING PASTE SURFACE

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Glass Technol., *A*,
49(4) (2008) pp. 179-182.

The paper is concerned with an investigation using scanning electron microscopy (SEM) of morphologies of frosted glass surfaces produced by using a new frosting paste. The new paste produces its effect by the physical process of surface ionic exchange and does not contain hydrofluoric acid or its compounds. The frosting process occurs at a temperature similar to 300^{o}C and is characterized by the appearance of a system of microblocks (similar to 50-150 μm in size) and microcracks (similar to 100-200 nm wide) at the glass surface. The microblock boundaries are essentially smooth and the front surfaces of the blocks are smooth. The surface morphology after the metal deposition on frosted glass carried out by chemical reduction in solution is also demonstrated. In particular, silver deposition was carried out by the chemical reduction of Ag+ to metallic Ag using a silvering solution based on ammoniac silver complexes in the presence of glucose as a reducing agent. Micrographs of the surface structures obtained with chemical etching and Sand blasting are compared in this paper with those of the structures formed diving frosting by the new frosting paste. This comparison indicates that the glass surface morphology after glass frosting with the new glass frosting paste differs substantially from that obtained with well known chemical etching and sand blasting processes.

PROPERTIES OF A GLASS SURFACE MODIFIED BY A NEW FROSTING PASTE. DISPERSION OF LIGHT IN THE GLASS NEAR-SURFACE LAYER

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Glass Ceram.,
11-12 (2008) pp. 384-389.

The results of an investigation of the optical properties of a 50-μm thick glass surface layer modified by a new frosting paste are presented. The action of the paste is based on a surface ion-exchange process that results in the formation of a system of microblocks and microcracks. The size distribution function of nonuniform scattering centers and the partial depolarization of the initially linearly polarized light are examined. It is noted that the light scattering characteristics of the modified glass layer are much different from the analogous characteristics of a glass surface which is frosted by chemical etching with a fluorine-containing etchant.

PERFORATED CENOSPHERE-SUPPORTED pH-SENSITIVE SPIN PROBES

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Russ. Chem. Bull.,
57(3) (2008) pp. 493-498.

Porous supports with an accessible internal volume and a shell providing the diffusive migration of pH-sensitive spin probes were obtained for the first time from hollow aluminosilicate cenospheres isolated from the coal fly ash. Using the methods of scanning electron microscopy and electron spin resonance, the morphology of different porous cenosphere modifications and its influence on the diffusion of spin probes from the internal volume were studied. When supporting aqueous solutions of a radical, the characteristic diffusion time for the mesoporous structure of the support is longer by a factor of 3–5 than that for the macroporous structure. Ferrospinel in a content of 6 wt % do not virtually affect the diffusion rate of spin probes. A constant rate of radical migration of ~1 μmol $\min^{-1}$, determined by radical solubility in water, is achieved when a radical in the solid aggregate state is supported on the magnetic cenospheres.

ELECTRONIC FINGERPRINTING OF ADSORBED SPECIES BY MEANS OF THE SUBSTRATE CORE LEVEL EXCITATION

A.R. Cholach

In "*Chemical Reactions on Surfaces*",
Eds. J.I. Duncan, A.B. Klein,
Nova Sci. Publishers, Inc., 2008,
Ch. 8, pp. 263-287.

The conjugate electron excitation as a novel kind of electron-solid interaction was developed recently in model studies. This phenomenon enables to fingerprint the electronic valence state structure and thus to ascertain the chemical nature of adsorbed species of any complexity. It also gives potentiality to determine an exact location of adsorbed particle on the composite substrate surface. Disappearance potential spectra duly reveal another substrate electronic peculiarity such as surface and bulk plasmon excitations in addition to regular data on density of the vacant state structure. Besides, the comparison of experimental data and results of adequate quantum-chemical calculations can reveal the location of adsorbed atoms with respect to the top substrate layer, and provides reliable information on the bond nature of adsorbed species. Presented results on the whole evidence for the considerable unity of substrate and adsorbate electronic structures as an essential quality of adsorptive system.

ADVANCED POWER OF DISAPPEARANCE POTENTIAL SPECTROSCOPY IN THE ADSORBED SPECIES IDENTIFICATION

A.R. Cholach

Chem. Phys. Res. J.,
2(3-4) (2008) ch. 2, 28 pp.

Advanced power of Disappearance Potential Spectroscopy for fundamental studies of adsorption and surface reaction mechanisms at the molecular level is highlighted. Electronic peculiarities of the adsorbed species can be characterized properly from an extended spectral structure processing due to following reasons. First, because of the pronounced sensitivity of this technique to precious few top sample layers those are exactly responsible for the course of surface reaction. Second, due to availability of the novel kind of electron-solid interaction, namely the conjugate electron excitation developed recently from the model studies. The latter phenomenon consists of ordinary substrate core level excitation accompanied by electron transition from the valence state of adsorbed particle to vacuum level. This is displayed experimentally as a set of spectral satellites localized by the respective ionization potential above the Fermi level of a given substrate component

CONTROL OF PARTICLE SIZE VIA CHEMICAL COMPOSITION: STRUCTURAL AND MAGNETIC CHARACTERIZATION OF Ni-Co ALLOY NANOPARTICLES ENCAPSULATED IN LAMELLAR MIXED OXIDES

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Microporous Mesoporous Mater.,
107(1-2) (2008) pp. 202-211.

Nanoparticles of Co-Ni alloys were prepared by thermal decomposition of layered double hydroxides (LDH) containing co-intercalated complexes of two metals. The precursor compounds $[LiAl_2(OH)_6]_2\{Ni_{1-x}Co_x(EDTA)\}\cdot 4H_2O$ (where EDTA is ethylenediaminetetraacetate) obtained by anion exchange from $[LiAl_2(OH)_6]Cl\cdot 1.5H_2O$ were treated at 450 °C in vacuum. The microstructure of the thermal products was studied using local (TEM, SAED, EDX) as well as integral (XRD, SAXS) methods. It was found that Ni-Co alloy nanoparticles are formed uniformly dispersed in the carbonized matrix of lamellar mixed oxides, and the increase of the relative cobalt content in $Ni_{1-x}CO_x$ from x = 0 to 0.86 leads to gradual enlargement of the average alloy particle size from 9 to 16 nm. According to magnetic measurements by SQUID magnetometry and FMR, all alloys, except $Ni_{0.14}Co_{0.86}$, are superparamagnetic at room temperature. The results on particle size obtained by different techniques are in good agreement. The variation of nanoparticle size via chemical composition in alloys and the use of LDH intercalation matrices is a promising way to synthesize nanocomposites with target properties.

NOVEL CARBONYL COMPLEXES OF RUTHENIUM WITH α-SUBSTITUTED OXIME DERIVATIVES OF TERPENES

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Russ. J. Coord. Chem.,
34(4) (2008) pp. 286-294.

The reactions of $Ru_3(CO)_{12}$ with *1R,4S,6S*-4-dimethylamino-4,7,7-trimethylbicyclo[4.1.0]heptane-3-one oxime (dimethylaminocaraneoxime) (**I**), *1R,4S,6S*-4-methylamino-4,7,7-trimethylbicyclo [4.1.0]heptane-3-one oxime (methylaminocarane oxime) (**II**), and *1R,2R,5R*-2-benzylthio-2,6,6-trimethylbicyclo[3.1.1]heptane-3-one oxime (benzylthiopinaneoxime) (**III**) were studied. The binuclear complex $Ru_2(CO)_4\{\mu\text{-}\eta^3(O,N,X)\text{-}L\}_2$ was formed as the main product in every reaction, when $Ru_3(CO)_{12}$ was heated with terpenoid to 80°C. In the above complex, two terpene ligands are coordinated in the form of 'head-to tail' bridge by the oxime groups at a binuclear metal fragment Ru–Ru. The heteroatom of the second functional group of every bridging ligand (nitrogen of amino group in I and II, sulfur of the thio group in III) is additionally coordinated to the ruthenium atom to give the chelate five-membered ring. Also the reactions of terpenoids **I**, **II**, **III** with $Ru_3(CO)_{12}$ were performed at room temperature using Me_3NO. In this case, as in the thermal reactions, the main product was the binuclear complex. However, in the reactions of $Ru_3(CO)_{12}$ with **I** and **II**, the trinuclear clusters were isolated that readily transformed to binuclear complexes in a solution. The complexes synthesized can exist as two diastereomers due to their chiral metal core. However, in all the cases, only one diastereomer was isolated, which indicates stereospecific nature of the above reactions. The compounds obtained were characterized by IR, ^1H-, $^{13}C\{^1H\}$-, COSY, and HXCOBI-NMR spectroscopy, the specific optical rotation angles were measured. For the binuclear complexes with ligands **I**, **III** and for trinuclear cluster with ligand **II**, single crystals were obtained and studied by X-ray diffraction.

HIGH VOLUME SYNTHESIS OF SILICON NANOPOWDER BY ELECTRON BEAM ABLATION OF SILICON INGOT AT ATMOSPHERIC PRESSURE

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Jpn. J. Appl. Phys.,
47(9) (2008) pp. 7019–7022.

The evaporation of high purity silicon ingot was performed in Ar, N_2, and air atmospheres using a power electron accelerator. The obtained powders with primary particle sizes of 10-500 nm were investigated using Brunauer-Emmett-Teller analysis

(BET), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence measurement, and Raman spectroscopy. The structure and photoluminescence properties of Si(Ar) nanopowder obtained at a large quenching rate differ substantially from those of Si(Ar) and Si(N_2) obtained at a smaller quenching rate. Photoluminescence peaks in the visible region of the spectrum are detected at room temperature for the Si(Ar) nanopowders.

STOICHIOGRAPHY AND CHEMICAL METHODS OF PHASE ANALYSIS OF MULTIELEMENT MULTIPHASE SUBSTANCES AND MATERIALS

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Russ. Chem. Rev.,
77(4) (2008) pp. 351-372.

The problems and achievements in the determination of the phase composition of multielement multiphase inorganic solid substances are considered. The problems of theory, methodology and practical use of two chemical methods of phase analysis, viz., selective dissolution and reference-free stoichiographic dissolution are discussed. The unique potential of stoichiography and differential dissolution method, which allows one to overcome many limitations and difficulties typical of modern phase analysis techniques, are demonstrated. Examples of using differential dissolution for the phase analysis of diverse substances and functional materials are given.

LASER-INDUCED LUMINESCENCE OF MODEL Fe/Al_2O_3 AND Cr/Al_2O_3 CATALYSTS

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Kinet. Catal.,
49(2) (2008) pp. 291-298.

The laser-induced luminescence of Cr^{3+} impurity ions in model Fe/Al_2O_3 and Cr/Al_2O_3 catalysts with different calcination temperatures was studied. It was found that an additional luminescence band at 770 nm appeared in the luminescence spectra of low-temperature samples as a result of the interaction of octahedrally coordinated Cr^{3+} ions with Fe^{3+} impurity ions. In the θ-Al_2O_3 phase with a concentration of Cr^{3+} ions higher than 0.1 wt %, the interaction of the Cr^{3+}- Cr^{3+} ion pairs in the immediate surroundings resulted in the appearance of N θ lines due to the splitting of R θ lines. The differences of these lines from the N α lines of α-Al_2O_3 were related to the individuality of the crystal lattice of the θ phase and the coordination of Cr^{3+} impurity ions in the immediate surroundings, which is different from that in the a phase. Based on the laser-induced luminescence spectroscopic data, it was found that regions with a local Cr^{3+} concentration higher than the average Cr^{3+} concentration in the bulk of a catalyst by one order of magnitude were formed in the α-Al_2O_3-Fe_2O_3 system with the bulk Fe and Cr concentrations of 2.5 and 0.04 wt %, respectively, which was calcined at 1220°C, as a result of the diffusion of chromium and iron ions.

Fundamental and Practical Approaches to Catalyst Preparation

MECHANOCHEMICAL SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF $La_{1-x}Ba_xFeO_{3-\delta}$ ($0 \leq x \leq 1$) PEROVSKITES

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Kinet. Catal.,
49(1) (2008) pp. 133-137.

$La_{1-x}Ba_xFeO_{3-\delta}$ (x = 0–1) perovskites were prepared by the mechanical activation of mixtures of binary oxides in a centrifugal planetary ball mill for 3 min followed by calcination at 1100°C for 4 h, and their phase composition was determined by X-ray diffraction. All samples up to $x = 0.8$ are single-phase oxides with a perovskite structure. The $x = 1$ sample is a mixture of perovskite- and brownmillerite-type phases. An orthorhombic-to-cubic morphotropic transition is observed at $x = 0.3$. The catalytic activity of the perovskite samples in CO oxidation, chosen as a model reaction, depends nonmonotonically on the barium content of the catalyst. High catalytic activities are shown by the $x = 0.8$ and 0.3 samples.

LOW-TEMPERATURE SYNTHESIS AND CHARACTERIZATION OF APATITE-TYPE LANTHANUM SILICATES

T.S. Kharlamova, S.N. Pavlova, V.A. Sadykov, O.B. Lapina, D.F. Khabibulin, T.A. Krieger, V.S. Muzykantov, M.V. Chaikina*, N. Uvarov*, J. Frade, Chr. Argirusis***** (**Institute of Solid State Chemistry, Novosibirsk, Russia; **University of Aveiro, Aveiro, Portugal; ***Clausthal University of Technology, Clausthal-Zellerfeld, Germany*)

Solid State Ionics,
179(21-26) (2008) pp. 1019-1023.

Al- and Sr-doped apatite-type lanthanum silicates (ATLS) have been prepared using mechanochemical activation (MA) and Pechini (Pe) methods, with some structural and electrical properties of doped samples being studied. MA provides ATLS formation already at room temperature after 20-35 min activation. Synthesis via Pe route occurs through the solid state reaction mechanism. MA of carbonate precursors obtained via Pe method results in the fort-nation of a single-phase ATLS after annealing at 900°C. For Al-doped apatite samples fort-nation of $LaAlO_3$ as a secondary phase is observed at high substitution levels depending on the sample stoichiometry, which affects properties of ceramics obtained.

LOW-TEMPERATURE SYNTHESIS METHODS OF DOPED APATITE-TYPE LANTHANUM SILICATES

T.S. Kharlamova, S.N. Pavlova, V.A. Sadykov, M.V. Chaikina*, T.A. Krieger, O.B. Lapina, D.F. Khabibulin, N. Uvarov*, J. Frade*, Chr. Argirusis** (**Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; **University of Aveiro, Aveiro, Portugal; ***Clausthal University of Technology, Clausthal-Zellerfeld, Germany*)

J. Chem. Eng. Jpn.,
40(13) (2007) pp. 1187-1191.

Doped apatite-type lanthanum silicates (ATLS) have been prepared using mechanical activation (MA) and Pechini (Pe) methods. MA was shown to give ATLS at essentially lower temperatures in comparison with conventional solid state technique with having great effect on apatite doping. Doped samples can be easily obtained after activation even at room temperature however milling as well as temperature treatment may cause some phase separation if there is an instability in the structure. Pe method was shown to require higher temperatures to be used for the silicate apatite synthesis. However MA of carbonate precursors for some minutes was shown to favour the reduction of synthesis temperature. Both methods allow to prepare dispersed powders with better concentration homogeneity being expected for samples synthesized via Pe method.

Al-DOPED APATITE-TYPE NANOCRYSTALLINE LANTHANUM SILICATES PREPARED BY MECHANOCHEMICAL SYNTHESIS: PHASE, STRUCTURAL AND MICROSTRUCTURAL STUDY

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Eur. J. Inorg. Chem.,
6 (2008) pp. 939–947.

Al-doped $La_{9.33+x/3}+ySi_{6-x}Al_xO_{26+3y/2}$ (x = 0–1.5, y = 0–0.67) apatite-type lanthanum silicates (ATLS) were synthesized with a high-power (1200 rpm) planetary ball mill that allows the formation of the lanthanum silicate phase after milling for 20–35 min at room temperature. The apatite phase already appears after milling for 5 min. Phase, structural and microstructural studies on the nanocrystalline lanthanum silicates were carried out by using XRD, TEM, and IR, ^{27}Al and ^{29}Si MAS NMR spectroscopy to clarify the mechanism of ATLS formation. The cluster-topotactic mechanism of the formation of apatite by mechanochemical treatment involving hydration of the starting compounds and acid–base reactions is suggested. Al-doping results in promoting the formation of apatite. However, a secondary $LaAlO_3$ phase may be present in the sample depending on its stoichiometry. This suggests the existence of a biphase domain in the La_2O_3–SiO_2–Al_2O_3 phase diagram at room temperature, in which Al-doped apatite and $LaAlO_3$ phases coexist.

DESIGN AND CHARACTERIZATION OF NANOCOMPOSITES BASED ON COMPLEX PEROVSKITES AND DOPED CERIA AS ADVANCED MATERIALS FOR SOLID OXIDE FUEL CELL CATHODES AND MEMBRANES

V.A. Sadykov, T.S. Kharlamova, L.Ch. Batuev, N.V. Mezentseva, G.M. Alikina, V.S. Muzykantov, T.A. Krieger, S.N. Pavlova, V.I. Zaikovsky, A.V. Ischenko, V.I. Zarubina, V.A. Rogov, O.F. Bobrenok*, N. Uvarov, J. Kilner***, J. Druce***, A. Smirnova****** (**Institute of Thermophysics, Novosibirsk, Russia; **Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; ***Imperial College London, South Kensington, London, UK; ****University of Connecticut, Connecticut, USA*)

In "*The Hydrogen Economy*",
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Mater. Res. Soc. Symp. Proc., 1098E, Warrendale,
PA, 2008, 1098-HH07-06.

$La_{0.8}Sr_{0.2}Fe_{0.6}Ni_{0.4}O_{3-x}$-$Ce_{0.9}Gd_{0.1}O_{2-x}$ and $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-x}$-$Ce_{0.9}Gd_{0.1}O_{2-x}$ nanocomposites were synthesized via ultrasonic dispersion of nanocrystalline powders of perovskite and fluorite oxides in acetone with addition of a surfactant, followed by drying and sintering at temperatures up to 1200°C. The evolution of the structure of samples with sintering temperature was studied by XRD and TEM with EDX and compared with the data on conductivity, oxygen isotope exchange, O_2 TPD, H_2 and CH_4 TPR. Preliminary testing of buttonsize cells with cathodes supported on thin YSZ layer covering Ni/YSZ cermet demonstrated a high and stable performance of LSNF-GDC composite promising for the practical application.

ANODE COMPOSITES BASED ON NiO AND APATITE-TYPE LANTHANUM SILICATE FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

T.S. Kharlamova, S.N. Pavlova, V.A. Sadykov, T.A. Krieger, G.M. Alikina, J. Frade*, Chr. Argirusis** (**University of Aveiro, Aveiro, Portugal; **Clausthal University of Technology, Clausthal-Zellerfeld, Germany*)

In "*The Hydrogen Economy*",
Eds. B. Choudhury, A. Dillon, J. Keller, C. Moen,
Mater. Res. Soc. Symp. Proc., 1098E, Warrendale,
PA, 2008, 1098-HH07-02.

Composite materials based on NiO and doped apatite-type lanthanum silicates (ATLS) that are new class of solid electrolytes were studied as anode materials for intermediate temperature solid oxide fuel cells (IT SOFC), with possibility to use both H_2 and CH_4 as a fuel being payed attention to. For cermets preparation different methods of Ni addition such as incipient wetness impregnation, modified Pechini methods or mechanical mixing were used. The composite materials were characterized by XRD, BET, TPO and methane steam reforming reaction. Doping with complex oxides possessing a high mobility of the lattice oxygen and partial Ni substitution by the mixed conductor were applied to improve anode stability to coking.

PEROVSKITE AND COMPOSITE MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

T.S. Kharlamova, S.N. Pavlova, V.A. Sadykov, T.A. Krieger, G.M. Alikina, N.V. Mezentseva, V.S. Muzykantov, A.I. Boronin, V.I. Zaikovsky, A.V. Ischenko, V.A. Rogov, N. Uvarov*, J. Frade, Chr. Argirusis***** (**Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; **University of Aveiro, Aveiro, Portugal; ***Clausthal University of Technology, Clausthal-Zellerfeld, Germany*)

In "*Nanophase and Nanocomposite Materials V*",
Eds. S. Komarneni, K. Kaneko, J.C. Parker,
P. O'Brien,
Mater. Res. Soc. Symp. Proc.,
1056E, Warrendale, PA, 2008, 1056-HH03-64.

$La_{0.8}Sr_{0.2}Fe_{0.6}Ni_{0.4}O_{2.9}$ (LSFN) and LSFN – $La_{9.83}Si_{4.5}Fe_{1.5}O_{26}$ (LSiF) nanocomposite were synthesized and investigated as cathode materials for intermediate temperature (IT) solid oxide fuel cells (SOFC). Phase and structure evolution with sample sintering temperature as well as their transport properties and catalytic activity in oxygen reduction were studied.

FABRICATION OF COATINGS BY THE CHARGED AEROSOL DEPOSITION METHOD

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Nanotech. Russ.,
3(5-6) (2008) pp. 311-320.

A novel low-cost, effective, and environmentally friendly method is proposed for depositing porous or dense coatings from a charged aerosol (a gas-dust plasma) onto different planar substrates. The generation of dense aerosols from charged aggregates consisting of nanoparticles and their deposition are performed using devices of the electromassclassifier type. Dense nanocoatings are most efficiently produced through mechanically assisted charged aerosol deposition from powders prepared with the use of the mechanochemical method. Modifications of the new method hold considerable promise for the fabrication of multilayer membranes intended for use in the design of solid-oxide fuel cells and catalytic membrane reactors. The relative density of thin coatings fabricated from dry nanopowders at room temperature can be as high as ~70%.

DEVELOPMENT OF CATALYSTS FOR DEHYDROGENATION OF C_3-C_4 PARAFFINS USING GIBBSITE THERMAL ACTIVATION PRODUCT

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Catal. Ind.,
Special Issue (2008) pp. 13-18.

A uniform approach is considered to preparation of aluminum-chromium catalysts for dehydrogenation of light C_3-C_4 paraffins based on the use of the products of gibbsite thermal chemical activation (TCA) in an industrial flow flush-reactor and centrifugal thermal activation (CTA) at the "Tseflar" plant. Catalytic characteristics in reaction of propane and butane dehydrogenation in fluidized and fixed beds over developed microspherical and granulated samples of catalyst exceed parameters of domestic industrial catalysts and do not yield to the best important catalysts.

NICKEL CATALYSTS BASED ON POROUS NICKEL FOR METHANE STEAM REFORMING

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Kinet. Catal.,
49(3) (2008) pp. 428-434.

The influence of synthesis conditions on the phase composition and texture of porous nickel supports as plates with a magnesium oxide underlayer were investigated by X-ray diffraction, low-temperature nitrogen absorption, and electron microscopy combined with X-ray microanalysis. Nickel catalysts supported on these plates were studied. Thermal treatment of $Mg(NO_3)_2$ in nitrogen yields a magnesium oxide underlayer with a small specific surface area (support I). The replacement of nitrogen with hydrogen leads to a larger surface area (support II). The formation of MgO is accompanied by the incorporation of Ni^{2+} cations from the oxide film into the underlayer. Upon subsequent reduction with hydrogen or under the action of the reaction medium, these cations form fine crystallites of nickel. The supports having an oxide underlayer show a higher activity in methane steam reforming than the initial metallic nickel. Nickel catalysts on supports I and II show similar activities. The activity of the catalysts was stable throughout 50-h-long tests; no carbon deposits were detected by TEM.

FORMATION OF INTERMETALLIC PHASES DURING MECHANICAL ALLOYING AND ANNEALING OF Cr + 20 wt % Al MIXTURES

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Inorg. Mater.,
44(6) (2008) pp. 587-591.

Phase-formation processes in mixtures of Cr and Al (20 wt %) powders in the course of mechanical alloying (MA) and the phase transformations of the samples during subsequent annealing at temperatures of up to 800°C has been studied. The resultant X-ray amorphous intermetallic phases were identified by a differential dissolution method, which allows one to follow the formation of X-ray amorphous and partially crystallized phases. During MA of Cr + Al mixtures, the first to form is X-ray amorphous Cr_4Al, which then converts to partially crystallized Cr_2Al through reaction with aluminum. The peritectoid decomposition of Cr_4Al during heating of the MA samples is accompanied by heat release at 330–350°C. Heating to 420°C leads to the formation of Cr_5Al_8. At 800°C, Cr_5Al_8 reacts with Cr to form Cr_2Al.

REDUCTIVE ANNEALING FOR GENERATING Se DOPED 20 wt % Ru/C CATHODE CATALYSTS FOR THE OXYGEN REDUCTION REACTION

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J. Appl. Electrochem.,
37(12) (2007) pp. 1515-1522.

Reductive annealing was chosen as a method for the syntheses of Se modified Ru/C catalysts. Initial preparation of a 20 wt % Ru/C was performed by impregnating $RuCl_3 \cdot 2H_2O$ on Vulcan XC72 with subsequent conditioning using H_2 at 250°C for 4 h. Surface treatment of Ru/C by SeO_2 followed by reductive annealing produced Se modified Ru/C catalysts with a pre-determined Ru:Se = 1:0.15 and 1:1 a/o. Structural characterization was carried out using HRTEM while electrochemical characterization was performed using RDE measurements. It is concluded that the presence of Se on Ru has a positive effect on the oxygen reduction reaction of RuSe/C catalyst systems with an optimal loading of Se close to a Ru:Se ratio of 1:0.15 a/o. Overloading of selenium led to neutralization of its promoting effect.

PHYSICOCHEMICAL FEATURES OF FORMATION OF SILICATE POROUS MESOPHASES

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Russ. Chem. Bull.,
57(1) (2008) pp. 29-35.

Silicate mesoporous mesophases analogous to SBA-3 or MCM-41 with the hexagonal (honeycomb) structure can be synthesized in a moderately acidic region (pH ~ 2.5-5). The synthesis was carried out using aqueous solutions of sodium silicate and a surfactant of the alkyltrimethylammonium bromide type as the starting precursors.

STRUCTURE AND ACID-BASE PROPERTIES OF HEXAALUMINATES

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React. Kinet. Catal. Lett.,
93(2) (2008) pp. 375-386.

Hexaaluminates $SrAl_{12}O_{19}$, $BaAl_{12}O_{19}$ and $LaAl_{11}O_{18}$ were prepared by co-precipitation of soluble nitrates of Sr, Ba, or La and Al using NH_4HCO_3 as a precipitating agent with subsequent calcination at 700–1400°C. The samples were characterized by adsorption methods, thermal analysis (TA and DTG), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy of adsorbed probe molecules (CO and $CDCl_3$). It was shown that calcination at 1200°C resulted in the formation of single-phase hexaaluminates in all the samples except for $LaAl_{11}O_{18}$, where an additional phase was found. The specific surface area of the samples was obtained in the range 16–22 m^2/g. After the treatment at comparable conditions, the total concentrations of both surface Lewis acid sites and basic sites were found to increase in the series: $BaAl_{12}O_{19} < SrAl_{12}O_{19} < LaAl_{11}O_{18}$. However, the strongest basic sites were detected on the surface of $BaAl_{12}O_{19}$.

EVOLUTION OF Cu-Zn-Si OXIDE CATALYSTS IN THE COURSE OF REDUCTION AND REOXIDATION AS STUDIED BY *IN SITU* X-RAY DIFFRACTION ANALYSIS, TRANSMISSION ELECTRON MICROSCOPY, AND MAGNETIC SUSCEPTIBILITY METHODS

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Kinet. Catal.,
49(6) (2008) pp. 821-830.

The reduced and reoxidized Cu–Zn–Si oxide catalysts as layered copper–zinc hydroxo silicates with the zincsilite structure were studied using *in situ* and *ex situ* X-ray diffraction analysis, transmission electron microscopy, and the temperature dependence of magnetic susceptibility. The catalysts were prepared by homogeneous deposition–precipitation. It was found that Cu^0 particles were formed on the surface of a layered hydrosilicate with the zincsilite structure upon reduction with hydrogen. The reoxidation of the reduced samples with a mixture of oxygen and an inert gas, which contained no more than 0.05 vol % O_2, resulted in the formation of individual Cu_2O and CuO phases; copper ions did not return to the hydrosilicate structure. Catalytic tests of Cu–Zn–Si catalysts in methanol synthesis indicate that the specific catalytic activity of copper metal particles grows linearly with increasing zinc loading. This fact suggests that copper metal particles, which were obtained by the reduction of Cu^{2+} ions from the copper–zinc hydroxo silicate with the zincsilite structure, were responsible for activity in methanol synthesis. Consequently, the ability to return copper ions to a precursor compound in reoxidation with oxygen at low concentrations, which is known for reduced Cu/ZnO catalysts (these catalysts are highly active in methanol synthesis), is not related to the catalytic activity in methanol synthesis.

PREPARATION OF Pd/C CATALYSTS VIA DEPOSITION OF PALLADIUM HYDROXIDE ONTO SIBUNIT CARBON AND THEIR APPLICATION TO PARTIAL HYDROGENATION OF RAPESEED OIL

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React. Kinet. Catal. Lett.,
95(1) (2008) pp. 3-12.

Pd/Sibunit catalysts were prepared by deposition of palladium hydroxide onto the support surface in an alkaline medium. It was found that the palladium distribution throughout the catalyst grain, and the dispersion of Pd particles depend on (*i*) the order of the addition of H_2PdCl_4 and Na_2CO_3 to carbon suspension, (*ii*) Na_2CO_3 to H_2PdCl_4 ratio, and (*iii*) aging time of the mixture H_2PdCl_4 + Na_2CO_3 before its addition to the carbon. The catalysts were tested in the hydrogenation of cyclohexene and rapeseed oil under static conditions. The yield of *trans*-isomers as products of partial hydrogenation of rapeseed oil was found to decrease with decreasing the Pd particle size in the catalysts, as well as with increasing the Pd concentration on the periphery of the support grains.

INFLUENCE OF THE TEXTURE AND ACID-BASE PROPERTIES OF THE ALUMINA-CONTAINING SUPPORT ON THE FORMATION OF Co(Ni)-Mo CATALYSTS FOR DEEP HYDRODESULFURIZATION OF THE DIESEL FRACTION

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Kinet. Catal.,
49(6 (2008) pp. 791–801.

The influence of the texture of γ-Al_2O_3 on the formation of Co(Ni)–Mo catalysts for hydrodesulfurization of the diesel fraction is studied. As shown by low-temperature N_2 adsorption, X-ray diffraction, IR spectroscopy of adsorbed molecules, and high resolution electron microscopy (HREM), use of a support with a larger specific surface and a lower total concentration of terminal OH groups makes it possible to prepare more active catalysts. The electron density radial distribution method shows that the finely dispersed cobalt-containing catalyst in its initial state contains $CoMoO_4$, $Al_2(MoO_4)_3$ and $CoAl_2O_4$, the last two phases being present in trace amounts. After the reaction, this catalyst contains cobalt-doped molybdenum sulfide. According to HREM data, the active phase of the cobalt-containing catalyst consists of layered sulfide association species $Co_{1.3}Mo_2S_{3.3}$, which differ in composition from the bulk phase $CoMo_2S_4$. It is assumed that, out of the 1.3 cobalt atoms in $Co_{1.3}Mo_2S_{3.3}$ 0.3Co occurs at the edges of the association species and 1.0 Co is intercalated into their interlayer space, and 0.7 S at the boundary between the association species and the Al_2O_3 phase is replaced by the corresponding amount of oxygen.

COMBINATORIAL APPROACH TO THE PREPARATION AND CHARACTERIZATION OF CATALYSTS FOR BIOMASS STEAM REFORMING INTO SYNGAS

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Catal. Today,
137(1) (2008) pp. 23-28.

A number of catalysts based on Al_2O_3 loaded with doped Ce-Zr mixed oxides and different active components (Cu, Cu-Ni, Ru, Pt, etc.) were synthesized via standard wet impregnation method using the robotic workstation. Ethanol (EtOH) was taken as a model compound of bio-oil and steam reforming of ethanol (ESR) as a model reaction. Activity screening experiments performed at 600–700°C in 0.5 vol % C_2H_5OH + 2.5 vol % H_2O + 97 vol % He mixture revealed that the most effective catalyst composition is $Ru/Ce_{0.4}Zr_{0.4}Sm_{0.2}/Al_2O_3$. Catalytic activity investigations at high reagent concentrations (10 vol % C_2H_5OH + 40 vol % H_2O + 50 vol % N_2) at 650–800°C confirmed this fact, revealing also that at high temperatures the activity of Cu-Ni catalysts is comparable with that of Ru-containing catalyst.

HYDROGEN PRODUCTION BY STEAM REFORMING OF METHANOL OVER Cu–CeZrYO$_x$-BASED CATALYSTS

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Catal. Today,
138(3-4) (2008) pp. 175-182.

Active and selective $Cu_x(CeZrY)_{1-x}O_y$ catalysts (pure and with addition of Al_2O_3 and Cr) for the steam reforming of methanol were synthesized via the urea–nitrate combustion method. Structural, surface and redox characteristics of these catalysts were investigated by XRD, BET, IR spectroscopy, differential dissolution, H_2-TPR and XPS methods. It was shown that addition of alumina and Cr leads to the steep increase in H_2 production due to appearance of highly dispersed copper species and stabilizes their activity. The parallel change of SRM rate constants and maximal rates of reduction with hydrogen characterizing mobility of lattice oxygen at variation of the catalyst composition was revealed that shows the importance of lattice oxygen mobility for steam reforming of methanol.

SPECIFIC FEATURES OF THE DEFECT STRUCTURE OF METASTABLE NANODISPERSE CERIA, ZIRCONIA, AND RELATED MATERIALS

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Kinet. Catal.,
49(6) (2008) pp. 840–858.

Models of the defect structure and microstructure of the CeO_2, ZrO_2, Ce–Me^1–O (Me^1 = La, Sm, Zr), and Zr–Me^2–O (Me^2 = Ca, Sr, Ba) nanomaterials are discussed. For ceria-based fluorite, the appearance of weakly bound oxygen and the mobility of bulk oxygen are due to distortions in the Ce–O coordination sphere and the appearance of interstitial oxygen atoms. For pure and doped zirconia, the phases forming in the intermediate temperature range are characterized by metastable structural networks differing from those observed in the equilibrium phases. The change in the local environment of the Zr cations (eight-atom coordination sphere) from a square antiprism in the initial salts to a distorted fluorite-like polyhedron in zirconia and the principle of structural conformity between hydrolyzed cations and the terminal hydroxyls of the Zr complexes in solution are the factors determining the genesis and structural features of the metastable phases. The defect structure and microstructure of the complex fluorite-like oxides have an effect on the state of the supported active component, favoring the formation of clustered species in the vicinity of extended defects in the support. Some examples of this effect in different types of reactions are provided.

ADSORPTION PROPERTIES OF ALUMINA-ALUMINUM CERMETS PREPARED IN THE ALUMINUM POWDER REACTION WITH WATER IN THE PRESENCE OF SURFACTANTS

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Prot. Met. Phys. Chem. Surf.,
44(4) (2008) pp. 382-385.

By a method of low-temperature nitrogen adsorption-desorption at the gas/solid interface, the trends in the adsorption and capillary-condensation properties of Al_2O_3/Al composites are studied as a function of the way of conjugate stages, namely, the metal hydrothermal oxidation and the replication of colloidal aluminum hydroxide by surfactants of the anionic, cationic, and non-ionogenic types.

SIZE EFFECTS IN CATALYSIS BY SUPPORTED METAL NANOPARTICLES

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Catal. Ind.,
Special Issue (2008) pp. 44-55.

The article presents the results of studies on size effects in low-temperature CO oxidation over $Au/\gamma\text{-}Al_2O_3$ и $Au/\delta\text{-}Al_2O_3$ catalysts and complete methane oxidation over $Pt/\gamma\text{-}Al_2O_3$ catalysts. For preparation of Au catalysts four methods (ionic adsorption, deposition-precipitation, liquid-phase chemical grafting and chemical vapor deposition) were tested. Platinum catalysts were prepared by impregnation of alumina with aqueous $H_2[Pt(OH)_6]$ solutions that contained, depending on preparation conditions, mono- or oligonuclear platinum hydroxycomplexes. Series of catalysts with narrow metal particle size distribution and average particle size varying from 0.5-1 to 20-25 nm were prepared and tested. It is shown that over the catalysts studied, the turnover frequencies of CO and CH_4 oxidation sharply increase with the decrease in Au or Pt particle size. The maximum catalytic activity is observed for supported metal particles of 2-3 nm in diameter. The data obtained demonstrate good prospects of nanosized Au and Pt catalysts as applied for combustion of CO contained in household air and diesel exhaust, methane utilization and energy production processes based on the burning of natural gas, as well.

A METHOD TO OBTAIN A HIGH LOADING OF NANO-SIZED Pt PARTICLES ON CARBON SUPPORT WITH A LOW SURFACE AREA

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Carbon,
46(3) (2008) pp. 549-552.

The use of Pt (IV) nitrate as a precursor to highly dispersed Pt particles on a carbon support has been evaluated. Platelet and herringbone-like carbon nanofibers (CNFs) with BET surface areas of 250 and 105 m^2/g have been used as the catalyst support, and preparations of Pt/C samples were carried out via impregnation of the supports with solution of $H_2Pt(OH)_6$ in conc. HNO_3, followed by evaporation of the solvent and reduction with hydrogen. Nitrogen adsorption/desorption data and TPD (CO, CO_2) have shown that treatment of CNFs with conc. HNO_3 has little effect on their texture but increases greatly the concentration of the surface oxygen groups. TEM showed presence of isolated Pt particles in the nitrate-derived catalysts even at a high Pt loading (25-30 wt %) but aggregated ones (clusters) in Pt/C samples prepared for comparison by hydrolysis method from H_2PtCl_6. Both TEM and CO chemisorption witnessed for resistance of Pt particles to sintering (e.g., $\langle d_n \rangle$ 2.7 nm, $\langle d_s \rangle$ 4.0 nm, and dispersion 27% after treatment of 25%Pt/C at 525°C, in H_2). Factors influencing the state of the metal and conditions enabling one to achieve the highest dispersions with the given method are discussed.

DEVELOPMENT OF CATALYSTS FOR HYDROGEN GENERATION FROM HYDRIDE COMPOUNDS

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Catal. Today,
138(3-4) (2008) pp. 253-259.

Catalytic hydrolysis of $NaBH_4$ and NH_3BH_3 has been studied. It was shown that the nature of the support and the active component of the catalyst affect the H_2 generation rate. Despite similar sizes of rhodium particles formed on the surface of different supports ($\gamma\text{-}Al_2O_3$, TiO_2, carbon), their reactivity is different. Rh/TiO_2 with low rhodium concentration (1 wt %) is the most active catalyst both in the hydrolysis of $NaBH_4$ and NH_3BH_3. The obtained results show that the rhodium chloride interaction with titania determines the reactivity of rhodium particles formed under action of $NaBH_4$ medium. TEM, DRS UV–vis and XPS were used to characterize the catalysts.

DEVELOPMENT OF THE METHOD FOR PREPARATION OF NANOSIZED PLATINUM GROUP METAL PARTICLES ON THE SURFACE OF CARRIER WITH THE AIM TO OBTAIN THE CATALYSTS FOR PORTABLE HYDROGEN GENERATORS BASED ON HYDROLYSIS OF SODIUM BOROHYDRIDE

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Vestnik of the Lomonosov Moscow Institute of Fine Chemical Technology,
3 (2008) pp. 64-71.

A method for deliberate synthesis of platinum group metal nanoparticles on the support surface was developed. The aim was to create active and stable catalysts for portable hydrogen generators based on hydrolysis of sodium boron hydride. From the results obtained, the process of Rh/TiO_2 catalyst preparation should include the following steps: incipient wetness impregnation of the support with the solution of the active component precursor, calcining at 300 °C, and reduction in the reaction medium of sodium boron hydride. The avoidance of the traditional step of high-temperature reduction of the catalytic composition with hydrogen allowed the preparation procedure to be simplified and nanodisperse metal particles to be obtained on the support surface, which are slightly increase in size with an increase in the metal loading in the catalyst.

VANADIUM-TITANIUM OXIDES: SOL-GEL SYNTHESIS AND CATALYTIC PROPERTIES IN CHLOROBENZENE OXIDATION

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Kinet. Catal.,
49(3) (2008) pp. 446-450.

Vanadium–titanium mixed oxides with V/Ti = 0.025, 0.050, and 0.100 have been synthesized by sol–gel processing. The anatase–rutile transition temperature decreases from 750 to 600°C as the vanadium content of the TiO_2 phase is increased. The most important texture parameters and the photoelectron and IR spectra of the oxides are reported. The oxides exhibit high catalytic activity in chlorobenzene oxidation, which is due to their specific electronic and crystal structures.

DISTRIBUTION OF THE COBALT-CONTAINING COMPONENT IN THE PORE SPACE OF HZSM-5 UPON A POSTSYNTHETIC MODIFICATION OF THE ZEOLITE WITH HYDROXO COMPOUNDS OF Co^{2+}

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Kinet. Catal.,
49(2) (2008) pp. 285-290.

The distribution of the cobalt-containing modifying component in the pore space of zeolite HZSM-5 depending on the total cobalt content of the samples (0.5–5.0 wt %) was quantitatively studied for the first time. At cobalt concentrations to 3.0 wt %, the cobalt-containing modifying component mainly occurred as isolated Co^{2+}_{Oh} ions in the micropores (channels) of HZSM-5 at the ion-exchange positions of the zeolite and in one-dimensional CoO and $CoAl_2O_4$ nanoclusters. A further increase in the cobalt concentration to 5.0 wt % resulted, in addition to the filling of micropores, in the partial filling of the mesopore space of the zeolite with a small amount of three-dimensional CoO and $CoAl_2O_4$ nanoparticles. Using sorption data and electronic diffuse reflectance spectra, the authors were the first to find that the effective density of a cobalt-containing modifying component in the pore space of a zeolite matrix was lower than the density of a bulk CoO phase by a factor of 6.

ISOBUTANE/BUTENE ALKYLATION ON SULFATED ALUMINA: INFLUENCE OF SULFATION CONDITION ON TEXTURAL, STRUCTURAL AND CATALYTIC PROPERTIES

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Appl. Catal., *A*,
344(1) (2008) pp. 107-113.

Samples of sulfated alumina with different sulfate contents were prepared by treatment of γ-alumina with an aqueous solution of a sulfate precursor (sulfuric acid or ammonium sulfate). Under conditions where no catalyst deactivation was observed, it was found that yield of C_{5+} products as well as C_5–C_7 products selectivity increase as the sulfate content increases up to 23 wt % and remain practically constant with further increase in sulfate content. Catalysts deactivation was studied at higher olefin WHSV and lower isoparaffin/olefin ratio in the feed. Increasing the sulfate content up to 14 wt % led to an increase in activity. A reduction in activity was observed when the sulfate content increased further. Samples with similar sulfate content obtained from different sulfate precursors exhibited similar butenes conversion and product distributions under both conditions. The differences in texture of sulfated alumina catalysts prepared from different sources of sulfate were determined by nitrogen adsorption. Different sulfate species, the formation of which is influenced by the source and sulfate content, were detected by DTG. Formation of sulfate-containing phases on the samples with sulfate content of more than 8 wt % was found by X-ray diffraction (XRD). The appearance of these phases resulted in a significant drop in surface area and pore volume.

THE ACTIVATION OF HETEROGENEOUS FENTON-TYPE CATALYST Fe-MFI

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Catal. Commun.,
9(3) (2008) pp. 381-385.

The activation of iron-containing zeolite of MFI structure with mineral and carboxylic acids in heterogeneous Fenton reaction was experimentally studied. The catalytic activity of the zeolite was tested in the hydrogen peroxide decomposition reaction. The activation effect of acids was observed in the following decreasing order: oxalic > acetic > hydrochloric > formic. The catalyst pre-treatment with nitric acid was ineffective. Optimum conditions for the most effective pretreatment of the zeolite with aqueous oxalic acid solutions were established.

STRUCTURAL PECULIARITIES OF COMPLEX OXIDE CeO_2 BASED SYSTEMS PROMISING FOR CATALYSIS

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Vestnik BGU,
ser. 2: Chemistry, Biology, Geography,
2 (2008) pp. 8-12.

Catalysts $Ce_{0.9}Sm_{0.1}O_{2-\delta}$, $Ce_{0.45}Zr_{0.45}La_{0.1}O_{2-\delta}$ and $Zr_{0.5}Ce_{0.5}O_{2-\delta}/\gamma\text{-}Al_2O_3$ were obtained by thermal treatment of xerogels of co-precipitated hydroxides. The structural characteristics and some properties of the developed catalysts were compared. The processes of structure formation during thermal treatment of the precipitates and xerogels were considered to show that the precipitate-to-sol transformation results in deceleration of the process of oxide system crystallization on calcining, in an increase in the dispersion and specific surface area and in a considerable increase in the concentration of defects, mainly that of Ce^{3+}, as well as in the improvement of the thermal stability of the phase structural stability of the oxide materials.

EFFECT OF THE BASIC SURFACE SITES OF CARBONS ON THE DEGREE OF DISPERSION OF PLATINUM CATALYSTS PREPARED BY H_2PtCl_6 ADSORPTION

A.N. Kholodovich, P.A. Simonov, R.I. Kvon,
A.V. Bukhtiyarov, V.I. Zaikovsky,
Yu.A. Chesalov, A.V. Romanenko

Kinet. Catal.,
49(6) (2008) pp. 886-892.

In the synthesis of Pt/C catalysts via H_2PtCl_6 adsorption onto a carbon support, NH_4Cl can be formed catalytically during the reduction of the precursor with H_2 at 250°C. This compound favors the sintering of metal particles. This effect is likely due to the weakening of metal–support bonding because of NH_4Cl adsorption on the Pt surface. The sources of nitrogen and chlorine atoms are basic surface sites of the support, which contain nitrogen atoms in their structure and adsorb Cl–ions from the precursor solution. This effect is typical of active carbons, whose surface contains chemically bound nitrogen as amino groups, and weakens as the Pt/N atomic ratio in the supported catalyst precursors is increased.

HETEROGENEOUS SELECTIVE OXIDATION OF FORMALDEHYDE TO FORMIC ACID ON V/Ti OXIDE CATALYSTS: THE ROLE OF VANADIA SPECIES

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E.V. Semionova, Yu.A. Chesalov, L.S. Dovlitova,
V.A. Rogov, V.N. Parmon

J. Mol. Catal. A: Chem.,
283(1) (2008) pp. 146-152.

The present work deals with the study of the role of vanadium species in the V/Ti-supported oxide catalysts for the oxidation of formaldehyde to formic acid. Two different series of catalysts were prepared, the first one consisting of catalysts of composition 20 wt % V_2O_5/80 wt % TiO_2 calcined at 400 and 450°C (series 1), and the second one was prepared by washing of series 1 samples with nitric acid (series 2). All the samples were characterized by XRD, IR spectroscopy, temperature-programmed reduction with H_2, and differential dissolution methods. In the catalysts of series 1, vanadium is represented by both monolayer species (monomeric and polymeric VO_x) and V_2O_5 phase in crystalline or X-ray amorphous state, depending on the calcination temperature. Washing the samples of series I with nitric acid removes the V_2O_5 phase, and the samples of series 2 contain only monolayer vanadium species. The monolayer vanadia-titania catalysts are highly active in the formaldehyde oxidation to formic acid, while crystalline and amorphous V_2O_5 exhibit a low activity in that reaction. Moreover, the presence of the V_2O_5 phase blocks the catalyst active sites and thus decreases the catalyst activity. The monolayer vanadium species are easier to be reduced by H_2 as compared to bulk V_2O_5.

RHEOLOGICAL PROPERTIES OF CATALYST PASTES OF BLOCK CATALYST IC-42-1 DEPENDING ON PREPARATION CONDITIONS

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Catal. Ind.,
5 (2008) pp. 41-49.

With the purpose of technology improvement authors studied rheological properties of plastic catalyst masses of block honeycomb catalyst IC-42-1 produced by mixture of α-iron oxide, a pseudoboehmite-containing binding agent (of various preparation ways) and water solutions of acetic acid, ethylene glycol and surface active agents. It is shown that rheological characteristics of formed pastes depend on an initial raw materials preparation way, humidity of the paste and its ageing in a hermetically sealed container before formation. It was found that qualitative (with a minimum number of defects) blocks were produced from pastes of the first or the second structural-mechanical types (SMT) characterized by dominating development of slow elastic deformations. It is shown that change of humidity even by 1% concerning optimum one leads during block forming to change of the paste SMT: to formation of "dragon tooth" defects (a drier paste) or wrinkling (a more damp paste). It is recommended to use in catalyst preparation technology a stage of daily paste ageing in a hermetically sealed container before formation.

OXIDE COPPER-CERIUM CATALYST ON ZIRCONIUM DIOXIDE FOR SELECTIVE OXIDATION OF CARBON MONOXIDE IN HYDROGEN

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Catal. Ind.,
2 (2008) pp. 13-19.

Catalytic properties of copper-cerium oxide catalysts with various ratious of active components supported on commercial monoclinic zirconium dioxide have been studied in order to create an effective catalyst for hydrogen purification from carbon monoxide by its preferential oxidation. It is shown that CO conversion in hydrogen-containing mixtures increases with the increase of cerium oxide content in the catalyst; the highest selectivity of catalyst is observed upon copper content 5-10% by weight. It is established that at 1,5 oxygen excess in gas mixtures in comparison with stoichiometry for CO oxidation (2 % CO, 1.5 % O_2, 96.5 % H_2), the optimum composition of catalyst corresponds to 10 % Cu-23 % CeO_2/ZrO_2. Commercial zirconium dioxide can be recommended as a promising carrier for oxide copper-cerium catalysts for hydrogen-containing mixture treatment from CO by its preferential oxidation under atmospheric pressure, temperature 100°C and rate of volume flow exceeding 12000 h^{-1}.

HIGH-SHRINKAGE-POTENTIAL POROUS GLASS-CERAMIC SUPPORTS FOR HIGH-TEMPERATURE OXIDE CERAMIC MEMBRANES

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Inorg. Mater.,
44(10) (2008) pp. 1130-1134.

The authors have optimized the composition of porous glass-ceramic supports compatible with conducting ceramics and have developed a procedure for the fabrication of such supports. High-shrinkage-potential porous supports in the form of dead-end tubes have been shown to be best suited for designing multilayered selective ceramic membranes. The authors have assessed the effects of various modifiers on the shrinkage curve of such supports. The factors that play a central role in determining the properties of supports have been identified: the amount of burnout additives determines the macroporosity, the addition of low-melting clay influences the shrinkage potential, leaching influences the microporosity, impregnation with a lanthanum salt determines the shape of the shrinkage curve and reactivity, and modification with Al_2O_3 sol determines the heat resistance of the supports.

HOFMEISTER ANION EFFECT ON THE FORMATION OF ZEOLITE BETA

A.V. Toktarev, G.V. Echevsky

Stud. Surf. Sci. Catal.,
174A (2008) pp. 167-172.

Influence of the anion X nature in tetraethylammonium compound $[N(C_2H_5)_4]X$ used as SDA in the non-seeded SiO_2 - A_2O_3 - Na_2O - $[N(C_2H_5)_4]X$ - H_2O reacting system on Beta zeolite formation selectivity was investigated. On the base of crystallization product phase composition as a function of synthesis time, the studied series of anions may be arranged in the following sequence: F^-, $SO_4^{2'}$, $PO_4^{3'}$, $(CH_2COO)_2^{2-}$> HCOO > $(COO)_2^{2-}$, CH_3COO <>>> Cl^- ~ NO_3^-<>>> Br^- <>>> I^- <>>> ClO_4^- with decreasing zeolite Beta-formation potency from left to right. Particularly, F', SO_4^{2-}, PO_4^{3-} and succinate anions facilitate formation of Beta zeolite in a wide range of the reaction gel chemical composition, while ClO_4^- I^-, Br anions prevent the zeolite crystallization. It was experimentally showed that zeolite-promoting anions allow to crystallize Beta zeolite in the same wide range of Si/Al composition as it is in TEAOH system, as well as to synthesize the substituted versions of Beta zeolite. The found sequence generally coincides with the well-known Hofmeister series of anions.

Carbon and Carbon Related Materials

SORBENTS AND SUPPORTS BASED ON NANOPOROUS CARBON XEROGELS

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Kinet. Catal.,
49(5) (2008) pp. 702-707.

The physicochemical properties of nanoporous carbon materials (TUMaNs) prepared by the carbonization of porous phenol–formaldehyde resin were studied. According to high-resolution electron microscopic data, these materials are nanographites composed of 5- to 10-μm globules, which form chaotically arranged microblocks 3–4 graphene layers in thickness. The materials have a developed system of 1.5 to 3.0 nm micropores and a specific surface area of 450–700 m^2/g. According to X-ray diffraction analysis, the samples consisted of strongly disordered graphite with uniquely large interlayer distances of 0.375–0.390 nm. The sorption properties of TUMaN toward hydrogen and light hydrocarbons were studied. The amount of absorbed hydrogen was higher than analogous values for materials with comparable or even larger specific surface areas. With respect to the sorption of light hydrocarbons, the properties of TUMaN were similar to those of silica and alumina. Nickel supported on TUMaN exhibited an unusually high activity and selectivity in butadiene hydrogenation to butenes. Palladium on TUMaN was highly effective in the hydrofining of ethylene for the removal of acetylene impurities.

PRODUCTION OF NANO-SIZE CARBON FILAMENTS BY CARBIDE CYCLE MECHANISM

I.V. Mishakov, R.A. Buyanov, V.V. Chesnokov,
I.A. Streltsov, A.A. Vedyagin

Catal. Ind.,
2 (2008) pp. 26-30.

The pilot plant with rotary reactor and the technology of nano carbon filaments synthesis (capacity 1-1.5 ton/year) is described. The suggested design and technology stipulate special features of the process, in which the initial volume of the catalyst grows by dozens times due to the formation of carbon phase. Conditions and technological parameters of obtaining carbon filaments with coaxial-conic and stack-like structure have been revealed.

CATALYTIC SYNTHESIS OF NANOSIZED FEATHERY CARBON STRUCTURES VIA THE CARBIDE CYCLE MECHANISM

I.V. Mishakov, R.A. Buyanov, V.I. Zaikovsky,
I.A. Streltsov, A.A. Vedyagin

Kinet. Catal.,
49(6) (2008) pp. 868-872.

The morphology of carbon nanostructures obtained by 1,2-dichloroethane decomposition on the 90% Ni/Al_2O_3 catalyst under different reaction conditions was studied by high-resolution transmission electron microscopy. A new carbon product was discovered, which received the name of feathery carbon. The product has an extremely loose disordered structure consisting of separate fragments of a graphite-like phase. The structural disordering is assumed to be caused by the variation of chlorohydrocarbon decomposition conditions on the frontal face of the metal particle. This changes the character of carbon atom diffusion from the frontal face to the backside face of the nickel particles and finally results in a feathery morphology of the carbon phase. The specific surface area of feathery carbon is 300–400 m^2/g.

DOUBLE LAYER SUPERCAPACITOR PROPERTIES OF ONION-LIKE CARBON MATERIALS

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Phys. Status Solidi B, 245(10) (2008) pp. 2296-2299.

This paper describes the electrochemical performance of carbon onions as electrode materials in electrical double layer capacitors with water electrolytes. Onion-like carbon (OLC) species were produced by vacuum annealing of detonation nanodiamonds (NDs) powder at 1170-2170 K. The material capability of the charge accumulation in the electric double layer was estimated using the voltammetric technique. The correlations between specific capacitance, surface area and conductivity were found. Charge-discharge measurements revealed a dependence of the specific capacitance of OLC on the degree of diamond particle graphitization and defectness of particle surfaces. Promising capacitance values, ranging within 20-40 F g^{-1} and within 70-100 F g^{-1} were found for the OLC materials operating respectively in acid electrolytic solution (1 M H_2SO_4) and alkaline electrolytic solution (6 M KOH).

INFLUENCE OF GAMMA IRRADIATION ON ELECTROPHYSICAL PROPERTIES OF ONION-LIKE CARBON

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J. Optoelectron. Adv. Mater., 10(7) (2008) pp. 1745-1748.

Temperature dependence of the conductivity of onion-like carbon (OLC) was investigated before and after gamma irradiation. It is found that the temperature dependence of the conductivity is described by the mechanism of variable range hopping conductivity (VRHC). The density of states on Fermi level N(E-F) is estimated on slope angle of curves δ(T) in coordinates ln[δ (T)/δ 293] - T-1/2. The gamma irradiation leads to the increase N(E-F) for OLC prepared by vacuum annealing of nanodiamond (ND) particles at temperatures 1400 K, 1650 K and to the decrease N(EF) for OLC produced by the annealing ND at temperatures 1850 K.

INFLUENCE OF GASES ON CONDUCTIVITY OF ONION-LIKE CARBON AND MULTIWALLED CARBON NANOTUBES

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J. Optoelectron. Adv. Mater., 10(7) (2008) pp. 1749-1753.

Temperature dependences of the conductivity of onion-like carbon (OLC) and catalytic multiwalled carbon nanotubes (MWNTs) were measured in various gas environments: helium, hydrogen, oxygen, air, methane. It has been found that in the vicinity of the melting and vaporization temperatures of oxygen and methane the conductivity sharply decreases for MWNTs (by 2-12%) and for OLC (by 4-12%). The observed reversible changes of the conductivity of investigated samples are discussed in the terms of processes of gases adsorption-desorption on the surface of nanotubes and OLC and breakup-recovery of contacts between nanotubes and particles of OLC as a result of melting and vaporization of environment gases.

CONTROLLABLE ELECTROMAGNETIC RESPONSE OF ONION-LIKE CARBON BASED MATERIALS

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Phys. Status Solidi B, 245(10) (2008) pp. 2051-2054.

Electromagnetic response of onion-like carbon (OLC) powders with variable ratio of decreasing in size diamond core and defective curved graphitic shells (sp^2/sp^3 nanocomposites) in Kα-band (26-37 GHz) is discussed. sp^2/sp^3 ratio in OLC was regulated by increasing of annealing temperature of explosive nanodiamond (ND) using as initial product. The observed one dimensional variable range hopping conductivity (4-300 K) combined with HR TEM data was attributed to the formation of variable length ribbon-like defective graphene scales. The increase of ND annealing temperature results in the increase of density states of conductive electrons and corresponding increase of conductivity of OLC produced. The increase of conductivity of OLC provides the increase of EM wave attenuation ability along with light increase of reflecting ability.

TERAHERTZ PROBING OF ONION-LIKE CARBON-PMMA COMPOSITE FILMS

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Diamond Relat. Mater.,
17(7-10) (2008) pp. 1608-1612.

Recently, superior electromagnetic attenuation of some types of onion-like carbon (OLC) in comparison to other carbon materials was reported, demonstrating a promising high potential of OLC for the design of electromagnetic shielding materials over a broad microwave (2−38 GHz) frequency range. This communication presents the first study of spectral features of OLC-polymethyl methacrylate (PMMA) composite films in the terahertz frequencies up to 3 THz, where the search of new operational materials and components is of particular importance for various promising applications.

ONION-LIKE CARBON FOR TERAHERTZ ELECTROMAGNETIC SHIELDING

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Diamond Relat. Mater.,
17(4-5) (2008) pp. 462-466.

It is demonstrated that onion-like carbon (OLC) provides efficient attenuation of the electromagnetic spectrum over the wavelength range 12–230 THz as compared to detonation nanodiamonds (DND) at similar or higher concentrations. Some characteristics of OLC important for the processing of polymer composites such as surface functional groups, zeta-potentials and agglomerate sizes are reported.

DETONATION NANODIAMOND AND ONION-LIKE CARBON: APPLICATIONS IN COMPOSITES

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Phys. Status Solidi A,
205(9) (2008) pp. 2245–2251.

Several properties and envisioned related applications in structural and functional composites of nanodiamond (ND) and their derivatives, onion-like carbon (OLC) are reported. The electromagnetic radiation shielding properties of the OLC-polyurethane composites had been characterized in the 120-165 GHz spectral range for 1-15 wt % OLC loading. It was also demonstrated that nanodiamond particles embedded to a polymer matrix attain photoluminescent properties when irradiated with a flux of MeV protons. This suggests an application of the ND-polymer coatings as fluorescence-induced indicators of a proton dose acquired by a spacecraft vehicle. Finally, the fabrication of novel composites of carbon nanotubes incorporated into a nanodiamond matrix obtained by electrophoretic codeposition of these two strongest nanocarbon components is reported.

EFFECT OF Fe/Ni CATALYST COMPOSITION ON NITROGEN DOPING AND FIELD EMISSION PROPERTIES OF CARBON NANOTUBES

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Carbon,
46(6) (2008) pp. 864-869.

Nitrogen-doped carbon (CN_x) nanotubes have been synthesized by acetonitrile vapor decomposition over catalyst nanoparticles produced in the result of thermolysis of solid solutions of Fe and Ni bimaleates. X-ray photoelectron spectroscopy revealed the nitrogen content in CN_x nanotubes grows from 0.4 to 1.2 at %, when Ni portion in catalyst increases. Nitrogen doping level of sample produced using bimaleates of Fe and Ni taken in a ratio of 7:3 is deviated from this dependence due to formation of two phases of metallic catalyst. N 1s-edge X-ray absorption spectra of samples showed three peaks, which by results of quantum-chemical calculation on nitrogen-containing carbon nanotube (CNT) model were assigned to pyridinic, graphitic, and molecular forms of nitrogen. Measurements of current–voltage characteristics of the samples found the electron emission threshold is reduced with amount of nitrogen incorporated into CN_x nanotubes.

TEXTURE AND SURFACE PROPERTIES OF CARBON-SILICA NANOCOMPOSITE MATERIALS PREPARED BY THE CARBONIZATION OF HIGH-ASH VEGETABLE RAW MATERIALS IN A FLUIDIZED CATALYST BED

P.M. Eletsky, V.A. Yakovlev, V.V. Kaichev, N.A. Yazykov, V.N. Parmon

Kinet. Catal.,
49(2) (2008) pp. 305-312.

A series of carbon–silica nanocomposite samples prepared by the carbonization of high-ash biomass (using rice husks as an example) in a fluidized-bed reactor with a deep oxidation catalyst at 450–600°C was studied by a set of physicochemical techniques (BET, IR spectroscopy, XPS, and TGA). The dependence of the chemical composition, texture characteristics, and main properties of the resulting materials on carbonization temperature was found.

TEXTURE AND ADSORPTIVE PROPERTIES OF MICROPOROUS AMORPHOUS CARBON MATERIALS PREPARED BY THE CHEMICAL ACTIVATION OF CARBONIZED HIGH-ASH BIOMASS

P.M. Eletsky, V.A. Yakovlev, V.B. Fenelonov, V.N. Parmon

Kinet. Catal.,
49(5) (2008) pp. 708-719.

Samples of microporous amorphous carbon materials with calculated BET specific surface areas of up to 3500 m^2/g, pore volumes of up to 3.0 cm^3/g, and micropore volumes of up to 1.9 cm^3/g were prepared using the chemical activation of rice hulls carbonized in a fluidized-bed reactor with a copper–chromium catalyst for deep oxidation. The effects of various activation parameters (temperature, activating agents, etc.) were studied, and optimum parameters were chosen. The resulting materials exhibited sorption capacities of up to 6.3 and 41 wt % for hydrogen at liquid nitrogen temperature and 50 atm and for methane at 0°C and 60 atm, respectively. Because of this, they are promising for use in the purification, storage, and transportation of fuel gases. Moreover, some aspects of the mechanism of the interaction of an activating agent with a carbon-containing precursor are proposed.

Composite Sorbents, Adsorption Heat Pumps

COMPOSITE SORBENTS “SALT INSIDE POROUS MATRIX”: SYNTHESIS, PROPERTIES, PRACTICAL APPLICATION

Yu. I. Aristov, L.G. Gordeeva, M.M. Tokarev

Ed. N.F. Uvarov, Publishing House SB RAS,
Novosibirsk, 2008, 359 pp.

The Book presents the conception of purposeful “nano design” of the properties of porous materials and new family of the composite sorbents “salt in porous matrix” developed for adsorption of water, methanol, ammonia and carbonic acid. A review of the current state-of-the art in the synthesis and studying of these materials and description of fundamental physicochemical properties of composites and their application for various processes and devices are given. Wide prospects of further development and application of suggested approach and new materials are revealed.

A NEW METHODOLOGY OF STUDYING THE DYNAMICS OF WATER SORPTION/DESORPTION UNDER REAL OPERATING CONDITIONS OF ADSORPTION HEAT PUMPS: EXPERIMENT

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Int. J. Heat Mass Transfer,
51(19-20) (2008) pp. 4966-4972.

In this paper a new methodology of studying the kinetics of water vapour sorption/desorption under operating conditions typical for isobaric stages of sorption heat pumps is proposed and tested. The measurements have been carried out on pellets of composite sorbent SWS-1L ($CaCl_2$ in silica KSK) placed on a metal plate. Temperature of the plate was changed as it takes place in real sorption heat pumps, while the vapour pressure over the sorbent was maintained almost constant (saturation pressures corresponding to the evaporator temperature of 5°C and 10°C and the condenser temperature of 30°C and 35°C). Near-exponential behaviour of water uptake on time was found for most of the experimental runs. Characteristic time τ of isobaric adsorption (desorption) was measured for one layer of loose grains having a size between 1.4 mm and 1.6 mm for different heating/cooling scenarios and boundary conditions of an adsorption heat pump. Maximum specific power estimated from the τ-values can exceed 1.0 kW/kg of dry adsorbent, that gives proof to the idea of compact adsorption units for energy transformation with loose SWS grains.

A NEW METHODOLOGY OF STUDYING THE DYNAMICS OF WATER SORPTION/DESORPTION UNDER REAL OPERATING CONDITIONS OF ADSORPTION HEAT PUMPS: MODELLING OF COUPLED HEAT AND MASS TRANSFER IN A SINGLE ADSORBENT GRAIN

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Int. J. Heat Mass Transfer,
51(1-2) (2008) pp. 246-252.

Here, the results are analysed obtained by mathematical modelling of the coupled heat and mass transfer in a single adsorbent grain which is in thermal contact with a metal plate subjected to a fast temperature jump/drop (at constant vapour pressure). The dynamic behaviour turns out to be closely linked with equilibrium properties of the adsorbent, in particular, with the initial/final temperatures and with the shape of the segment of water sorption isobar (convex or concave) between these temperatures.

DYNAMICS OF WATER SORPTION ON A SINGLE ADSORBENT GRAIN CAUSED BY A LARGE PRESSURE JUMP: MODELLING OF COUPLED HEAT AND MASS TRANSFER

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Int. J. Heat Mass Transfer,
51(25-26) (2008) pp. 5872-5876.

A mathematical model of coupled heat and mass transfer in the course of water adsorption on a single adsorbent grain, which is in thermal contact with an isothermal metal plate is presented. Adsorption is caused by a large jump of vapour pressure over the grain. The radial profiles of the grain temperature and the water concentrations in the adsorbed and gas phases were calculated as a function of time. Strong interrelationship between the shapes of the water sorption isotherm and the radial uptake profile was revealed. The best fit to the experimental data of [B. Dawoud, Yu. I. Aristov, Experimental study on the kinetics of water vapour sorption on selective water sorbents, silica–gels and alumina under typical operating conditions of sorption heat pumps, Int. J. Heat Mass Transfer, 46(2) (2003) 273–281] corresponds to the water diffusivity $D_e = 6.0 \times 10^{-6}$ m^2/s and the coefficient of the heat transfer $\alpha_p = 70$ W/(m^2 K) which are larger than those measured in quasi-equilibrium experiments.

KINETICS OF WATER ADSORPTION ON LOOSE GRAINS OF SWS-1L UNDER ISOBARIC STAGES OF ADSORPTION HEAT PUMPS: THE EFFECT OF RESIDUAL AIR

I.S. Glaznev, Yu.I. Aristov

Int. J. Heat Mass Transfer,
51(25-26) (2008) pp. 5823-5827.

In this paper the effect of a non-adsorbable gas (air) on kinetics of water adsorption on loose grains of the composite adsorbent SWS-1L (silica modified by calcium chloride) (grain size 0.8–0.9 and 1.4–1.6 mm) was studied. The adsorbent grains were placed on the surface of isothermal metal plate at $T = 60$°C and equilibrated with the mixture of water vapor at $P_{H2O} = 10.3$ mbar and air at a certain partial pressure P_A. After that the metal plate was subjected to a temperature drop down to 35°C at almost constant pressure over the grains. Reduction of the adsorption rate was revealed even at the partial pressure of residual air P_A as low as 0.06 mbar. At $P_A > 0.4$ mbar the kinetic curves were near-exponential and the characteristic adsorption time τ did not depend on the grain size and increased as $\tau = \tau_0 + AP_A$, where $A = 700 \pm 50$ s/mbar. Desorption stage was less affected by the residual air. The specific cooling power generated during the isobaric adsorption stage was estimated as a function of the residual air pressure.

CHEMICAL AND ADSORPTION HEAT PUMPS: CYCLE EFFICIENCY AND BOUNDARY TEMPERATURES

Yu.I. Aristov

Theor. Found. Chem. Eng.,
42(6) (2008) pp. 873-881.

The efficiency of an ideal three-temperature (3T) cycle of a chemical heat pump (CHP) is considered. For a reversible CHP 3T cycle, the maximal efficiency can be determined using the ratio of the heat of evaporation of the working fluid and the heat of the chemical reaction or using the boundary temperatures of the cycle. The boundary temperatures of the reversible CHP cycle are not independent variables relative to each other. As they are related by the Clausius–Clapeyron equation for the equilibrium of the pure fluid and by the van't Hoff equation for the chemical reaction, the choice of one of these temperatures completely determines the two others. Comparison of the efficiencies of the CHP cycle and the cycle of an adsorption heat pump (AHP) shows that the CHP efficiency can theoretically reach the Carnot-cycle efficiency whereas the AHP efficiency is always less than the Carnot-cycle efficiency because of the generation of entropy due to the transfer of heat to (from) the adsorber at a finite temperature difference. The minimal temperature of the external heat source needed for the operation of the CHP (AHP) cycle, the minimal evaporator temperature, and the maximal condenser temperature are calculated. These temperatures are determined for CHP (AHP) applications such as heating, air conditioning, ice production, and deep freezing in different climatic zones.

CHEMICAL AND ADSORPTION HEAT PUMPS: COMMENTS ON THE SECOND LAW EFFICIENCY

V.E. Sharonov, Yu.I. Aristov

Chem. Eng. J.,
136(2) (2008) pp. 419-424.

The thermodynamic analysis of an ideal cycle of chemical and adsorption heat pumps was performed in order to compare two definitions of the cycle efficiency used in literature and estimate the maximal efficiency that can be reached for particular non-regenerative cycle. It was shown that the efficiency equal to the Carnot efficiency can be, in principle, obtained for a chemical heat pump that results from a monovariant equilibrium of a gas-solid reaction. This was confirmed for various chemical reactions between salts and ammonia (or water). For a divariant equilibrium in adsorption heat pump there is inevitable degradation of the efficiency due to the thermal entropy production caused by the external thermal coupling. Simple estimation of the efficiency reduction is suggested.

STATUS QUO AND PROSPECTS OF DEVELOPMENT OF CHEMICAL AND SORPTION HEAT ENGINES IN THE RUSSIAN FEDERATION AND THE REPUBLIC OF BELARUS

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(**Luikov Heat and Mass Transfer Institute, Minsk, Belarus; **Kutateladze Institute of Thermal Physics, Novosibirsk, Russia*)

J. Eng. Thermophys.,
81(1) (2008) pp. 17-47.

The basic principles of operation of chemical and adsorption heat engines have been described. The advantages and new aspects of their application have been considered. A review of the state of the art in sorption technologies in different countries, as well as of the features of their application in Russia and Belarus is given.

NANOCOMPOSITE SORBENTS "SALT INSIDE POROUS MATRIX": DESIGN OF PHASE COMPOSITION AND SORPTION PROPERTIES, PRACTICAL APPLICATIONS

L.G. Gordeeva, **Yu.I. Aristov**

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G. Vayssilov, Heron Press, Sofia, 2008, pp. 1-11.

In this communication the authors suggest and discuss the new approach of design of water sorbents "salt in porous matrix" for various applications. In frame of this approach the demands of particular application are formulated at first step. Then the composite adsorbent with properties meeting the requirements is synthesized. Practical tools available to design such optimal sorbent are suggested and discussed: the chemical nature and content of confined salt, the porous structure of the host matrix and synthesis conditions. All these tools can be used to adjust the real composite adsorbent to the optimal one. This paper gives a review of the current state-of-the art on the new family of the composite sorbents for various applications.

COMPOSITES “LITHIUM HALIDES IN SILICA GEL PORES”: METHANOL SORPTION EQUILIBRIUM

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Microporous Mesoporous Mater.,
112(1-3) (2008) pp. 254-261.

This paper presents the methanol sorption equilibrium and phase composition of two composite sorbents “LiCl and LiBr confined to mesopores of silica gel”. Chemical phase analysis of the samples was performed by the differential dissolution method. Phase transformation of the composites during methanol sorption was characterized *in situ* by X-ray diffraction analysis. The isobars of methanol sorption on the composites were measured in the temperature range T=293-423 K and for methanol pressure P_{MeOH} = 21-300 mbar using a thermo-gravimetric technique. It was found that the two composites showed an outstanding sorption capacity w_{max}=0.8 g/g and an energy storage ability E_{max}=1.0 kJ/g, which could be attractive for development of efficient adsorptive cooling/heating and energy storage systems driven by a low temperature heat source.

COMPOSITE SORBENTS “LITHIUM NITRATE IN SILICA PORES” FOR LOW TEMPERATURE HEAT TRANSFORMATION

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Int. Sci. J. Alternative Energy Ecol.,
11 (2008) pp. 95-99.

Basing on the detailed thermodynamic analysis of an adsorption heat transformation process, it was proposed that composite sorbents “$LiNO_3$ confined to silica mesopores” can be used in adsorption heat-transformers (AHT) in mild climate conditions.

It was found out that the isolation of $LiNO_3$ in the pores of SiO_2 resulted in the significant changes in physical-chemical properties of the salt. These changes are due to the increase of the contribution of a surface energy of the salt in the total Gibbs energy of the system, when $LiNO_3$ is dispersed to the nano-sized pores. This effect can be used for nanotailoring new adsorbents with desirable sorption properties which fit requirements of particular AHT cycle. Besides, the hydration rate was significantly increased for confined salt. Moreover, the hydration mode changed form reaction controlled to diffusion controlled.

Theoretical analysis of the AHT thermodynamic cycle based on the composite SWS(Li)-15 showed that the regeneration of this sorbent can be performed with the external heat source of quite low temperature (about 60–700°C). Thus, composite sorbents based on lithium nitrate and silica are perspective for cold production and heat storage in the mild climate conditions, like it is a case for the Central Russia and the South of the Eastern and Western Siberia.

DECARBONATION RATES OF CYCLED CaO ABSORBENTS

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Energy Fuels,
22(3) (2008) pp. 1911-1916.

Decarbonation rates of cycled CaO sorbent were measured for a wide range of particle sizes (0.25−4 μm), temperatures (747−830°C), and relative CO_2 concentrations (0−95%). The decarbonation rate was found to decay exponentially with an increase in partial CO_2 pressure that can be explained by assuming CaO nuclei formation is the rate-limiting step. A differential particle model using two variable parameters was successfully applied to fit the experimental data. An approximate analytical expression is put forward for the decarbonation rate as a function of sorbent texture, temperature, CO_2 pressure, particle size, and Sherwood number.

INFLUENCE OF STRUCTURAL DEFECTS ON THE ELECTROCATALYTIC ACTIVITY OF PLATINUM

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J. Solid State Electrochem.,
12(5) (2008) pp. 497-509.

Structural defects play major role in catalysis and electrocatalysis. Nanocrystalline (or nanostructured) materials composed of nanometer-sized crystallites joined via grain boundaries have been recognized for their specific structure and properties, differentiating them from single crystals, coarsely grained materials or nanometer-sized supported single-grained particles (Gleiter, Nanostruct. Mater. 1:1-19, 1992). In this paper, Pt electrodes were used, prepared by electrodeposition on glassy carbon and gold supports, as model nanocrystalline materials to explore the influence of grain boundaries and other structural defects on electrocatalysis of CO and methanol oxidation. The authers build on the recently established correlations between the nanostructure (lattice parameter, grain size, and microstrains) of electrodeposited Pt and the deposition potential (Plyasova et al., Electrochim. Acta 51:4447-4488, 2006) and use the latter to obtain materials with variable density of grain boundary regions. The activity of electrodeposited Pt in the oxidation of methanol and adsorbed CO exceeds greatly that for Pt(111), polycrystalline Pt, or single-grained Pt particles. It is proposed that active sites in nanostructured Pt are located at the emergence of grain boundaries at the surface. For methanol electrooxidation, the electrodes with optimal nanostructure exhibit relatively high rates of the “direct” oxidation pathway and of the oxidation of strongly adsorbed poisoning intermediate (CO_{ads}), but not-too-high methanol dehydrogenation rate constant. These electrodes exhibit an initial current increase during potentiostatic methanol oxidation explained by the CO_{ads} oxidation rate constant exceeding the methanol decomposition rate constant.

CO MONOLAYER OXIDATION ON Pt NANOPARTICLES: FURTHER INSIGHTS INTO THE PARTICLE SIZE EFFECTS

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J. Electroanal. Chem.,
599(2) (2007) pp. 221-232.

This paper provides further insights into the particle size effects in CO monolayer oxidation. Strong particle size effects are confirmed in the size range from 1.8 to 5 nm. The discrepancies in the literature concerned with the particle size effects in CO monolayer oxidation are reconciled by exploring the influence of the experimental conditions on the stripping voltammograms and chronoamperograms. Evidence supporting the contribution of slow non-electrochemical step to the overall mechanism of CO oxidation is presented. The particle size effects in CO monolayer oxidation are attributed to the size-dependent $CO_{ads} + OH_{ads}$ interaction as well as to the size-dependent CO_{ads} surface diffusion coefficient.

ON THE INFLUENCE OF THE METAL LOADING ON THE STRUCTURE OF CARBON-SUPPORTED PtRu CATALYSTS AND THEIR ELECTROCATALYTIC ACTIVITIES IN CO AND METHANOL ELECTROOXIDATION

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Phys. Chem. Chem. Phys.,
9(40) (2007) pp. 5476-5489.

PtRu (1:1) catalysts supported on low surface area carbon of the Sibunit family ($S_{BET} = 72\ m^2\ g^{-1}$) with a metal percentage ranging from 5 to 60% are prepared and tested in a CO monolayer and for methanol oxidation in H_2SO_4 electrolyte. At low metal percentage small (<2 nm) alloy nanoparticles, uniformly distributed on the carbon surface, are formed. As the amount of metal per unit surface area of carbon increases, particles start coalescing and form first quasi two-dimensional, and then three-dimensional metal nanostructures. This results in a strong enhancement of specific catalytic activity in methanol oxidation and a decrease of the overpotential for CO monolayer oxidation. It is suggested that intergrain boundaries connecting crystalline domains in nanostructured PtRu catalysts produced at high metal-on-carbon loadings provide active sites for electrocatalytic processes.

ON THE ENHANCED ELECTROCATALYTIC ACTIVITY OF Pd OVERLAYERS ON CARBON-SUPPORTED GOLD PARTICLES IN HYDROGEN ELECTROOXIDATION

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Phys. Chem. Chem. Phys.,
10(44) (2008) pp. 6665-6676.

Palladium-gold particles with varied composition were prepared by Pd electrochemical deposition on Au nanoparticles immobilized on model carbon support. Pd-Au/C catalysts were characterized *ex situ* by transmission electron microscopy, energy dispersive X-ray analysis and X-ray photoelectron spectroscopy, and *in situ*, by underpotential deposition of hydrogen and copper adatoms, and CO stripping. Hydrogen oxidation reaction on pristine and CO-poisoned Pd-Au/C particles was studied using rotating disk electrode (RDE) technique. It was found that the decrease of the effective Pd overlayer thickness below ca. two monolayers resulted in a two-fold increase of the exchange current density of the hydrogen oxidation reaction and in significant increase of CO tolerance.

SURFACE ELECTROCHEMISTRY OF CO AS A PROBE MOLECULE ON CARBON-SUPPORTED Se-SURFACE MODIFIED Ru NANOPARTICLES VIA INFRARED REFLECTION ABSORPTION SPECTROSCOPY

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Phys. Chem. Chem. Phys.,
9(42) (2007) 5693-5699.

The carbon monoxide molecule is used to probe the electronic properties of Ru/C and Se surface-modified Ru/C nanocatalysts. Coordination of a Se to a Ru surface strongly affects the vibrational properties and reactivity of the CO adsorbed. Marked alteration of the CO stretching frequency; increase of the Stark tuning rate for C-O vibration; and a positive shift of the onset of CO oxidation are observed for Se-modified Ru particles and attributed to the electronic effect of Se.

Catalysis by Heteropoly Compounds and Polyoxometalates

SYNTHESIS OF MOLYBDOVANADOPHOSPHORIC HETEROPOLY ACID SOLUTIONS HAVING MODIFIED COMPOSITION

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R.I. Maksimovskaya

Appl. Catal. A,
342(1) (2008) pp. 126-130.

A new practically wasteless method of synthesis of high-vanadium Mo-V-phosphoric heteropoly acids aqueous solutions having modified composition $H_aP_zMo_yV_{x'}O_b$ (HPA-$x'_{z\mathrm{P}}$) has been developed. These solutions are used as thermally stable catalysts of oxidation of organic compounds with O_2. At the first stage of the synthesis, V_2O_5 is dissolved in the cooled H_2O_2 to form peroxy vanadium compounds, which spontaneously decompose to yield $H_6V_{10}O_{28}$ solution. The latter is stabilized by addition of an excess of H_3PO_4. The prepared ($H_9PV_{14}O_{42}$ + H_3PO_4) solution is added to a gradually evaporating suspension of (MoO_3 + H_3PO_4) to form the HPA-$x'_{z\mathrm{P}}$ solution. The catalysts based on HPA-$x'_{z\mathrm{P}}$ solutions do not yield V-containing deposits up to 170°C. Syntheses of HPA-$x'_{z\mathrm{P}}$ solutions can be realized both in a lab and pilot scale.

A NOVEL METHOD OF THE SYNTHESIS OF MOLYBDOVANADOPHSPHORIC HETEROPOLY ACID SOLUTIONS

V.F. Odyakov, E.G. Zhizhina

React. Kinet. Catal. Lett.,
95(1) (2008) pp. 21-28.

A novel eco-friendly method of the synthesis of aqueous solutions of the Keggin-type Mo-V-P heteropoly acids $H_{3+x}PV_xMo_{12-x}O_{40}$ (HPA-x) is proposed. At the first stage, V_2O_5 is dissolved in cooled H_2O_2 to form peroxyvanadic compounds, which spontaneously decompose to yield an $H_6V_{10}O_{28}$ solution. The latter is stabilized by the addition of H_3PO_4 to yield an $H_9PV_{14}O_{42}$ solution that is added to a boiling aqueous suspension of (H_3PO_4 + MoO_3). This suspension is gradually evaporated producing the HPA-x solution. This safe and practically wasteless method holds much promise for the preparation of HPA-x solutions with x = 2–6.

ALTERATION OF PHYSICOCHEMICAL PROPERTIES OF CATALYSTS BASED ON AQUEOUS SOLUTIONS OF Mo-V-P HETEROPOLY ACIDS IN REDOX PROCESSES

E.G. Zhizhina, V.F. Odyakov

React. Kinet. Catal. Lett.,
95(2) (2008) pp. 301-312.

Selective catalytic oxidation of various organic substrates with O_2 in the presence of aqueous solutions of Mo-V-P heteropoly acids (HPA) is carried out via two stages in separate reactors. In stage (1), a substrate is oxidized into a desired product while HPA is reduced. The reduced form of HPA is oxidized with O_2 in stage (2). A set of physicochemical properties of the homogeneous catalyst has been found to alter continuously during these redox processes. Using a solution of the modified high-vanadium HPA ($H_{12}P_3Mo_{18}V_7O_{85}$), the authors demonstrate that density, viscosity, and pH of this solution reach their maxima after reaction (1) and attain their minima after reaction (2). On the contrary, the redox potential of the solution is minimal after reaction (1) and maximal after reaction (2). All alterations of physicochemical properties of the catalyst are found completely reversible.

CATALYTIC OXIDATION OF ORGANIC COMPOUNDS WITH OXYGEN IN THE PRESENCE OF Mo-V-PHOSPHORIC HETEROPOLY ACID SOLUTIONS

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Kinet. Catal.,
49(6) (2008) pp. 773-781.

The studies carried out at the Institute of Catalysis on the selective catalytic oxidation of organic compounds with oxygen in the presence of aqueous solutions of Mo–V–phosphoric heteropoly acids (HPAs) are reviewed. Both Keggin-type HPA-x solutions ($H_{3+x}PV_xMo_{12-x}O_{40}$, x = 2–6), and modified HPA-x' solutions ($H_aP_zMo_yV_{x'}O_b$, $1 \le x' \le 12$; $8 \le y \le 20$; $1 \le z \le 3$; $40 \le b \le 89$; $a = 2b - 6y - 5\,(x' + z)$) are used as catalysts. In the presence of HPA, alkylphenols are oxidized into 1,4-quinones with a selectivity of 85–99%, and C_2–C_4 olefins in the presence of Pd complexes are oxidized into carbonyl compounds with a selectivity of 98–99%. The bifunctional (acidic and oxidizing) properties of HPA solutions are used for the first time to synthesize anthraquinones and vitamin K_3. High thermal stability of modified HPA-x' solutions permits to develop a whole series of important oxidative processes of basic and fine organic syntheses.

SUPPORTED POLYOXOMETALATE-BASED HETEROGENEOUS CATALYSTS FOR LIQUID PHASE SELECTIVE OXIDATIONS

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In *"Heterogeneous Catalysis Research Progress"*,
Ed. M.B. Gunther,
Nova Sci. Publishers, Inc., 2008, ch. 6.

The design of active, selective, stable and easily recyclable heterogeneous catalysts is a challenging goal of liquid phase oxidation catalysis. Early transition-metal oxygen-anion clusters or polyoxometalates (POMs) have received increasing attention as oxidation catalysts because of their unique ensemble of properties, such as inorganic nature, metal oxide-like structure, thermodynamic stability to oxidation, thermal and hydrolytic stability, tunable acidities, redox potentials and solubility, etc. The apparent structural analogy of POMs and metal oxide surfaces allows considering POMs as discrete, soluble fragments of extended metal oxide lattices, which can be comprehensively investigated at the atomic level. In the structure of transition-metal-monosubstituted POMs (M-POMs), the active center M is isolated in and strongly bound to an inert metal oxide matrix and is thus prevented from hydrolysis and oligomerization, which makes M-POMs perspective building blocks for designing single site heterogeneous catalysts. The development of strategies for converting homogeneous POMs to solid, true heterogeneous catalysts is of primary importance. A simple wet impregnation usually did not allow obtaining catalysts which would be stable to leaching in polar reaction media. In the past decade, a great deal of work was directed to immobilize POMs on specially modified supports *via* the formation of a chemical bond (ionic, covalent or dative). Embedding POM into an inert matrix using sol-gel method may also lead to stable heterogeneous catalysts. Importantly, the molecular structure of POM can be maintained after immobilization, which ensures uniformity of spatially separated active centers on the catalyst surface or inside pores. In this review paper, the authors survey recent achievements in the synthesis of POM-based heterogeneous catalysts using different immobilization techniques, their characterization, and application for liquid phase selective oxidation of organic compounds. Special attention is paid to analyze the frequently success-limiting issues of catalyst activity and selectivity after immobilization and, especially, after recycling, catalyst stability to leaching and nature of catalysis.

KINETICS AND MECHANISM OF THE OXIDATION OF 2,3,6-TRIMETHYLPHENOL WITH HYDROGEN PEROXIDE IN THE PRESENCE OF Ti-MONOSUBSTITUTED POLYOXOMETALATES

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Kinet. Catal.,
49(3) (2008) pp. 371-378.

The product composition and reaction kinetics are reported for 2,3,6-trimethylphenol (TMP) oxidation with hydrogen peroxide in acetonitrile catalyzed by a Ti-monosubstituted polyoxometalate (Ti-POM) with a Keggin structure ($[Bu_4N]_4[PTi(OMe)W_{11}O_{39}]$) and for the stoichiometric reaction between TMP and the peroxo complex $[Bu_4N]_4[HPTi(O)_2W_{11}O_{39}]$ (**I**). The main products of the stoichiometric reaction are 2,3,5-trimethyl-1,4-benzoquinone (TMBQ) and 2,2',3,3',6,6'-hexamethyl-4,4'-biphenol (BP). The TMBQ yield increases as the TMP/**I** molar ratio is decreased. The catalytic reaction is first-order with respect to H_2O_2 and the catalyst and has a variable order (1–0) with respect to TMP. The rate of the reaction increases as the water concentration in the reaction mixture is raised. The stoichiometric reaction is first-order with respect to peroxo complex **I** and has a variable order (1–0) with respect to TMP. There is no kinetic isotope effect for this reaction (k_{ArOH}/k_{ArOD} = 1). A TMP oxidation mechanism is suggested, which includes the coordination of a TMP molecule and peroxide on a Ti site of the catalyst with the formation of a reactive intermediate. The one-electron oxidation of TMP in this intermediate yields a phenoxyl radical. The subsequent conversions of these $ArO^{\bullet}$ radicals yield the reaction products.

SYNTHESIS AND PHYSICOCHEMICAL STUDY OF THE $PMo_{11}(TiO)O_{39}^{5-}$ HETEROPOLYANION

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Russ. J. Inorg. Chem.,
53(9) (2008) pp. 1359-1365.

Procedures were developed for the synthesis of the guanidinium (Gua) and tetrabutylammonium (TBA) salts of 11-molybdotitano(IV)phosphate heteropolyanion (MTPH) from solutions with the stoichiometric ratio P : Mo = 1 : 11 and in excess of titanium(IV) ions, Ti : P ≥ 1.5, at pH 1.85–1.90. MTPH was isolated as the $(Gua)_5PMo_{11}(TiO)O_{39}$ and $(TBA)_5PMo_{11}(TiO)O_{39}$ salts. The composition and formula of MTPH were established by chemical analysis, electronic absorption spectroscopy in the visible region of the oxidized and reduced MTPH forms, IR spectroscopy, and ^{31}P NMR. $H_5PMo_{11}(TiO)O_{39}$, obtained by ion exchange of the Gua salt in an aqueous–organic medium, is a strong pentabasic acid. MTPH reacts with H_2O_2 to form a peroxo complex with limited stability in an aqueous solution. In aqueous–organic media, the peroxo complex is more stable. In acetonitrile, MTPH persists for several days.

HETEROGENEOUS SELECTIVE OXIDATION CATALYSTS BASED ON COORDINATION POLYMER MIL-101 AND TRANSITION METAL SUBSTITUTED POLYOXOMETALATES

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J. Catal.,
257(2) (2008) pp. 315-323.

Titanium- and cobalt-monosubstituted Keggin heteropolyanions, $[PW_{11}CoO_{39}]^{5-}$ and $[PW_{11}TiO_{40}]^{5-}$, were electrostatically bound to the chromium terephthalate polymer matrix MIL-101. The MIL-supported polyoxometalate (POM) catalysts were characterized by elemental analysis, XRD, N_2 adsorption, and FT-IR-spectroscopy. The catalytic performance of both MIL-101 and the novel composite materials M-POM/ MIL-101 was assessed in the oxidation of three representative alkenes, α-pinene, caryophyllene and cyclohexene, using molecular oxygen and aqueous hydrogen peroxide as oxidants. Ti-POM/MIL-101 demonstrated fairly good catalytic activity and selectivity in α-pinene allylic oxidation and caryophyllene epoxidation with hydrogen peroxide, while Co-POM/MIL-101 catalyzed α-pinene allylic oxidation by molecular oxygen. Both composite materials are stable to POM leaching, behave as true heterogeneous catalysts, and can be used repeatedly without suffering a loss of activity and selectivity in oxidations with O_2 and H_2O_2, provided rather mild reaction conditions ($T < 50^{o}C$, $[H_2O_2] < 0.2$ M) are used with the latter oxidant.

BIMETALLIC PALLADIUM(II) AND IRON(III), TITANIUM(IV), VANADIUM(V), COBALT(II), AND COPPER(II) COMPLEXES WITH THE $[As_2W_{19}O_{67}(H_2O)]^{14-}$ HETEROPOLYANION

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Russ. J. Inorg. Chem.,
53(5) (2008) pp. 690-695.

The formation of bimetallic Pd(II) and M = Fe(III), Ti(IV), V(V), Co(II), or Cu(II) complexes with the two-vacancy $[As_2W_{19}O_{67}(H_2O)]^{14-}$ heteropolyanion (HPA) (below referred to as As_2W_{19}) has been studied by UV/Vis and IR spectroscopy and differential dissolution. In an aqueous solution at pH 6 and a Pd:M:As_2W_{19} molar ratio of 1:1:1, heteropoly complexes (HPC) incorporating two different metals one being Pd(II) are formed. The resulting complexes were precipitated from solution as cesium salts. In the case of Pd(II) and M = Fe(III), Co(II), or Cu(II) ions, the precipitate contained bimetallic HPC $[As_2W_{19}FePdO_{67}(H_2O)_2]^{9-}$ (65.9 wt %), $[As_2W_{19}CoPdO_{67}(H_2O)_2]^{10-}$ (45.6 wt %), and $[As_2W_{19}CuPdO_{67}(H_2O)_2]^{10-}$ (50.7 wt %) mixed with monometallic HPC $[As_2W_{19}M_2O_{67}(H_2O)_2]^{(14-2m)-}$ ($As_2W_{19}M_2$). In the case of Pd(II) and Ti(IV) or V(V), bimetallic HPC of a different composition were precipitated, namely, $[As_2W_{19}Ti_2O_{67}(OH_x)_2\ PdO]^{(10-2x)-}$ (76.8 wt %) and $[As_2W_{19}V_2O_{67}(OH_x)_2\ PdO]^{(8-2x)-}$ (15.0 wt %), where palladium ions are not incorporated in the HPC structure but are attached to the HPC surface, possibly, as hydroxide species. Using M = Pd(II), Ti(IV), V(V) ions and the HPA As_2W_{19} ([M]:[As_2W_{19}] = 2:1, pH 6), new monometallic HPC, $[As_2W_{19}Pd_2O_{67}(H_2O)_2]^{10-}$, $[As_2W_{19}Ti_2O_{67}(OH_x)_2]^{(10-2x)-}$, and $[As_2W_{19}V_2O_{67}(OH_x)_2]^{(8-2x)-}$ (x = 0, 1, or 2), were obtained.

LIQUID-PHASE OXIDATION OF BENZOTHIOPHENE AND DIBENZOTHIOPHENE BY CUMYL HYDROPEROXIDE IN THE PRESENCE OF CATALYSTS BASED ON SUPPORTED METAL OXIDES

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Kinet. Catal.,
49(5) (2008) pp. 644-653.

The liquid-phase oxidation of benzothiophene and dibenzothiophene by cumyl hydroperoxide in the presence of supported metal oxide catalysts was carried out in octane in an N_2 atmosphere at 50–80°C. The cumyl hydroperoxide, benzothiophene, and dibenzothiophene conversions and the yield of sulfones were determined for catalysts of various natures. In the presence of MoO_3/SiO_2, the most efficient and most readily regenerable catalyst, the benzothiophene conversion was ~60% and the dibenzothiophene conversion was as high as 100% upon almost complete consumption of cumyl hydroperoxide. The influence of unsaturated and aromatic compounds (oct-1-ene, toluene) on the catalytic effect was studied. The kinetics of substrate oxidation and cumyl hydroperoxide decomposition and an analysis of the cumyl hydroperoxide conversion products suggested a benzothiophene and dibenzothiophene oxidation mechanism including the formation of an intermediate complex of the hydroperoxide with the catalyst and the substrate and its transformation via heterolytic and homolytic routes.

INTERACTION OF ARSENITE IONS WITH MOLYBDATE IN AQUEOUS SOLUTION

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Russ. J. Inorg. Chem.,
53(4) (2008) pp. 649-654.

Interaction of arsenite ions with molybdate ions in aqueous $HClO_4$ at pH of 3–5 were studied using spectrophotometry. A heteropoly anion (HPA) with the $AsMo_4$ stoichiometry was revealed. Elemental analysis, X-ray photoelectron spectroscopy, and IR spectroscopy were used to characterize the composition and structure of the cesium salt of As(III)–Mo(VI) HPA precipitated from solution. The comparison of the IR spectra of cesium salts of the synthesized HPA and dimethylarsenite HPA $(CH_3)_2AsMo_4O_{15}H^{2-}$, whose structure is known, implies that $AsMo_4O_{15}^{3-}$ has a similar structure, where the AsO_2^- group is linked by four connected molybdenum octahedra $(Mo_4O_{12})O^{2-}$.

TITANIUM-SALAN-CATALYZED ASYMMETRIC OXIDATION OF SULFIDES AND KINETIC RESOLUTION OF SULFOXIDES WITH H_2O_2 AS THE OXIDANT

K.P. Brylyakov, E.P. Talsi

Eur. J. Org. Chem.,
19 (2008) pp. 3369-3376.

Asymmetric oxidation of sufides to sulfoxides by aqueous hydrogen peroxide with catalysis by titanium-salan complexes is presented. Optically active sulfoxides have been obtained with good to high enantioselectivities (up to 97 % *ee*) by a tandem enantioselective oxidation and kinetic resolution procedure, the catalyst performing over 500 turnovers with no loss of enantioselectivity.

THE NATURE OF ACTIVE SPECIES IN CATALYTIC SYSTEMS BASED ON NON-HEME IRON COMPLEXES, HYDROGEN PEROXIDE, AND ACETIC ACID FOR SELECTIVE OLEFIN EPOXIDATION

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Kinet. Catal.,
49(3) (2008) pp. 379-385.

The catalytic systems $[(BPMEN)Fe^{II}(CH_3CN)_2](ClO_4)_2/H_2O_2/CH_3OOH$ and $[(TPA)Fe^{II}(CH_3CN)_2](ClO_4)_2/H_2O_2/CH_3OOH$, where BPMEN = *N*,*N'*-dimethyl-*N*,*N'*-bis(2-pyridylmethyl)-1,2-diaminoethane and TPA = tris(2-pyridylmethyl)amine, provide selective olefin epoxidation. Proton NMR studies showed that the mononuclear iron(IV) oxo complexes $[(L)Fe^{IV}=O]^{2+}$, with L = BPMEN or TPA, are present in the cited catalytic systems. These intermediates are the decomposition products of the acylperoxo complexes $[(L)Fe^{III}\_O_3CCH_3]^{2+}$. Such a complex was observed by the ^2H NMR technique at low temperatures. The $[(L)Fe^{IV}=O]^{2+}$ and $[(L)Fe^{V}=O]^{3+}$ oxo complexes are possible active species in the studied catalytic systems.

Photocatalytic and Related Processes

PHOTOCATALYTIC TRANSFORMATIONS OF ORGANIC SULFUR COMPOUNDS AND H_2S

A.V. Vorontsov

Russ. Chem. Rev.,
77(10) (2008) pp. 909-926.

Modern views on the products, pathways and kinetic features of liquid- and gas-phase photocatalytic reactions of sulfur compounds in the presence of heterogeneous and homogeneous photocatalysts are generalised. Attention is focused on the aliphatic and aromatic reduced sulfur compounds and pesticides. The reaction rate in the liquid and gas phases are analysed as function of solution pH, temperature, catalyst content, substrate concentration, solvent type, air moisture and added oxidants. Photocatalyst deactivation and the ways for recovery of its activity are considered.

A MULTIFOLD INCREASE IN THE PHOTOCATALYTIC ACTIVITY OF TITANIUM DIOXIDE VIA THE COMBINATION OF A MESOPOROUS STRUCTURE WITH PLATINUM NANOPARTICLES

E.A. Kozlova, A.V. Vorontsov

High Energ. Chem.,
42(7) (2008) pp. 583-585.

The purpose of this work was template synthesis of titanium dioxide from organic and inorganic precursors, including titanyl sulfate and titanium tetrabutoxide, with the use of ionic and nonionic templates. Platinum was deposited on the synthesized materials by two methods, (1) the photodeposition (PD) of platinum and (2) the impregnation with the subsequent mild chemical reduction (MCR). The photocatalytic activity of the obtained catalysts has been tested in the reaction of the gas-phase oxidation of acetone and liquid-phase oxidation of a model organophosphorous substance, dimethyl methylphosphonate. The obtained samples have shown a high activity in both reactions.

To reveal the reason for the higher activity of the platinized catalysts obtained by photodeposition, their structure was investigated by means of transmission electron microscopy. The deposition of platinum by means of MCR results in the formation of extended metal particles with a length of 10–20 nm; platinum aggregates of ~20 nm in size composed of spherical platinum particles of 2–3 nm in diameter. It is likely that this shape of particles with a small diameter is favorable for mediation of photocatalytic reactions, presumably, owing to a higher specific surface area of platinum particles of a smaller size.

SULPHURIC ACID AND Pt TREATMENT OF THE PHOTOCATALYTICALLY ACTIVE TITANIUM DIOXIDE

D.V. Kozlov, A.V. Vorontsov

J. Catal.,
258(1) (2008) pp. 87-94.

The study focuses on preparation, surface sites characterization and catalytic activity testing of pure (TiO_2), sulfated (TiO_2-S), loaded with 1 wt % Pt (TiO_2-Pt) and platinized/sulfated (TiO_2-Pt-S) high surface area anatase TiO_2 (100% anatase, 340 m^2/g). Sulfation was performed in 4 M H_2SO_4 solution and was not followed by a high temperature calcination. TEM images reveal the formation of a 3 Å amorphous layer over TiO_2 and TiO_2-Pt surface after their sulfation. Infrared spectrum of TiO_2-S contains additional absorption bands at 1235, 1333 and 1378 cm^{-1} that are assigned to S═O stretch and distorted adsorbed SO_4^{2-} vibrations. Low temperature CO adsorption and organic species adsorption from heptane solutions was performed for characterization of surface sites. TiO_2-S showed 3–5 cm^{-1} shift of adsorbed CO absorption band compared to initial TiO_2. The quantity of adsorbed CO increased by a factor of 1.5 for TiO_2-S indicating the increase of the quantity of surface Lewis sites. Sulfation also resulted in disappearance of OH groups having absorption band at 3690 cm^{-1} that was attributed to substitution by monodentate and bidentate sulfates. Four bases and two acids with different p*K* were used as probes in solution titration revealing that the quantity of different acid sites in TiO_2-S increases 1.07–2.17 times. Unexpectedly the quantity of acid and base sites in TiO_2-Pt-S decreases relatively to other catalysts studied.

Catalytic activity of the samples in acetone deep photooxidation was measured as a function of acetone vapor concentration in a flow-circulating reactor. All dependences are well described by the one site Langmuir–Hinshelwood kinetic model. The maximum oxidation rate was similar for all samples and was observed at acetone concentration above 1500 ppm. However, in the range of low acetone concentration the activity of TiO_2-Pt-S was about triple of pure TiO_2 activity. The high activity of sulfated/platinized and sulfated TiO_2 is due to the much increased acetone adsorption constant.

FAST ELIMINATION OF ORGANIC AIRBORNE COMPOUNDS BY ADSORPTION AND CATALYTIC OXIDATION OVER AEROSOL TiO_2

A.S. Besov, A.V. Vorontsov

Catal. Commun.,
9(15) (2008) pp. 2598-2600.

High concentration TiO_2 aerosol was generated by a sonic method and applied for the first time to air purification from vapors of organic compounds. Reactive adsorption and photocatalytic oxidation over aerosolized TiO_2 nanoparticles result in comcompared with the acid-base surface properties of plete elimination of acetone and dimethyl methylphosphonate vapors over the timescale of few minutes, which demonstrates a good prospect of this novel method for practical air treatment.

THE EVALUATION OF ACTIVITIES OF TWO TYPES OF PHOTOCATALYSTS AT INACTIVATION/DISINTEGRATION OF MICROORGANISM AEROSOL

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Chem. Eng. Transactions,
16 (2008) pp. 275–282.

Photocatalytic processes are more and more widely used to remove different pollutants including microorganisms from liquid and gaseous media. However, methods for evaluating the efficiency of photocatalysts at inactivation/disintegration of microorganisms in the liquid film have limitations at predicting their efficiency for microorganism-containing aerosols. The comparison of two types of photocatalysts was performed on *Mycobacterium smegmatis bacterium* and *vaccinia virus* using these new methods for evaluating the efficiency of photocatalysts at inactivation/disintegration of microorganisms in aerosols deposited on photocatalytic coatings. It has been shown that the photocatalyst based on platinized TiO_2 displays a higher activity at inactivation/disintegration of aerosols of both microorganisms than the photocatalyst based on "pure" titanium dioxide.

WATER DELIGNIFICATION BY ADVANCED OXIDATION PROCESSES: HOMOGENEOUS AND HETEROGENEOUS FENTON AND H_2O_2 PHOTO-ASSISTED REACTIONS

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Appl. Catal., B,
84(3-4) (2008) pp. 821-826.

The oxidation of lignin in synthetic aqueous solutions as well as in the biologically treated pulp-and-paper mill wastewater with hydrogen peroxide was studied in various methods: hydrogen peroxide UV-photolysis, homogeneous, heterogeneous and UV-assisted heterogeneous Fenton reactions, catalysed by FeZSM-5 zeolite. Contrasting the low-molecular organic contaminants, the oxidation of lignin in aqueous solutions was drastically slowed down in presence of heterogeneous FeZSM-5 zeolite, showing the superior performance of acidic homogeneous Fenton and hydrogen peroxide photolysis. This is explained by steric hindrance in oxidation of lignin with OH radicals on the catalyst surface and possible deactivation of lignin molecules adsorbed on the zeolite. The hydrogen peroxide photolysis among the studied delignification methods appeared to be the most efficient one in a wide range of pH.

PHOTOCHEMICAL ACTIVITY OF SOME COMPLEX OXIDES - PHASE COMPONENTS OF TROPOSPHERIC AEROSOL

V.S. Zakharenko, I.R. Abdulin

Atmos. Oceanic Opt.,
21(6) (2008) pp. 483-485.

Powdered samples of complex oxides (potassium niobates of the layered structure) were obtained by high temperature synthesis and subsequent grinding. Action spectra of photoinduced processes were determined over potassium niobates of the different phase composition for water and water-organic systems. It is shown that oxygen formation is caused by its photodesorption and is observed under illumination near the red boundary of intrinsic absorption band region. Hydrogen is formed as a result of photocatalytic dehydrogenation of residual adsorbed organic compounds, whereas photocatalytic decomposition of water does not occur. The quantum efficiency of photocatalytic dehydrogenation increases by an order of magnitude after adding the mixture of a hydrogen-containing organic compound to the reaction.

STUDY OF THE SURFACE PROPERTIES OF SILICON AND CALCIUM OXYGEN COMPOUNDS

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T.S. Minakova*, V.S. Zakharenko (**Tomsk State University, Tomsk, Russia*)

Atmos. Oceanic Opt.,
21(6) (2008) pp. 490-492.

The acid-base surface state of samples of the silicon oxide and calcium oxygen compounds was investigated. Adsorption of freon on calcium compounds has been studied. Adsorption data were calcium oxygen compounds. To estimate the expected freon adsorption on the calcium compound surfaces, approximated to the conditions of the troposphere, experiments were carried out with samples exposed to air for a long time.

INTERACTION OF FREON-22 WITH ALUMINUM AND MAGNESIUM OXIDES

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Protection Met. Phys. Chem. Surf.,
44(2) (2008) pp. 198-201.

It is known that Freons can be destructively adsorbed by magnesium and calcium oxides under the effect of mild ultraviolet radiation. Insofar as these oxides along with the silicon, aluminum, and iron oxides are typical components of solid tropospheric aerosols, photo- and dark adsorption processes may represent an efficient channel of the Freon removal from the atmosphere. In this work, dark adsorption of Freon-22 on aluminum and magnesium oxides, which were treated in a vacuum at room temperature, is studied. Experiments with the specimens that have been exposed to air for a long time are especially important in estimating the probable adsorption of a Freon on aluminum or magnesium oxide under conditions close to the tropospheric ones.

Catalysis for Organic Chemistry

ACTIVITY OF COBALT SULFIDE CATALYSTS IN THE HYDROGENOLYSIS OF DIMETHYL DISULFIDE TO METHANETHIOL: EFFECTS OF THE NATURE OF A SUPPORT AND THE PROCEDURE OF SUPPORTING A COBALT PRECURSOR

A.V. Mashkina, O.P. Krivoruchko,
L.N. Khairulina

Kinet. Catal.,
49(1) (2008) pp. 103-109.

The conversion of dimethyl disulfide to methanethiol on various catalysts containing supported cobalt sulfide in an atmosphere of hydrogen was studied at atmospheric pressure and T = 190°C. On CoS introduced into the channels of zeolite HSZM-5, the process occurred at a high rate but with a low selectivity for methanethiol because the proton centers of the support participated in a side reaction with the formation of dimethyl sulfide and hydrogen sulfide. Under the action of sulfide catalysts supported onto a carbon support, aluminum oxide, silicon dioxide, and an amorphous aluminosilicate, the decomposition of dimethyl disulfide to methanethiol occurred with 95–100% selectivity. The CoS/Al_2O_3 catalysts were found to be most efficient. The specific activity of alumina–cobalt sulfide catalysts only slightly depended on the phase composition and specific surface area of Al_2O_3. The conditions of the thermal treatment and sulfurization of catalysts and, particularly, the procedure of supporting a cobalt precursor onto the support were of key importance. Catalysts prepared through the stage of supporting nanodispersed cobalt hydroxide were much more active than the catalysts based on supported cobalt salts.

ACTIVITY OF CATALYSTS IN THIOPHENE SYNTHESIS FROM FURAN AND HYDROGEN SULFIDE

A.V. Mashkina, L.N. Khairulina

Kinet. Catal.,
49(2) (2008) pp. 245-252.

Thiophene synthesis from furan and H_2S over acid catalysts is reported. Proton donor catalysts are low-active, nonselective, and prone to deactivation. Alumina-supported catalysts having Lewis acid sites, such as alumina-supported catalysts, are more efficient. With these catalysts, the thiophene formation rate per Lewis acid site increases with increasing site strength. It is assumed that the reaction proceeds via the formation of a surface intermediate consisting of an acid site bonded to an α carbon atom of the furan ring and an H_2S molecule nondissociatively adsorbed on a basic site. At atmospheric pressure, T = 250-450°C, initial furan concentrations of 1–20 vol %, and H_2S/furan = 0.4–20 (mol/mol), the thiophene formation reaction is first-order with respect to both reactants and its rate constant increases with increasing temperature. The thiophene formation rate depends on the H_2S/furan molar ratio. Under optimal conditions, the thiophene yield is 95–98 mol % and the thiophene formation rate is high.

CONVERSION OF DIMETHYL DISULFIDE IN THE PRESENCE OF ZEOLITES

A.V. Mashkina, E.A. Paukshtis,
O.P. Krivoruchko, L.N. Khairulina

Kinet. Catal.,
49(2) (2008) pp. 253-260.

Dimethyl disulfide conversion in the presence of zeolites was studied at atmospheric pressure and T = 190–350°C. For all catalysts, the products of the reaction at T = 190°C - methanethiol, dimethyl sulfide, and hydrogen sulfide - result directly from dimethyl disulfide. The relative reaction rate and the dimethyl sulfide selectivity decreases in the order HZSM-5 ≥ CoHZSM-5 > HNaY > NaX, NaY. The methanethiol formation selectivity changes in the reverse order. The highest methanethiol selectivity at T = 190°C is shown by the sodium zeolites; the highest dimethyl sulfide selectivity by the high-silica zeolite HZSM-5. Raising the reaction temperature increases the reaction rate and changes the process route: at high temperatures, dimethyl disulfide decomposes to methanethiol, which then condenses to yield dimethyl sulfide and hydrogen sulfide. The observed regularities are explained in terms of the different acidic properties of the zeolite surfaces.

CATALYTIC CONVERSIONS OF DIALKYL DISULFIDES

A.V. Mashkina

Kinet. Catal.,
49(6) (2008) pp. 802-811.

The results of the studies of catalytic conversions of lower dialkyl disulfides performed at the Boreskov Institute of Catalysis are summarized. The selective hydrogenolysis of dimethyl and diethyl disulfides with the formation of alkanethiols occurs in a hydrogen medium on transition metal sulfides. Dimethyl disulfide turns into dimethyl sulfide in an inert gas medium on oxide catalysts with acid and basic sites on their surface. Lower dialkyl disulfides are dehydrocyclized to thiophene under the action of sulfide catalysts. In an oxygen medium on the metal oxides and salts, diethyl disulfide and a lower disulfide concentrate are selectively oxidized to form alkanethiolsulfinates, alkanethiolsulfonates, and alkanesulfonic acids.

DESIGN OF SCHIFF BASE-LIKE POSTMETALLOCENE CATALYTIC SYSTEMS FOR POLYMERIZATION OF OLEFINS: VIII. SYNTHESIS OF *N*-(*o*-CYCLOALKYLPHENYL) 2-HYDROXYNAPHTHALENE-1-CARBALDEHYDE IMINES

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Russ. J. Org. Chem.,
44(1) (2008) pp. 103–106.

Substituted o-cycloalkylanilines reacted with 2-hydroxynaphthalene-1-carbaldehyde in methanol in the presence of formic acid to give the corresponding Schiff bases as ligands for the synthesis of titanium(IV) complexes.

DESIGN OF SCHIFF BASE-LIKE POSTMETALLOCENE CATALYTIC SYSTEMS FOR POLYMERIZATION OF OLEFINS: IX. SYNTHESIS OF SALICYLALDEHYDES CONTAINING AN ISOBORNYL SUBSTITUENT AND HYDROXYPHENYL IMINE LIGANDS BASED THEREON

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Russ. J. Org. Chem.,
44(1) (2008) pp. 107-113.

Reactions of substituted 2-(1,7,7-trimethylbicyclo[2.2.1]hept-exo-2-yl)phenols with paraformalde-hyde in the presence of tin(IV) chloride and 2,6-dimethylpyridine gave the corresponding salicylaldehydes which reacted with primary amines to produce a series of new Schiff bases as ligands for complex formation with transition metals.

CATALYTIC OXIDATION OF BETULIN AND ITS DIACETATES WITH ECOLOGY FRIENDLY REAGENTS

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J. Siberian Federal Univ. Chem.,
1(3) (2008) pp. 277-285.

The conditions of betulin and betulin diacetate oxidation with 35 % H_2O_2 into their epoxides were studied. In the two-phase water-organic medium the oxidation reactions are carried out at mild conditions: atmosphreric pressure and temperature 60-80°C. The reaction of betulin diacetate oxidation was realized with high yield of epoxide (90 %) and degree of the conversion 98 % in the presence of soluble catalyst $[CH_3(n\text{-}C_8H_{17})_3N]_3\{PO_4[WO(O_2)_2]_4$.

LIQUID PHASE CATALYTIC PROCESSES OF “GREEN CHEMISTRY” FOR FINE ORGANIC SYNTHESIS

Z.P. Pai, V.N. Parmon

In “*Chemical Reagents, Reactants and Processes of Low Tonnage Chemistry*”, Institute of Chemistry of New Materials, Minsk, Belarus,
Eds. V.A. Agabekov, E.V. Koroleva,
2008, 346 pp.

Single-stage synthesis of epoxides, mono- and dicarbonic acids using renewable resources, containing fatty unsaturated acids, terpenes and their derivatives opens up possibilities of development of up-to-date technologies to provide innovative solutions to environmental challenges.

The results of the studying of oxidative functionalization of organic compounds of natural origin by method of phase-transfer catalysis carried out in two-phase system using environmentally friendly oxidizers are concidered.

CATALYTIC OXIDATION OF ORGANIC SUBSTRATES WITH HYDROGEN PEROXIDE IN TWO-PHASE SYSTEMS IN THE PRESENCE OF PEROXO-POLYOXOTUNGSTATES CONTAINING ORGANIC LIGANDS

Z.P. Pai, P.V. Berdnikova, A.G. Tolstikov, O.N. Roor, T.B. Khlebnikova, N.K. Gusarova*, S.F. Malysheva*, N.I. Ivanova*, B.A. Trofimov*
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React. Kinet. Catal. Lett.,
94(2) (2008) pp. 319-326.

The prospects of using of bifunctional homogeneous metal-complex catalysts based on the peroxopolyoxotungstates with organic ligands (tertiary phosphine oxides) were exemplified by oxidation of benzyl alcohol and cyclooctene with hydrogen peroxide in two-phase systems (organic phase – liquid phase).

CATALYTIC EPOXIDATION OF α,β- AND β,γ-UNSATURATED BICYCLIC KETONES WITH HYDROGEN PEROXIDE

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2100-2103.

The possibility of preparing epoxides from α,β- and β,γ-unsaturated bicyclic ketones formed as by-products in liquid-phase oxidation of cyclohexane with atmospheric oxygen (a stage in production of caprolactam, adipic acid, and other products) was examined. The reaction products were analyzed by gel chromatography and mass spectrometry.

CATALYTIC OXIDATION OF α,β- AND β,γ-UNSATURATED BICYCLIC KETONES WITH HYDROGEN PEROXIDE

Z.P. Pai, P.V. Berdnikova, A.A. Nosikov*, B.M. Khlebnikov (**Tomsk Polytechnic University, Tomsk, Russia*)

Chem. Sustain. Devel.,
16(4) (2008) pp. 421-426.

The possibility of oxidation of the compounds of light fraction of X-oils - α,β- and β,γ-unsaturated bicyclic ketones was studied with the aim of utilization of by-products in liquid-phase oxidation of cyclohexane with atmospheric oxygen (a stage in production of caprolactam. adipic acid, and other products). Oxidation was performed using 30% hydrogen peroxide under temperature 55–65ºC and atmospheric pressure, in two-phase solutions (water phase - organic phase) in the presence of a homogeneous bifunctional nanostructured catalyst based on tetra(oxodiperoxotungstato)phosphate in combination with quaternary ammonium cations. The reaction products were analyzed by GC-MS, TLC, GC.

HIGHLY REGIOSELECTIVE NICKEL-CATALYZED HYDRODEFLUORINATION OF PENTAFLUOROACETANILIDE

S.A. Prikhodko, N.Yu. Adonin, D.E. Babushkin, V.N. Parmon

Mendeleev Commun.,
18(4) (2008) pp. 211-212.

A highly regioselective reaction of pentafluoroacetanilide hydrodefluorination which proceeds under the action of zinc in the presence of nickel complexes leading to the formation of 2,3,4,5-tetra- and 3,4,5-trifluoroacetanilide was observed.

THE EFFECT OF N-HETEROCYCLIC CARBENE LIGANDS IN THE PALLADIUM-CATALYZED CROSS-COUPLING REACTION OF $K[C_6F_5BF_3]$ WITH ARYL IODIDES AND ARYL BROMIDES

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Tetrahedron,
64(25) (2008) pp. 5920-5924.

The effect of N-heterocyclic carbene (NHC) ligands on the catalytic activity of *in situ* generated palladium complexes in the model cross-coupling reaction of $K[C_6F_5BF_3]$ with $4\text{-}FC_6H_4I$ was studied. Based on the obtained results, a series of pentafluorobiphenyls $C_6F_5C_6H_4X$ were prepared from $K[C_6F_5BF_3]$ and XC_6H_4I or $4\text{-}CF_3C_6H_4Br$ in high yields under aerobic conditions.

POLYFLUOROORGANOBORON-OXYGEN COMPOUNDS: V FEASIBLE ROUTES TO PERFLUOROALKYLTRIMETHOXYBORATES $M[C_nF_{2n+1}B(OMe)_3]$ (n = 3)

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ZAAC,
633(4) (2007) pp. 647-652.

A well applicable preparative method for lithium perfluoroalkyltrimethoxyborates, $Li[C_nF_{2n+1}B(OMe)_3]$ (n = 3, 4, 6), was elaborated which is based on the reaction of $B(OMe)_3$ with $C_nF_{2n+1}Li$ generated from $C_nF_{2n+1}H$ and *t*-BuLi. Alternative perfluoroalkylation reactions of $B(OMe)_3$ with perfluoropropyllithium generated from C_3F_7I and RLi, perfluoropropylmagnesium bromide, or perfluoropropyltrimethylsilane and potassium fluoride gave less satisfactory results for $M[C_3F_7B(OMe)_3]$. The conversion of $M[C_nF_{2n+1}B(OMe)_3]$ salts (M = Li, BrMg) into $K[C_nF_{2n+1}B(OMe)_3]$ salts and basic properties of the new salts are reported.

POLYFLUOROORGANOBORON-OXYGEN COMPOUNDS: VII. STUDIES OF CONVERSION OF $[C_6H_nF_{5n-1}B(OMe)_3]^-$ INTO $[(C_6H_nF_{5-n})_2B(OMe)_2]^-$ (n = 0, 1)

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Collec. Czech. Chem. Commun.,
73(12) (2008) pp. 1681-1692.

Conversion of salts $Li[(C_6H_nF_{5-n})B(OMe)_3]$ (n = 0, 1) into $(Li{\cdot}DME)[(C_6H_nF_{5-n})_2B(OMe)_2]$ was studied in dichloromethane-DME solution. The observed rate constants k decrease from $(21.4 \pm 0.9) \times 10^{-3}$ l mol^{-1} s^{-1} ($Li[C_6F_5B(OMe)_3]$) over $(6.99 \pm 0.11) \times 10^{-3}$ l mol^{-1} s^{-1} ($Li[(2,3,5,6\text{-}C_6HF_4)B(OMe)_3]$) to $(2.94 \pm 0.05) \times 10^{-3}$ l mol^{-1} s^{-1} ($Li[(2,3,4,6\text{-}C_6HF_4)B(OMe)_3]$), while $Li[(2,3,4,5\text{-}C_6HF_4)B(OMe)_3]$ does not undergo any transformation. Hydrolysis of $(Li{\cdot}DME)[(C_6H_nF_{5-n})_2B(OMe)_2]$ leads to corresponding borinic acids, whereas treatment of them with aqueous solution of $M[HF_2]$ (M = Bu_4N, K) acidified with HF results in $M[(C_6H_nF_{5-n})_2BF_2]$ in high yields.

(FLUOROORGANO)FLUOROBORANES AND – BORATES: XVI. PREPARATION OF BIS(PERFLUOROALKYL)DIMETHOXYBORATE AND BIS(PERFLUOROALKYL)DIFLUOROBORATE SALTS, $M[(C_nF_{2n+1})2BX_2]$ (M = K, NMe_4; X = OMe, F)

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Organometallics,
26(9) (2007) pp. 2420-2425.

Potassium bis(perfluoroalkyl)dimethoxyborate salts, $K[(C_nF_{2n+1})_2B(OMe)_2]$ (n = 3, 4, 6), were prepared in 60−76% yield by the reaction of (perfluoroalkyl)lithium with chlorodimethoxyborane and subsequent metathesis of the cation with KF. Reactions of $K[(C_nF_{2n+1})_2B(OMe)_2]$ with 42−73% aqueous HF resulted in the salts $K[(C_nF_{2n+1})_2B(OR)F]$ (R = H, CH_3), which were converted into $K[(C_nF_{2n+1})_2BF_2]$ by the treatment with anhydrous HF. Metathesis of potassium salts with $[NMe_4]OH$ in water yielded the corresponding borates $[NMe_4][(C_nF_{2n+1})_2BF_2]$.

A WELL FEASIBLE AND GENERAL ROUTE TO (ORGANOETHYNYL)DIFLUOROBORANES, $R_HC{=}CBF_2$, AND THEIR PERFLUORINATED ANALOGUES, $R_FC{=}CBF_2$

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J. Fluorine Chem.,
128(7) (2007) pp. 699-702.

A representative series of (organoethynyl)difluoroboranes $RC{\equiv}CBF_2$ ($R{=}C_4H_9$, $(CH_3)_3C$, CF_3, C_3F_7, $(CF_3)_2CF$, $CF_3CF{=}CF$, $C_4F_9CF{=}CF$, C_6F_5) was prepared by abstraction of fluoride from the corresponding $K[RC{\equiv}CBF_3]$ salts with BF_3 in appropriate solvents (1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane, or dichloromethane).

CONDENSATION OF NAPHTHALENEDIOLS WITH BENZENE IN THE PRESENCE OF ALUMINUM BROMIDE: AN EFFICIENT SYNTHESIS OF 5-, 6-, AND 7-HYDROXY-4-PHENYL-1- AND 2-TETRALONES

K.Yu. Koltunov

Tetrahedron Lett.,
49(24) (2008) pp. 3891-3894.

Isomeric 1,5-, 1,6-, 1,7-, 2,6-, and 2,7-naphthalenediols react smoothly with benzene at room temperature in the presence of an excess of aluminum bromide to give 5-, 6-, and 7-hydroxy-4-phenyl-1-tetralones and 5- and 6-hydroxy-4-phenyl-2-tetralones, respectively. The mechanism of these reactions is interpreted in terms of key di- or tri-cationic (superelectrophilic) intermediates.

EFFICIENT CLEAVAGE OF CUMENE HYDROPEROXIDE OVER HUSY-ZEOLITES: THE ROLE OF BRØNSTED ACIDITY

K.Yu. Koltunov, V.I. Sobolev

Appl. Catal., A,
336(1) (2008) pp. 29-34.

The cleavage of cumene hydroperoxide in the presence of H-form USY zeolites to form phenol and acetone has been examined. For comparison, the same reaction, catalyzed by Y-, ZSM-5, β-zeolites, as well as sulfuric and heteropolyacids is performed. As appeared, HUSY zeolites of high Si/Al ratio (15 and 40) are sufficiently active catalysts, and their efficiency is comparable to that of sulfuric acid. Such outstanding catalytic performance of HUSY should be attributed to combination of favourable porous topology, sorption properties and relatively strong acidity of the internal surface. The acid strength of HY and HUSY zeolites is roughly estimated in terms of H/D exchange between deuterated acetone and water over the solid acid, while their sorption properties are estimated based on H_2O-TPD measurements.

SYNTHESIS OF BIODIESEL VIA DEOXYGENATION OF STEARIC ACID OVER SUPPORTED Pd/C CATALYST

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Catal. Lett.,
122(3-4) (2008) pp. 247-251.

High catalytic activity was achieved in the deoxygenation of stearic acid in dodecane in a temperature range of 270–300°C under 17 bar helium over palladium on nanocomposite carbon Sibunit. Besides *n*-heptadecane, which was obtained previously in this reaction with palladium on activated carbon, *n*-pentadecane was also formed in significant amounts.

CATALYTIC HYDROGENATION OF LINOLEIC ACID TO STEARIC ACID OVER DIFFERENT Pd AND Ru SUPPORTED CATALYSTS

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Appl. Catal., *A*,
345(2) (2008) pp. 201-212.

Catalytic hydrogenation of linoleic acid in *n*-decane as a solvent was studied over several Pd- and Ru-supported catalysts in order to achieve complete conversion of linoleic acid into stearic acid. Catalyst deactivation by coking was, however, rather prominent. Supported ruthenium, was more prone to deactivation than palladium, which was also confirmed in the catalyst reuse tests with technical grade linoleic acid. The mesoporous structure of the catalyst was preferable to achieve fast hydrogenation of the intermediate products, thus promoting formation of stearic acid.

REDUCTIVE DEBENZYLATION OF HEXABENZYLHEXAAZAISOWURTZITANE — THE KEY STEP OF THE SYNTHESIS OF POLYCYCLIC NITRAMINE HEXANITROHEXAAZAISOWURTZITANE

A.P. Koskin, I.L. Simakova

Russ. Chem. Bull.,
56(12) (2007) pp. 2370-2375.

Main features of the reductive debenzylation of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane were studied. This process is the key step of the synthesis of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [$5.5.0.0^{3,11}.0^{5,9}$]dodecane (hexanitrohexaaza isowurtzitane, CL-20), a compound with unique energetic and explosive characteristics. The use of the latter is restricted so far by the high cost of the two-step process of debenzylation during which the compound is rapidly deactivated. The expensive Pd/C catalyst is deactivated in the first step of the process, which limits the use of this polycyclic nitramine. The influence of the solvent nature; loadings of the reactants, catalyst, and cocatalyst; the hydrogen pressure and reaction temperature on the general features of the process and the yield of the target precursor of CL-20 was studied.

KINETIC ASPECTS OF STEREOSELECTIVITY IN HYDROGENATION OF FATTY ACIDS

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J. Mol. Catal. A: Chem.,
286(1-2) (2008) pp. 156-161.

Kinetic peculiarities of stereoselectivity in hydrogenation of fatty acids are discussed. The reaction mechanism should be able to account for independence of the reaction rate on hydrogen pressure and conversion, stereoselectivity on conversion as well as an increase in *cis*/*trans* ratio with pressure increase. Various mechanisms advanced in the literature for formation of *cis*- and *trans* mono-unsaturated acids and their derivatives are considered, showing behavior contradicting with experiments. A reaction mechanism is proposed, which is consistent with experimental observations.

CATALYTIC SYNTHESIS OF THIOPHENE FROM DIALKYL DISULFIDES AND *n*-BUTANE

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Pet. Chem.,
48(2) (2008) pp. 112-118.

A promising new method for thiophene synthesis on the basis of dialkyl disulfides (byproduct of demercaptanization of hydrocarbon feedstocks) catalyzed by a modified magnesia–chromia–alumina catalyst was developed.

TITANIUM AND CERIUM-CONTAINING MESOPOROUS SILICATE MATERIALS AS CATALYSTS FOR OXIDATIVE CLEAVAGE OF CYCLOHEXENE WITH H_2O_2: A COMPARATIVE STUDY OF CATALYTIC ACTIVITY AND STABILITY

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Appl. Catal., A,
345(2) (2008) pp. 195-200.

Catalytic properties of transition-metal-containing silicate materials with hexagonally packed mesopores-channels, Ti-MMM-2 and Ce-SBA-15, have been studied in oxidative cleavage of cyclohexene (CyH) to adipic acid using aqueous H_2O_2 as oxidant. In a solvent-free system, the yield of adipic acid reached 10-15 % at H_2O_2/CyH 3.6 mol·mol^{-1} and 80°C after 72 h. The stepwise addition of the oxidant to the reaction mixture allowed increasing the yield of the target product up to 33 and 18% for Ti-MMM-2 and Ce-SBA-15, respectively. For both catalysts, the yield of adipic acid decreased significantly in the second run despite CyH conversion attained 100%. The catalyst stability and the reasons of the deactivation have been explored. For both catalytic materials, partial decrease of the mesopore surface area and mesopore volume was observed after the CyH oxidation run. DRS-UV-vis study revealed irreversible formation of oligomerized TiO_2 like species on the Ti-MMM-2 surface due to interaction of Ti centres with the oxidant and the reaction products. The elemental analysis data showed that adipic acid causes leaching of titanium from Ti-MMM-2 into solution. Ce-SBA-15 was found to be more stable with respect to the active metal leaching but prone to deactivation due to agglomeration of cerium ions to form cerium oxide nanocrystallites; partial reduction of Ce(IV) to Ce(III) also occurred.

Polymerization Catalysts and Polymer Materials

SUPPORTED TITANIUM-MAGNESIUM CATALYSTS FOR PROPYLENE POLYMERIZATION

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Kinet. Catal.,
49(6) (2008) pp. 782-790.

The results of studies of the synthesis and properties of supported titanium–magnesium catalysts for propylene polymerization are considered. The composition of the catalysts is $TiCl_4/D_1/MgCl_2–AlEt_3/D_2$, where D_1 and D_2 are stereoregulating donors. With the use of the procedure proposed for the synthesis of titanium–magnesium catalysts, the morphology of catalyst particles depends on the stage of the preparation of a Mg-containing support. The titanium–magnesium catalysts developed afforded polypropylene (PP) in a high yield; this PP was characterized by high isotacticity and excellent morphology. The controllable fragmentation of the catalyst by the polymer is of crucial importance for the retention of the morphology of titanium–magnesium catalyst particles in PP. The fragmentation of catalyst particles to microparticles occurred in the formation of more than 100 g of PP per gram of the catalyst. The surface complexes were studied by DRIFT and MAS NMR spectroscopy and chemical analysis. It was shown that the role of internal donors is to regulate the distribution of $TiCl_4$ on different $MgCl_2$ faces and, thereby, to influence the properties of PP. It was found that chlorine-containing complexes of aluminum compounds were formed on the catalyst surface by the interaction of the catalyst with AlEt; these complexes can block the major portion of titanium chloride. Data on the number of active sites and the rate constants of polymer chain propagation (k_p) at various sites indicate that donor D_1 increases the stereospecificity of the catalyst because of an increase in the fraction of highly stereospecific active sites, at which k_p is much higher than that at low-stereospecificity active sites. Donor D_2 enhances the role of D_1. Similar values of k_p at sites with the same stereospecificity in titanium–magnesium catalysts and $TiCl_3$ suggest that the role of the support mainly consists in an increase in the dispersity of titanium chloride.

TITANIUM-MAGNESIUM CATALYSTS FOR OLEFIN POLYMERIZATION - EFFECT OF TITANIUM OXIDATION STATE ON CATALYST PERFORMANCE

T.B. Mikenas, A.A. Tregubov, V.A. Zakharov, L.G. Echevskaya, M.A. Matsko

Polimery,
53(5) (2008) pp. 353-357.

The influence of oxidation state of titanium and the effect of ethoxy groups' introduction into titanium compounds on the catalytic properties of $MgCl_2$ - supported catalysts [with triisobutylaluminum (TIBA) or triethylaluminum (TEA) as cocatalyst] in ethylene polymerization and ethylene 1-hexene copolymerization, and on the polymer characteristics is investigated. To prepare solutions, soluble compounds of titanium in different oxidation states [η^6-benzene-$Ti^{2+}Al_2Cl_8$, $Ti^{3+}Cl_3$.nDBE, and $Ti^{4+}(OEt)_2Cl_2$] were synthesized, analyzed by ESR and ^{13}C NMR methods, and immobilized on the highly dispersed magnesium chloride. The data were obtained on the effects produced by composition and oxidation state of titanium compounds (covering also commonly used $TiCl_4$) on the activity, control of PE molecular weight by hydrogen, copolymerization ability, and molecular weight distribution (MWD) of polyethylene. The results obtained demonstrate that different titanium precursors comprising Ti(II), Ti(III) and Ti(IV) compounds supported on $MgCl_2$ allow preparing the highly active catalysts for ethylene polymerization or ethylene/1-hexene copolymerization. It was found that titanium oxidation state in the initial titanium compounds had a weak effect on the molecular weight and MWD of PE, whereas the ligand environment of titanium affected this parameter more strongly.

ETHYLENE POLYMERIZATION OVER SUPPORTED TITANIUM-MAGNESIUM CATALYSTS: HETEROGENEITY OF ACTIVE CENTERS AND EFFECT OF CATALYST COMPOSITION ON THE MOLECULAR MASS DISTRIBUTION OF POLYMER

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Macromol. Symp.,
260(1) (2007) pp. 184-188.

New experimental approach was used for analysis of molecular weight distribution (MWD) of polymers produced over titanium-magnesium catalysts (TMC). Polymers were fractionated on to fractions with narrow MWD (polydispersity (PD) values $M_w/M_n < 2$). Then some of these fractions were combined to get the minimal quantity of fractions with PD values close to 2 (Flory components). It was found that three fractions corresponding to three groups of active centers are sufficient for proper fitting experimental MWD curve for PE obtained over TMC with different Ti content and with different hydrogen concentration in polymerization.

SUPPORTED ZIEGLER-NATTA CATALYSTS FOR ETHYLENE SLURRY POLYMERIZATION AND CONTROL OF MOLECULAR WEIGHT DISTRIBUTION OF POLYETHYLENE

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Chin. J. Polym. Sci.,
26(5) (2008) pp. 553-559.

The effect of chemical composition of highly active supported Ziegler-Natta catalysts with controlled morphology on the MWD of PE has been studied. It was shown the variation of transition metal compound in the $MgCl_2$-supported catalyst affect of MWD of PE produced in broad range: Vanadium-magnesium catalyst (VMC) produce PE with broad and bimodal MWD ($M_w/M_n = 14-21$). MWD of PE, produced over titanium-magnesium catalyst (TMC) is narrow or medium depending on Ti content in the catalyst ($M_w/M_n = 3.1-4.8$). The oxidation state of the initial titanium compounds in TMC has only slight effect on MWD of PE produced. Based on MWD data of PE heterogeneity of active centers of TMC and VMC was studied. The results of resolution of experimental GPC curves into Flory components indicated three Flory components are sufficient to describe MWD curve of PE, produced with TMC; six

Flory components are required in the case of VMC. In the case of copolymerization of ethylene with 1-hexene over TMC the addition of 1-hexene leads to decrease of MW and to slight effect on Mw/Mn values. On the contrary the strong effect of 1-hexene on MWD of PE produced over VMC was found: the introduction of 1-hexene results in considerable broadening of MWD due to the shifting of the main MWD peak to low MW region. At that comonomer doesn't affect the position of high molecular weight shoulder. The results indicate that some of active centers of VMC producing high MW polymer are not active in the reaction of chain transfer with comonomer.

NOVEL ZIRCONOCENE HYDRIDE COMPLEXES IN HOMOGENEOUS AND IN SiO_2-SUPPORTED OLEFIN-POLYMERIZATION CATALYSTS MODIFIED WITH DIISOBUTYLALUMINUM HYDRIDE OR TRIISOBUTYLALUMINUM

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Macromol. Chem. Phys.,
209(12) (2008) pp. 1210-1219.

Reactive species in SiO_2-supported, zirconocene-based olefin-polymerization catalysts have been characterized by comparison of their UV-vis spectra with those of related, NMR-spectroscopically identified catalyst species in homogeneous solution. Neutral zirconocene dihydride complexes are found to arise in hydrocarbon solutions as well as on SiO_2 supports when catalyst systems that contain *rac*-$Me_2Si(ind)_2ZrCl_2$ and methylaluminoxane (MAO) are modified by addition of diisobutylaluminum hydride or triisobutylaluminum. These complexes, tentatively formulated as adducts with Lewis-acidic alkylaluminum species AlR_2X, *rac*-$Me_2Si(ind)_2ZrH_2 \cdot \{nAlR_2X\}$, are reconverted into the initial reactive zirconocene cations upon addition of isobutene to these reaction systems.

ETHYLENE POLYMERIZATION OVER HOMOGENEOUS AND SUPPORTED CATALYSTS BASED ON BIS(IMINO)PYRIDINE Co(II) COMPLEX: DATA ON THE NUMBER OF ACTIVE CENTERS AND PROPAGATION RATE CONSTANT

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

Macromol. Chem. Phys.,
209(24) (2008) pp. 2510-2515.

The number of active centers (C_P) and propagation rate constant (k_P) for ethylene polymerization with homogeneous catalyst $LCoCl_2$ + MAO and supported catalyst $LCoCl_2/SiO_2$ + Al(*i*-Bu)$_3$, where L is 2,6-(2,6-$(Me)_2C_6H_3N = CMe)_2C_5H_3N$, have been determined using the method of polymerization quenching by radioactive carbon monoxide (^{14}CO). The unstable rate profile of the reaction was attributed to a decrease in the number of active centers from 0.23 to 0.14 $mol \cdot mol^{-1}(Co)$ corresponding to an increase in the reaction time from 5 to 15 min, whereas the k_P value remained constant, amounting to $3.5 \bullet 10^3$ $L \cdot mol^{-1} \cdot s$ at 35°C. A narrow molecular weight distribution of the obtained polyethylene (PE) samples ($M_w/M_n = 1.9$) testifies that the homogeneous catalyst $LCoCl_2$ + MAO can be regarded as a single-site system. The activity of the supported catalyst was stable and noticeably lower than that of the homogeneous catalyst due to the low concentration of the active centers (0.02-0.03 $mol \cdot mol^{-1}(Co)$). PE with a broad molecular weight distribution ($M_w/M_n = 36$) and noticeably higher molecular weight is formed in the presence of the supported catalysts. The activity of the supported catalyst increases sharply at polymerization in the presence of hydrogen. The data obtained on the C_P and k_P values allow suggesting the formation of the "dormant" centers at polymerization without hydrogen and regeneration of the active centers in the presence of hydrogen. The average k_P values for the supported catalyst containing multiple active centers were determined to be $5.9 \bullet 10^3$ and $10.5 \bullet 10^3$ $L \cdot mol^{-1} \cdot s$, respectively, at 35 and 50°C.

EFFECT OF TEMPERATURE ON THE NUMBER OF ACTIVE SITES AND PROPAGATION RATE CONSTANT AT ETHYLENE POLYMERIZATION OVER SUPPORTED BIS(IMINO)PYRIDINE IRON CATALYSTS

A.A. Barabanov, G.D. Bukatov, V.A. Zakharov

J. Polym. Sci. A Polym. Chem.,
46(19) (2008) pp. 6621–6629.

The inhibition of ethylene polymerization with radioactive carbon monoxide (^{14}CO) was used to obtain data on the number of active sites (C_P) and propagation rate constant (k_P) at ethylene polymerization in the temperature range of 35-70°C over supported catalysts $LFeCl_2/Al_2O_3$, $LFeCl_2/SiO_2$, and $LFeCl_2/MgCl_2$ (L: $2,6\text{-}(2,6\text{-}(Me)_2C_6H_3N = CMe)_2C_5H_3N$) with activator Al(*i*-Bu)$_3$. The values of effective activation energy (E_{eff}), activation energy of propagation reaction (E_P), and temperature coefficients of variation of the number of active sites ($E_{Cp} = E_{eff} - E_P$) were determined. The activation energies of propagation reaction for catalysts $LFeCl_2/Al_2O_3$, $LFeCl_2/SiO_2$, and $LFeCl_2/MgCl_2$ were found to be quite similar (5.2-5.7 kcal/mol). The number of active sites diminished considerably as the polymerization temperature decreased, the E_{Cp} value being 5.2-6.2 kcal/mol for these catalysts at polymerization in the presence of hydrogen. The reactions of reversible transformations of active centers to the surface hydride species at polymerization in the presence and absence of hydrogen are proposed as the derivation of E_{Cp}.

THE NUMBER OF ACTIVE CENTERS AND PROPAGATION RATE CONSTANT IN ETHYLENE POLYMERIZATION WITH A HOMOGENEOUS CATALYST BASED ON COBALT 2,6-BIS[IMINO]PYRIDYL COMPLEX WITH METHYLALUMINOXANE ACTIVATOR

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Polymer Sci., *ser. B*,
50(11-12) (2008) pp. 326-329.

The number of active centers *Cp* and propagation rate constant *kp* upon ethylene polymerization with a homogeneous catalyst based on a cobalt complex with bis[imino]pyridyl ligands ($LCoCl_2$, where L is $2,6\text{-}(2,6\text{-}(Me)_2C_6H_3N{=}CMe)_2C_5H_3N$) using methylaluminoxane as an activator was determined by quenching by radioactive carbon monoxide (^{14}CO). It was found that the drop in activity during polymerization on the above catalyst is due to the decreasing number of active centers (from 0.23 to 0.14 mol/mol Co within 15 min of polymerization); the propagation rate constant remained unchanged, $3.5 \bullet 10^3$ l/(mol s) at 35°C, which is substantially lower than for a catalyst based on an iron complex with analogous bis[imino]pyridyl ligands. It follows from the data on molecular mass characteristics of the produced polymer that the homogeneous catalyst $LCoCl_2$/methylaluminoxane is of monocenter type, and the obtained value of the propagation rate constant reflects the true reactivity of its active centers.

COPPER(II) AND COBALT(II) COMPLEXES WITH A CHIRAL 5-PYRAZOLONE DERIVATIVE OBTAINED FROM THE TERPENE (+)-3-CARENE: SYNTHESIS AND PROPERTIES

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Russ. J. Coord. Chem.,
34(10) (2008) pp. 766–771.

The complexes $[CuLCl_2]$ (**I**), $[CoLCl_2]$ (**II**), and $CuLBr_2$ (**III**) (where L is the derivative of optically active 5-pyrazolone prepared from the terpene (+)-3-carene) were obtained and characterized. According to X-ray diffraction data, crystal structures **I** and **II** (orthorhombic crystal system) are built from mononuclear acentric molecules. In the resulting complexes, the Cu^{2+} or Co^{2+} ion coordinates two N atoms of the chelating bidentate ligand L and two Cl atoms, thus making a distorted tetrahedron. Intermolecular contacts and the hydrogen bonds Cl(1)…H–O(1) give rise to columns parallel to axis *y*. For complexes **I** and **III**, μ_{eff} = 1.83 and 1.81 μB, respectively; these values correspond to the electronic configuration d^9. For complex **II**, μ_{eff} = 4.42 μB, which suggests the tetrahedral structure of the coordination entity $CoCl_2N_2$. Complexes **I** and **III** were studied by EPR spectroscopy.

Fe(II) COMPLEX WITH CHIRAL PYRAZOLYLQUINOLINE L AND Fe(II), Co(II), AND Cu(II) COMPLEXES WITH ACHIRAL PYRAZOLYLQUINOLINE L^1: SYNTHESIS AND PROPERTIES. THE CRYSTAL STRUCTURES OF [ML^{1}Cl$_2$] (M = Fe, Co, AND Cu)

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Russ. J. Coord. Chem.,
34(4) (2008) pp. 278-285.

The complexes FeLCl$_2$ (I), [FeL^{1}Cl$_2$] (II), [CoL^{1}Cl$_2$] (**III**), and [CuL^{1}Cl$_2$] (**IV**) (where L and L^1 are chiral and achiral pyrazolylquinolines, respectively) were obtained. Complexes **II–IV** were structurally characterized by single-crystal X-ray diffraction analysis. Crystals of complexes **II** and **III** are triclinic (space group $P\bar{1}$) and crystals of complex **IV** are monoclinic (space group $P2_1/n$). Structures **II–IV** are built from discrete mononuclear acentric molecules. In these complexes, the M^{2+} ion (M = Fe, Co, and Cu) coordinates two N atoms of the bidentate chelating ligand L^1 and two Cl atoms. The coordination cores MCl$_2$N$_2$ are distorted tetrahedra. For complexes **I** and **II**, μ_{eff} = 5.05 and 5.07 μ_B, respectively, correspond to the high-spin configuration d^6. For complex **III**, μ_{eff} = 4.51 μ_B (high-spin configuration d^7) and for complex **IV**, μ_{eff} = 1.80 μ_B (configuration d^9).

STRAIGHT-CHAIN SEGMENT LENGTH DISTRIBUTIONS IN UHMWP REACTOR POWDERS OF DIFFERENT MORPHOLOGICAL TYPES

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Int. J. Polym. Anal. Charact.,
12(3) (2007) pp. 221-230.

A series of reactor powders of ultrahigh molecular weight polyethylene obtained using supported and unsupported Ziegler catalysts were studied with the help of low-frequency Raman spectroscopy. This experimental technique allows one to calculate the length distribution of straight-chain segments (SCS) in a polymer sample without differing between the SCS localized in either crystalline or amorphous regions of the sample. A comparison of the scanning electron microscopy images of powders with their SCS distributions showed that the samples with pronounced fibrous morphology exhibit bimodal distribution functions, while the granular morphological pattern yields unimodal SCS length distributions.

STRUCTURE AND PROPERTIES OF ORGANIC NANOCOMPOSITES FOR QUANTUM ELECTRONICS

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High Energ. Chem.,
42(7) (2008) pp. 597-600.

Considerable progress in the creation of polymer materials for optical technologies has been achieved in the recent years. These materials are used to design tunable-laser active media, optical sensors, optical radiation limiters, and organic electronic devices. One of the most promising polymers for the fabrication of optical materials based on organic compounds is poly(methyl methacrylate) (PMMA), since it is highly transparent in the visible spectral region, is compatible with a variety of organic compounds, and exhibits a high radiation resistance.

The goal of this study was to fabricate poly(methyl methacrylate)-based optical materials for quantum electronics and to investigate their properties.

The optical polymer material was designed and its structure and properties were investigated. The studies have shown that these materials offer promise for creation of solid-state active media of tunable lasers based on organic compounds.

PROTON-CONDUCTING MEMBRANES BASED ON MULTICOMPONENT COPOLYMERS

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Russ. J. Appl. Chem.,
81(7) (2008) pp. 1213-1219.

Preparation of proton-conducting polymeric composites via copolymerization of multicomponent monomeric systems using the interpenetrating polymer network preparation procedure is studied.

The products are characterized by the protonic conductivity, water-retaining capacity, and mechanical properties. The approach used allows fabrication of membranes with a reasonable protonic conductivity over the temperature range 20–90°C. A possibility of modification of the proton-conducting materials with small additions of hydrolyzable organosilicon comonomers is analyzed. The structure of the resulting systems is examined by small-angle neutron scattering.

HYDROGELS BASED ON INTERPENETRATING NETWOORKS

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Preprint №2770, Konstantinov Petersburg Nuclear Physics Institute, Gatchina, Russia, 2008, pp. 1-38.

Properties of new hydrogels based on interpenetrating networks (IPN), which are built up from vinyl- and hydride-containing oligosiloxanes and polyvinyl alcohol (PVA), were characterized. While the PVA network swelling in water is determined by the nature and concentration of the cross-linking monomer, the swelling degree was shown to increase anomalously with an increase in the number of the monomer units. The optical transparency of the material was observed in the systems with the most tightly cross-linked network where the structural IPN units were no more than 100 nm in size. The structure of hydrogels contrasted through swelling in heavy water was characterized using small-angle neuron scattering that allowed the distribution of water-filled nanopores through the hydrogel network to be studied. The multilevel model of the hydrogel structure was constructed as a complex packing of water-saturated pored of ca. 10 nm diameter; the model agrees with the relevant atomic-force microscopic data. The structure of ion exchange PVA-based materials was considered.

Biology Related Catalysis

IMMOBILIZED NON-GROWING CELLS *RHODOCOCCUS RUBER* AS HETEROGENEOUS BIOCATALYSTS FOR HYDRATION OF ACRYLONITRILE TO ACRYLAMIDE

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Catal. Ind., 1 (2008) pp. 44-50.

The adsorptive capacity of carbon-containing supports towards non-growing cells *Rhodococcus ruber* strain gt1 possessing nitrile hydratase activity was studied. This was used to prepare heterogeneous catalysts for enzymatic hydration of acrylonitrile to acrylamide. It was shown that *Rhodococcus* immobilization is determined by the value of accessible area and surface roughness of supports. For adsorbents ("Sapropel" and "Sibunit") an amount of absorbed microorganisms reached 20-25 mg of dry cells per 1 g of a support. It was shown that when microorganism is adsorbed on supports with a rough surface (on which carbon nanofibers or pyrocarbon deposits were synthesized) nitrile hydratase activity increased by a factor of 2-3 in comparison with cell activity in suspension, while adsorption on supports with smooth graphite-like surface led to decrease by a factor of 1.5-2 of enzyme activity. Highest stability of cells *Rhodococcus ruber* immobilized on supports with a synthesized layer of catalytic fiber carbon was ascertained. Productivity of heterogeneous process of acrylamide formation is 6-fold or higher than productivity of homogeneous one.

IMMOBILIZATION OF GLUCOAMYLASE BY ADSORPTION ON CARBON SUPPORTS AND ITS APPLICATION FOR HETEROGENEOUS HYDROLYSIS OF DEXTRIN

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Carbohydr. Res., 343(7) (2008) pp. 1202-1211.

Glucoamylase (GA) was immobilized by adsorption on carbon support: on Sibunit, on bulk catalytic filamentous carbon (bulk CFC) and on activated carbon (AC). This was used to prepare heterogeneous biocatalysts for the hydrolysis of starch dextrin. The effect of the texture characteristics and chemical properties of the support surface on the enhancement of the thermal stability of the immobilized enzyme was studied, and the rates of the biocatalyst's thermal inactivation at 65-80°C were determined. The thermal stability of glucoamylase immobilized on different carbon supports was found to increase by 2-3 orders of magnitude in comparison with the soluble enzyme, and decrease in the following order: GA on Sibunit > GA on bulk CFC >

GA on AC. The presence of the substrate (dextrin) was found to have a significant stabilizing effect. The thermal stability of the immobilized enzyme was found to increase linearly when the concentration of dextrin was increased from 10 wt/vol % to 50 wt/vol %. The total stabilization effect for glucoamylase immobilized on Sibunit in concentrated dextrin solutions was about 10^5 in comparison with the enzyme in a buffer solution. The developed biocatalyst, "Glucoamylase on Sibunit" was found to have high operational stability during the continuous hydrolysis of 30-35 wt/vol % dextrin at 60°C, its inactivation half-time ($t_{1/2}$) exceeding 350 h. To improve the starch saccharification productivity, an immersed vortex reactor (IVR) was designed and tested in the heterogeneous process with the biocatalyst "Glucoamylase on Sibunit". The dextrin hydrolysis rate, as well as the process productivity in the vortex reactor, was found to increase by a factor of 1.2-1.5 in comparison with the packed-bed reactor.

GLUCOSE ISOMERASE ACTIVITY IN SUSPENSIONS OF *ARTHROBACTER NICOTIANAE* CELLS AND ADSORPTION IMMOBILIZATION OF THE MICROORGANISMS ON INORGANIC CARRIERS

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Appl. Biochem. Microbiol.,
44(2) (2008) pp. 174-181.

Kinetics of monosaccharide isomerization has been studied in suspensions of intact, non-growing *Arthrobacter nicotianae* cells. Under the conditions of the study, glucose and fructose were isomerized at the same maximum rate of 700 μ mol/min per 1 g dried cells, which increased with temperature (the dependence was linear at 60–80°C). The proposed means of adsorption immobilization of *A. nicotianae* cells involve inorganic carriers differing in macrostructure, chemical nature, and surface characteristics. Biocatalysts obtained by adsorbing the cells of *A. nicotianae* on carbon-containing foamed ceramics in the course of submerged cultivation were relatively stable and retained original activity (catalysis of monosaccharide isomerization) throughout 14 h of use at 70°C. Maximum glucose isomerase activity (2 μ mol/min per 1 g) was observed with biocatalysts prepared by adsorption of non-growing *A. nicotianae* cells to the macroporous carbon–mineral carrier Sapropel and subsequent drying of the cell suspension together with the carrier.

PROPERTIES OF BIOCATALYST OBTAINED BY ENTRAPMENT IN SiO_2-XEROGEL OF *ARTHROBACTER NICOTIANAE* BACTERIA PRODUCING CELL-BOUND GLUCOSE ISOMERASE

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Doklady NAN Belarus,
52(6) (2008) pp. 76-80.

The original technique for immobilization of *Arthrobacter nicotianae* cells having glucose isomerase activity was developed, and biocatalyst by entrapment of bacterial cells into silica xerogel was obtained. It was found that the rate of the enzymatic reaction of monosaccharide isomerization was not limited by both internal and external diffusion of substrate to immobilized bacterial cells. For biocatalyst the values of Michaelis constant, half-life time at different temperatures and temperature coefficient for the enzymatic reaction of monosaccharide isomerization were established. The obtained results can be applied to develop a modern technology of glucosefructose syrups production using immobilized glucose isomerase.

PREPARATION AND CHARACTERIZATION OF SUPPORTS WITH A SYNTHESIZED LAYER OF CATALYTIC FILAMENTOUS CARBON: III. SYNTHESIS OF CARBON NANOFIBERS ON NICKEL SUPPORTED ONTO ALUMINUM OXIDE

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Kinet. Catal.,
49(4) (2008) pp. 506-514.

The synthesis of catalytic filamentous carbon (CFC) on catalysts prepared by supporting Ni^{2+} compounds onto the surface of various alumina modifications (macroporous α-Al_2O_3 and mesoporous θ-Al_2O_3 and δ-Al_2O_3) using two procedures (impregnation and homogeneous precipitation) was studied. The texture characteristics (specific surface area and pore structure) of the parent supports and adsorbents with a CFC layer were compared. The effect of the supporting procedure on the surface morphology of Ni/Al_2O_3 catalysts and the synthesized CFC layer was studied by scanning electron microscopy. It was found that the carbon yield on a macroporous catalyst prepared by homogeneous precipitation was higher than that on a catalyst prepared by impregnation by a factor of ~2. The CFC layer exhibited a mesoporous structure because of a chaotic interlacing of carbon nanofibers, and the synthesis of CFC on macroporous supports resulted in the formation of a bidisperse pore structure of the adsorbent. Active and stable heterogeneous biocatalysts were prepared by the adsorptive immobilization of enzymatically active substances (glucoamylase and nongrowing baker's yeast cells) on CFC.

HYDROGENATION OF VEGETABLE OILS OVER Pd ON NANOCOMPOSITE CARBON CATALYSTS

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Ind. Eng. Chem. Res.,
47(19) (2008) pp. 7219-7225.

Catalytic hydrogenation of vegetable oils was studied over Pd on nanocomposite carbon catalysts. The mesoporous structure of the carbon support was beneficial to achieve fast hydrogenation rates and the desired cis/trans ratio of monoenic products of edible oil hydrogenation. The preparation procedure developed for a slurry catalyst was successfully utilized for fixed bed applications. Industrial experience of Pd/nanocomposite carbon utilization in selective hydrogenation of edible and total hydrogenation of nonedible oils is described.

ENVIRONMENTAL-FRIENDLY SYNTHESIS OF VITAMINS AND FUNCTIONALIZED QUINONES

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Rossiisky Khimichesky Zh.,
52(2) (2008) pp. 57-66.

Development of environmental-friendly synthesis of oxygen-containing products of fine organic synthesis is important today because stoichiometric oxidation with toxic reagents is widely used in this field of chemical industry. Two types of heterogeneous catalysts are tested in reaction of selective liquid-phase oxidation of phenols to quinones – important intermediates in vitamins and medical products synthesis. Comparative tests of catalytic properties of silica supported Fe-containing polymeric phthalocyanine, FePcS-SiO_2, and mesoporous mesophase material Ti-MMM-2 in reaction of oxidation of 2-methyl-1-naphtol to 2-methyl-1,4-naphtoquinone (vitamin K_3), and some other functionalized phenols to quinines with reactive groups, such as alcohol, groups with double or triple bond are carried out. Mechanism of oxidation of alkyl substituted phenols is studied using chromatography, mass-spectrometry, isotopic methods, ESR-spectroscopy. The results evidence different mechanisms of phenol oxidation in catalytic systems.

PREBIOTIC CARBOHYDRATES AND THEIR DERIVATES

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In *"Biosphere Origin and Evolution"*,
Eds. N. Dobretsov et al., Springer, 2008,
Part 2, pp. 103-118.

The most significant experimental results on the putative synthesis of various carbohydrates and their derivates from simple substrates in plausible prebiotic conditions are summarized and discussed. The synthesis of monosaccharides from formaldehyde and lower carbohydrates (glycolaldehyde, glyceraldehyde, dihydroxyacetone) can be catalyzed by different compounds such as lead, phosphate and borate ions and several natural minerals. Lower carbohydrates can be directly formed in aqueous formaldehyde solutions under the action of UV-irradiation. The possible role of carbohydrates and their derivates in the chemical evolution and development of presumable abiogenic metabolism is illustrated as well.

NANODIAMOND BIOCONJUGATE PROBES AND THEIR COLLECTION BY ELECTROPHORESIS

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Diamond Relat. Mater.,
17(11) (2008) pp. 1858-1866.

The application of detonation nanodiamonds (NDs) as probes for protein capture and electrophoretic collection was investigated. NDs were chemically modified in a series of reactions to produce a ND-NH_2 product that had increased chemical homogeneity. The product was characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). FTIR spectra were taken using an IR vacuum cuvette and the samples were dehydrated at different temperatures. The ND-NH_2 product was capable of conjugating to

N-hydroxysuccinimide derivatives of TAMRA and biotin. The number of chemically attached TAMRA molecules on ND-NH_2 was calculated to be ~ 1 molecule/nm^2. The singly conjugated TAMRA-ND (T-ND) and doubly conjugated TAMRA-ND-Biotin (T-ND-B) products formed stable aqueous colloidal suspensions. T-ND and T-ND-B were collected on planar electrodes and silicon field tip arrays using a field of 10 V/cm. The rate of collection for the aminated ND is dependent upon field strength and an exponential decrease in current was observed as a function of time. Streptavidin was captured by the T-ND-B bioconjugate probe and this nanoparticle–protein complex was collected from solution by electrophoresis.

Chemical Engineering. Mathematical Simulation of Processes and Reactors

FIXED BED REACTORS WITH GRADIENT CATALYSTS

V.M. Khanaev, E.S. Borisova, A.S. Noskov

Nova Sci. Publishers, Inc.,
2008, 103 pp.

At present, the ideas of gradient catalysts are used for creation the new type of afterburning catalysts, for microchannel reactors. In the theoretical investigation the attention is being increasingly focused on the complex approach based on the optimization of heat- and mass transfer and of the activity of the whole catalyst bed through the optimal bed packing, granule shape, distribution of the active component, heat conductivity etc., i.e. through creation of some optimal gradient medium for conducting the catalytic process. Fundamentals for optimization of the spatial bed structure, in particular for optimization of the active component distribution through the bed length, are developed intensively with regard to synthesis of new materials and creation of new methods for arranging reaction beds (for example, in microchannel reactors). The authors of the present paper are the first who proposed to use the variational approach for solving these problems, so they theoretically formulated the problem of a catalytic process optimization by means of non-uniform spatial active sites distribution and obtained the analytic solutions for several cases.

In the present paper, the following points are discussed:

1. Setting the optimization problem for a catalytic fixed bed reactor, development of theoretical methods for analysis of the obtained mathematical problem with different reaction rate equations under conditions of intensive heat and mass transfer. Theoretical analysis of the influence of gradient catalysts on:

- Economy of the total active component amount;
- Improvement of the reactant conversion;
- Optimization of the temperature profile;
- Changes in the reaction selectivity.

2. Evaluation of influences of optimal active component distribution on the conversion and selectivity in real processes, in particular in the selective oxidation of methane.

THEORETICAL AND EXPERIMENTAL FUNDAMENTALS FOR OPTIMAL CATALYST BED ARRANGING IN TUBULAR REACTOR

O.P. Klenov, V.M. Khanaev, E.S. Borisova, A.A. Sviridonov, A.S. Noskov

Catal. Ind.,
Special Issue (2008) pp. 38-46.

The article presents the results of catalyst granular layer structure studying, estimation of its effect on catalytic reactions and demonstrates the practical use of the obtained results for natural gas steam conversion in tubular reactors.

An effect of loading of catalyst particles on the spatial bed structure of a fixed bed of a tubular reactor tube has been proved theoretically and experimentally. An effect of catalyst loading on technological parameters of the process has been shown on the example of commercially important reaction of natural gas steam conversion. In particular, it is shown that optimum loading of a bed can reduce temperature of the external walls of the reactor of steam conversion by some tens of degrees. This ensure longer service of pipes operating at 700-1000°C.

On the basis of the results obtained a loading device was developed and the largest Russian reactors for natural gas steam conversion at M-750 units for methanol production (Tomsk, Gubakha) were loaded.

SPATIALLY RESOLVED NMR THERMOMETRY OF AN OPERATING FIXED-BED CATALYTIC REACTOR

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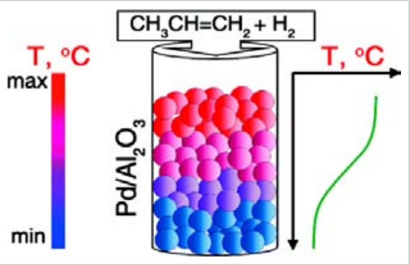
J. Amer. Chem. Soc.,
130(32) (2008) pp. 10452-10453.

An MRI-based approach for the thermometry of an operating packed-bed catalytic reactor was implemented. This approach was employed for the spatially resolved NMR thermometry of the bed of $Pd/\gamma\text{-}Al_2O_3$ catalyst beads in the course of propylene hydrogenation reaction. This was achieved by detecting the spatially resolved axial 1D profiles of the ^{27}Al NMR signal intensity of Al_2O_3 in the course of the reaction. The experimental results demonstrate a clear correlation between the ^{27}Al NMR signal intensity and the catalyst temperature measured with a thermocouple (25−250°C), and reveal the existence of pronounced temperature gradients along the catalyst bed.



STUDY OF DEEP METHANE OXIDATION KINETICS USING AN IMPROVED FLOW-CIRCULATION METHOD

I.Yu. Pakharukov, N.N. Bobrov, V.N. Parmon

Catal. Ind.,
6 (2008) pp. 11-16.

A flow-circulation method appreciably improved in recent years is the most correct method to study stationary kinetics features of heterogeneous reactions. The improvements consist in providing the possibility to determine reaction rate at given composition of a contact reaction mixture (catalytic activity) directly. The improved flow-circulation method was used for the first time to study the process of methane deep oxidation by molecular oxygen with the purpose to obtain one-parametrical dependences of catalytic activity against temperature and reaction medium component concentration as well as to solve an inverse kinetic problem. Catalyst IC-12-72 with composition 16±2 mass % of Sr_2O_3, 4±0.6 mass % of MgO (the rest - Al_2O_3) was studied. Apparent activation energy of reaction (110 kJ/mol) was determined in kinetic area. An equation well describing experimental data in the given range of concentrations (relative mean deviation was 8%) was formulated based on the experiments and conception of the mechanism of Langmuir-Hinshelwood competitive adsorption reaction. Simplicity of realization of the improved flow-circulation method allows recommending it for selection the most active catalysts and analysis of the dependences of stationary rates of heterogeneous catalytic reactions against various process parameters.

OXIDATION OF ORGANIC COMPOUNDS IN A MICROSTRUCTURED CATALYTIC REACTOR

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Chem. Eng. J.,
135(1) (2008) pp. S57-S65.

A microstructured catalytic reactor for the oxidation of organic compounds has been fabricated from aluminum alloy AlMgSiCu1 (6082 series, Al51st). The catalyst section was assembled of 63 microstructured plates with catalytic coating. In each plate of 416 µm thickness, 45 semicylindrical microchannels of 208 µm in radius with a distance in between of 150 µm were electrodischarge machined. A porous alumina layer of 29±1 µm thickness was produced on the plates by anodic oxidation. The resulting coatings were impregnated with an aqueous solution of copper dichromate followed by drying and calcination at 450°C to produce active catalysts. Kinetics of deep oxidation of organic compounds *n*-butane, ethanol, and isopropanol was studied in the reactor at 150–360°C and of 1,1 dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH) at 200–375°C. Intermediate reaction products in the reactions of alcohols and UDMH oxidation were identified. For UDMH, these are methane, dimethylamine, formaldehyde 1,1-dimethylhydrazone, and 1,2-dimethyldiazene. Nitrogen atoms from the UDMH and N-containing intermediates were shown to convert mainly to N_2. Kinetic parameters of the reactions of *n*-butane and alcohols (rate constants and apparent activation energies) were calculated using kinetic modeling based on a modified method of quickest descent.

DEVELOPMENT AND TESTING OF GRANULAR CATALYSTS FOR COMBUSTORS OF REGENERATIVE GAS TURBINE PLANTS

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A.N. Zagoruiko, S.R. Khairulin,
M.A. Kerzhentsev, V.N. Korotkikh, V.N. Parmon,
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Kinet. Catal.,
49(6) (2008) pp. 873-885.

Two types of granular catalysts for effective methane combustion in combustors of gas turbine plants (GTPs) were developed: (1) catalysts based on noble metals with a low Pd content (1–2 wt %), characterized by a low methane ignition temperature, and (2) catalysts based on manganese oxides and hexaaluminates, which have an increased thermal stability. The methane oxidation kinetics was investigated, and combustion in the catalyst chamber of the GTP was simulated. For optimizing the combustion technology, the following two-step process using a combined catalytic package is suggested. The inlet zone of the combustor is filled with a highly active Pd catalyst, which initiates methane oxidation and ensures that the temperature at the exit of this zone is the initial temperature of methane combustion. This takes place in the next zone, which is filled with an oxide catalyst tolerant to high temperatures. The pilot testing of the catalysts was carried out in a model catalytic combustor. The results are in satisfactory agreement with calculated data. Long-term tests indicate the high stability of the catalysts. The Pd catalyst was demonstrated to retain its high activity and to provide an ignition temperature of 240^{o}C. The initial activity of the hexaaluminate-based catalysts remains unchanged after tests at 930^{o}C. The use of a combined charge of the palladium (7–15%) and manganese (85–93%) catalysts in the model GTP combustor allows a high natural gas combustion efficiency to be achieved at a low level of hazardous emissions (NO_x, 0–1 ppm; CO, 1–3 ppm; hydrocarbons, 3–10 ppm).

CATALYTIC PROCESSES AND CATALYSTS FOR ELEMENTAL SULFUR PRODUCTION FROM SULFUR-CONTAINING GASES

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G.A. Bukhtiyarova

Catal. Ind.,
Special Issue (2008) pp. 52-62.

The article presents an analytical review of modern technologies for elemental sulfur production from gases. Along with wide application of the conventional alumina catalyst in conventional Claus process some new trends which may significantly affect technology of gaseous sulfur production are formulated and generalized: active development of Claus tail gases cleanup process with the stress on replacement of low-temperature processes of "Sulfreen" type with the processes of selective hydrogen sulfide oxidation by oxygen; development of novel highly-efficient technologies for hydrogen sulfide decomposition to sulfur and hydrogen; application of new catalyst types (first of all, on microfiber supports) for Claus and selective H_2S oxidation processes; wider application of titania and vanadia catalysts at new constructed units; development of technologies and catalysts for selective hydrogen disulfide oxidation for direct purification of H_2S-containing gases and for catalytic reduction of SO_2 for sulfur recovery from smelter gases.

DEVELOPMENT OF NEW CATALYSTS AND IMPROVEMENT OF CATALYTIC METHODS OF PURIFICATION OF FUEL GASES FROM VANYUKOV AND FLASH SMELTING FURNACES

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Catal. Ind.,
Special Issue (2008) pp. 80-85.

Two types of structured catalysts were developed and studied: 1) thermal conductive composite plates (TCP) for one-stage WGSR, and 2) permeable composite materials (PCM) for preferential CO methanation in hydrogen-containing gas in the presence of CO_2 (up to 20 vol %). TCP based on a thermally stable Cu-containing catalyst have high thermal conductivity – up to 2.5-5.0 $W/(m^xK)$; catalyst grain use rate for the TPC is higher than in granules of traditional commercial Cu-containing catalysts. It is shown that in one-stage process with TCP use the CO content can be reduced from 12 to 0.9-1 vol % at gas feed rate of 6300-6900 h^{-1} and temperature change along a catalyst bed from 380 to 250^{o}C. PCM based on Ni-Cr-oxide catalyst has high mechanical strength and thermal conductivity as high as 5÷10 $W/(m^xK)$; provides CO content less than 2^x10^{-3} % at 200-220^{o}C and producer gas flows from 6000 to 17000 h^{-1}, preference to CO hydrogenation is above 0.5; as a result of CO hydrogenation less than 50 % of CH_4 are produced from CO.

For purification of 1 m^3 of hydrogen-containing gas from 11-12 vol % to residual CO content less than

2^x10^{-4} vol % it is necessary: 1) 0.26 l of a Cu-based catalyst bed in the form of TCP (incl. voids among TPC) for WGSR, and 2) 0.1 l of Ni-based PCM for preferential CO methanation.

Structured catalysts may be used for production of a hydrogen-containing gas for fuel elements. Additionally, they allow carrying out the catalytic processes in conditions of intensive heat- and mass exchange that is especially important for the reactions high selectivity of which is only possible in a narrow temperature interval and in kinetic area.

ANALYSIS OF THE ACTIVITY OF AN ALUMINUM OXIDE CLAUS CATALYST IN COMMERCIAL OPERATION

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2031-2035.Activity dynamics of an AO-MK-2 aluminum oxide catalyst in conversion of hydrogen sulfide and carbonyl sulfide during four years of service in an industrial Claus reactor was analyzed. The rate constants of the Claus reaction were determined and changes in the active surface area of the catalyst were examined.

CLAUS CATALYST ACTIVITY CONTROL IN SULPHUR RECOVERY UNITS

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Catal. Ind.,
6 (2008) pp. 30-34.

The work states methodical principles of catalyst activity control in Claus reactors based on determination of a constant of hydrogen sulfide conversion reaction rate at temperatures of the catalyst less than 280°C. The considered methods have been proved by the data of laboratory researches (in a concentration range of $[H_2S]_0 = 1.5\text{-}7$ vol %), pilot tests ($[H_2S]_0 = 0.8\text{-}37.4$ vol %) of an alumina catalyst of AO-NKZ-2 produced at JSC "Novomichurinsk Catalyst Plant" and the results of its approbation in the Claus reactor of the coke-oven gas treating plant at OJSC "Magnitogorsk Iron and Steel Works". It is recommended to use them for authentic control of current activity and forecasting of a residual resource of catalysts in commercial Claus reactors operating in conditions of considerable variations of process gas composition as well as for comparative assessment of catalysts activity in Claus process.

BIOETHANOL AS A PROMISING FUEL FOR FUEL CELL POWER PLANTS

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V.A. Sobyanin, V.D. Belyaev, Yu.I. Amosov,
N.A. Kuzin, A.S. Bobrin

Theor. Found. Chem. Eng.,
42(1) (2008) pp. 1-11.

The catalytic reaction of steam reforming of bioethanol for the production of a hydrogen-containing gas in a temperature range from 300 to 700°C is studied. Copper-, nickel-, cobalt-, platinum-, and rhodium-containing catalysts supported on different substrates, including metal grids, are tested. Comparative analysis of the methods of bioethanol processing to a hydrogen-enriched gas for feeding high-temperature proton-exchange polymer electrolyte membrane fuel cells is performed.

HYDROGEN PRODUCTION FROM DIMETHYL ETHER AND BIOETHANOL FOR FUEL CELL APPLICATIONS

S.D. Badmaev, P.V. Snytnikov

Int. J. Hydrogen Energy,
33(12) (2008) pp. 3026-3030.

Dimethyl ether (DME) and water-ethanol mixtures are promising and attractive sources of hydrogen for fuel cell applications. Copper-cerium oxide systems have been studied as the catalysts for DME steam reforming to hydrogen-rich gas mixtures. Hydrogen and carbon dioxide were the main reaction products, CO content was insignificant. For CO removal to 10 ppm – the level tolerated by low-temperature fuel cells in the hydrogen-rich feed gas, the reaction of preferential CO methanation in the presence of CO_2 has been used. Nickel-cerium oxide system was used as the catalyst. Steam reforming of water-ethanol mixtures was performed using supported Rh catalyst. Reaction products of ethanol steam reforming at 400°C contained H_2, CH_4 and CO_2. As the temperature increased to 600-700°C, the CH_4 concentration decreased considerably. The obtained hydrogen-rich gas mixture can be used as a feed for high-temperature solid-oxide fuel cells.

CATALYTIC PRODUCTION OF HYDROGEN FROM METHANOL FOR MOBILE, STATIONARY AND PORTABLE FUEL-CELL POWER PLANTS

B.N. Lukyanov

Russ. Chem. Rev.,
77(11) (2008) pp. 995-1016.

Main catalytic processes for hydrogen production from methanol are considered. Various schemes of fuel processors for hydrogen production in stationary, mobile and portable power plants based on fuel cells are analysed. The attention is focused on the design of catalytic reactors of fuel processors and on the state-of-the-art in the design of catalysts for methanol conversion, carbon monoxide steam conversion and carbon monoxide selective oxidation. Prospects for the use of methanol in on-board fuel processors are discussed.

MICROCHANNEL CATALYTIC SYSTEMS FOR HYDROGEN ENERGETICS

L.L. Makarshin, V.N. Parmon

Russ. J. General Chem.,
77(4) (2007) pp. 676–684.

The concept of hydrogen energetics envisages economically reasonable hydrogen production from various organic compounds in stationary and mobile devices of low and medium performance, called fuel processors. Fuel processors with a high specific performance in hydrogen can be developed with the aid of microchannel catalytic systems. The paper considers the present situation with microchannel catalytic reactors for fuel processors.

DEVELOPMENT OF HIGH-EFFICIENT COMPACT FUEL PROCESSOR WITH MICROCHANNEL REFORMER

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In *"Advanced Energy Technologies for the Earth and Outer Space"*, Eds. A.S. Koroteeva,
M: ZAO "Svetlitsa", 2008, 208 pp.

According to the order of the National Innovation Company "New Energy Projects" a partial methane oxidation fuel processor has been developed and tested, which generates synthesis gas in amounts necessary to provide power source of a high temperature fuel cell battery of electric power of 2 kW. The fuel processor is integrated by heat with the battery using anode gas heat. The fuel processor reformer is manufactured using the microreactor technology. The technological unit incorporates a sulfur cleaning unit providing cleaning of natural gas from hydrogen sulfide to a level of 5 mg/m^3 within a half a year in addition to the reformer and heat exchangers. The unit feeding air to the technological unit of the fuel processor incorporates a membrane pump, a filter and a device making it possible to control the air flow rate by the variation of pump current frequency. A control unit has been developed and manufactured for the fuel processor, which enables the operating parameters to be monitored by means of computer. The control unit is able as well to cut off methane and air feed to the fuel processor in the case of emergency situations.

Tests as conducted demonstrated the fuel processor serviceability.

With nominal fuel flow rate the operating temperature of the fuel processor is at a level of 800–850°C. The time the reformer needs to attain 850°C at startup is 30–40 min. Depending on the fuel flow rate and methane-air proportion the temperature of the reformer and synthesis gas can be below or above the above mentioned value. The analysis results on reformate composition at the fuel processor exit indicate that the methane conversion at Reformer temperatures of 850–900°C, when the catalyst activity is high, is equal to 95%. Yield in terms of hydrogen and carbon oxide is close to the calculational indices. As temperature decreases, the catalyst activity drops and, consequently, the methane conversion decreases. At present the fuel processor is being tested for its performance and lifetime in "Keldysh Center". Tests are being conducted according to the NIC"NEP" program. The created specimen may serve as a basis for the development of the fuel processor for a high capacity power unit.

HYDROGEN PRODUCTION BASED ON THE SELECTIVE CATALYTIC PYROLYSIS OF PROPANE

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Theor. Found. Chem. Eng.,
42(5) (2008) pp. 611-621.

Catalytic decomposition of propane with producing hydrogen in a temperature range of 400–

700°C is investigated. Optimal production parameters (temperature, catalyst composition), which provide the production of a mixture of hydrogen and propane with a low methane content free of carbon oxides for a long time, are established.

DIRECT CONVERSION OF METHANE ON Mo/ZSM-5 CATALYSTS TO PRODUCE BENZENE AND HYDROGEN: ACHIEVEMENTS AND PERSPECTIVES

Z.R. Ismagilov, E.V. Matus, L.T. Tsykoza

Energy Environ. Sci.,
1 (2008) pp. 526-541.

Development of highly effective catalysts for one-stage conversion of light hydrocarbons with high selectivity to valuable products will solve such problems as efficient utilization of natural and oil-associated gases, and environmental protection. Methane dehydroaromatization (DHA) over Mo/ZSM-5 catalysts is a promising process for direct production of valuable aromatic compounds and hydrogen from methane. This review focuses on the range of issues dealing with the effect of catalyst composition, preparation, pretreatment and operation conditions on the physicochemical properties and activities of Mo/ZSM-5 catalysts in DHA reaction. The concepts of the reaction mechanism and the nature of the active molybdenum forms are reviewed. Various aspects of the Mo/ZSM-5 deactivation under reaction conditions and methods of their regeneration are discussed. Some approaches for improvement of the Mo/ZSM-5 performance in DHA reaction are addressed in the review in detail.

$LiCoO_2$-BASED CATALYSTS FOR GENERATION OF HYDROGEN GAS FROM SODIUM BOROHYDRIDE SOLUTIONS

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Catal. Today,
138(3-4) (2008) pp. 260-265.

The catalytic performance of lithium cobaltite, $LiCoO_2$, in sodium borohydride hydrolysis has been studied and compared with catalytic properties of Co_3O_4, $CoCl_2$ and $Co(NO_3)_2$. Activation times and observed H_2 generation rates were found dependent on the chemical nature and dispersion of the catalysts, as well as on the reaction temperature. The magnetic susceptibility method was used to demonstrate that all studied cobalt compounds, including cobalt oxides and soluble salts, are being reduced under catalytic conditions to form catalytically active cobalt boride phases. Impregnating $LiCoO_2$ with Pt and Rh chlorides increases only the initial catalytic activity, which then quickly declines during cyclic stability tests and in just a few cycles approaches that of the starting $LiCoO_2$ material.

HYDROGEN PRODUCTION BY CATALYTIC HYDROCARBON DECOMPOSITION VIA CARBIDE CYCLE MECHANISM

V.V. Chesnokov, R.A. Buyanov, V.V. Molchanov

Catal. Ind.,
Special Issue (2008) pp. 19-23.

Method of hydrogen production by catalytic decomposition of hydrocarbons via carbide cycle mechanism is considered. The reasons of generation of methane in equilibrium concentration as an admixture to hydrogen are explained. A catalyst with productivity up to 600 l of hydrogen per 1 g of the catalyst during 1 cycle at maximum possible temperature (700-750^{o}C) was developed to reduce the depending on the temperature methane equilibrium concentration. A method was suggested for catalyst regeneration using water steam with possibility of its cycle operation.

SORPTION ENHANCED HYDROCARBONS REFORMING FOR FUEL CELL POWERED GENERATORS

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Int. J. Hydrogen Energy,
33(12) (2008) pp. 3061-3066.

The single-step sorption enhanced reforming of methane, propane–butane mixture, ethanol, methanol over an admixture of CaO sorbent with a Ni reforming catalyst have been experimentally studied in a periodically operated quasi-adiabatic fixed bed reactor. The bed temperature profile during reforming step drastically influences the purity of product hydrogen. The best results were obtained for the temperature decrease downstream the reactant flow. In the case of the alcohols reforming the hydrogen purity was 98–99 vol % with both CO and CO_2 impurities of about 10–20 ppm. A proton exchange membrane fuel cells (PEMFC) stack was successfully fed with the hydrogen produced by the single-step sorption enhanced reforming of ethanol without any loss of efficiency. Both the sorbent and the catalyst maintained sufficient activity level during 1500 h on stream and more than 600 cycles.

DEVELOPMENT OF Cu- AND Ni-CONTAINING STRUCTURED CATALYSTS FOR PURIFICATION OF H_2-RICH GASES FROM CARBON MONOXIDE BY STEAM CONVERSION AND PREFERENTIAL HYDROGENATION

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Catal. Ind.,
Special Issue (2008) pp. 24-30.

Two types of structured catalysts were developed and studied: 1) thermal conductive catalyst plates (TCP) for one-stage WGCR and 2) permeable composite material (PCM) for reaction of preferential CO methanation in hydrogen rich gas in CO_2 excess (up to 20 vol %). TCP based on a thermally stable Cu-containing catalyst possesses high thermal conductivity - up to 2.5-5.0 W(m^{x}K); catalyst grain use for TCP is higher than in the granules of traditional commercial Cu-containing catalysts. It is shown that in one-stage process with TCP CO concentration can be reduced from 12 to 0.9-1 vol % at the gas feed rate of 6300-6900 h^{-1} and temperature change along the catalyst bed from 380 to 250°C. PCM based on a Ni-Cr-oxide catalyst has high mechanical strength; thermal conductivity as high as 5÷10 W/(m^{x}K); provides CO residual content less than 2x10^{-1} % at 200-220°C and gas flow 6000÷17000 h^{-1}; CO preference hydrogenation above 0.5; CO_2 hydrogenation results in no more than 50% of CH_4.

For purification of 1 m^3 of hydrogen containing gas from 11-12 vol % to residual CO content less than 2x10^{-4} it is necessary: 0.26 *l* of Cu-based TCP (including voids among TCPs) and 2) 0.1 *l* of Ni-based PCM for preferential CO methanation.

Structured catalysts may be used for production of hydrogen-containing gas for fuel cells. Additionally, they allow carrying out the catalytic processes in conditions of intensive heat- and mass exchange that is especially important for reactions which are selective only in narrow temperature interval and in kinetic area.

PREFERENTIAL CO OXIDATION OVER A COPPER–CERIUM OXIDE CATALYST IN A MICROCHANNEL REACTOR

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Appl. Catal., *A*,
350(1) (2008) pp. 53-62.

The activity of a 5 wt % Cu/CeO_{2-x} catalyst during preferential CO oxidation in hydrogen-rich gas mixtures was studied in a microchannel reactor. The CO concentration dropped from 1 vol % to 10 ppm at a selectivity of 60%, at a temperature of 190°C, and a WHSV of 55,000 cm^{3}g^{-1}h^{-1}. Both the CO concentration and the temperature increased when the WHSV was increased from 50,000 to 500,000 cm^{3}g^{-1}h^{-1}. An increase of the O_2 concentration from a 1.2 to 3 fold excess reduced the CO concentration to 10 ppm in a broad temperature interval of 50°C at WHSVs up to 275,000 cm^{3}g^{-1}h^{-1}. The preferential CO oxidation could be carried out at higher flow rates and at higher selectivities in the microchannel reactor compared to a fixed-bed flow reactor.

COMPARATIVE STUDY ON CONVERSION OF C_8 AND C_{16} PARAFFINS ON ZSM-5 CATALYSTS

D.G. Aksenov, O.V. Kikhtyanin, G.V. Echevsky

Stud. Surf. Sci. Catal.,
174A (2008) pp. 1211-1214.

A comparative study of conversion of n-octane and n-hexadecane in conditions of BIMF process was performed to follow reaction pathways and to estimate advantages to use heavier distillates for obtaining high-quality fuels. It was found that the conversion of both n-octane and n-hexadecane depends on reaction pressure, and the yield of liquid reaction products is higher in the case of heavier feed. However products of n-octane conversion demonstrate more stable behavior with TOS (Time On Stream). Benzene content is lower in the case of n-hexadecane. A positive effect of heavier hydrocarbons in minimizing dealkylated aromatics content was demonstrated by special experiments.

DEVELOPMENT OF CATALYST Pt-SAPO-31 FOR HEAVY HYDROCARBON FRACTION HYDROISOMERIZATION PROCESSES

O.V. Kikhtyanin, G.V. Echevsky

Catal. Ind.,
3 (2008) pp. 47-53.

Catalyst Pt-SAPO-31 was obtained on the basis of synthesized silicoaluminophosphate with the structure of SAPO-31 and applied for hydroisomerization of heavy hydrocarbon fractions. Activity and selectivity of the catalyst of various chemical compositions in conversion of n-octane, diesel fraction and slack wax were investigated. Optimum structure of the catalyst has been revealed. Pt-SAPO-31 catalyst considerably reduces turbidity and freezing temperatures of reaction products by reducing content of n-paraffins, not being inferior by these parameters to an industrial catalyst on the basis of silicoaluminophosphate SAPO-11 in production of low cold-test diesel and oil fractions. Presence in raw materials of sulfur up to 500 ppm reduces activity of the catalyst and requires rise of reaction temperature by 10-15°C for production of products with necessary temperature characteristics. Laboratory tests were a basis for carrying out catalyst pilot tests.

SYNTHESIS OF SAPO-31 WITH di-n-PENTYLAMINE: INFLUENCE OF CHEMICAL COMPOSITION AND CRYSTALLIZATION CONDITIONS

O.V. Kikhtyanin, A.V. Toktarev, A.B. Ayupov, G.V. Echevsky

Stud. Surf. Sci. Catal.,
174B (2008) pp. 245-248.

SAPO-31 materials were prepared using di-n-pentylamine. Both composition of reaction mixture and hydrothermal treatment conditions exhibit an influence on the crystallization kinetics. Thus, low silica content accelerates crystallization, however high silica content has an opposite effect. Calculation of unit cell parameters for samples with different crystallinities may help in understanding of crystallization mechanism. The obtained results are discussed using data of physico-chemical methods.

PILOT TESTS OF Pt-SAPO-31 CATALYST IN GASOIL ISOMERIZATION

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Catal. Ind.,
Special Issue (2008) pp. 30-38.

The article presents the results of pilot tests of a pre-production prototype of catalyst Pt-SAPO-31, mass. % Pt – (0.5-1), Al_2O_3 – 46, P_2O_5 – 38, SiO_2 – 16, completely confirmed results of earlier laboratory studies of this material in hydroisomerization of heavy hydrocarbon fractions. The purpose of the tests was: selection of an optimal regime for isomerization of gasoils with various sulfur content; determination of product properties according to requirements of standards; estimation of catalyst operation stability. It is shown that the catalyst is highly active and selective in conversion of initial gasoil. It is proved by decreasing of freezing and cloud point temperature by 30-35°C at diesel fuel output 96-98%. Resource tests of the catalyst in processing of raw material with sulfur content $5x10^{-3}$ % at 335-340°C showed high stability of its operation during 800 hours without change of catalytic activity and temperature characteristics of the product.

Pilot tests showed advantages of the pre-production prototype Pt-SAPO-31 and prospects of its practical use in hydroisomerization of gasoils with sulfur content up to $35x10^{-2}$ %. Properties of the end products are defined by a temperature regime of the process. Large-scale technology is developed. Organization of industrial production of the catalysts is possible at existing catalyst plants having experience of zeolite synthesis.

HYDROTREATMENT OF DIESEL FEEDSTOCK OVER Pt-SAPO-31 CATALYST: FROM LAB TO PILOT SCALE

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Stud. Surf. Sci. Catal.,
174B (2008) pp. 1227-1230.

High effective hydroisomerization properties of Pt-SAPO-31 catalyst were demonstrated both in laboratory experiments and on pilot scale. Activity of the catalyst is suppressed by sulfur (100-500 ppm), but it may be restored by temperature rise. Long-term run of Pt-SAPO-31 catalyst have confirmed its high activity and stability. Group compositions of feedstock and reaction products were examined by ^{1}H and ^{13}C NMR method and properties of the catalyst in dependence on reaction properties are discussed.

INFLUENCE OF THE HEAT TREATMENT CONDITIONS ON THE ACTIVITY OF THE CoMo/Al$_2$O$_3$ CATALYST FOR DEEP HYDRODESULFURIZATION OF DIESEL FRACTIONS

A.V. Pashigreva, G.A. Bukhtiyarova, O.V. Klimov, G.S. Litvak, A.S. Noskov

Kinet. Catal.,
49(6) (2008) pp. 812-820.

The effect of the heat treatment temperature on the sulfidation and activity of CoMo/Al$_2$O$_3$ catalysts designed for deep hydrodesulfurization of diesel fuel was studied. The catalysts were prepared using citric acid as a chelating ligand. The organic ligands present in the samples heat-treated at 110 and 220°C retard the decomposition of dimethyl disulfide and the formation of the sulfide phase but make the catalyst more active than the samples calcined at higher temperatures.

MODERN CATALYSTS FOR DEEP HYDROTREATING FOR PRODUCTION OF LOW-SULFUR DIESEL FUELS BY EURO-3 AND EURO-4 STANDARDS AT THE RUSSIAN PETROLEUM PROCESSING PLANTS

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Catal. Ind.,
Special Issue (2008) pp. 6-13.

For production of diesel fuels with sulfur content according to Euro-3 and Euro-4 standards at the Russian petroleum processing plants without reconstruction of existing hydrotreating units it is necessary to replace catalysts by more active ones. Most of the Russian catalysts can be used for production of diesel fuels with sulfur content $3.5\text{x}10^{-2}$ mass. %, or higher. For production of fuel with sulfur content less than $5.0^{\text{x}}10^{-3}$, and residual sulfur content less than $1.0^{\text{x}}10^{-3}$ mass. %, it is necessary to use catalysts of the latest generation, surface compounds of which represent a highly active Co(Ni)-Mo-S phase of the second type. Domestic catalyst IC-GO-1 that has been produced at the CJSC "Promyshlennye Katalizatory" since 2007 under the license of the Boreskov Institute of Catalysis is a typical representative of such catalysts. Upon commercial operation of the catalyst at the JSC "Saratovskii NPZ" hydrotreating parameters guaranteed both by the developer and the manufacturer were confirmed. Production of IC-GO-1 can reach 600 t/year that is enough for re-equipment of 10 typical Russian hydrotreating plants within a year.

FINE HYDROTREATMENT OF OIL DISTILLATES OF PRIMARY AND SECONDARY ORIGIN OVER NEW GENERATION CATALYSTS

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Neftepererabotka i Neftekhimiya,
10 (2007) pp. 19-23.

The possibility of synthesis of high-quality low-sulfur diesel fuels from straight-run oil distillate and from the mixture of the straight-run distillate with gasoil of the catalytic cracking was studied in the presence of new generation Co-Mo/Al$_2$O$_3$ sulfide catalysts. Catalytic properties of these catalysts and of a number of the best Russian and imported catalysts were compared. It was shown that the hydrotreatment process, when achieved over the new-generation catalysts under conditions typical of the Russian refineries, allows the EURO-4 diesel fuel to be produced from the straight-run oilfeed. When the feed is a mixture containing 30% of the catalytic cracking gasoil, the properties of the resulting hydrogenizates are somewhat out the EURO-4 standards. The obtained data on the transformations of organosulfur and condensed aromatic compounds lead to expect the stable yield of diesel fuels satisfying the EURO-4 standards at a decreased proportion of catalytic cracking gasoil in the feed.

PRECIOUS METALS FOR CATALYST PRODUCTION

V.N. Parmon, V.I. Simagina, L.P. Milova

Catal. Ind.,
Special Issue (2008) pp. 46-52.

Application of precious metals (platinum and palladium) for catalyst production taking into account creation and development of new catalytic technologies is reviewed. Production of domestic catalysts on the basis of precious metals is reduced. Annual production of these catalysts is a little more than 300 t which corresponds to approximately 25-30% use of existing capacities for production of these catalysts. Construction of new and modernization of existing plants that use catalysts containing precious metals is carried out with the participation of foreign companies. The share of imported catalysts containing Pd and Pt for various process still remains significant (up to 60%). The level of precious metals consumption in production of organic synthesis products and medical products remains at the level of 1990s. Potentialities of extended applications of platinoids are reviewed both for creation of new generations of traditional catalysts in petroleum processing, petroleum chemistry, organic synthesis, protection of environment competitive with import ones and for areas new for Russia such as creation of nanocomposite materials for hydrogen power engineering, medical products, membrane technologies.

UNIVERSAL RELATION BETWEEN THE BOUNDARY TEMPERATURES OF A BASIC CYCLE OF SORPTION HEAT MACHINES

Yu.I. Aristov, M.M. Tokarev, V.E. Sharonov

Chem. Eng. Sci.,
63(11) (2008) pp. 2907-2912.

For analyzing a basic cycle of an adsorption heat machine (AHM) an empiric rule was suggested, which manifests that adsorption isosters and equilibrium line lnP(1/T) for the pure sorbate intersect at T approaching infinity. This rule prompts how to plot the cycle, gives a link between the boundary temperatures of the cycle and allows estimation of a minimal temperature T^{min}_{σ} of an external heat source that is necessary to drive the cycle. In this paper the validity of the T^{min}_{σ} estimation was justified for working pairs which are most commonly used for adsorption units: water-silica gel, water-zeolite 13X, water-zeolite 4A, water-selective water sorbents (SWSs), CO_2-carbon, methanol-carbons (AC-35, TA90), methanol-hydrophobic zeolite CBV 901 Y and ammonia-carbon PX31. Four main working pairs for absorption heat machines-ammonia-water, water-LiBr, methanol-LiBr and R22-isobutylacetate are also analyzed. This allowed the formulation of requirements to an optimal adsorbent to be used in a single-effect non-regenerative cycle of an AHM. The accuracy of the T^{min}_{σ} estimation was examined for each pair. Moreover, it was shown that Trouton's rule is always valid if sorption equilibrium obeys the Polanyi potential theory, i.e., the equilibrium sorption is a unique function of the sorption potential $AF = -RT \ln(P/P_0)$. For chemical reactions between various salts and sorbates this rule is violated because of a large difference between the standard changes of the entropy and enthalpy in the course of reaction and evaporation. In this case T^{min}_{σ} can be calculated from the Clausius-Clapeyron and Vant-Hoff equations.

HYBRID AUTOWAVES IN FILTRATION COMBUSTION OF GASES IN A CATALYTIC FIXED BED

A.P. Gerasev

Combust., Explosion, Shock Waves,
44(2) (2008) pp. 123-132.

A mathematical model of autowave processes in a heterogeneous medium with chemical reactions in the gas phase and on the catalyst is constructed. The coefficients of heat and mass transfer between the phases and the thermal conductivity of the solid phase are determined from the current values of system parameters. The model describes three types of autowaves: waves due to filtration combustion of gases in the low-velocity regime, waves due to a catalytic reaction, and hybrid waves. The behavior of phase trajectories of the dynamic system is studied by methods of qualitative and numerical analysis, and an effective technique is developed for searching for a physically grounded autowave solution of the problem. The laws of propagation of autowaves due to filtration combustion of gases and hybrid autowaves are numerically examined, and the effect of system parameters on the basic technological characteristics of autowave processes is studied.

MATHEMATICAL MODELING OF THE CONTINUOUS PROCESS FOR SYNTHESIS OF NANOFIBROUS CARBON IN A MOVING CATALYST BED REACTOR WITH RECIRCULATING GAS FLOW

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Chem. Eng. J.,
137(3) (2008) pp. 681-685.

A continuous process for synthesis of nanofibrous carbon from methane in a reactor with a moving bed of the $Ni-Al_2O_3$ catalyst (90 wt % Ni) and intensively recirculated gas flow is considered. Dependencies for calculating outlet characteristics of the gas mixture and catalyst are suggested. Comparison of various types of continuous reactors shows that the suggested reactor is preferable.

MODELING OF CONTROLLED COMBUSTION OF HIGH-ENERGETIC MATERIALS ON STRUCTURED CATALYSTS

V.M. Khanaev, E.S. Borisova, N.N. Kundo

Combust., Explosion, Shock Waves,
44(5) (2008) pp. 535-542.

A mathematical model of combustion of high-energetic materials on structured catalysts is developed. Numerical studies are performed for combustion of a typical material: aminoguanidine nitrate. An increase in catalytic activity, as well as an increase in the thermal conductivity of the catalyst, is found to expand the range of real-time controlling of the burning rate of the condensed substance.

NUMERICAL STUDY OF A MATHEMATICAL MODEL OF A CATALYTIC FUEL PROCESSOR WITH COCURRENT OXIDATION AND CONVERSION FLOWS

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J. Appl. Ind. Math.,
2(3) (2008) pp. 329-340.

The results are presented of the numerical study of a mathematical model in the form of a nonlinear boundary value problem describing the stationary regimes in a catalytic fuel processor. The authors study a two-dimensional model for the endoblock, with the longitudinal heat and mass transfer by the gas and the transversal heat conductivity along the catalyst in the two-temperature approximation. For the exochannel, a model is considered with the longitudinal heat and mass transfer by the gas flow and the longitudinal heat transfer along the catalytic wall. These two blocks are related to each other through the equality of the temperature and heat flux on the boundary. The results obtained are in good agreement with experimental data.

STOCHASTIC SIMULATION OF PHYSICOCHEMICAL PROCESSES PERFORMANCE OVER SUPPORTED METAL NANOPARTICLES

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J. Comput. Chem.,
29(1) (2008) pp. 79-86.

The statistical lattice model has been proposed which permits one to take into account the change in the shape and surface morphology of the nanoparticle under the influence of the reaction media. The influence of monomolecular and dissociative adsorption on the particles equilibrium shape and surface morphology has been studied. It has been shown that by taking into account of attraction "adsorbate-metal" the reshaping of the initial hemispheric particle into cone-shaped one occurs induced by adsorption, similar to the experimentally observed reversible reshaping of active nanoparticles. The model reaction $A+B_2$ has been studied taking into account the roughening of the active particle surface and the spillover phenomena of the adsorbed A_{ads} species over the support surface.

PRODUCTION OF NANOMATERIALS BY VAPORIZING CERAMIC TARGETS IRRADIATED BY A MODERATE-POWER CONTINUOUS-WAVE CO_2 LASER

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J. Appl. Mech. Techn. Phys.,
48(2) (2007) pp. 292-302.

The efficiency of utilization of CO_2 laser energy for vaporization of Al_2O_3 ceramics is evaluated using a mathematical model for the interaction of laser radiation with materials. It is shown that the calculated efficiency of radiation-energy utilization is not higher than 15% at a radiation power density of 10^5 W/cm^2 on the target. On the experimental facility designed for the synthesis of nanopowders, a vaporization rate of 1 g/h was achieved for Al_2O_3, which corresponds to a 3% efficiency of radiation-energy utilization. The dependence of the characteristic particle size of a zirconium oxide nanopowder on helium pressure in the range of 0.01–1.00 atm was studied. Results of experiments on vaporization of multicomponent materials ($LaNiO_3$ and the Tsarev meteorite) are given.

THE SPECIAL FEATURES OF PHASE EQUILIBRIA IN α-PINENE-WATER BINARY MIXTURES IN THE SUB- AND SUPERCRITICAL STATES

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Russ. J. Phys. Chem. A,
82(6) (2008) pp. 928-932.

Phase equilibria in α-pinene–water binary mixtures under sub- and supercritical conditions were studied by thermodynamic modeling. The compositions and boiling points of three-phase heteroazeotropic mixtures were calculated as functions of pressure. The T and p regions of the existence of liquid–liquid and vapor–liquid two-phase mixtures were determined. The $T_{c\ \mathrm{mix}}$ and $p_{c\ \mathrm{mix}}$ critical curve coordinates depending on mixture composition were found. The $T_{c\ \mathrm{mix}}$ curve exhibited an anomaly in the form of a minimum. The $T_{\mathrm{Az}}p_{\mathrm{Az}}$ heteroazeotropic line ended at the minimum point of the critical curve.

CALCULATION OF PHASE DIAGRAMS OF HETEROPHASE TWO- AND THREE-COMPONENT LIQUID MIXTURES 'α-PINENE – WATER' AND 'α-PINENE – WATER – ETHANOL'

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Chem. Eng. Sci.,
63(24) (2008) pp. 5854-5859.

Phase behaviors of two- and three-component mixtures 'α-pinene–water' and 'α-pinene–ethanol–water' were studied over a wide range of their composition, temperature, and pressure. Conditions were found that provide heteroazeotropic states of binary mixture 'α-pinene–water' and ternary mixture 'α-pinene–ethanol–water' depending on the ratio of 'water/(α-pinene+ethanol)' fractions at the 'α-pinene+ethanol' ratio of 1:1. Critical curves were calculated to demonstrate an anomalous dependence of these curves on the mixture composition, with the temperature minimum points typical of the mixtures that form heteroazeotropes.

THE KINETICS OF THERMAL ISOMERIZATION OF β-PINENE AND A MIXTURE OF β- AND α-PINENES IN SUPERCRITICAL ETHANOL

A. Yermakova, A.M. Chibiryaev*, I.V. Kozhevnikov, V.I. Anikeev

J. Supercrit. Fluids,
45(1) (2008) pp. 74-79.

Thermal isomerization of p-pinene and equimolar mixture of α- and β-pinenes in supercritical ethanol was studied experimentally. The reactivity of structurally similar α- and β-pinenes were compared in the same supercritical solvent. It was shown that both pinenes undergo thermal transformations independently of one another upon co-thermolysis in supercritical (SC) ethanol. Conversion of α-pinene yields monocyclic limonene as the main product, and p-pinene gives acyclic p-myrcene. This study allowed developing the first kinetic model of p-pinene thermolysis in SC ethanol.

THE INFLUENCE OF WATER ON THE ISOMERIZATION OF α-PINENE IN A SUPERCRITICAL AQUEOUS-ALCOHOLIC SOLVENT

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Russ. J. Phys. Chem. A,
82(1) (2008) pp. 62-67.

The influence of water as a cosolvent and catalyst of the isomerization of α-pinene in a supercritical aqueous–alcoholic (ethanol) solvent was studied experimentally. At T=657 K and p = 230 atm, an increase in the concentration of water in the reaction mixture was found to increase the rate of the reaction and its selectivity with respect to the desired product, limonene. Water exhibited the properties of an acid catalyst because of its ionization. Mathematical experimental data processing was performed to evaluate and separate the contributions of the radical and ionic paths to the total rate of the reactions that occurred during the thermal isomerization of α-pinene.

MODELING OF REVERSE-FLOW REACTOR FOR VOC INCINERATION WITH ACCOUNT OF REVERSIBLE ADSORPTION: THE WAY TO MINIMIZE THE NEGATIVE INFLUENCE OF DESORPTION PHENOMENA

A.N. Zagoruiko

Int. J. Chem. Reactor Eng.,
vol. 6: A110 (2008).

The paper discusses the influence of adsorption/desorption phenomena on the purification performance of the reverse-flow catalytic incinerator for abatement of volatile organic compounds (VOC). It is shown that the reversible adsorption of VOC at the catalyst surface may occur at the catalyst bed inlet in the end of the cycle, followed by desorption into outlet gases after flow reversal leading to decrease of the process purification efficiency. The mathematical modelling results showed that inert material beds in combination with proposed process control strategy are needed to avoid negative influence of adsorption effects.

ANAEROBIC CATALYTIC OXIDATION OF HYDROCARBONS IN MOVING HEAT WAVES. CASE SIMULATION: PROPANE OXIDATIVE DEHYDROGENATION IN A PACKED ADIABATIC V–Ti OXIDE CATALYST BED

A.N. Zagoruiko

Chem. Eng. Sci.,
63(20) (2008) pp. 4962–4968.

The model simulation study has shown that the anaerobic process of oxidative dehydrogenation of propane under periodic alteration of feeding between propane and air may be realized in adiabatic catalyst beds in a stable continuous cyclic mode in a two-reactor scheme. In the case of an appropriate choice of process parameters (cycle duration and feeding flow rates) the process appears to be autothermal, i.e. it does not require any inlet gas preheating for stable operation. Compared with a similar steady-state adiabatic process, the proposed process is characterized with much lower maximum catalyst temperatures, giving the way to process pure propane without diluting it with inert gases, thus simplifying the downstream procedure of product separation. Predicted propylene yield is competitive with the one for the steady-state adiabatic process, while sufficient technological benefits of the new technology are expected (decrease in energy consumption and minimization of heat-exchange environment, process safety improvement, suppression of coke formation and efficient coke incineration).

DEVELOPMENT AND APPLICATION OF SOFTWARE FOR THE AGENT MODEL OPTIMIZATION

O.A. Zasypkina, O.P. Stoyanovskaya, I.G. Chernykh

Numer. Methods Program.,
9 (2008) pp. 19-25.

A new technology for the model construction of physico-chemical processes of agents is proposed. This technology gives a possibility of searching and adaptation of kinetics scheme for chemical reactions. A new version of the ChemPAK software package is discussed as an application of this technology. The package was used to study the Butlerov reaction scheme and the ethane and methane pyrolysis schemes.

STUDYING INSTABILITY OF 3D COLLISIONLESS SYSTEMS ON STOCHASTIC TRAEJECTORIES

V.N. Snytnikov, E.A. Kuksheva

In "*Collective Phenomena in Macroscopic Systems*",
Eds. G. Bertin, R. Pozzolli,
World Scientific Pub. Co Inc., 2007, pp. 280-285.

A practical method for distinguishing stochastic and regular subsystems in the entire set of particles for numerical modeling of the development of physical instabilities in collisionless systems with self-consistent fields is proposed. The method of subdividing the phase space into subsystems is based on the comparison of the results of two computational experiments with identical initial conditions but different realizations of rounding errors. An example of establishing the spatial and temporal domains of the development of collective instability and determining the instability increments is offered by a gravitating disk.

A CAPILLARY GAS CHROMATOGRAPHIC COLUMN WITH A POROUS LAYER BASED ON A MESOPOROUS MATERIAL

Yu.V. Patrushev, V.N. Sidelnikov, M.K. Kovalev, M.S. Melgunov

Russ. J. Phys. Chem. A,
82(7) (2008) pp. 1202-1205.

A procedure for synthesizing an MSM-41-type mesoporous mesophase material (MMM) layer, that is, a layer of a solid porous material with a regular arrangement of nanoscale calibrated pores and a unified geometry, on the inner wall of a capillary column was developed. Because of the high specific surface area of silica, capillary columns with a porous MMM layer on the basis of silica allow the amount of samples introduced to be increased by an order of magnitude compared with the known capillary porous-layer columns. An example of the separation of light hydrocarbons is described. The properties of columns with MMM porous layers are discussed.

GAS-CHROMATOGRAPHIC STUDY OF THE RETENTION OF COMPONENTS OF THE REACTION OF THE CATALYTIC OXIDATION OF PROPYLENE ON POROUS POLYMERS

E.Yu. Yakovleva, O.V. Skrypnik

J. Anal. Chem.,
63(5) (2008) pp. 455-459.

The gas-chromatographic retention of oxygen, carbon dioxide, propane, propylene, water, propylene oxide, acrolein, acetone, and acetaldehyde on polar and nonpolar adsorbents was studied. A procedure was proposed for the gas-chromatographic determination of gaseous and liquid components of the reaction of the catalytic oxidation of propylene using one column.

A GAS-CHROMATOGRAPHIC STUDY OF THE RETENTION OF REACTION COMPONENTS IN THE CATALYTIC OXIDATION OF β-PICOLINE TO NICOTINIC ACID

E.Yu. Yakovleva, V.Yu. Belotserkovskaya, O.V. Skrypnik

J. Anal. Chem.,
63(9) (2008) pp. 863-866.

The gas-chromatographic retention of pyridine, β-picoline, 3-pyridinecarbaldehyde, 3-pyridinenitrile, nicotinic acid, and nicotinamide on polar stationary phases was studied. A scheme was proposed and a procedure was developed for the determination of the reaction components of the catalytic oxidation of β-picoline to nicotinic acid on a column (3 m × 3 mm) packed with Chromosorb WAW + 10 wt % FFAP. The separation time was 28 min. The detection limits were 0.01 and 0.37 ppm for 3-pyridinenitrile and nicotinic acid, respectively.

CONTACT LENSES

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Eds. V.F. Danilichev, S.A. Novikov,
St. Petersburg, advertising agency "Veko",
2008, 271 pp.

The monograph reflects the state-of-the-art in the ophthalmocontactology. Particular attention is paid to the possibility of application of remedial contact lenses. Under consideration is the creation of new materials, saturation of the lenses with antibiotics, their application depending on the presence of certain microflora, application of remedial soft contact lenses for perioperational prophylaxis of intraocular infection and for delivering medical care at injuries of the organ of vision, as well as for eye protection under extreme conditions including high smoke content and exposure to unfavorable chemical factors.

A NEW APPROACH TO REGENERATING HEAT AND MOISTURE IN VENTILATION SYSTEMS

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Energy Buildings,
40(3) (2008) pp. 204-208.

For countries with a cold climate the large difference (30-60°C) in winter between indoor and outdoor temperatures leads to (a) large heat losses in ventilation systems; (b) moisture freezing at the systems exit; (c) great reduction in the indoor humidity. Here is presented a new approach for regenerating heat and moisture in ventilation systems in cold climates which allows resolution of these problems. The method has been tested under climatic conditions of West Siberia (winter 2005-2006). The prototype system requires very little maintenance, has a low capital cost, is compact and energy efficient. Technical, economic and social aspects of this method are discussed.

FOCUSING AEROGEL RICH OPTIMIZATION

A.Yu. Barnyakov*, M.Yu. Barnyakov*, V.S. Bobrovnikov*, A.R .Buzykaev*, A.F. Danilyuk, V.V. Gulevich*, V.L. Kirillov, S.A. Kononov*, E.A. Kravchenko*, A.P. Onuchin*, S.I. Serednyakov*, V.V. Porosev*
(**Budker Instituнte of Nuclear Physics, Novosibirsk, Russia)*

Nucl. Instrum. Meth. Phys. Res., *Sect. A*,
595(1) (2008) pp. 100-103.

The method of improvement of Cherenkov angle resolution in RICH detectors using 'focusing' aerogel radiators (FARICH) is under investigation. The 'focusing' three-layer aerogel radiator was investigated using a digital radiographic device. The Monte Carlo calculations of velocity resolution based on measured variations of the refractive index in aerogel tile are presented. With the observed variations, π- and K-mesons can be separated up to 8.4 GeV/*c*, π- and μ-mesons can be separated up to 1.6 GeV/*c*. The use of sodium fluoride radiator in a RICH detector was studied. NaF radiator extends the working momentum region for the π/K identification down to 0.6 GeV/*c*. It has been shown that a RICH detector with NaF radiator can achieve a competitive velocity resolution up to 5 GeV/*c* as compared to single-layer aerogel RICH.

RESULTS FROM R&D OF CHERENKOV DETECTORS AT NOVOSIBIRSK

A.Yu. Barnyakov*, M.Yu. Barnyakov*, K.I. Beloborodov*, V.S. Bobrovnikov*, A.R. Buzykaev*, A.F. Danilyuk, V.B. Golubev*, V.V. Gulevich*, V.L. Kirillov, S.A. Kononov*, E.A. Kravchenko*, A.P. Onuchin*, S.I. Serednyakov* (**Budker Institunte of Nuclear Physics, Novosibirsk, Russia)*

Nucl. Instrum. Meth. Phys. Res., *Sect. A*,
581(1-2) (2007) pp. 410-414.

The group produces silica aerogels with refractive indices of 1.006–1.13 with good optical transparency. The particle identification systems for the KEDR and the SND detectors based on threshold aerogel counters are described. Cosmic test results for the SND counters are presented. The possibility of employing a RICH with a sodium fluoride crystal radiator for π/K separation up to 5 GeV/c momentum is explored. The combined NaF-aerogel radiator is proposed to decrease the minimum working momentum of the RICH below the Cherenkov threshold in aerogel.

MEMBRANES AND NANOTECHNOLOGIES

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Nanotech. Russ.,
3(11-12) (2008) pp. 656-687.

The today's state of membrane science, as well as membrane applications and trends in the studies related to nanotechnology are discussed. The detailed analysis is carried out of the use of highly permeable polymer glasses, metallic and ceramic membranes for gas separation, alcohols, ultra pure substances and hydrogen production, as well as aqueous and organic media nanofiltration. The technology and mechanism of the nuclear pore membrane formation are outlined. The approaches are mentioned to form the channels with complex geometry. The ion exchange membranes and polymeric proton-conducting electrolytes are specially discussed. The feature of polyelectrolytes for membranes, membrane structure and transport properties are considered. The membrane modification with organic and inorganic components are described. The achievements in ion exchange membrane use for the pure and deionized water production are discussed. The problems related the fuel cell membrane are outlined. The significant attention is paid to asymmetry transport in nanosize membranes. The mechanisms responsible for the asymmetry in gas and electrolyte transport are discussed.

FLUORINATED PROTON-CONDUCTING NAFION-TYPE MEMBRANES, THE PAST AND THE FUTURE

S.S. Ivanchev

Russ. J. Appl. Chem.,
81(4) (2008) pp. 569-584.

By now, considerable advances have been made in the field of fuel cells (FC) operating with polymeric electrolytes in the form of thin membranes. The development in this area is governed by the wide variety of application fields of membrane FC. As for solid-oxide FC, their use is presumably limited to development of high-power installations in which the loss of heat into the environment can be minimized. The authors analyze in what follows the problems solely associated with polymeric electrolytes for membrane FC. A strong stimulus to activation of research in the field of membrane FC was given by the agreement on hydrogen energetics, concluded by the Russian Academy of Sciences and Noril'skii Nikel' combine. In accordance with this agreement, the research program envisaged a wide variety of studies in hydrogen energetics and fuel cells, including development of polymeric proton-conducting membranes for FC, improvement of catalytic systems on FC electrodes, improvement of the FC design, and fabrication of FC batteries. Taking into account the wide diversity of the problems associated with these tasks, the authors consider in more detail the development of polymeric membrane FC and analyze the synthesis and fabrication of proton-conducting polymeric (primarily fluoropolymeric) membranes for FC.

ASTROCATALYSIS HYPOTHESIS FOR ORIGIN OF LIFE PROBLEM

V.N. Snytnikov

In "*Biosphere Origin and Evolution*",
Eds. N. Dobretsov et al., Springer US, 2008,
Part 2, pp. 45-53.

Analysis of the available natural science data has allowed the astrocatalysis hypothesis to be formulated. The hypothesis indicates the pre-planetary circumstellar disk as the most probable time and place of the primary abiogenic synthesis of prebiotic organic substances from simple molecules along with the "RNA world" and the life origin. The sequence of self-organization stages that gave rise to the Earth biosphere is determined. Results of computational experiments with supercomputers are used to determine conditions of abiogenic organic compounds in the Earth's biosphere. In handling the problem of the origins of the Earth's biosphere, it is necessary to establish and study the role of abiogenic synthesis of prebiotic compounds in the sequence of key stages of the self-organization of matter. The sequence is the evolution of the surroundings from the point of Big Bang towards organic life and further to humans.

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2. **(V.F. Danilichev, S.A. Novikov, N.A. Ushakov, V.N. Pavlyuchenko, E.V. Boiko, M.S. Polyak, E.V. Muravieva, I.N. Okolov, V.A. Reituzov, G.V. Gorelova, V.M. Dolgikh), S.Ya. Khaikin, (V.S. Proshina, G.G. Rodionov, T.G. Sazhin, S.V. Sosnovskii, S.V. Chepur, S.V. Churashov), S.S. Ivanchev, (A.A. Koltsov),**
“Contact Lenses”,
Eds. V.F. Danilichev, S.A. Novikov, St. Petersburg, advertising agency “Veko”, 2008,
271 pp. (in Russian).
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Status Quo and Prospects of Development of Chemical and Sorption Heat Engines in the Russian Federation and the Republic of Belarus,
J. Eng. Thermophys.,
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Catalytic Production of Hydrogen from Methanol for Mobile, Stationary and Portable Fuel-Cell Power Plants,
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Stoichiography and Chemical Methods of Phase Analysis of Multielement Multiphase Substances and Materials,
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Catalytic Conversions of Dialkyl Disulfides,
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Catalytic Technologies for Enhancement of Fuel and Energy Resources of Russia by Using Non-Traditional Sources of Hydrocarbon Fuel,
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Liquid Phase Catalytic Processes of "Green Chemistry" for Fine Organic Synthesis,
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In "*Development of Life upon Changes in the Earth's Abiotic*",
Publishing House SB RAS, Novosibirsk, 2008, pp. 242-258 (in Russian).

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Astrocatalysis Hypothesis for Origin of Life Problem,
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Modelling of Astrocatalysis on Supercomputers,
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Publishing House SB RAS, Novosibirsk, 2008, 192 pp. (in Russian).

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In "*Collective Phenomena in Macroscopic Systems*", Eds. G. Bertin, R. Pozzolli,
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Russ. Chem. Rev.,
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Catalytic Processes and Catalysts for Elemental Sulfur Production from Sulfur-Containing Gases,
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"*Physical Chemistry of Solid State*",
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"*Catalytic Processes in Fixed Bed Reactors*",
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Collec. Czech. Chem. Commun.,
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Polyfluoroorganoboron-Oxygen Compounds: V. Feasible Routes to Perfluoroalkyltrimethoxyborates $M[C_nF_{2n+1}B(OMe)_3]$ (n = 3),
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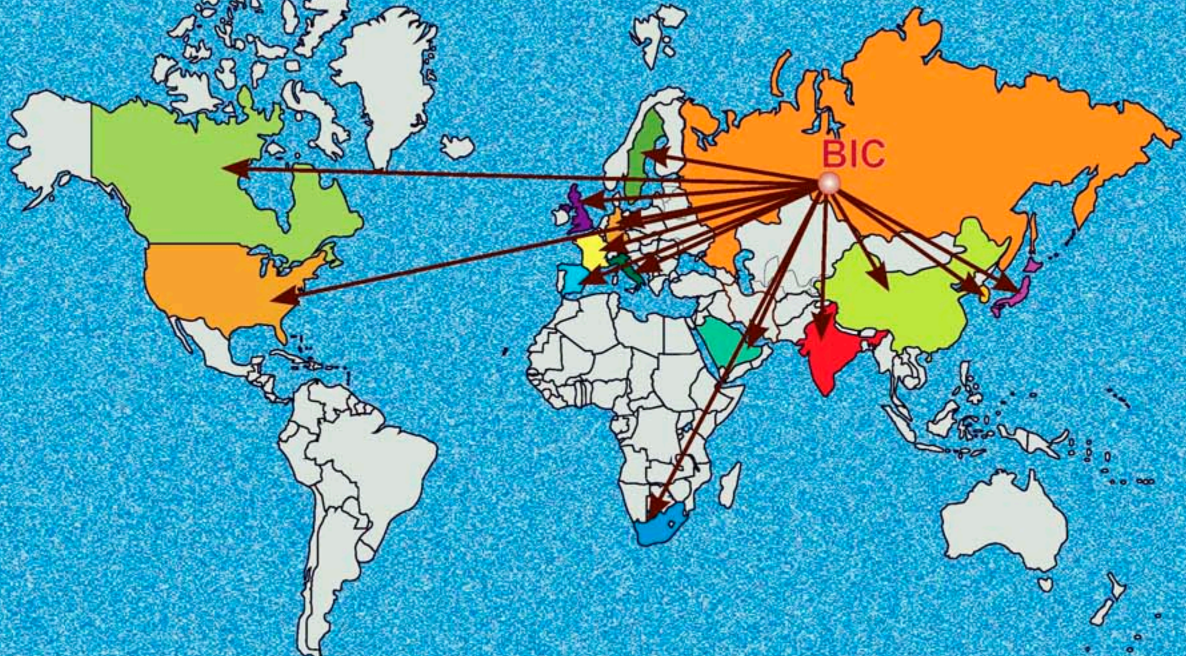

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