BORESKOV INSTITUTE OF CATALYSIS

SIBERIAN BRANCH OF RUSSIAN ACADEMY OF SCIENCES

ANNUAL REVIEW '99

ANNUAL REVIEW

of Activities in Fundamental Areas

1999

BORESKOV INSTITUTE OF CATALYSIS
SIBERIAN BRANCH OF RUSSIAN ACADEMY OF SCIENCES

Novosibirsk

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Pr. Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia

Phone: (007) 383 2 34 32 69
FAX: (007) 383 2 34 30 56
E-mail: parmon@catalysis.nsk.su
http: //www.catalysis.nsk.su

Dear Colleagues,

This is a real pleasure for me to present already the sixth issue of annual reviews of the Boreskov Institute of Catalysis in the main fields of its academic and R&D activities covering the year 1999.

The Boreskov Institute of Catalysis is well known to experts in both academic and industrial catalysis not only in Russia and CIS, but also in many western and oriental countries. Since the sixties it has remained the largest chemical research institution in the Asian part of Russia having many deep and stable traditions and providing research in nearly all fields of catalysis. Its interests spread from the sophisticated purely academic research to the real applied problems, including commercial catalysts and catalytic technologies.

During the last years according to numerous changes in Russia and its stepwise approach to the market economy, there were also some sufficient changes in the behavior and life of the Boreskov Institute of Catalysis. However, in spite of general instability in the country, the Institute could survive as a high quality specialized organization. Moreover, the intensity and quality of the research and engineering activity at the Institute became even higher. 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 impulse of its creator and first director Academician Georgii K. Boreskov. Hope, the readers will feel that themselves, when comparing the materials of this and previous issues of the Annual Review.

The year 1999 was very important for the life of the Institute in many aspects. First of all, the Institute has condoned to sustain successfully in the extremely high financial instability of Russia in the mid of 1998. This appeared possible only due to a very high professional value of the Institute among the industries both in Russia and abroad that helped financial self-maintenance of the Institute. Thus, since 1996 nearly one quarter of the Institute's budget originates as royalties or license fees from the industries, mainly the western ones. The total income from the Russian and foreign industries into the overall budget of the Institute has approached the value of 75 % in 1999. Also, since the mid 1990’s there was established a really strategic partnership with some world leading industrial companies.

Since 1998 the Institute has been operating in the status of the Key Russian institution and federal coordinator in the field of catalysis and catalytic technologies, i.e. in the very high federal status, the same as the Institute had in the former USSR. From that year the Institute succeeded also in reestablishing the National Russian R&D program in new generation of catalysts and catalytic technologies sponsored by the Ministry of Science and Technologies of the Russian Federation.

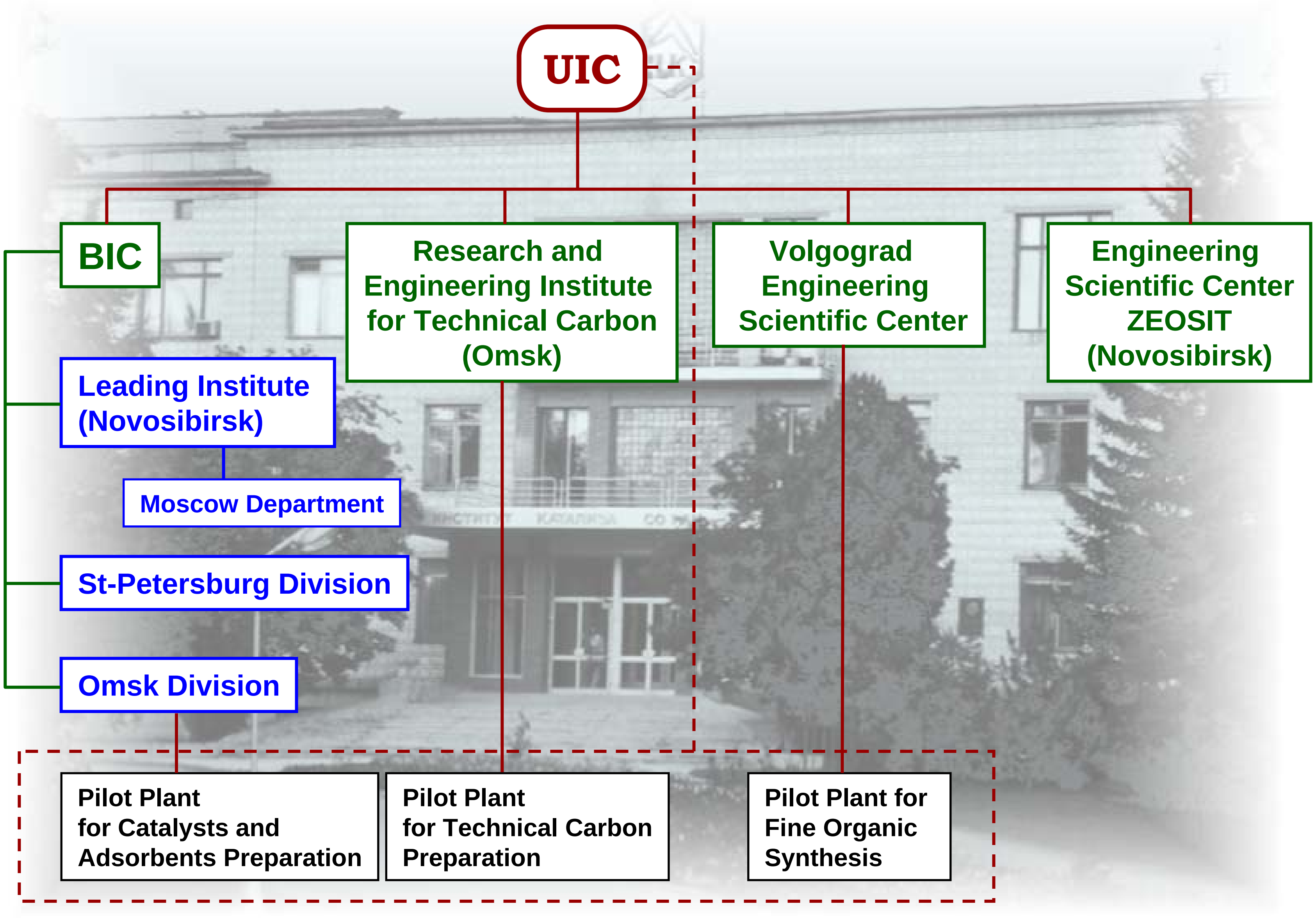
Since 1998 the Institute has been united with some other R&D chemical institutions of the Siberian Branch of the Russian Academy of Sciences in the frame of a new R&D association: the United Institute of Catalysis headed by the director of the Boreskov Institute of Catalysis. Now the United Institute of Catalysis (UIC) includes the Boreskov Institute of Catalysis with its Omsk and St. Petersburg Divisions, the Research and Engineering Institute for Technical Carbon in Omsk as well as Scientific-Engineering Center “Zeosit” in Novosibirsk and Volgograd Scientific-Engineering Center on the Volga River. The facilities of the UOC include now three powerful pilot plants capable of providing manufacturing of the first industrial batches of various catalysts and specialty chemicals.

The year 1999 was the fifth year of activity of the third generation of the directorate of the Institute. According to the Bylaw of both the Institute and the Russian Academy of Sciences, in the spring of 2000 there was accomplished a procedure of reelection of the Director of the Institute for the next five-year period. V. Parmon has remained the position of the Director. According to the Bylaw the next step has to be renovation also of the staff of both the Board of Directors as well as the Scientific Council of the Institute up to year 2005. Indeed, these changes will be very important, since even now the main research and administrative management in the Institute belongs to a sufficiently young generation of researches. However, one can be sure that the new management of the Institute will also recognize well all the existing problems taking the maintenance of high activity and productivity of R&D of the Institute in both fundamental and applied areas as the goals of the highest priority.

Hope this issue of the Annual Review of the Boreskov Institute of Catalysis is exhibiting many sides of the current Institute’s capacity 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 before, we publish special issue of the Institute’s reviews.

May, 2000 Valentin N. Parmon

United Institute of Catalysis (UIC)



UIC

BIC

Research and Engineering Institute for Technical Carbon (Omsk)

Volgograd Engineering Scientific Center

Engineering Scientific Center ZEOSIT (Novosibirsk)

Leading Institute (Novosibirsk)

Moscow Department

St-Petersburg Division

Omsk Division

Pilot Plant for Catalysts and Adsorbents Preparation

Pilot Plant for Technical Carbon Preparation

Pilot Plant for Fine Organic Synthesis

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

The Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences (BIC) still remains the largest specialized institute working in the field of catalysis not only at the territory of Asian part of Russia, but in the world too. It is the only institution in the country fully specialized on the problems of catalysis and encompasses all its aspects from fundamental and theoretical to industrial mastering of new catalysts.

The Institute was founded in 1958. 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 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 (up to 1000 people in staff) 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) includes the Boreskov Institute of Catalysis with its Omsk and St. Petersburg Divisions, the Research and Engineering Institute for Technical Carbon in Omsk as well as Scientific-Engineering Center “Zeosit” in Novosibirsk and Volgograd Scientific-Engineering Center on the Volga River.

STRUCTURE OF THE INSTITUTE

The Institute of Catalysis with its Omsk and St. Petersburg Divisions currently has 1000 employees, of these 5 Corresponding Members of the RAS, more than 50 Professors, about 200 have a Ph.D. degree, and about 30 Ph.D. students. The Institute presents the unique society of specialists in broad spectra of catalysts problems, able to solve any questions related to phenomena of catalysis, from theoretical problems like quantum-chemical calculations up to designing of industrial catalysts and processes.

The structure of the Institute incorporates 7 scientific-research departments, Department of Applied Catalysis Problems, Center for Catalyst Characterization and Testing, and Information Center. The structure of the Institute includes also scientific-supportive units, manufacturing facilities, administration and services.

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, including data on their chemical and phase composition, dispersity and pore structure, nature of active components, etc.
- Joint investigations with foreign firms and organizations in order to design new catalysts, processes and technologies; search for new prospect catalytic systems.
- Development of modern standard experimental methods and equipment for catalyst studies and tests. Design of catalysts and materials with certificated properties.

In its work Center bases on high potential of the Institute, its fundamental and applied studies in all fields of catalysis, its outdated instrumentation and methods for catalytic systems studying.

The Information Center of the Institute comprises the Library of Scientific Literature and the Group of mathematical and programm support.

The Information Center was established to support WWW-server of the Institute http://www.catalysis.nsk.su and the United server SB RAS on Chemical Sciences http://www.catalysis.nsk.su/chem**.**

Data bank included 8 Databases on Russian and foreign catalysts, catalyst supports, catalytic processes, etc.

Department of Applied Catalysis Problems with a complex bench of adoption and testing of processes and catalysts provides commercialization of new developments in shortest time.

STRUCTURE OF THE INSTITUTE

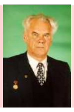
Directorate:
G.M. Matveev, B.S. Bal'zhinimaev,
V.I. Bukhtiyarov, B.I. Ermakov, S.P. Kil'dyashev,
A.S. Noskov, V.A. Likholobov, V.N. Parmon,
V.A. Sobyanin

DIRECTOR

Directorate

Scientific Council

Research Departments



DEPARTMENT OF HETEROGENEOUS CATALYSIS
7 laboratories and 4 groups Head: Prof. R.A. Buyanov

DEPARTMENT OF HOMOGENEOUS AND COORDINATION CATALYSIS
3 laboratories and 4 groups Head: Prof. V.A. Likholobov

DEPARTMENT OF MATHEMATICAL MODELING OF CATALYTIC PROCESSES
3 laboratories Head: Prof. V.A. Kirillov

DEPARTMENT OF NONTRADITIONAL CATALYTIC PROCESSES AND TECHNOLOGIES
3 laboratories and 7 groups Head: Acad. V.N. Parmon

DEPARTMENT OF CATALYTIC METHODS FOR ENVIRONMENTAL PROTECTION
2 laboratories and 2 groups Head: Prof. Z.R. Ismagilov

DEPARTMENT OF CATALYTIC PROCESS ENGINEERING
5 laboratories and 3 groups Head: Prof. A.S. Noskov

DEPARTMENT OF PHYSICOCHEMICAL METHODS FOR CATALYST INVESTIGATION
9 laboratories and 3 groups, Center for Catalyst Characterization and Testing Head: Prof. D.I. Kochubey

DEPARTMENT OF APPLIED CATALYSIS PROBLEMS
Head: Dr. A.A. Kirchanov

THE INFORMATION CENTER OF THE INSTITUTE
Head: Dr. V.L. Kuznetsov

Scientific-Supportive Units

Manufacturing Facilities

Administration and Services

SCHOOLS OF THE BORESKOV INSTITUTE OF CATALYSIS

The Boreskov Institute of Catalysis has numerous and deep traditions and continues intensive fundamental and applied investigations. It possesses an actively and fruitfully working school of specialists in catalysis.

Many works by the school of **Acad. Georgii K. Boreskov** in the field of deep and partial oxidation processes are well known in our country and far from its frontiers.

The principal importance has the concept of chemical nature of phenomenon the decisive role in which belongs to the intermediate chemical interaction between the reagents and catalysts. The fundamentals of the theory of heterogeneous oxidative catalysis are:

- The key importance of the energy of reagent bonding to the catalyst for the rate and rote of oxidation reactions;

- The influence of cation nearest environment on catalytic properties;

- A viewpoint on reaction medium and catalyst as an indivisible system;

- An idea of stepwise and concerted mechanisms of redox reactions.

Under the guidance of **Prof. Mikhail G. Slin'ko** a school raised famous not only in Russia, but abroad as well.

M.G. Slin'ko developed a method of mathematical modeling of catalytic reactors and processes, based on hierarchical principle. This method was developed for multi-phase processes and reactors with fixed and fluidized beds.

Design of real industrial catalysts with optimum strength, pore structure; providing their reproducibility on a large scale are the necessary elements of all aspects in the field of applied catalysis. **Prof. Vera A. Dzis'ko** contributed significantly to the development of methods of preparation and studying the regularities of oxide catalysts formation.

The revealed correlation of preparation conditions and physico-chemical properties of oxide systems allowed to formulate the criteria to control phase composition, surface area, stability, and acid-base properties, that appeared to be the basis for creation of a number of industrial catalysts and carriers.

At the end of the 60s big progress was in the field of homogeneous catalysis and catalysis by transition metal complexes. Of essential importance in this field not only for our country were the works by **Prof. Yurii I. Yermakov**.

Yu.I. Yermakov formulated the conception of the surface metal-organic compounds as active sites precursors for the supported catalysts. It served as a basis for the new approach in catalysis - application of principles used in homogeneous catalysis to study fundamental problems of heterogeneous catalysis. Methods for purposeful synthesis of supported catalysts of desired composition and dispersity have been developed.

In the 1977-1978 a big team of chemical physicists of the younger generation headed by **Acad. Kirill I. Zamaraev** came from Moscow. The flow of these specialists significantly enlivened the atomic-molecular studies of catalytic reaction mechanisms and catalytic properties of heterogeneous catalysis by physicochemical methods.

The school by K.I. Zamaraev contributed much to:

- *Development of theory of electron tunneling in condensed media;*
- *Coordination chemistry of metal-complexes solutions;*
- *Step-wise description of homogeneous catalytic reactions;*
- *The works in photochemistry, photocatalysis and solar-to-chemical energy conversion.*

The main principle of these works is the complex application of modern physico-chemical technique to mechanistic studies of heterogeneous and homogeneous reactions, studies of the structure and the active sites at the molecular level, search of new nontraditional directions in catalysis.

This year the teams headed by Prof. Roman A. Buyanov, Prof. Vladimir A. Likholobov, Acad. Valentin N. Parmon, Prof. Georgii M. Zhidomirov won the competitive Program "Leading Scientific Schools" supported by Russian Foundation for Basic Research (RFBR).

Prof. Roman A. Buyanov developed the home school of fundamentals for catalyst preparation and technology**.**

The main research areas covered are:

- *Design and application of new methods to increase solid phases activity at catalysts preparation and to control their activity and selectivity;*
- *Study of catalysts deactivation and carbon-mineral compositions formation;*
- *Development of the theory of non-branched radical chain reactions in the absence of oxygen (pyrolysis);*
- *Design of industrial catalysts.*

The works by school of **Prof. Vladimir A. Likholobov** initiated development of methodological and fundamental approaches to the synthesis of effective homogeneous and heterogeneous catalysts for organic synthesis.

The main conceptions of this school are:

- *Molecular design of catalytic compositions on all hierarchical levels;*
- *"Assembly" of active centers of metal complex catalysts;*
- *Synthesis of porous supports with desired texture and surface properties.*

The works of school by **Acad**. **Valentin N. Parmon** relate to:

- *Design and study of novel and nontraditional catalytic processes, first of all, photocatalytic and thermochemical methods for the direct conversion of solar energy and ionizing radiation energy;*
- *Development of an original approaches to description of catalytic processes by methods of nonequilibrium thermodynamics;*
- *Study of a possible impact of photocatalysis over the troposphere aerosols on the global chemistry of the Earth atmosphere.*

The school of **Prof. Georgii M. Zhidomirov** develops the quantum-chemical direction in theoretical spectroscopy and molecular theory of catalysis:

The methodological basis for molecular (cluster) modeling of catalytic systems is formulated, the cluster approximation is widely used to calculation of electronic structure and reactivity of active sites on zeolites and oxide catalysts.

R&D ACTIVITY OF THE INSTITUTE

Fundamental catalysis

- Determination of general physico-chemical regularities of catalysis
- Development of scientific basis for molecular design of substances and materials
- Development of the theoretic basis for realization of catalytic processes.

Applied catalysis

- Design of highly efficient catalysts of new generation for the production of key chemicals and oil processing
- Design of catalytic compositions and technologies for innovative application areas
- Development of innovative catalysts and catalytic technologies manufacturing complex chemicals and polymers with preconceivable properties
- Design of sorbents, catalysts and technologies for detoxication of hazardous technogenous wastes.

In the context of future research program, the Institute will continue to study the mechanisms and kinetics of actually important catalytic reactions, improve physicochemical and quantum-chemical methods used in catalysis, develop the research basis for purposeful synthesis of a number of catalysts, supports and sorbents (including non-traditional mechanochemical, plasma, radiation-thermal methods, etc.), study the regularities of formation of new materials (carbon-carbon composite materials of globular and fibrous structure, polymer-inorganic composites, composite membranes, etc.) as well as supports and adsorbents with the optimum geometry and controlled structure and mechanical properties (monolith multichannel ceramics, honeycomb carbon and ceramic monoliths); design new and improve the existing catalytic processes (cracking, alkylation, polymerization, etc.) and novel reactors, study the possibilities of using catalysis in such non-traditional fields as thermocatalytic conversion of solar and other types of energy; design of adsorption materials for freon-free air conditioners, accumulators of low-potential heat, active cooling systems; technologies with the use of low-energy fuels; various types of heaters with catalytic fuel cells, etc.

INSTRUMENT 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

COMMERCIAL CATALYSTS AND TECHNOLOGIES OWNED BY THE BORESKOV INSTITUTE OF CATALYSIS

CATALYSTS FOR CONVERSION OF LIQUID ORTHO-HYDROGEN TO PARA-HYDROGEN

1970 - Uzbekistan

VANADIUM CATALYSTS FOR SULFURIC ACID PRODUCTION

1970 - Russia

CATALYSTS FOR ENVIRONMENTAL PROTECTION

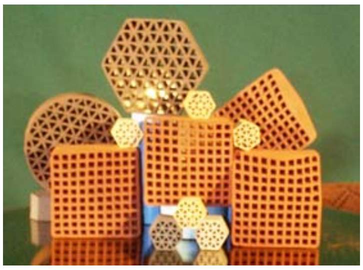
1990 - Russia

FORMALDEHYDE PRODUCTION FROM METHANOL OVER OXIDE CATALYST

1972 - Russia
1982 - Czech Republic, Bulgaria

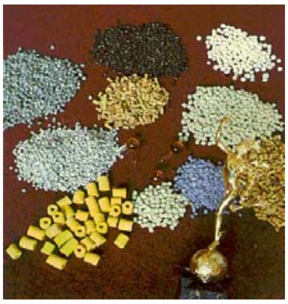
DEHYDROGENATION CATALYSTS FOR ELASTOMERS PRODUCTION

1974 - Russia



TECHNOLOGY OF ALUMINA PRODUCTION: NITRATE-AMMONIA TECHNOLOGY, THERMAL DECOMPOSITION WITH THE USE OF CHG, THERMOCHEMICAL AND MECHANOCHEMICAL ACTIVATION

1975 - Germany, 1990 - Kazakhstan,
1992 - Russia



CATALYSTS FOR PROPYLENE POLYMERIZATION

1980 - Kazakhstan, 1987 - Russia
1995 - The Netherlands, USA

CATALYST FOR NITROUS GASES PURIFICATION FROM OXYGEN IN HYDROXYLAMINE SULFATE PRODUCTION

1981 - Russia, 1995 - Germany

TECHNOLOGIES AND REACTORS BASED ON REVERSE-PROCESS

1982 - Russia, 1985 - Kazakhstan,
1989 - Japan, 1990 - Bulgaria,
1991 - Uzbekistan, 1993 - China,
1995 - USA, 1998 - Australia

CATALYTIC HEATING PLANTS

1982 - Russia

NEW CARBON MATERIAL - SIBUNIT AND SIBUNIT BASED CATALYSTS

1984 - Russia

CATALYSTS FOR METHIONINE PRODUCTION

1986 - Russia

“ZEOFORMING” PROCESS FOR THE PRODUCTION OF HIGH-OCTANE GASOLINES (BIC - SEC “ZEOSIT)

1992 - Russia, 1997 - Poland

NONPLATINUM HONEYCOMB CATALYSTS TO PRODUCE NITRIC ACID

1995 - Russia

CATALYSTS FOR CLAUS PROCESS

1996 - France

Industrial Reverse-Plant for processing of waste gases of metallurgy to H_2SO_4. Capacity up to 100 000 m^3/h ("Pechenganickel” Metallurgy Plant)

CATALYSTS FOR LOW-TEMPERATURE CONVERSION OF CARBON MONOXIDE IN AMMONIA PRODUCTION

1996 - Kazakhstan

Reactor for ammonia oxidation with IC-42-1 catalyst (AO “Azot”, Berezniki)

DEVELOPMENTS OF THE BORESKOV INSTITUTE OF CATALYSIS AT SEMI-COMMERCIAL SCALE

TECHNOLOGIES BASED ON "CATALYTIC HEAT GENERATORS" - COMBUSTION, DRYING AND THERMAL TREATMENT

1984 - Russia, Ukraine, Lithuania

DEVICES AND INSTALLATIONS FOR CATALYSTS TESTING

1985 - Russia, 1992 - USA

ENVIRONMENTALLY FRIENDLY AIR HEATER

1986 - Russia, Uzbekistan

CATALYSTS FOR PLANT OILS HYDROGENATION, PRODUCTION OF MEDICINES (LIDOCAIN, SULPIRID)

1988 - Russia

PROCESSES FOR GASES AND WASTE WATER PURIFICATION FROM SULFUR-CONTAINING SUBSTANCES

1989 - Russia

CATALYIC NEUTRALIZER FOR PURIFICATION OF AUTOMOTIVE EXHAUSTS

1990 - Russia

NOVEL COMPOSITE SORBENTS BASED ON CARBON MATERIALS, ALUMINAS, SILICA GELS FOR WASTE WATER PURIFICATION, PRECIOUS METALS EXTRACTION, FRESH WATER RECOVERY

1995 - Russia

CATALYSTS FOR ACRYLIC ACID PRODUCTION

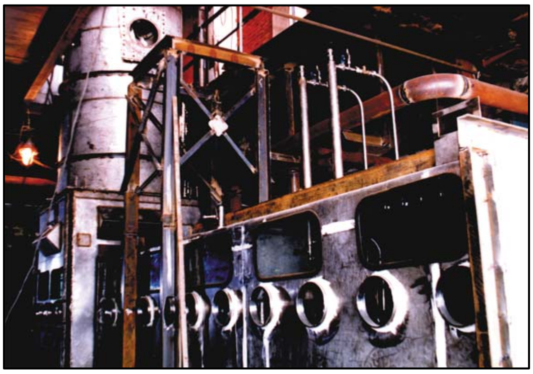
1992- Russia

ALKYLATION OF AROMATICS OVER ZEOLITE CATALYSTS

1990 - Russia

CATALYSTS FOR PRODUCTION OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE) AND ETHYLENE-PROPYLENE COPOLYMERS

1997 - Russia



Industrial plant for destruction of mixed organic wastes containing natural uranium with a capacity of 50 t/y (Novosibirsk Chemical Concentrates Plant Ltd.)

Pilot plant for synthesis of phenol from benzene, with nitrous oxide used as the oxidant (ALPHOX, USA)

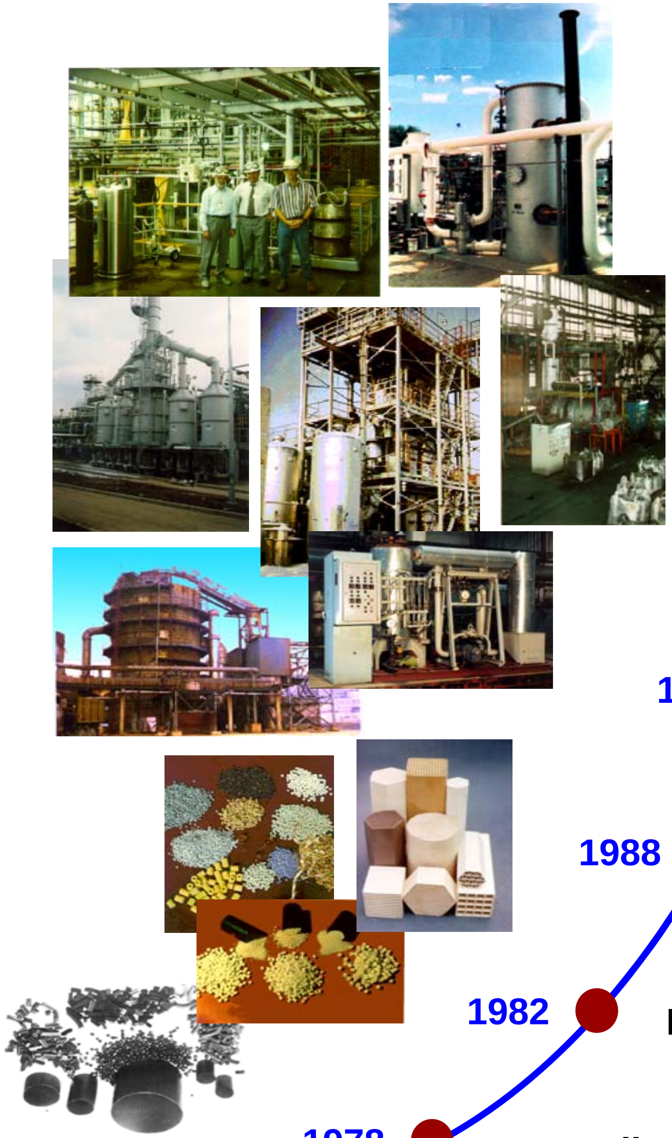
CATALYTIC PROCESS TO DESTRUCT ORGANIC RADIOACTIVE WASTES

1995 - Russia

ONE-STAGE PROCESS OF BENZENE TO PHENOL OXIDATION (ALPHOX)

1996 - USA

Catalytic Processes from Molecular Level to Industrial Plants



1999 Catalyst for hydropurification of terephthalic acid
Developed in cooperation with Samsung Chemicals

1998 One-step technology for production of nicotinic acid
Licensed to European company

1997 Non-platinum catalyst for production of nitric acid, Russia

1996 BtoP technology (benzene + [N_2O] → phenol)
Jointly designed with Monsanto

1995 Catalyst for oil cracking, Russia

1993 Carbon material SIBUNIT, Russia
Sibunit for phosgene synthesis, DuPont, 1994

1992 ZEOFORMING process for synthesis of gasoline, Russia
Lurgi, 1997

1988 Catalysts for polypropylene polymerization, Russia
DSM, 1995

1982 REVERS-Process
Monsanto Enviro Chem. Systems, 1992

1978 Vanadium catalysts for sulfuric acid production, Russia

1958

Kinetic

Gradientless and integral differential reactors
Fast relaxation technique
Stop flow technique
Radiochemical 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*
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 research fellows, visiting scientific centers, and participating in congresses and symposia on theoretical and applied catalysis.

During the year 1999 43 scientists took part in 20 measures abroad: 5 researchers participated in the 2nd *China-Russia Symposium on Catalysis,* China; 13 participants visited the *4th European Congress on Catalysis, "EUROPACAT-IV",* Italy; 4 scientists took part in the *Seminar on Organometallic Complexes*, Poland.

Long-term visits of the spesialists from the Boreskov Institute of Catalysis to foreign institutions

Germany	14	France	12	The Netherlands	13
UK	5	Spain	3	Switzerland	4
Poland	5	Greece	7	Italy	20
USA	20	Israel	1	India	4
Canada	1	China	5	Bulgaria	1
South Korea	1	Czech Republic	1	Mexico	1

Visits of foreign specialists to the Boreskov Institute of Catalysis:

Germany	6	France	11	The Netherlands	7
Belgium	1	Spain	1	Switzerland	2
USA	13	China	4	Republic of South Africa	5
South Korea	10	Japan	7		

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.

The Boreskov Institute of Catalysis invites all researchers interested in collaboration for mutual-benefit cooperation in the field of catalysis.

SCIENTIFIC COOPERATION WITHIN THE FRAMEWORK OF CONTRACTS AND AGREEMENTS WITH SCIENTIFIC CENTERS OF FOREIGN COUNTRIES

ITALY

The cooperation in the frame of the agreement between **Russian Academy of Sciences** (RAS) and **National Council on the Scientific Research** of Italy:

- **Institute of Energy Conversion and Storage, TAE**, Messina – **BIC**, Novosibirsk, “*Catalysis for Solving the Energy Problem”;*
- **Institute of Researches of Membranes and Chemical Reactors Modeling, IRMMRC**, Calabri – **BIC**, Novosibirsk, **“***Researches on Membranes”.*

FRANCE

According to the agreement between RAS and CNRS **BIC** collaborates with the **Institute de Recherches sur la Catalyse**, Villeurbanne, and **Université Pierre et Marie Curie**, Paris.

YUGOSLAVIA

The agreement between **Interacademic Board on Catalysis of the Serbian Academy of Sciences and Arts** and **BIC** in the field of fundamentals of catalyst preparation and catalytic processes.

POLAND

In the frame of **RAS-PAS** agreement **BIC** cooperates with the **Institute of Chemical Technology,** Glivitse, and the **Institute of Physics**, Krakow

COOPERATION WITH FOREIGN ORGANIZATIONS IN THE FRAMEWORK OF BILATERAL AGREEMENTS

GERMANY

Cooperation in the frame of RAS-DFG agreement with the **Munich University**, Munich**;** **Munich Technical University**, Garching; **Fritz-Haber-Institut MPG**, Berlin.

THE NETHERLANDS

The cooperation with the research institutions of The Netherlands is:

- *"Creation of Membrane-Catalytic Process for Fat Acids Eterification"***, Agricultural-Technological Scientific and Research Institute**, Vageningen;
- **"***New Catalysts and Catalytic Processes for Gas Treatment and Solid Fuels Gasification*", **Energetic Research Center of The Netherlands**, Petten;
- **"***Safety of Chemical Reactors***", Twente University**, Twente.

COOPERATION IN THE FRAMES OF PROJECTS FINANCED BY INTERNATIONAL FOUNDATIONS

INTAS SUPPORTED PROJECTS

I. Formation and Development of Microporosity in Precursors and Polymer-Pyrolysed Activated Carbons with Regards to the Separation Concentration and Storage of Methane

Project Coordinator:

Prof. B. McEnaney, University of Bath, UK.

Participants:

Dr. D.K. Efremov, Boreskov Institute of Catalysis, Novosibirsk, Russia;

Prof. M. Molina-Sabio, University of Alicante, Spain; **Dr. A. Bagreev**, Institute of Sorption and Problems of Endoecology, Kiev, Ukraine.

II. Combustion Processes in Porous Media as a Base for New Industrial Technologies

Project Coordinator:

Prof. G. Sivashinskii, Tel-Aviv University, School of Mathematical Sciences, Department of Applied Mathematics, Israel.

Participants:

Prof. A.S. Noskov, Boreskov Institute of Catalysis, Novosibirsk, Russia; **Prof. V.S. Babkin**, Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia; **Prof. D. Bradley,** University of Leeds, UK; **Prof. A. Sagindykov**, Combustion Problem Institute, Almaty, Kazakhstan; **Prof. V. Sobolev**, Samara State University, Samara, Russia.

III. Dynamic Behavior of Hydrocarbons Entrapped in Zeolite Pores

Project Coordinator:

Prof. C.R.A. Catlow, The Royal Institution of Great Britain, London, UK.

Participants:

Dr. A.A. Shubin, Boreskov Institute of Catalysis, Novosibirsk, Russia; **Dr. H. Jobic**, Institut de Recherches sur la Catalyse, Villeurbanne, France; **Prof. V.D. Skirda**, Kazan State University, Kazan, Russia.

IV. Electronic, Magnetic and Adsorption Properties of Carbon Nanostructured

Project Coordinator:

Prof. J. Marc-Bonard, Ecole Polytechnique Federale de Lausanne, Switzerland

Participants:

Dr. V.L. Kuznetsov, Boreskov Institute of Catalysis, Novosibirsk, Russia; **Dr. O. Klein**, Ecole Polytechnique, Palaiseau, France; **Dr. A.V. Okotrub**, Institute of Inorganic Chemistry, Novosibirsk, Russia; **Dr. T. Kononenko**, General Physics Institute, Moscow, Russia.

V. Novel Nanostructured Catalysts for the Selective Reduction of NO_x by Heavy Hydrocarbons

Project Coordinator:

Prof. J. Ross, University of Limerick, Ireland.

Participants:

Prof. V.A. Sadykov, Boreskov Institute of Catalysis, Novosibirsk, Russia;
Prof. A.Ya. Rosovskii, Topchiev Institute of Petrochemical Synthesis, Moscow, Russia;
Prof. V.A. Matyshak, Semenov Institute of Chemical Physics, Moscow, Russia;
Prof. B. Andersson, Chalmers University of Technology, Göteborg, Sweden.

GRANTS PROVIDED BY INTAS-RFBR

I. Theoretical and Experimental Studies on the Catalytic Activity of the V_2O_5-TiO_2 System

Project Coordinator:

Prof. K. Jug, Universität of Hannover, Germany.

Participants:

Prof. O.B. Lapina, Boreskov Institute of Catalysis, Novosibirsk, Russia;
Prof. V.Yu. Borovkov, Institute of Organic Chemistry, Moscow, Russia; **Prof. C. Minot,** Université Pierre et Marie Curie, Paris, France.

II. Silica and Zirconia Based Mesoporous Mesophases: Synthesis, Structure, and Catalytic Properties

Project Coordinator:

Prof. G. Poncelet, Universite Catholique de Louvain, Belgium.

Participants:

Dr. V.N. Romannikov, Boreskov Institute of Catalysis, Novosibirsk, Russia;

Prof. F. Schuth, Universität Frankfurt, Germany; **Prof. S.D. Kirik,** Institute of Chemistry and Chemical Engineering, Krasnoyarsk.

GRANT PROVIDED BY DUTCH ORGANIZATION FOR SCIENTIFIC RESEARCH (NWO):

I. Clusters in Zeolite Materials

Project Coordinator:

Prof. R.A. van Santen, Eindhoven University of Technology, Eindhoven, The Netherlands.

Participants:

Prof. G.M. Zhidomirov, Boreskov Institute of Catalysis, Novosibirsk, Russia;

Prof. V.B. Kazansky, Zelinsky Institute of Organic Chemistry, Moscow, Russia.

COPERNICUS

I. Novel Approach to the Application of Unsteady-State Catalysis to Advanced Process and Reactor Design

Project Coordinator:

Prof. M. Baerns, Institute of Applied Catalysis, Berlin, Germany.

Participants:

Boreskov Institute of Catalysis, Novosibirsk, Russia (**Dr. A.A. Ivanov**); **Institute of Chemical Technology**, Lausanne, Switzerland; **Gent University**, Gent, Belgium; **Institute of Physical Chemistry**, Kiev, Ukraine; **Institute of Physical Chemistry**, Moscow, Russia.

II. Wood Biomass and Wastes Upgrading: Development and Application of Clean Processes for Fine Chemicals, Oils and Carbon Sorbents Production

Project Coordinator:

Prof. R. Gruber, University of Metz, Metz, France

Participants:

Boreskov Institute of Catalysis, Novosibirsk, Russia **(Prof. A.N. Startsev), Krasnoyarsk Institute of Chemistry**, Krasnoyarsk, Russia; **Paris VI University**, Paris, France**; Universitaire de Technologie de Metz**, Metz, France; **Nancy University**, Nancy, France; **Orléans University**, New Orleans, France; **Bruxelles University**, Brussels, Belgium; **Imperial College,** University of London, London, UK; **CSIC Institute of Carbochemistry**, Zaragoza, Spain; **Kassel University**, Kassel, Germany; **Krasnoyarsk Technological Academy,** Krasnoyarsk, Russia; **Donetsk Institute of Coal Chemistry** NAU, Donetsk, Ukraine; **Warszawa Institute of Organic Chemistry PAN**, Warszawa, Poland; **Gliwice Institute of Coal Chemistry**, Gliwice, Poland.

NATO: SCIENCE FOR PEACE PROGRAM

I. Catalytic and Electrochemical Processes for SO_2 and NO_x Emission Abatement

Project Coordinator from a NATO Country:

Dr. S. Boghosian, Institute of Chemical Engineering and High Temperature Chemical Processes, Patras, Greece.

Project Coordinator from a Partner Country:

Prof. B.S. Bal'zhinimaev, Boreskov Institute of Catalysis, Novosibirsk, Russia.

II. Development of Shaped Steam Reforming Catalyst

Project Coordinator from a NATO Country:

Prof. K.R. Westerterp, Twente University, The Netherlands.

Project Coordinator from a Partner Country:

Prof. V.N. Parmon, Boreskov Institute of Catalysis, Novosibirsk, Russia.

NATO SCIENCE PROGRAMME

Cooperative Science & Technology Sub-Programme

Mechanism of Donor Molecules Activation over the Sulfide Hydrotreating

Project Coordinator from a NATO Country:

Dr. M. Lacroix, Institut de Recherches sur la Catalyse, Villeurbanne, France.

Project Coordinator from a Partner Country:

Prof. A.N. Startsev, Boreskov Institute of Catalysis, Novosibirsk, Russia.

INTERNATIONAL SCIENCE AND TECHNOLOGY CENTER (ISTC)

I. Development of the Technology of Catalytic Fluidized Bed Destruction of Organic Wastes Containing Radionuclides

Project Coordinator:

Prof. Z.R. Ismagilov, Boreskov Institute of Catalysis, Novosibirsk, Russia.

II. Creation of Ecological Autonomous Domestic Unit Heater of 25-50 kW Capacity, Based on Catalytic Oxidation of Gaseous Hydrocarbon Fuel

Project Coordinator:

Prof. Valerii A. Kirillov, Boreskov Institute of Catalysis, Novosibirsk, Russia.

CRDF COOPERATIVE GRANTS PROGRAM

I. Investigation of Nanoscale Alkaline-Earth Metal Oxides as Destructive Adsorbents and Catalysts in Reactions of Halogenated Hydrocarbon

Project Coordinator:

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

Project Head from the Russian Side:

Prof. A.M. Volodin, Boreskov Institute of Catalysis, Novosibirsk, Russia.

Participants:

Dr. R.M. Richards, Kansas State University, Manhattan, USA;

A.V. Timoshok, Prof. V.V. Chesnokov, I.V. Mishakov, Dr. V.I. Zaikovskii,

Prof. V.B. Fenelonov, M.S. Mel'gunov, Boreskov Institute of Catalysis, Novosibirsk, Russia.

II. Formation Mechanism and Electron Field Emission Properties of Carbon Films Containing Multi-Walled Nanotubes

Project Coordinator:

Prof. B. Segall, Gase Western Reserve University, Cleveland, USA.

Project Head from the Russian Side:

Dr. V.L. Kuznetsov, Boreskov Institute of Catalysis, Novosibirsk, Russia.

Participants:

Dr. A.N. Obraztsov, **Dr**. **I.Yu. Pavlovskii**, **A.P. Volkov**, Moscow Lomonosov State University, Moscow, Russia;

Dr. E.D. Obraztsova, Institute of General Physics, Moscow, Russia;

Yu.V. Butenko, Dr. A.L. Chuvilin, A.N. Usoltseva, K.T. Murzakhmetov, Boreskov Institute of Catalysis, Novosibirsk, Russia.

III. Experimental and Theoretical Investigations of Chemical Reactivity of Reversible Reaction in Supercritical Water

Project Coordinator:

Dr. J.A. Manion, National Institute of Standards and Technology, Gaithersburg, USA.

Project Head from the Russian Side:

Prof. V.I. Anikeev, Boreskov Institute of Catalysis, Novosibirsk, Russia.

Participants:

Prof. A. Yermakova, A.V. Gudkov, M.V. Gudkov, Boreskov Institute of Catalysis, Novosibirsk, Russia

BIC-IRC TWINNING PROGRAM

(COOPERATION BETWEEN BORESKOV INSTITUTE OF CATALYSIS (BIC) AND INSTITUT DE RECHERCHES SUR LA CATALYSE (IRC), VILLEURBANNE, FRANCE)

I. Synthesis of New Catalytic Materials

1.1. ***Zeolite Membranes for New Catalytic Reactors***

Participants:

BIC: Z.R. Ismagilov, R.A. Shkrabina
IRC: J.-A. Dalmon, S. Miachon

1.2. ***Catalytic Membrane Reactors for Gas-Liquid Applications***

Participants:

BIC: L.V. Nosova, O.M. Il'initch
IRC: J.-A. Dalmon, S. Miachon

II. Reaction Mechanism

2.1. ***Epoxidation of Ethylene***

Participants:

BIC: B.S. Bal'zhinimaev, L.G. Pinaeva, E.M. Sadovskaya, A.P. Suknev, V.B. Goncharov
IRC: C. Mirodatos, Y. Schuurman, T. Decamp

2.2. ***Modeling***

Participants:

BIC: V.I. Elokhin, E.D. Resnyanskii, E.V. Kovalev
IRC: M. Kolb, Y. Boudeville, S. Mathieu

2.3. ***NO-CH_4 Reaction***

Participants:

BIC: B.S. Bal'zhinimaev, L.G. Pinaeva
IRC: C. Mirodatos, Y. Schuurman, T. Decamp

III. Hydrodechlorination

Participants:

BIC: V.A. Likholobov, V.I. Simagina
IRC: G. Bergeret, M.T. Gimenez, A. Renouprez

IV. Molecular Dynamic in Zeolites

Participants:

BIC: A.G. Stepanov, A.A. Shubin, M.V. Luzgin
IRC: H. Jobic, A. Tuel

CONFERENCE AND EXHIBITION ACTIVITIES

Solution of many specific problems requires joint efforts in order to promote its fastest accomplishing. International congresses, symposia, conferences, and seminars are most productive to familiarize scientists with innovations outside their own research and to disseminate the information about the results achieved to a wider audience.

EXHIBITION ACTIVITY

Participation in exhibitions illustrates the research and social activities of an institution, promotes an increase in its rating, and expands the scope of scientific and commercial partners. Besides, the level and consumer properties of the scientific achievements may be evaluated in more realistic manner.

Our Institute, while owing numerous items in the field of applied catalysis, exercises the attending at exhibitions to promote its developments to the consumer market, to advertise its R&D activities and search for potential customers.

In 1999, BIC's developments were exposed at:

- 15 Exhibitions, including international ones (27th International Invention Show in Geneva, Italy; "Great Rivers-99", N. Novgorod, Russia; "HI TECH. Investments. Innovations", St. Petersburg, Russia; "Chemistry-99", Moscow, Russia, "VTTV-Omsk-99", Omsk, Russia; "Innovations in the Field of Chemical Technologies and Novel Materials", Delhi, India);
- Two panel discussions participated by the Novosibirsk Region Administration ("Heat Power Engineering", "Transfer of Science Intensive Technologies into Chemical Industry");
- Two conferences and workshops in Novosibirsk (International Memorial K.I. Zamaraev Conference "Physical Methods for Catalytic Research at the Molecular Level", The Workshop "Domestic Catalysts and Technologies for Nitric Acid Industry").

The most important BIC's achievements in the area of applied catalysis were presented at the exhibitions. The most attractive were the developments suggested for social fields such as medicine, heat power engineering, food industry and environmental protection; innovative technologies (synthesis of nicotinic acid and formaldehyde, REVERS-process, catalysts for cracking, reforming, new carbon materials, *etc.*) being of interest to big enterprises and foreign companies. The concern of representatives of smaller enterprises was focused on chemicals which do not need sophisticated facilities and heavy expenses for their production and are properly certified (for the case of medications); these are "Amisorb", "Sulfacrilate", "Entero- and Hemosorbents", catalytic heaters, moisture absorbing and heating insoles, *etc.* Lately, representatives of the defense establishment have shown great interest in the high-tech innovations for practicing them at the conversion enterprises.

The high scientific and engineering level of developments of our Institute, the manner of presenting them at the exhibitions is always attractive to numerous visitors (including journalists).

Among the awards are:

Diploma for a honeycomb oxide catalyst for ammonia oxidation (St. Petersburg)

Golden medal and Certificate of the First Degree for “Composite Materials of the SWS Family” (Geneva)

Diploma for a set of the most important BIC’s developments presented at the exhibition “Chemistry-99” (Moscow)

Certificate of Laureate of the Investment Project Competition at the exhibition “Investment Potential of Novosibirsk on the Eve of XXI Century”.

Participation in various exhibitions, discussion of commercial prospects of the displayed innovations promotes expanding of the potential market for new technologies and materials.

CONFERENCE ACTIVITY

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 scientists from CIS, but International as well.

International Memorial K.I. Zamaraev Conference “Physical Methods for Catalytic Research at the Molecular Level”

Novosibirsk, Russia, June 28–July 2

The Conference, devoted to the memory of Academician K.I. Zamaraev and scheduled to his 60 years anniversary, took place in a specially rented resort “Lazurnyi” situated in a picturesque site on the shore of the Ob’ Lake near Akademgorodok, convenient for both meetings and recreation.

The Conference was organized by:

- Boreskov Institute of Catalysis, Novosibirsk, Russia
- International Association for the Promotion of Cooperation with Scientists from the New Independent States of the former Soviet Union (INTAS)
- International Union of Pure and Applied Chemistry (IUPAC)
- Russian Foundation for Basic Research (RFBR)
- Russian Mendeleev Chemical Society, Novosibirsk Department, Russia
- The Russian Scientific Council on Catalysis, Moscow, Russia

177 participants from 15 countries attended the Conference, and Russia was presented by the largest delegation.

The subject of International Memorial K.I. Zamaraev Conference “Physical Methods for Catalytic Research at the Molecular Level” maximum concerned K.I. Zamaraev research interests such as catalysts investigation on atomic-molecular level and application of physical methods, especially spectral, for this purpose:

- ♦ Quantum-chemical studies on the electronic structure of active components in catalysts, and molecular adsorption on active sites
- ♦ Physical methods for surface science studies and studies of adsorption processes

- Experimental studies on the structure of active sites of heterogeneous catalysts and on the elementary mechanisms of heterogeneous catalytic reactions
- Experimental studies on elementary mechanisms of homogeneous catalytic reactions
- Development of new methods and approaches to *in situ* catalytic studies.

Most presentations discussed the experimentally studied structure of catalyst active sites, as well as the mechanisms of heterogeneous and homogeneous catalysis, investigated with physical methods. The atomic molecular description of catalysts and related processes is one of determining trends in the modern theory of chemical catalysis.

In the whole, presented were 12 plenary lectures, 12 special subject lectures, 32 oral reports and 98 posters.

Leading world scientists and closest followers of K.I. Zamaraev were among the invited plenary lecturers and special subject lecturers.

Plenary lectures were given by:

R. Schlögl (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany) – *"Experimental Studies on the Structure of Active Sites in Heterogeneous Catalysis";*

D.I. Kochubey (Boreskov Institute of Catalysis, Novosibirsk, Russia) – "*Determination of the Structure of the Catalytic Active Centers by EXAFS";*

E.G. Derouane, Heyong He, Sharifah Bee Derouane-Abd Hamid (The University of Liverpool, Liverpool, UK), I.I. Ivanova (Moscow Lomonosov State University, Moscow, Russia) – *"In situ MAS NMR Investigations of Molecular Sieves and Zeolite-Catalyzed Reactions";*

E.P. Talsi, D.E. Babushkin, A.P. Sobolev, K.P. Brylyakov, N.V. Semikolenova, V.A. Zakharov (Boreskov Institute of Catalysis, Novosibirsk, Russia) – *"NMR and EPR Spectroscopic Studies of the Reactive Intermediates of Homogeneous Catalytic Oxidation and Polymerization*;

J. Fraissard, M.A. Springel-Huet, J.L. Bonardet, A. Gedeon (Universite Pierré et Marie Curie, Paris, France) – *"Xe-NMR of Adsorbed Xenon Used as a Probe of Solid Catalysts";*

E.A. Paukshtis (Boreskov Institute of Catalysis, Novosibirsk, Russia) – *"Infrared Spectroscopy to Study the Mechanism of Catalytic Reaction on Molecular Scale. From Diffusion to Limiting Stage Kinetics*";

G. Mestl (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany) – *"In Situ Raman Spectroscopy – a Valuable Tool to Understand Operating Catalysts";*

R. Imbihl (Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Germany) – "*Model Studies for Catalysis with Microstructured Bimetallic Surfaces*";

Ya. Iwasawa (Graduate School of Science, The University of Tokyo, Tokyo, Japan) – *"Characterization and Catalytic Performance of Designed Surfaces";*

L.D. Marks (Northwestern University, Evanston, USA) – *"New Methods for Determining Surface Structures";*

K.V. Shalyaev, J.T. Groves, Ning Jin, Tomoko Kitago (Princeton University, Princeton, USA) – *"Rapid and Selective Catalytic Oxygenation of Hydrocarbons with Ruthenium and Manganese Porphyrins";*

M.Yu. Sinev, V.Yu. Bychkov (N.N. Semenov Institute of Chemical Physics, Moscow, Russia) – *"Application of High-Temperature Differential Scanning Calorimetry to in situ Studies of Gas-Solid Reactions and Catalytic Processes".*

Special **subject lectures** were presented by

I.I. Moiseev (N.S. Kurnakov Institute of General and Inorganic Chemistry, Moscow, Russia);

O.V. Krylov (N.N. Semenov Institute of Chemical Physics, Moscow, Russia);

Z.R. Ismagilov, V.K. Ermolaev (Boreskov Institute of Catalysis, Novosibirsk, Russia);

O.B. Lapina, A.A. Shubin, V.V. Terskikh (Boreskov Institute of Catalysis, Novosibirsk, Russia);

A.G. Stepanov (Boreskov Institute of Catalysis, Novosibirsk, Russia);

V.B. Kazansky (N.D. Zelinsky Institute of Organic Chemistry, Moscow, Russia);

G. Spoto, A. Zecchina, G. Berlier, S. Bordiga (Dipartimento di Chimica IFM dell'Universita di Torino, Torino, Italy), M.G. Clerici (EniTecnologie SpA, Italy), L. Basini (SnamProgetti SpA, Italy);

B.E. Nieuwenhuys, C.A. de Wolf, P.D. Cobden, N.M.H. Janssen (Leiden Institute of Chemistry, Leiden, The Netherlands), V.V. Gorodetskii, M.Yu. Smirnov (Boreskov Institute of Catalysis, Novosibirsk, Russia), A.G. Makeev (Moscow Lomonosov State University, Moscow, Russisa), M.G. Slin'ko (Institute of Chemical Physics, Moscow, Russia);

A.T. Bell, A. Khodakov, K. Chen, J. Yang, B. Olthof, E. Iglesia (University of California, Berkeley, USA)**;**

J.P. Breen, F.C. Meunier, J.R.H. Ross (Centre for Environmental Research, University of Limerick, Limerick, Ireland);

V.A. Benderskii (Institute of Chemical Physics Problems, Chernogolovka, Russia);

M.N. Vargaftik, N.Yu. Kozitsyna, M.V. Martens, I.P. Stolyarov, M.K. Starchevsky, I.I. Moiseev (N.S. Kurnakov Institute of General and Inorganic Chemistry, Moscow, Russia)

On importance is that Russian works, performed with physical methods, conform to the world standards regarding ideology and creativity. Modern equipment supply is the most critical factor for the Russian scientists due to the well-known economic crisis in Russia. However, at present many leading Russian research teams work in a tight cooperation with foreign universities and institutions well supplied with the most advanced equipment.

Estimating the results obtained with physical methods and presented at the Conference, one may understand that in most cases physical methods provided a better and qualitatively new understanding of catalysts' performance.

Regarding that many Russian and foreign scientists are interested in the Conference subject and considering the fact that only Gordon conferences arranged in the USA regularly discuss the above mentioned problems in a concentrated form, the participants of International Memorial K.I. Zamaraev Conference “Physical Methods for Catalytic Research at the Molecular Level” recommended to arrange this conference once in four years in different countries.

Special **Scientific INTAS Session** took place in the frame of the Conference. 19 project participants presented their brief reports on the done work during the intensive work of the INTAS Session, informed about collaboration between groups. The participants (37 participants from CIS and 6 from foreign countries) got to know with the allied projects and obtained new information about last advances.

During the Conference holding the exhibition of advertising materials of **Shimadzu Europa GmbH** producing analytical equipment and devices for physico-chemical characterization of catalysts, supports and porous materials, as well as analytical tools for catalyst testing took place.

The Boreskov Institute of Catalysis exposed its achievements in the area of applied catalysis.

Regional Workshop “State-of-Art in Chemical and Pharmaceutical Industry”
Novosibirsk, Russia, 16-18 November

The Workshop was organized by

- Boreskov Institute of Catalysis SB RAS
- Administration of Novosibirsk Region
- Russian D.I. Mendeleev Chemical Society, Novosibirsk Division
- Joint Council on Chemical Sciences SB RAS

Three days of meetings included the diverse program - plenary lectures, oral reports, panel discussions on several directions: low-tonnage chemical products and processes of their production; medicines and food; chemical processes in a fuel and energy complex; chemistry in agriculture; destruction and processing of industrial and agricultural wastes, and so on.

Acad. V.N. Parmon opened the Workshop. He underlined an extreme importance of this meeting for the developers and consumers of new technologies.

The Head of the Department of a science, higher and vocational education **Prof. P.V. Reshedko** told about those steps of regional administration, that are undertaken and will be undertaken to facilitate the position of a science.

The plenary lecture by **Acad. V.N. Parmon** “*Experience of Innovation Activity of the Boreskov Institute of Catalysis*” appeared to be a real handbook how to organize the work in the conditions of market economy.

Prof. V.A. Semikolenov gave a lecture “Strategy and Tactics for Design of Catalytic Processes to Produce Valuable Organic Substances”.

The Vice-president of the Siberian branch of RAS, Director of the Novosibirsk Institute of Organic Chemistry, **Acad. G.A. Tolstikov** paid attention to the problem of reconstruction of chemical industry of the country, development of new technologies and revival of the old. Special attention was paid to the domestic drugs industry. This theme Acad. G.A. Tolstikov has continued in his plenary lecture "*Perspectives of Researches in the Development of Medicines in the Siberian Branch of RAS*".

Design of medicines is considered to be the main direction of fundamental studies and applied developments. The next plenary lectures also related to this problem:

B.A. Trofimov, **V.K. Stankevich,** Irkutsk Institute of Chemistry, Irkutsk, Russia – *"Medicines by the Irkutsk Institute of Chemistry";*

A.V. Dushkin, N.Z. Lyakhov, V.V. Boldyrev, Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia - *"Mechanochemistry for Pharmaceutical Disperse Systems";*

V.P. Chetverikov, Novokuznetsk Chemical-Pharmaceutical Research Institute, Novokuznetsk, Russia – *"Experience of NCPRI in Design of Medicines: State of Art and Prospects of Development"*.

The works in the field of synthesis of organic compounds, alongside with a solution of theoretical problems, provide for realization of biological researches. This approach has allowed not only to reveal a lot of substances, perspective for medicine, but also to get over rather labor-consuming process of production of the new medicinal forms.

Interesting reports and lively discussions made this Workshop very useful for all participants.

RFBR Seminar "Modern Trends in Development of Low-Tonnage Chemical Materials; Scientific Foundations of Employment, Integration of Investigations and Innovations for Creation of Competitive Technologies"

Nizhnekamsk, Russia, 16-18 September

Organizers:

The Ministry of Science and Technologies of Russian Federation, Moscow, Russia
Russian Foundation on Basic Researches, Moscow, Russia
Scientific Council on Catalysis and its Industrial Application of the RAS, Moscow, Russia
Russian D.I. Mendeleev Chemical Society, Moscow, Russia
Kazan Scientific Center of the Russian Academy of Sciences, Kazan, Russia
Kazan State Technological University, Kazan, Russia
Boreskov Institute of Catalysis, Novosibirsk, Russia
JSC "Nizhnekamskneftekhim", Nizhnekamsk, Russia

This Seminar was the fifth in the cycle "Results of Fundamental Researches for Investments". 79 participants – scientists form Academic Institutes and Institutes of Higher Education, representatives from industrial enterprises - took part in the Seminar. The main developments presented at the Seminar were directed to the solution of the problems of petroleum industry, production of tires, synthetic rubber. New materials, different dopants (stabilizers, ozonizers, modifiers, etc.), novel catalytic processes and efficient catalysts were the subjects of plenary lectures and oral presentations.

Of the most interest was the lecture presented by **Prof. A.S. Noskov,** Boreskov Institute of Catalysis: V.N. Parmon, A.S. Noskov, "Catalytic Processes at Manufacturing of the Products for Organic Synthesis" concerning new catalytic processes and catalysts owned by the Institute.

The Workshop "Domestic Catalysts and Technologies for Nitric Acid Industry"

Novosibirsk, Russia, 5-9 October

The Workshop was organized by the Boreskov Institute of Catalysis and "Katalizator Co", Novosibirsk. 70 leading specialists from 22 first-rate chemical plants participated in it.

The lectures by Deputy director of the Boreskov Institute of Catalysis **Prof. A.S. Noskov** and Director of the "Katalizator Co" **Dr. M.G. Makarenko** were listened to with great interest. The lectures presented the main developments by the Boreskov Institute of Catalysis and the "Katalizator Co" and outlined the prospects of designing of catalysts and catalytic processes.

The technology of two-step ammonia oxidation for nitrogen acid production over non-platinum oxide catalysts was presented in the lecture by **I.A. Zolotarskii** (Boreskov Institute of Catalysis).

Dr. O.P. Klenov (Boreskov Institute of Catalysis) stated the technical suggestions on the catalyst charging into the reactor with the help of special feeder, which provided the homogeneity of the physico-mechanical and hydrodynamic properties of the catalyst layer.

The lecture by **Prof. T.M. Yurieva** (Boreskov Institute of Catalysis) was devoted to the development of the catalysts for low-temperature carbon oxide conversion.

T.V. Borisova ("Katalizator Co") stated in her lecture that the main part of the catalysts and supports produced at the "Katalizator Co" is based on the alumina obtained by the methods of thermochemical and mechanochemical hydrargillite activation. Efficient technologies to produce aluminum oxides and hydroxides with the wide range of properties were developed at the "Katalizator Co".

The lecture by **A.V. Kachkin** ("Katalizator Co") related to the experience in the development and application of aluminum-palladium catalyst for gas purification from nitrogen oxides.

Dr. G.V. Isaeva ("Katalizator Co") gave a lecture "Low-Percentage Palladium Catalyst for Ejection Gases Purification from NO_x", devoted to the design of novel catalyst.

The lecture by **Dr. V.A. Chumachenko** ("Katalizator Co") was of interest for those who are concerned with the design of the catalysts for environmental protection, and presented the catalysts developed jointly with the Boreskov Institute of Catalysis.

BORESKOV INSTITUTE OF CATALYSIS AS AN EDUCATIONAL CENTER

With deep belief that people are a decisive factor and the best way to study yourself is to teach others, many researchers of the Institute participate in the training of specialists in chemistry and, of course, in catalysis. The majority of them ensure closest and time-tested links of the Institute with the main source of researchers – Novosibirsk State University (NSU). The others develop dynamic contacts with other Siberian schools, primarily, with Novosibirsk State Technical University (NSTU).

BIC – NSU

Boreskov Institute of Catalysis is a key element in the training of specialists in chemistry at NSU. More than 35 researchers of the Institute are currently part-time teachers at the Department of Natural Sciences (DNS) at NSU. They present lectures, give seminars and practical classes, participate in the organization and renovation of the educational process at four out of eight chemical chairs of DNS, namely, chairs of physical chemistry, general chemistry, analytical chemistry, adsorption and catalysis.

The chair of adsorption and catalysis 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. Twenty five to thirty students of the IV, V and VI years of the Chemical Department of DNS are trained at the chair annually. Its graduates obtain Bachelors, Specialists and Masters diplomas. 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.

From the first years, the strategy of the training of students at the chair is formed 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, 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 curricula allow for a significant widening of the sphere of the working activity of its graduates. They can work as technologists, production managers, researchers at various research organizations, teach at universities.

All this allows the students to prepare their graduation study 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.

The year 1999, Novosibirsk State University commemorates its 40th anniversary!

Novosibirsk State University was established as an essential part of the Siberian Branch of the Academy of Sciences; at present 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. Novosibirsk State University is not large against traditional universities; there are 5000 people, including undergraduate and postgraduate students, and 10.000 people, including students of the Physical and Mathematical School and of the Higher College of Informatics, who study there. The University keeps holding competitions to choose the most talented children throughout the Siberian Region and to nurture the intellectual elite of Russia. During forty years, about 26,000 researchers skilled in modern fields of mathematics, physics, chemistry, biology, geology, economy, humanities and social sciences graduated from the University.

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. The University was among pioneers of application of computer facilities and up-to-date information technologies for students' training and research. And the *third* principle means that the students master theoretical disciplines during their first to third years and do their practical research in academic institutes of the Siberian Branch during the last years.

Celebration of the fortieth anniversary took a week. Every day was reach in very different events; these were scientific conferences, exhibitions, presentations, KVN shows, sport competitions and brain-rings, grand meetings, banquets, discotheques. And the final point was a grandiose meeting in front of the University building: bonfire, shows of popular artists, festive salute…

BIC – NSTU

Training of the personnel in the field of technology of catalytic processes is of special importance for practical application of fundamental knowledge in the field of catalysis. To meet this task, work in two main directions is under way. First, corresponding courses ("Bases of chemical technology", "Mathematical modeling of catalytic reactors") are prepared for students studying at the chair of adsorption and catalysis. Further progress in this direction is connected with the training of students specializing in "Engineering environment protection" started at NSTU in 1998. It is one of the steps in realization of the program of joint training of specialists at NSTU and institutes of the Siberian Branch of RAS. The basic training is conducted by a chair founded at the Boreskov Institute of Catalysis. Researchers of BIC present courses on industrial ecology and technology of the environment protection, basics of manufacturing and catalytic methods.

Today there are about 40 students of IV and V years studying at the chair. The first graduation of engineers majoring in engineering environment protection will be held at NSTU in 2000.

BIC – graduate school

Besides teaching students of a number of Russian universities, researchers of the Institute participate in the training of young scientists of the highest qualification capable of independent fundamental, search and applied studies 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 graduate school of SB RAS and graduate school of NSU. Annually 20-30 graduates are trained at the graduate school working at the Institute. Supervised by the researchers of the Institute, graduate students conduct their Ph.D. studies in chemical kinetics and catalysis, physical chemistry, chemical engineering in the BIC laboratories.

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

SCIENTIFIC SOCIAL LIFE

☆

February 8, 1999 was announced the **Day of Russian Science** in commemoration of 275th anniversary of the foundation of Academy of Sciences in Russia.

According to the edict of the President of Russian Federation the following scientists of the Boreskov Institute of Catalysis and its Omsk Division were awarded for valuable contribution to the science, training of highly skilled personnel and in honor of 275th anniversary of the Russian Academy of Sciences:

Acad. V.N. Parmon - Order of Honor

Prof. V.A. Likholobov and **Prof. V.K. Duplyakin – Medal of "Merits for Fatherland"**

Prof. G.M. Zhidomirov and **Prof. Z.R. Ismagilov - Honorary title "Honored Worker of Sciences of Russian Federation"**

59 persons got the **Diploma of RAS and Trade Union of Workers of RAS,** and 58 got the **Official thanks** by President.

☆

May 20, 1999 was a memorial date for international community of scientists - the 60th anniversary of Kirill I. Zamaraev. The Institute has been prepared for this historical date in advance. The selected articles by K.I. Zamaraev were issued. The photo exposition represented Kirill Ilyich with his colleagues and friends; with his family; enjoying the rare moments of contact with nature. It was a great day – the scientific presentations by the followers of K.I. Zamaraev, flowers, music, and poetry.

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:

- Boreskov Institute of Catalysis, Novosibirsk
- Institute of Semiconductors Physics, Novosibirsk
- Russian D.I. Mendeleev Chemical Society, Moscow
- Scientific-Industrial Company «Altay», Biysk

- «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.

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. The Fund has organized the competition for awarding by the scholarships of Zamaraev International Charitable Scientific Foundation. In 1999 the post-graduates scholarships were obtained by the following young researchers of the Boreskov Institute of Catalysis: K.P. Brylyakov, O.V. Vassil'tsova, E.I. Vovk, M.S. Mel'gunov, E.A. Podgornov, Yu.V. Potapova, L.Yu. Khitrina.

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 1999 the Foundation became one of the organizers of International Ecological Student Scientific Conference *"Ecology of Russia and Contiguous Territories. Ecological Catalysis"*. This year it was held in memory of K.I. Zamaraev, who attached a vital importance to the role of catalysis in environmental protection. On proposal of Foundation organizers the section "Ecological Catalysis" was included in the scientific program of the Conference. Students from 13 higher educational institutions presented 22 oral and 9 poster presentations at this section.

✯

In October, 1999, after a long interruption, the **Council of Scientific Youth** began to work. At present 8 Ph.D. students and researchers of the Institute and also representative of the students form the personnel of the Council; Dr. A.G. Okunev is the Chairman. The main principle of the Council is submission of the interests of the youth in the Institute. It includes organization of competition of the youth projects, support of the young lecturers of higher educational establishments – employees of the Institute, organization of training for qualifying examinations for the Ph.D. degree, improvement of living conditions of the young scientists, and other directions of activity connected with the improving of a position of the young researchers of the Institute.

✯

The Competition among the young scientists of Novosibirsk Scientific Center SB RAS has been organized to mark the 275th anniversary of RAS. The following participants from the Boreskov Institute of Catalysis presented their works:

V.V. Galvita – “Gas-Phase Electrocatalysis with the Use of Solid Electrolytes: Oxidative Methane Conversion”

O.N. Martyanov – “Thin Structure of the Ferro-Magnetic Resonance Spectra of the Surface of Magnetics and Heterogeneous Catalysts on its Bases”

M.M. Tokarev – “Physico-Chemical Bases of Novel Nanocomposite Sorbents. Theoretical and Experimental Analysis of their Practical Application: Accumulation of Low-Potential Heat, Adsorption Heat Pamps, Freone-free Refrigeration Machines, Deep Gases Drying, Obtaining of Fresh Water from Atmosphere”

S.I. Propkopiev – “Kinetic and Thermodynamic Analysis of Thermochemical Accumulation of Heat and Nuclear Energy with the Use of Reversible Catalytic Reactions and Physico-Chemical Processes”

M.V. Luzgin – “Low-Temperature Reactions of Olefins and Alcohols on Acid Zeolites”

A.O. Kuzmin - “Partial Oxidation of Low Hydrocarbons in Soft Conditions”

I.L. Simakova – “Development of Catalytic Processes for N-Ethyl-2-Aminomethylpirrolidone – Key Semiproduct for “ Sulpyrid” Synthesis”

A.V. Simakov – “Catalytic Conversion of Nitrogen-Containing Compounds over Oxide Catalysts”

M.Yu. Smirnov – “Study of Mechanism of Reactions $NO+H_2$ and NO+CO over the Structurally Non-Uniform Surfaces of Pt (100)”

A.F. Bedilo – “Study of Electron-Acceptor Surface Centers of the Catalysts Based on Sulfated ZrO_2 by ESR and Regularities of Catalysts Synthesis by Aerogel Method”

I.G. Danilova – “Development and Application of IR Spectroscopy of Diffuse Reflectance for Non-Destructive Analysis of Composition and Properties of the Surfaces of Monoliths, Minerals and Polymerization Catalysts”

A.R. Cholach – “Study of the Surface Waves, Generated in the Course of Catalytic Nitrogen Oxide Reduction by Hydrogen over Rhodium”.

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According to the Decision of the Presidium of SB RAS on awarding of Prize of Eminent Scientists, the G.K. Boreskov Prize was awarded to **Dmitrii Yu. Zemlyanov** for his work “Study of Model Catalytic Reactions over the Metal Surface on the Molecular Level” and K.I. Zamaraev Prize – to **Victor V. Terskikh** for his work "Application of NMR-Spectroscopy in Heterogeneous Catalysis”.

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Results of the XXXVII Annual BIC’s Competition of the Research Works

I Prize

- **G.Ya. Popova, T.V. Andrushkevich, Yu.A. Chesalov, I.I. Zakharov, E.S. Stoyanov, G.A. Zenkovets** – “Mechanism of Selective Formaldehyde Transformations over V-Ti-Oxide System” (95 points)

II Prizes

- **I.I. Il'ina, O.G. Arkhipova, I.L. Simakova, V.A. Semikolenov** – "Catalytic Processes to Produce Linalool from α-Pinene: Kinetic Regularities and Reaction Mechanism" (84 points)
- **V.V. Kaichev, E.A. Podgornov, (M. Hävecker, A. Knop-Gericke), V.I. Bukhtiyarov** – "The Nature of Active Particle in Reaction of Ethylene Epoxidation over Silver. Study by X-Ray Absorption Spectroscopy, Photoemission, Temperature-Programmed Desorption" (81 points)
- **V.V. Goidin, V.V. Molchanov, A.I. Lukashevich -** "Development of the Method to Produce Citronellol and Citronellal from Turpentine Components" (77 points)
- **G.N. Kryukova, S.V. Tsybulya, A.S. Ivanova, G.S. Litvak** – "Microstructure of Low-Temperature Species of Alumina of Boehmite and Pseudoboehmite Family and its Transformation under Thermal Treatment" (76 points)
- **L.G. Simonova, E.A. Paukshtis, O.B. Lapina, A.V. Toktarev, V.I. Zaikovskii, B.B. Goncharov, A.P. Suknev, V.I. Bukhtiyarov, V.L. Kirillov, V.V. Terskikh, V.V. Kaichev, D.A. Arendarskii, (V.A. Chumachenko)** – "New Type of the Catalyst Based on Fibre Glass" (76 points)
- **A.R. Cholach, V.M. Tapilin** – "New Possibilities of Disappearance Potential Spectroscopy (DAPS) in Study of the Electron Properties of Solid Surface" (74 points)

III Prizes

- **V.P. Talsi, S.V. Ignashin** – "Physical Methods for Petrochemical Industry" (69 points)
- **R.A. Shkrabina, L.T. Tsykoza, S.A. Yashnik, V.A. Sazonov, V.V. Kuznetsov, N.V. Shikina, Z.R. Ismagilov, V.B. Fenelonov, E.A. Paukshtis, M.V. Luzgin, A.V. Kalinkin, I.E. Abroskin** – "Synthesis and Investigation of Poison-Proof and Stable Monolith Cu-Substituted Zeolite Catalysts for the Processes of Selective Reduction of Nitrogen Oxides with Hydrocarbons" (69 points)
- **G.M. Maksimov, M.N. Timofeeva, V.V. Molchanov, V.V. Goidin, R.I. Maksimovskaya** – "Development of Heteropolyacid Catalyst for Sorbose Acetonation" (67 points)
- **O.N. Kovalenko, P.N. Kalinkin, L.V. Gogina, V.M. Novopashina, N.N. Kundo** – "Peculiarities of Kinetics and Mechanism of Low-Temperature H_2S Oxidation with Oxygen" (66 points)
- **G.A. Kovalenko** – "Medicines of Prolonged Action Based on Immobilized Drug Substances" (66 points)

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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. Geogii 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 were 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 Institute (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 Gerogii 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.

BRIEF HISTORY OF THE INSTITUTE, 1969-1978

(a sequel to "Annual Review-98")

In 1968 the Institute reached the 10-year mark. It has got a very individual, attractive "face" of its own. Considering of all aspects of its life allowed regard the Institute as a useful and successful institution.

In 1969-1978 the Institute continues its investigations on the R&D directions:

- **Development of general theory of catalytic action**
- **Development of scientific bases for catalysts preparation**
- **Development of new and improvement of existing commercial catalytic processes**
- **Development of the methods of mathematical modeling of catalytic reactors**.

To the end of the 70th the number of the researchers increased form 220 in 1969 to 306 in 1978, the total staff – from 695 in 1969 to 850 in 1978. The structure of the Institute included about 20 laboratories and groups, which fell into five departments. Most of the laboratories undertook research work in the theory of catalysis, simultaneously solving a series of applied problems.

DEPARTMENT OF HETEROGENEOUS CATALYSIS

Laboratory of Oxidation

Head: Georgii K. Boreskov

The Laboratory undertakes investigation on the mechanisms of catalytic reactions of complete and selective oxidation. The Laboratory has succeeded in elaborating a concept based on estimation of energies and the character of bonds that are broken or made during the catalytic process. Various methods – calorimetry, thermodesorption, isotopic, pulse-technique, direct measurements of the rates of some stages of the catalytic processes are used.

Catalysts and catalytic processes are developed for obtaining sulfuric acid, formaldehyde, acrylic acid, acrylonitrile, and phthalic anhydride.

Laboratory of Semiconductor Catalysts

Head: Nadezhda P. Keier

The main objective of the Laboratory is to investigate the interrelations between the electronic structure and catalytic properties of the oxide semiconductor catalysts. The variation of the electronic structure of catalysts is achieved via methods of “doping”, “field effect” and illumination with photons. The relative role of “collective” and “local” properties of surface catalysts in the chemisorption and catalytic processes was clarified. Among the successful results of this Laboratory are elaboration of a method to determine absolute quantum yields of photocatalytic reactions and study of the mechanism of CO photocatalytic oxidation on a series of oxides.

Laboratory of Catalysts Preparation

Head: Vera A. Dzis’ko

As a result of systematic study it has been shown that the activity of single-component catalysts is approximately constant and does not depend on preparation technique. The activity of most catalysts of complex composition depends on products of their interaction. The Laboratory undertakes research on the regularities of surface generation of hydroxide systems, silica gel, and supported metal catalysts. It develops technology of catalysts preparation for sulfuric acid production (vanadium-containing catalysts IC-1-1 and IC-1-2), propylene ammoxidation (bismuth-molybdate based catalysts) and hydrogenation (Ni-catalysts).

Laboratory of Dehydrogenation

Head: Roman A. Buyanov

The Laboratory is responsible for designing and improving catalysts and catalytic processes for the petrochemical industry. Also it carries out studies on kinetics of dehydrogenation, coking, regeneration and some other processes for their simulation and optimization.

New and improved catalysts for oxidative dehydrogenation of n-butylene to divinyl are under pilot tests. Four industrial catalysts for liquid p-hydrogen production are developed based on fundamentals of low-temperature o-hydrogen conversion. The crystallization mechanism of the slightly soluble hydrogels named "mechanism of oriented growing" is revealed.

Laboratory of Metal Catalysts

Head: Aleksandr V. Khasin

As a result of the investigation performed mechanism of molecular nitrogen activation during catalytic synthesis of ammonia over iron and molybdenum nitride and forms of adsorbed hydrogen on nickel have been revealed, and data on equilibrium and kinetics of oxygen chemisorption on silver have been obtained.

Laboratory of Gas-Purification Processes (up to 1978 - Laboratory of High-Temperature Catalytic Processes)

Head: Vladislav V. Popovskii

The Laboratory undertakes research works in two main directions: development of highly active and stable catalysts for exhausted gases purification (IC-12-1 for complete oxidation of exhausted gases, "crust" IC-12-3) and elucidation of the main factors affecting the reactivity of the molecules.

The Laboratory works in close cooperation with chemical, automobile, electromechanical, pulp and paper industries.

Laboratory of Catalytic Conversion of Sulfur Compounds

Head: Anna V. Mashkina

The main scientific problem is the establishment of general regularities of some classes of reactions of sulfur-organic compounds. Sulfides, sulfoxides, sulfones, and thiophenes are used as model materials. Regularities found are applied to develop processes and catalysts to obtain sulfur organic compounds promising for practical use: IC-1-7 catalyst for sulfolene hydrogenation; sulfides oxidation to sulfoxides in diesel oil; IC-232 catalyst for oil sulfoxides production.

Laboratory of Zeolites

Head: Kazimira G. Ione

The Laboratory undertakes research on the catalytic properties of metal-zeolite systems in dependence of the nature, valence state, dispersity and mode of distribution of transition metal for reactions of polifunctional catalysis. As a result, zeolites with high catalytic activity in reactions of complete oxidation, hydrogenation and hydrocracking have been obtained.

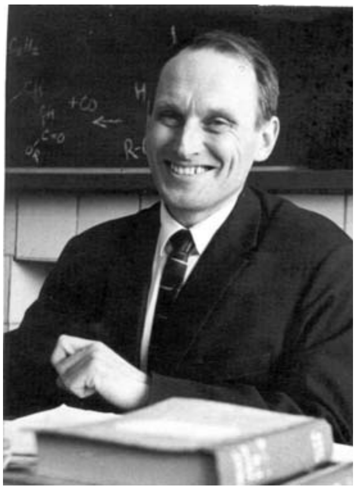
DEPARTMENT OF HOMOGENEOUS AND COORDINATION CATALYSIS

The Department was organized in 1972 to consolidate the laboratories and groups studying catalytic processes with transition metal complexes.

Laboratory of Catalysis by Metal Complexes

Head: Klavdii I. Matveev

The Laboratory carries out theoretical investigations on the regulation of catalytic activity of metal complexes by ligands in redox reactions. The Laboratory has succeeded in developing new catalytic systems for oxidation of ethylene and higher olefins to acetaldehyde and ketones, respectively. New homogeneous catalyst based on phosphour-molybdate heteropoly acids for cumene hydroperoxide decomposition has been developed. The mechanism of molecular oxygen activation with heteropoly acids is under developing.



Laboratory of Catalytic Polymerization

Head: Vladimir A. Zakharov

The Laboratory undertakes research on the heterogeneous catalysts for olefin polymerization. The Laboratory has developed a method to determine the number of active centers - transition metal-carbon bonds in the surface coordination compounds - by their interaction with radioactive inhibitors.

A new type of one-component catalysts for olefin polymerization was obtained by the interaction of π-allylic complexes of transition metals with oxide support. The Laboratory has developed highly active catalysts for gas-phase and slurry olefin polymerization including titanium-containing catalysts supported on polyethylene and magnesium compounds.

Laboratory of Metal-Organic Catalysts

Head: Yurii I. Yermakov,

Deputy director on the scientific work

The major aim of the Laboratory is to develop methods for synthesis of catalysts with transition metal complexes fixed on the support, which combine the advantages of homogeneous systems with those of heterogeneous, using organometallic compounds. The Laboratory solves a problem of purposeful synthesis of bi- and trimetallic catalysts for hydrocarbon conversion.

DEPARTMENT OF PHYSICAL METHODS

Laboratory of Structural Investigations

Head: Vsevolod N. Kolomiichyk

This Laboratory has at its disposal a variety of methods, which permit determination of phase composition and crystal structure of catalysts and supports by means of X-ray (high temperature X-ray, analysis of the profile of the diffraction patterns, method of radial distribution of atoms to characterize the structure of poorly crystallized and amorphous catalysts and supports), electron microscopy, ESCA to study the state of surface layers of the catalyst.

Laboratory of Optical Spectroscopy

Head: Lembit G. Karakchiev

Laboratory undertakes studies on variation of catalyst composition in the processes of its preparation and thermal treatment by means of electronic spectroscopy in ultraviolet and visible spectral regions and IR spectroscopic studies in the range from 10 to 5000 cm^{-1} at temperatures from –196 to 700 ^{o}C.

Laboratory of Radiospectroscopy

Head: Vyatcheslav M. Mastikhin

The Laboratory has succeeded in the study of solid catalysts, especially active component of vanadium catalysts and mechanism of ligand exchange in paramagnetic complexes by ESR. By means of NMR the Laboratory studies adsorption, the nature of proton centers on the catalyst surface, and reagent interaction with soluble catalysts.

Radiochemical Laboratory

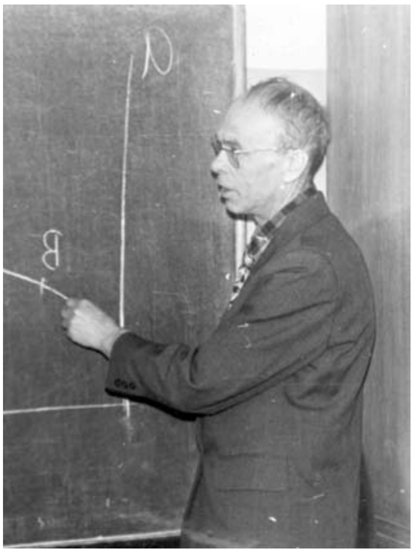
Head: Leonid A. Sazonov

Radioactive and stable isotopes are used to investigate the reaction mechanisms of heterogeneous catalysis. By means of ionizing radiation the Laboratory studies the nature of radiation defects in solids, adsorption forms and reactivity of surface compounds.

Due to wide experimental possibilities the Laboratory can carry out joint work not only with the laboratories of the Institute, but with other institutes as well.

Laboratory of Adsorption

Head: Anatolii P. Karnaukhov



The Laboratory’s activities are divided into two main parts:

- Study of the geometric parameters of catalysts: surface area determination by argon thermodesorption in a highly efficient set-up developed in the Laboratory; determination of dispersion of supported metallic catalysts using the chemisorption of hydrogen, oxygen and carbon monoxide; porous structure determination by mercury porosimetry, adsorption and capillary condensation
- Study of the interaction energy of chemisorbed reagents by a sensitive macrocalorimeter with electric compensation for heat effects and by differential microcalorimeter of the Kalve type.

Analytical Laboratory

Head: Vladislav V. Malakhov

The Laboratory includes the group of physico-chemical methods of analysis, the gas chromatography group, and the thermo-analytical group developing necessary methods to investigate catalysts and directly performing the analyses. The available analytical techniques are being continuously perfected with a view to increasing their precision, sensitivity, resolution, rate and efficiency.

Laboratory of Mechanisms of Catalytic Reactions (organized in 1977)

Head: Kirill I. Zamaraev

The Laboratory studies the mechanism of catalytic reactions and structure of active centers of catalysts of homogeneous and heterogeneous reactions by NMR and ESR mnethods.

DEPARTMENT OF INDUSTRIAL CATALYSTS

Laboratory of the Scientific Bases of Catalysts Technology

Head: Aleksandr A. Samakhov

The major task of the Laboratory is to investigate the physico-chemical nature of the processes of catalyst production and to develop on this basis methods of efficient selection, simulation and technological calculations for equipment, which provides catalysts of needed quality. The studies carried out allowed to create the largest commercial plant in the USSR for production of vanadium catalysts.

Laboratory for the Industrial Catalysts Study

Head: Naum M. Zaidman

The Laboratory carries out scientific-organizational work on improvement the quality of commercial catalysts. The Laboratory makes detailed examinations of standards and technical conditions for commercial catalysts developed by all organizations of the USSR, undertakes work on standardization of methods for determining operation parameters of catalysts and on development of testing apparatus for catalysts.

Laboratory for Synthesis of Supports

Head: Emmanuil A. Levitsky

- Principally new methods are developed for obtaining dispersed alumina and silica gel, intended for large scale production of supports and adsorbents;
- The processing line to produce active alumina of various forms and size of granules by the technology of liquid formation is put into operation;
- The new method of adsorption-contact catalyst drying is suggested;
- The models of catalytic heat generators for powder adsorbents regeneration are developed.

DEPARTMENT OF KINETICS AND SIMULATION

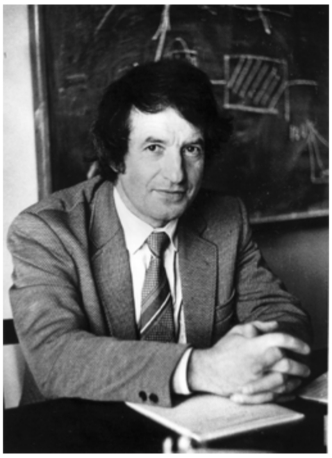
Laboratory for Catalytic Processes Simulation

Head: Mikhail G. Slin'ko

The basic direction of the Laboratory's work is simulation of processes of the following kinds: stationary bed, liquid phase, fluidized bed, nonstationary, and complex with varying catalyst states. It also studies problems of stability and aerodynamic simulation of chemical reactors. By 1974 the Laboratory succeeded in simulation about 40 commercial processes.

Laboratory of Process Simulation in Fixed Bed (organized in 1976)

Head: Yurii Sh. Matros



The Laboratory is active in the mathematical modeling of chemical reactors. It develops the theoretic bases for catalytic processes under unsteady-state conditions.

Laboratory of Kinetics of Catalytic Reactions

Head: Vyatcheslav I. Timoshenko

The Laboratory undertakes analyses of the dynamic system of chemical kinetics, and studies kinetic regularities of individual stages of heterogeneous catalytic reactions and the effect of the reaction media on the variation of catalytic properties. Theoretical, experimental and mathematical methods are being developed. The Laboratory works to create systems for automation of kinetic investigations.

Laboratory of Computing Techniques

Head: Vladimir B. Skomorokhov

The major aim of this Laboratory is automation of chemical experiments, improving existing and developing new means of mathematical simulation, and perfecting computer hardware and software. The Laboratory has at its disposal computers “Minsk-32”, “Minsk-2”, “Dnepr-2”; a third generation hybrid computing system HCS-100. By combining the “Minsk-2” digital computer and “MN-14” analog computer an analog-digital computing system, ACDS, has been created which combines all the advantages of analog and digital machines.

Laboratory for Simulation of Processes with Phase Conversions

Head: Aleksandr S. Shmelev

The Laboratory develops methods of simulation for such processes as polymerization, crystallization, hydrocracking, esterification, decomposition of some chemical products, etc., which are complicated by the appearance or disappearance of one of the phases of the reaction system in order to increase yields of commercial production.

Laboratory for Simulation of Catalytic Processes in a Fluidized Bed

Head: Valentin S. Sheplev

On the basis of mathematical simulation and studies of local and integral characteristics of fluidized bed a method for increasing the degree of uniformity of the bed has been developed and tested in a series of important catalytic processes on pilot and semi-commercial scales. The Laboratory works in close cooperation with other laboratories of the Institute, trade institutes and commercial plants.

Pilot-Chemical Shop of the Institute has equipment, which allow testing of catalyst activity at low and high (up to 700 atm) pressures mainly in flow circulating equipment. The experimental data are analyzed by computer.

The equipment of the **Division of Catalysts Preparation** allows production of catalysts in 10-20 kg quantities for testing, and allows study of some technological stages of catalyst preparation.

At the Institute there is a centralized system for creation of experimental equipment. The **Design Office** develops the projects and assemblies for equipment.

The **Library of Scientific Literature** of the Institute has about 15000 books and 55000 scientific-technical journals basically on chemistry, chemical technology, physics and mathematics.

The **Glass-Blowing Shop** produces complex products of glass and quartz.

The **Office of Measuring Instruments** and **Technical Division** provide the laboratories with measuring and analytical apparatus and perform a great variety of information-measuring techniques. The Institute has succeeded in the development and production of a series of special assemblies for equipment to carry out catalytic investigations. Particularly, the Institute shops make circulating pumps for flow-circulating equipment for testing catalytic activity.

THE MOST IMPORTANT CATALYTIC PROCESSES AND CATALYSTS DEVELOPED BY THE INSTITUTE OF CATALYSIS

➢ **Oxidation processes**

♦ Oxidation of sulfur dioxide on high-temperature and low-temperature vanadium catalysts. On the basis of the technology for production of vanadium catalysts the largest in Europe commercial plant has been built in Voskresensk;

♦ Oxidation of methanol to formaldehyde over the oxide catalyst instead of industrial silver catalysts. A set with a combine gear was created at the Novosibirsk Chemical Plant. This process with the capacity up to 50.000 t/year was also marketed in Czecho-Slovakia (1973);

For the first time in the world practice a new gear with 4 adiabatic layers of the catalyst was developed, and started at the Kemerovo Plant;

♦ Unmatched two-step oxidation of propene to acrylic acid in fluidized bed (Jointly with the Saratov branch of the Institute of Polymers) and ammoxidation of propane and propene to acrylonitrile. The catalysts pilot tests have been conducted at Polotsk Chemical Center (1975);

♦ Soluble catalytic systems for olefin oxidation to carbonyl compounds.

➢ **Petrochemical and oil-refining processes**

♦ Production of basic monomers (from C_2 to C_5 and styrene);

♦ One-step production of diolefins from paraffins. Jointly with the Institute of Monomers (Yaroslavl) a series of new catalysts for olefin dehydrogenation was developed. High-performance thee-layered device for butulene dehydrogenation to divinyl were put into operation jointly with Tol'yatti plant (1975).

➢ **Catalytic reactions involving sulfur compounds** – synthesis of thioethers, sulfoxides, sulfons and thiophenes; producing alkylthiophenes, thiophanes, dimethylsulfoxides and sulfons, sulfolans; catalyst for hydrogenation of sulfolene to sulfolane.

➢ **Production of synthetic liquid fuel**

♦ Synthesis of petrol or Diesel fuels by direct hydrogenation of carbon monoxides with the use of low-temperature catalyst based on carbonyl complexes and clusters of transition metals;

♦ Production of liquid hydrocarbon fuel from natural gas and methanol with the use of zeolite catalysts.

➢ **Polymerization of olefins**

Highly active catalysts (titanium-magnesium systems and zirconium systems) for ethylene polymerization in suspension, gas-phase regimes and in solution without stage of washing were tested at the pilot scale at Kyibushevsk plant.

- **Catalysis for ecological problems**

- ♦ Detoxication of exhaust gases containing vapors of organic solvents over the Cu-based catalysts, stable to sulfur poisons;
- ♦ Liquid-phase process with a homogeneous phthalocyanine catalyst for recovery of hydrogen sulfide from natural and other gases;
- ♦ Catalyst for combustion of noxious wastes of aromatic compounds;
- ♦ An industrial installation (created in collaboration with Technical Design Office and Novosibirsk Chemical Plant) for catalytic purification of wastes of methanol-free formaldehyde production was put into operation at Novosibirsk Chemical Plant (1976).

- **Different sorts of silica gel supports and alumina support.**

  Pilot installation for amorphous aluminum hydroxide production by thermal treatment of hydrargillite was put into operation at Gorkii Pilot Plant; processing line for active alumina production by method of fluid moulding was started at Ryazan Oil-Processing Plant (1974). A decision is adopted about construction of series of large-scale installations for active alumina production.

- **Thermally stable supported nickel catalysts for hydrogenation**
- **Supported highly active catalysts for ethylene production**
- **Catalytic system for one-step synthesis of ethylene glycol**

SCIENTIFIC-SOCIAL LIFE OF THE INSTIUTE. KEY DATES

1969

March. The presidium of the Supreme Soviet of the USSR awarded the Institute the ORDER OF THE RED BANNER OF LABOUR.

April. The “Days of Science” devoted to the advances of the Institute of Catalysis took place at the House of Sciences. The leading scientists of the Institute presented lectures during the scientific conference. Of big interest was the exhibition of novel catalysts and processes developed by the Institute.

1970

April. At the suggestion of R.A. Buyanov the Memorial Square dedicated to the 100^{d} anniversary of V.I. Lenin was implanted. The Siberian pines, blue firs, limes, oaks, rowans, nut-trees planted by the collaborators of the Institute formed the beautiful square.

1970-1971

The Institute has got a number of new devices and equipment produced domestically and imported: Electron microscopy (Czech republic), X-ray spectrometer and mass-spectrometer (USSR), Auger-spectrometer (UK), tablet compressing machine (UK), spray drier (Denmark), spectrometers of Raman scattering (USSR), ESR- and NMR-spectrometers (Japan), electronic computer “Minsk-32”.

1972

Fundamental and applied works of the Institute were presented in the section "Contribution of Chemists of SB AS USSR to the Development of Soviet Science" at the "Exhibition of National Economic Achievements". The Institute has got the Award.

1973

December. The Scientific session devoted to the 15 anniversary of the Institute took place. Academician G.K. Boreskov opened the session. The leading scientists of the Institute gave their lectures. The first Booklet "The Institute of Catalysis" was issued. It presented the structure of the Institute and main directions of the research work of the divisions and subdivisions of the Institute.

On the proposal of Scientific Council of the Institute the Council of young scientists was created, which united the researchers of age limit up to 33 years. P.A. Zhdan was elected the chairman of the council.

1977

Prof. K.I. Zamaraev entered the Institute and became a deputy director of the Institute and the head of the Laboratory of Mechanisms of Catalytic reactions, organized in the same year.

Right after the group of his teammates – the graduates from the Moscow Physico-Technical Institute - arrived: V.N. Parmon, V.M. Nekipelov, V.P. Zhdanov, D.I. Kochubey, E.N. Savinov, E.P. Talsi, S.V. Lymar, Yu.I. Aristov.

1978

June 23, 1978 – 20 years since the day of adoption of the decision about organization of the Institute of Catalysis in the Siberian Branch of the USSR AS.

During the scientific session devoted to the 20^{th} anniversary of the Institute the leading scientists – G.K. Boreskov, K.I. Zamaraev, R.A. Buyanov, V.A. Dzis'ko, V.D. Sokolovskii, V.V. Popovskii, Yu.I. Yermakov, K.I. Matveev, K.G. Ione, Yu.Sh. Matros – presented key lectures on the main directions of the investigations.

A picnic was organized ashore of the Ob' River to celebrate the occasion.

October. Presidium of the SB AS USSR adopted a resolution about organization of Division of Catalytic Hydrocarbon Conversion in Omsk. V.K. Duplyakin was appointed the head.

December. For the first time the competition of research works by young scientists took place.

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INTERNATIONAL COOPERATION

The scientific cooperation of the Institute with the scientific centers of other countries is effected in

- Conducting of joint seminars and participating in congresses and symposia on theoretical and applied catalysis. The Institute initiated the organization of Soviet-Japan and Soviet-French Seminars on Catalysis;
- Exchanging of research fellows. Every year nearly 50 scientists from other countries pay short visits to the Institute of Catalysis to get acquainted with its activities. In the Institute there is a regular program of visits by junior scientists from foreign countries;
- Visiting scientific centers.

The broadening of international scientific and engineering relations proceeded in **1969** along the path of establishing the connections with the industrial enterprises of German Democratic Republic: the programs in the field of chemical reactors modeling and development of new processes.

In **1970** the program of scientific and engineering cooperation with the scientific centers of France on the problem “Application of Computer Technique in Catalytic Investigations” was elaborated, which specified the holding of Soviet-French Symposia, exchange of specialists, joint development of industrial processes (Project Coordinator – M.G. Slin’ko).

1971. In accordance with an agreement signed by Bulgaria, Hungary, the German Democratic Republic, Cuba, Poland, Rumania, the USSR, Czechoslovakia, and Yugoslavia, the Institute of Catalysis was charged with the function of a Coordination Center for the problem “Development of new industrial catalysts and improvement of the quality of catalysts applied in industry”. The total leadership of the activities of the Coordination Center was performed by the Council of Representatives, made up of appointed representatives from each member-country. Academ. G.K. Boreskov represents the Soviet Union, the Director of the working body became A.A. Samakhov, the Scientific Secretary – G.I. Panov.

The main directions of the work were:

1) Collection and summarizing information on commercial catalysts and supports;
2) Developing improved and standardized methods of catalyst testing;
3) Developing and improving commercial catalysts and supports.

The Center undertook the organization work to fulfil the program of cooperation: it participated in developing detailed workable plans, mediated negotiations, organized meetings and conferences of specialists. In 1973 the first number of Materials of Coordination Center - “Industrial Catalysts” – was issued. It contains data on 159 catalysts and supports. A stock of catalysts and supports manufactured in collaborating countries were created.

Since **1973** the Institute became an active participant in the USSR-USA cooperation Program “Chemical Catalysis”. G.K. Boreskov and M.G. Slin’ko took part in elaboration of the research plan: catalysis by coordination and metal-organic compounds; modeling of the chemical reactors; application of catalysis in life-support systems of spaceships; catalysis for environmental protection. In the frame of cooperation the Soviet-American workshops were organized and exchanging of research fellows took place.

An edition of the Soviet-Hungary Journal "Reaction Kinetics and Catalysis Letters" was started in **1974** (Editors: G.K. Boreskov (USSR) and F. Nagy (Hungary).

In **1975** in the frame of intergovernmental agreements on the scientific and technical cooperation on the problem “Chemical Catalysis” the first long-term visits to the capitalist countries took place: A.A. Davydov - France, Lyon, Institute de Recherches sur la Catalyse; V.M Tapilin – USA, California Technological Institute; V.M. Mastikhin – USA, Princenton University; B.N. Kuznetsov – USA, Stenford University.

CONFERENCE AND EXHIBITION ACTIVITY

Year	Date	Event
1969	**April, 12-18**	Seminar *"Fundamentals of Catalysts Preparation"* (more than 70 specialists of applied-research centers and enterprises)
1971	**March, 19-22**	Soviet-French Seminar "*Application of Mathematical Methods and Electronic Computers in Catalytic Investigations"*. A decision was adopted about regular holding of Seminars on the general problem "Informatics" with participation of foreign specialists. Next Seminars were organized by the Institute jointly with Computer Center of AS USSR in 1975 (Novosibirsk) and in 1978 (Odessa).
	June, 7-11	IV All-Russian *Conference on Chemical Reactors* (about 180 scientists and specialists from academician and applied-research institutes)
	July, 4-9	The 1st Soviet-Japan *Seminar on Catalysis*
1972	**March, 13-20**	1st French-Soviet *Seminar on Mechanism of Oxidative Reactions,* (France). G.K. Boreskov presented the lecture "Study of Mechanism of Oxidative Dehydrogenation of Butene-1 with Oxide Catalysts"
	July	2nd All-Russian *Seminar on Application of Oscillating Spectroscopy in Adsorption and Catalysis* (10 papers were presented by the specialists from the Institute)
	August, 20-26	G.K. Boreskov, M.G. Slin'ko, Yu.I. Ermakov, A.M. Lazutkin, V.I. Savchenko participated in the V International *Congress on Catalysis* (USA). Acad. G.K. Boreskov was elected the President of International Congress on Catalysis for 1972-1976.
	November, 14-16	All-Russian Seminar *"Adsorbed Oxygen in Catalysis"* (Researchers from the Institute gave 15 reports).
1973	**April**	All-Russian *Meeting on Isotope Exchange on Solid Catalysts* (more than half of the lectures were given by the participants from the Institute).
1974	**May, 21-23**	Soviet-American Meeting *"Catalysis for Environmental Protection"*.
	July, 16-19.	1st Soviet-American Symposium *"Chemical Catalysis*"
	October, 9-11	1st All-Russian Seminar *"Photoadsorption and Photocatalytic Phenomena in Heterogeneous Systems"* (36 leading scientists from Moscow, Leningrad, Kiev, Tomsk and Novosibirsk)
1975	**July, 14-16**	2nd All-Russian *Conference on Kinetics of Heterogeneous Reactions* "Kinetics-2" was organized jointly with Scientific Council on Catalysis (120 participants from 46 academician and applied-research institutes)

1976	**March, 21-24**	1st All-Russian Conference “*Application of Zeolites in Catalysis*” organized jointly with the Scientific Council on Catalysis (150 participants from Moscow. Leningrad, Groznii, Alma-Ata and other cities).
	June, 12-18	The *Scientific Session* of Scientific Council on Catalysis dedicated to the problems of designing and application of novel efficient catalysts (180 specialists from academician and applied-research institutes, industrial enterprises and ministries).
1977	**April, 18-20**	1st Symposium *“Siberian Catalytic Readings”* in honor of 70th anniversary of Acad. G.K. Boreskov. The Subject of the Symposium was “Modern Problems of Catalysis”. The reviews on urgent questions of catalysis were given by G.K. Boreskov, D.V. Sokolskii, B.A. Dolgoplosk, O.V. Krylov, F.T. Shilov, V.B. Kazanskii, O.M. Poltorak, K.I. Zamaraev, and foreign scientists – K. Tamaru (Japan), J. Haber (Poland), P. Putanov (Yugoslavia), D. Shopov (Bulgaria).
	June, 23-25	All-Russian Meeting *“Synthesis and Catalytic Properties of Transition Metals Complexes, Anchored on the Surface of Supports*”
	June, 27 – July, 1	International Seminar *“Catalysis in Environmental Protection”* with participation of specialists from socialist countries
1978	**May, 29-31**	All-Russian Conference “*Supported Metal Catalysts of Hydrocarbon Conversion (New Approach to Synthesis and Studying*) (120 participants, among them 29 foreign specialists).
	September, 23-25	All-Russian Meeting *“Synthesis, Structure and Application of Heteropolycompounds in Catalysis*”

SCIENTIFIC DEPARTMENTS

DEPARTMENT OF HETEROGENEOUS CATALYSIS

HEAD OF THE DEPARTMENT PROF. ROMAN A. BUYANOV

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

Laboratory of Heterogeneous Selective Oxidation
Head: Prof. Tamara V. Andrushkevich

Laboratory of Dehydrogenation
Head: Prof. Roman A. Buyanov

Laboratory of Catalysts Preparation
Head: Prof. Oleg P. Krivoruchko

Laboratory of Catalytic Conversion of Carbon Oxides
Head: Prof. Tamara M. Yurieva

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

Laboratory of Adsorbents and Supports
Head: Prof. Boris P. Zolotovskii

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

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

Group of Dynamics of Surface Transformations
Head: Dr. Andrei V. Simakov

Group of Catalytic Synthesis of Oxygen-Containing Compounds
Head: Dr. Galina G. Volkova

The **Laboratory of Oxidative Catalysis over Zeolites** (headed by Prof. Gennadii I. Panov) proceeded in studying the mechanism of deactivation of Fe-ZSM-5 zeolite in the course of oxidative hydroxylation of benzene by nitrogen monoxide. The deactivation was shown to result from poisoning of the active sites (α-sites) by coke, the concentration of α-sites being linearly decreased with an increase in the coke concentration. Even if the catalyst activity is many times decreased, the activity of an individual α-site remains constant that argues the absence of diffusion hindrances and the absence of blocking the microporous space of the zeolite.

Poisoning ability of coke was determined. The amount of coke equivalent to 100-120 benzene molecules was shown to cause poisoning of one α-site.

During the past year the research activities of the **Laboratory of Heterogeneous Selective Oxidation** (headed by Prof. Tamara V. Andrushkevich) have been concentrated on three major research fields:

- An efficient way to synthesize isonicotinic acid (initial compound for production of antituberculous preparation) by direct 4-methylpyridine oxidation over the binary oxide catalyst has been developed (jointly with the Laboratory of Catalysts Preparation headed by Prof. O.P. Krivoruchko).
- V-Ti-O system has been shown to be the most efficient for ammoxidation of methylpyrasine. The surface complexes of methylpyrasine and ammonia have been detected using Fourrier IR spectroscopy and the mechanism of amido pyrasine formation through carboxyl and amide complexes interaction has been established (jointly with the Laboratory of Zeolites and Acid Base Catalysis headed by Prof. E.A. Paukshtis).
- The formation of formic acid and carbon oxides from the surface compounds of the same structure – symmetric bidentate formiates - has been shown by TPD and TPR coupled with Fourrier IR spectroscopy (jointly with the Laboratory of Spectral Methods headed by

Prof. D.I. Kochubey). The first is formed as a result of interaction of weakly bonded formiates with the oxygen, and carbon oxides are formed as a result of strongly bonded formiates decomposition.

The **Laboratory of Dehydrogenation** (headed by Prof. Roman A. Buyanov) was active in research under two main subject areas:

- Regular features and mechanisms of radical-chain non-branched reactions over heterogeneous catalysts were discovered and investigated. Basic principles of a new fundamental theory of these processes were formulated.
- Fundamentals of the theory of formation of metal-carbon composite materials, catalysts and adsorbents were formulated. The said processes proceed through catalytic decomposition of hydrocarbons according to the “carbide cycle mechanism” on microparticles of metals of the sub-group of iron and the alloys with other metals.

Researches of the **Laboratory of Catalysts Preparation** (headed by Prof. Oleg P. Krivoruchko) have been applied to a variety of problems:

- The genesis of Fe-Zr system ($[Fe^{3+}]/[Zr^{4+}]=0.123$) has been studied in dependence of nature and content of surface-active substances and thermal treatment conditions. It has been shown that thermolysis of the materials depends upon pH of their precipitation. The formation of cubic zirconia was observed at high pH, and formation of monoclinic zirconia – at low pH.
- An effect of vanadium and molybdenum concentrations on the microstructure of V-Mo-Ti-O system has been studied and formation of V-Mo compound with the layer structure active in a series of reactions of partial oxidation has been revealed.
- A set of methods (BET; IR spectroscopy; ^{29}Si, ^{23}Na, ^{27}Al, ^{133}Cs and ^{129}Xe NMR) has been used to study physico-chemical properties and structure of silica glass fiber supports formed upon glasses leaching. The SiO_2 matrixes formed differs significantly from the typical globular silica gels. Its structure and properties are mostly adequately described by a pseudo-intercalation model of layered matter including alternating layers of 3-4 silica-oxygen tetrahedrons. The possibility of pillarging-effect has been revealed.
- Fe-containing particles in the matrixes of amorphous carbon first were shown to catalyze its graphitization at 600-800 ^{o}C in the inert medium. The three-stage mechanism of amorphous carbon to graphite transformation has been suggested based on experimental data.

It was established by the researchers of the **Laboratory of Catalytic Conversion of Carbon Oxides** (headed by Prof. Tamara M. Yurieva) that $Cu\text{-}Zn/SiO_2$ catalysts represent a mixed zinc-copper hydroxysilicate with the zincsilite structure: $M2[(M1)\ \square Si_4O_{10}](OH)_2{\bullet}nH_2O$, where M1 are Zn^{+2} ions in octahedral positions in layers formed by two layers of $[Si_4O_{10}]$ tetrahedrons, M2 - zinc ions in interlayers; $\square$ are cation vacancies. Copper ions are constituents of the zincsilite structure. The aim of the study was to determine the structure positions of copper ions substituting for zinc ions and the dependence of the redox and catalytic properties of these copper ions on the localization positions.

Various physicochemical techniques such as TA, XRD, EM, IRS, DD (Differential Dissolution) were used for the study. Copper ions were shown to substitute for zinc ions located both at octahedral positions of the layers (position M1) and in the water interlayer (position M2). Different properties with respect to interaction with hydrogen are characteristic of the copper ions at different structure positions: (a) Copper ions in octahedral positions in layers are reduced starting with the temperature of 280-300 °C, about a half of these ions being reduced at 450 °C; (b) Copper ions, which are in the water interlayer, are reduced at a constant activation energy at the temperature range between 230 and 260 °C; all of them may be reduced at these temperatures.

Catalytic properties of hydroxysilicates Cu-Zn-SiO_2 reduced by hydrogen at different temperatures were studied with respect to dehydrogenation of methanol. The catalytic properties, *i.e.* selectivity to methyl formiate and activity, were shown to depend on the mode of copper stabilization. A higher selectivity to methyl formiate was observed for copper ions substituting for zinc ions in the octahedral positions in the layers.

An important part of the research program of the **Laboratory of Catalysts for Deep Oxidation** (headed by Prof. Vladislav A. Sadykov) was the development of effective monolith catalysts for oxidative dehydrogenation of propane into olefins at short contact times. The catalysts were synthesized based on new platinum-free active components. The influence of the composition and arrangement of the catalyst bed on the process route and yield of olefins was studied. The role of gas-phase reactions in the process of oxidative dehydrogenation of propane was first demonstrated for the honeycomb catalysts. Optimization of the catalyst bed composition and of the operation parameters allowed the yields of propylene and ethylene to be remarkably increased.

Also methods for production of monoliths of commercial dimension-types from corundum using different feedstocks and procedures for supporting active components for production of honeycomb catalysts were elaborated. These catalysts are effective to selective oxidation of methane into syngas. In cooperation with the Laboratory of Industrial Catalytic Processes headed by I.A. Zolotarskii, the catalysts were tested using the real natural gas in the autothermal mode; they revealed high activity and selectivity.

The **Laboratory of Adsorbents and Supports** (headed by Prof. Boris. P. Zolotovskii) has accomplished the development of a low-waste technology for synthesis of alumina supports (ICT-02-6M, ICT-02-7 produced by “Katalizator Co”, Novosibirsk). The technology is adopted in industry.

The **Group of Reactions of Oxidation on Metals** (headed by Prof. Aleksandr V. Khasin) has detected two essentially different species of hydrogen adsorbed on a copper-zinc oxide catalyst pre-reduced by hydrogen (the model catalyst for methanol synthesis) at the range from room temperature to 493 K at the hydrogen pressure from 10 to 10^5 Pa. A low energy of the chemisorption bond is characteristic of the first one, which is formed in a considerable equilibrium quantity at high hydrogen pressures close to atmospheric. Species of the second type are more strongly bonded to the surface of the reduced catalyst; they are readily formed at the whole range of conditions under study, and the equilibrium is established between the adsorbed and gaseous hydrogen.

Adsorption of oxygen on silver films prepared in vacuum was studied at 473 K at the range of oxygen pressures between 1 and 1000 Pa. Oxygen was found to be adsorbed in a considerable equilibrium quantity, which reached and then went above (as a function of oxygen pressure) the value corresponding to the monolayer. The results obtained allowed the assumption that the high quantity resulted from oxygen adsorption at the inner grain boundary surfaces.

The **Group of Catalytic Conversion of Sulfur-Containing Compounds** (headed by Prof. Anna V. Mashkina) has developed the catalyst ICT-31-7 for synthesis of methylmercaptan from methanol and hydrogen sulfide (in cooperation with "Katalizator Co", Novosibirsk). If compared to the currently used catalyst ICT-31-1, this one provides a higher (by 20%) productivity to methylmercaptan at the same high selectivity. The kinetics of the high-pressure reaction was studied to recommend the process conditions using the improved catalyst. The results obtained are of interest to set up a high-capacity production of methionine (birdseed supplement).

The application of a wide number of physicochemical methods and purposeful synthesis of samples made it possible for the **Group of Dynamics of Surface Transformations** (headed by Dr. Andrei V. Simakov) to characterize the state of Cu^{2+} ions in Cu-Ti-O catalysts and to establish the following:

- The structure of copper oxide forms on the TiO_2 surface is determined by its morphology, the copper concentration and the catalyst preparation method.
- At low copper concentrations Cu^{2+} ions preferably interact with low-coordinated oxygen atoms of the anatase lattice with the formation of chain structures of variable length with low number of isolated Cu^{2+} ions. The concentration of these forms and the geometry of the nearest oxygen environment of Cu^{2+} ions are determined by the structure of TiO_2 faces. The most energetically favorable structures are formed on face (001).
- As the copper concentration grows, some of the surface oxide copper-titania forms become nucleation centers of oxide clusters. The size of the latter seems to be limited by the size of anatase pores.
- Noticeable growth of bulk CuO phase takes place after completion of the formation of surface-stabilized Cu^{2+} ions and oxide clusters.
- The ratio of the forms of copper can be changed in favor of more energetically favorable ones by the application of another preparation method – equilibrium adsorption technique.
- The investigation performed made it possible to make quantitative evaluation of the contents of different copper forms on the anatase surface.

The novel high effective biocatalyst for continuous starch hydrolysis into glucose on the basis of glucoamilase immobilized on carbon-ceramic monolithic support has been developed.

The **Group of Catalytic Synthesis of Oxygen-Containing Compounds** (headed by Dr. Galina G. Volkova) has been formed in November, 1999. The basic research program of the group includes design of heterogeneous catalysts for halide-free carbonylation of dimethyl ether, methanol and methyl acetate.

DEPARTMENT OF HOMOGENEOUS AND COORDINATION CATALYSIS

HEAD OF THE DEPARTMENT PROF. VLADIMIR A. LIKHOLOBOV

Laboratory of Catalysis by Complex Metal Compounds
Head: Prof. Vladimir A. Likholobov

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

Laboratory of Catalytic Polymerization
Head: Prof. Vladimir A. Zakharov

Laboratory of Sulfide Catalysts
Head: Prof. Anatolii N. Startsev

Group of Catalysts and Processes Based on Heteropoly Acids
Head: Prof. Klavdii I. Matveev

Group of Catalysts on Carbon Supports
Head: Prof. Vladimir A. Semikolenov

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

Members of the **Laboratory of Catalysis by Complex Metal Compounds** (headed by Prof. Vladimir A. Likholobov) were active in research under two main subjects:

Design of heterometallic active sites of supported catalysts for low temperature chemical fixation of molecular nitrogen

Bimetallic 5%Fe-M and 9%Ru-M (M=Pt, Rh, Ir, Co) catalysts with different M contents (0.2 to 7.1 wt %) were studied. The catalyst were prepared by successive supporting complexes of H_2PtCl_6, $RhCl_3{\cdot}4H_2O$, $H_3IrCl_6{\cdot}xH_2O$ or $Co_2(CO)_2$ and anion carbonyl clusters $K_2[Fe_2(CO)_8]$ or $K_2[Ru_4(CO)_{13}$ on MgO followed by decomposition of the supported component in flowing hydrogen at high temperature. Potassium metal as promoter was introduced into the prepared catalysts to be tested at the Institute of Organoelement Chemistry (Moscow) using a flow reactor at 150-400 °C, atmospheric pressure of $1N_2+3H_2$ mixture and flow rate 10 *l*/h. Platinum and, in particular, rhodium and iridium additives to iron were established to accelerate considerably the process of ammonia synthesis over a wide temperature range (200-400 °C), the synergistic effect being the most apparent at the low temperature range (200-250 °C). Addition of cobalt to iron also results in an increase in the ammonia synthesis rate, although the synergistic effect becomes observed at above 300 °C. The rate of formation of ammonia was studied as a function of M content at a constant content of potassium metal in catalysts (Fe-M)+K/MgO. The catalytic activity to ammonia synthesis at 250-350 °C was found to increase continuously as the content of M increases from 0 to 5-7 wt %. Addition of the second metal M to ruthenium results in either no change in the catalyst activity or has an inhibiting effect. The data obtained demonstrate that iron rather than ruthenium is disposed to form synergistic pairs for synthesis of ammonia.

Studies of complex formation of ions Fe(III) and Co(II) with arsenic(III)-tungsten(VI) heteropoly anions as systems prospective for mild hydroxylation of aromatic compounds

Interaction of unsaturated heteropoly anions (HPA) $[AsW_9O_{33}]^{9-}$ (AsW_9), $[As_2W_{19}O_{67}(H_2O)]^{14-}$ (As_2W_{19}) and $[As_2W_{20}O_{68}(H_2O)]^{10-}$ (As_2W_{20}) with Fe^{3+} and Co^{2+} ions was studied in order to synthesize new polyoxometallates comprising clusters of transition metal ions. Spectrophotometric studies showed that the As(III)-heteropolytungstates are capable of stabilizing an overstoichiometric number of Fe^{3+} ions (counting per one HPA) in the solutions at $pH \geq 6$. As_2W_{19} (pH 6) adopts up to 12 ions of Fe^{3+}, whereas the number of adopted Co^{2+} ions equals no more than the number of 'vacancies' in the lattices of As_2W_{19} and As_2W_{20} (pH 2), *i.e.* 2 and 1, respectively. AsW_9 (pH 7.5), upon formation of M-containing complex $[As_2W_{18}M_3O_{66}]^{12-}$, can stabilize additionally up to 3 Fe^{3+} or Co^{2+} ions. Complexes of HPA with Fe^{3+} and Co^{2+} ions were isolated from the solutions as solid salts with Cs^+ cations. The salt compositions were determined by differential dissolution to correspond to complexes in the solution. IR spectra of the Cs^+ salts showed that all the prepared complexes fall into the same structural type of heteropoly anion As_2W_{21}, in which the metal ions substitute for one, two or three WO groups. The overstoichiometric Fe^{3+} ions are constituents of the Fe(III)-containing HPA; they are oligomer hydroxyl species tailored to heteropoly anions $[As_2W_{18}Fe_3(H_2O)_xO_{66}]^{9-}$ and $[As_2W_{19}Fe_2(H_2O)_xO_{67}]^{8-}$.

Researches by the **Group of Aerogel Materials** (headed by Dr. Aleksandr F. Danilyuk) have been concerned with the preparation and characterization of the silica aerogels.

Monolithic blocks of transparent silica aerogels are used as radiators of Cherenkov counters for charged particles identification. The effects of processing parameters on optical and structural properties of aerogels have been studied by *in situ* measurements of light scattering intensity and small angle X-ray scattering technique. For the first time the dependence of light scattering intensity on gelation time is shown to have a nonlinear character with a minimum. A qualitative description of the creation and evolution of the gel network during an aging is developed that takes into account a rigidity of the formed gel and its susceptibility to deformations.

The kinetics of the supramolecular crystallization of concentrated suspensions of monodispersed spherical silica particles was studied. It is three-dimensional and follows the Avrami-Erofeev equation: $A=1 -\exp[-(kt)^m]$, where $m=4$. The rate constant k is proportional to the probability of the appearance of a crystallization center in unit volume in unit time and the linear crystal growth rate, which is determined experimentally.

The **Laboratory of Catalytic Polymerization** (headed by Prof. Vladimir A. Zakharov) was active under the following main subject areas:

Determination of the number of active sites and the rate constant of growth of the active sites of different stereoregulating ability at polymerization of propylene over titanium-magnesium catalysts of various compositions

Radiochemical method was first used for obtaining experimental data on the number and ratio of active sites of different stereospecificity and on the reactivity (constant of growth rate, K_e) of these sites. The following series of K_e was observed: atactic sites < stereoblock sites < isotactic sites. Constant K_e of the sites with equal stereospecificity was found to be practically independent of the catalyst composition (the presence of the support and a stereoregulating agent). Introduction of a stereoregulating agent does not influence a total of the active sites but causes a sharp increase in the proportion of stereoactive sites.

Study of supported metallocene catalysts in ethylene polymerization and co-polymerization

The influence of the composition of the supports of different nature (SiO_2/MAO[I] and $MgCl_2$[II]), containing Lewis acidic cites of various types and concentration, and composition of the supported zirconocene (Cp_2ZrCl_2, $Me_2Si(Ind)_2ZrCl_2$) on the activity to polymerization of ethylene and co-polymerization of ethylene with hexane-1 was studied. It has been revealed that the nature of active cites of support (I) strongly differs from that of the support (II). For the support (I) the reaction ability of active cites and molecular structure of obtained polymers are similar to corresponding homogeneous system. An effect of method of preparation and composition of support (I) on catalytic activity and morphology of polymers formed has been revealed.

Generation of active centers in homogeneous catalytic system $CpZrMe_2/Ph_3CB(C_6F_5)_4$ in methylene-chloride medium and toluene medium was studied by NMR technique.

The $[Cp_2ZrMe(\mu\text{-}Me)Zr(Me)Cp_2]^+[B(C_6F_5)_4]^-$ complex of low thermal stability (earlier described in literature) is formed upon low temperature (-60 ^oC) in both solvents. Formation of new complex (hypothetically, $[Cp_2ZrMe]^+[B(C_6F_5)_4]^-$), which is, probably, precursor of active centers, was observed at room temperatures when toluene was used as a solvent.

The members of the **Laboratory of Sulfide Catalysts** (headed by Prof. Anatolii N. Startsev) are focussed on the following problems:

Development of the theory of formation and action of the active sites of sulfide catalysts for hydrorefining of oil fractions

New method based on thermodesoprtive measurements of hydrogen content in sulfide catalysts was developed for experimental checking the hypotheses suggested earlier on the determining role of occluded hydrogen in the formation of electron structure of active nickel and cobalt atoms.

Development of method for preparation of (Ni, Mo) sulfide catalysts for hydrotreatment of oil fractions

For continuing the previous research, genesis of catalysts supported on Al_2O_3 was studied; the catalysts were prepared by successive anchoring of molybdenum complexes followed by sorption of nickel or cobalt compounds. Application of EXAFS and FTIR techniques allowed the mechanism based on surface assembly of the direct precursor of the active component to be proved. Conditions of synthesis of surface sulfides from metal complexes were optimized.

New high selective catalysts based on P-Mo-V heteropoly acids for oxidation of alkyl phenols by oxygen into alkyl-1,4-benzoquinones and the corresponding processes were developed by the **Group of Catalysts and Processes Based on Heteropoly Acids** (headed by Prof. Klavdii I. Matveev). The reactions were achieved by mixing the two-phase systems in oxygen atmosphere. The catalyst and reactants were in the immiscible (aqueous and organic) solutions. New methods for controlling the catalyst activity and selectivity were discovered. The control was achieved through variations in the HPA-n composition, also the nature of organic solvents and the reaction conditions.

The selectivity 82-85% was attained for oxidation of 2,6-dimethylphenol and 2,6-ditertbutylphenol into the corresponding dialkyl-1,4-benzoquinones (DAQ), semiproducts of medicines and perfumes, and the selectivity higher than 98% for oxidation of 2,3,6-trimethylphenol into 2,3,5-trimethyl-1,4-benzoquinone (TMQ), a semiproduct of vitamin E. The developed method for synthesis of TMQ will be the basis of a new ecologically friendly technology for production of vitamin E. The developed methods for synthesis of DAQ are promising for production of medicines and perfumes.

Technical data were developed based on the recent investigations for assembling a pilot installation for methylation of 1-naphthol into 2-methyl-1-naphthol, which is a semiproduct of the VICASIB technology for synthesis of vitamins K. Such an installation of the capacity 1 t Vicasol/y will be assembled and started-up in the Pilot Chemical Plant at the Institute to adopt the technology for industry and to launch the production for the Novosibirsk Region.

The **Group of Catalysts on Carbon Supports** (headed by Prof. Vladimir A. Semikolenov) developed the technologies of catalytic stages of hydrogenation of N-vinylpyrrolidone-s into N-ethylpyrrolidone-2 and of N-ethyl-2-nitromethylenepyrrolidine into N-ethyl-2-aminomethylpyrrolidine, which are the key semiproducts for synthesis of psychotropic medicament Sulpyride. In cooperation with the Chemical-Pharmaceutical Research Institute (Novokuznetsk), the technologies were adopted and a pilot batch of the Sulpyride tablet medication was synthesized. The Pharmacological Committee of the Russian Federation approved the clinical test of the medication.

Kinetic regularities of the multistage process for transformation of α-pinene into linalool, the key product for synthesis of wide latitude of fragrant substances, were studied. The stages of the process are hydrogenation of α-pinene into *cis*-pinane, oxidation of *cis*-pinane into pinane hydroperoxide, hydrogenation of pinane-2-hydroperoxide into pinane-2-ol and thermal isomerization of pinane-2-ol into linalool. The method for synthesis of linalool was achieved at the pilot scale.

DEPARTMENT OF MATHEMATICAL MODELLING OF CATALYTIC PROCESSES

HEAD OF THE DEPARTMENT PROF. VALERII A. KIRILLOV

Laboratory of Catalytic Processes in Dynamic Bed
Head: Prof. Gennadii G. Kuvshinov

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

Laboratory of Catalytic Processes for Desulfurization
Head: Prof. Nikolai N. Kundo

A new method for preparation of a catalyst for synthesis of catalytic filamentous carbon (CFC) from methane was developed by the **Laboratory of Catalytic Processes in Dynamic Bed** (headed by Prof. Gennadii G. Kuvshinov).

Also a method was suggested for deliberate synthesis of metal catalysts, including nickel catalysts for methane decomposition. The catalysts were synthesized by impregnation of the porous metal oxide with the precursor of a textural promoter followed by reduction. The required texture of NiO was provided by pre-calcination of the oxide at a certain temperature ranging between 300 and 900°C. A number of nickel-based catalysts with different concentrations of the active component, size of metal particles and stability to deactivation in the course of formation of CFC were prepared. The carbon yield and the strength of carbon granules formed on the catalyst during methane decomposition were shown to increase with the nickel concentration in the catalyst to reach the maximum at the range of 90-96% of nickel. The highest yield of carbon (375-384 g of carbon per gram of nickel) was established to occur when the initial active particles were 10 to 40 nm in average diameter. The studies of efficiency of catalysts comprising different textural promoters (SiO_2, Al_2O_3, MgO and ZrO_2) revealed that the highest carbon yield was attained with ones comprising SiO_2 as the textural promoter.

The concepts of achieving strongly exothermic reactions in gas-liquid-solid systems using multifunctional reactors were developed by the **Laboratory of Multiphase Processes Modeling** (headed by Prof. Valerii A. Kirillov). The reactors combine functions of different technological apparatuses, such as heat exchanger, separator, circulation pump and catalytic contactor. The reactors operate in the gas lift mode to achieve the contact of the gas-liquid mixture with a regular catalytic packing, which is constructed like monolith units with such channel size as to provide the low pressure drop of the two-phase flow and the intensive interphase transfer. The suggested design of the gas lift reactor with regular catalytic packing allows high consumption of the catalyst and reaction volume. The highly intensive heat sink from the reaction zone at high rates of mass transfer makes reactor of this type practicable for strongly exothermic processes, which require high uniformity of the temperature filed. The low pressure drop is also among the advantages. These reactors possess all the advantages of slurry reactors but not their principal drawback, *i.e.* the problem of the catalyst separation from the reaction products.

The research work of the **Laboratory of Catalytic Processes for Desulfurization** (headed by Prof. Nikolai N. Kundo) was aimed at the following subjects:

- Low temperature processes of oxidation of hydrogen sulfide were studied in solutions and in the gas phase. Analysis of the data obtained revealed the formation of polysulfides as intermediate products; the further transformation of the intermediates determined the rate and selectivity of hydrogen sulfide oxidation. A model was suggested to explain unsteady state phenomena observed during catalytic oxidation of H_2S, *viz.* critical phenomena, oscillation processes. The catalyst requirements were formulated for the process of low temperature oxidation of hydrogen sulfide.
- Theoretical assessment of practicability of the catalysts in gas-turbine processes demonstrated potentialities of improving efficiency of power installations and decreasing concentrations of toxic compounds in waste gases.

DEPARTMENT OF NONTRADITIONAL CATALYTIC TECHNOLOGIES

HEAD OF THE DEPARTMENT ACAD. VALENTIN N. PARMON

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

Laboratory of Energy Transforming Materials
Head: Dr. Yurii I. Aristov

Group of Energy-Chemical Technology
Head: Prof. Vladimir I. Anikeev

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

Group of Stereoselective Catalysis
Head: Dr. Oxana A. Kholdeeva

Group of Biocatalysis
Head: Dr. Galina A. Kovalenko

Group of Catalytic Synthesis of Biologically Active Compounds
Head: Prof. Aleksandr G. Tolstikov

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

Group of Photocatalysis on Semiconductors
Head: Prof. Eugenii N. Savinov

Membrane Research Group
Head: Prof. Oleg M. Il'initch

The **Laboratory of Catalytic Methods of Solar Energy Conversion** (headed by Acad. Valentin N. Parmon) continues to study the properties of the first working analog of prosthetic group of nonheme enzymes of the methane monooxygenase type: the colloid and supported Fe and Cu hydroxides appeared to catalyze the oxidation of light alkanes, including methane, in aqueous solutions with hydrogen peroxide.

Collaborators of this laboratory continue to success this year in studying the phenomena of mass transport of liquid fluids inside the pore catalyst granules during their drying as well as in bulk beds of catalysts by NMR-tomography technique.

New results were obtained in the field of studying the photoinduced sorption phenomena on the surface of solid aerosols of the Earth's atmosphere.

A set of complimentary physicochemical techniques (TG, DSC, NMR, IRS, DMTA, DES) were used in the **Laboratory of Energy Transforming Materials** (headed by Dr. Yurii I. Aristov) for studying common features of water sorption in 'hygroscopic salt dispersed in a porous host matrix' composites at variations in the natures of both salt and matrix over wide ranges. General conclusions on regularities of the sorption and state of water in these systems were made.

The reasons for non-physical values of surface dimensions of different kinds of silica were investigated. A simple model was suggested to involve the presence of steric hindrances upon formation of a monolayer of organic molecules (aliphatic alcohols and carbonylic acids).

Regularities of aerogels dissolution, synthesized according to one- and two-stage procedures, in NaOH aqueous solution were studied in cooperation with the Group of Aerogel Materials headed by Dr. A.F. Danilyuk. The threshold desintegration of the secondary structure of the aerogel was shown to occur as soon as the critical dissolution level was reached. For description of the S-like kinetic curves of the dissolution, a modification of the Delmon model was suggested to take into account the final size of the primary dissolution center.

Pilot-scale production of composite sorbents SWS-1L and IC-011-1 was adopted in cooperation with the Omsk Division of the Boreskov Institute of Catalysis; the sorbents in amount of 2.6 ton were manufactured and supplied to customers. Technical data for the sorbent manufacturing were prepared in cooperation with the Laboratory of Coordination and Expertise.

Thermodynamic methods to modeling the multiphase chemical processes and reactors operating under supercritical and phase transition conditions were developed in the **Group of Energy Chemical Technology** (headed by Prof. Vladimir I. Anikeev). The main results obtained during 1999 year:

- Mathematical modeling of the diffusion processes on a single catalyst granule for the acetic acid oxidation in supercritical water was carried out.
- Kinetic and mechanism of 2-propanol hydration reaction in supercritical water were studied. It was first found that the reaction rate and equilibrium constant of this reversible reaction depends remarkably on the fluid density.
- Experimental kinetic data on the Fischer-Tropsch reaction in the presence of a commercial iron oxide-based catalyst were used for developing the kinetic model involving the influence of

the non-ideal reaction mixture on the reaction rate. Equations were derived to describe two Schultz-Flory distribution functions (for saturated and unsaturated hydrocarbons) depending on the fugacities of CO and H_2 in the reaction mixtures. The suggested model describes the reaction kinetics at 523-623 K and P=6-100 atm. A method to choose the nature and optimal concentration of the supercritical solvent was suggested based on calculation critical parameters of the mixture. Considerable increase of the reaction rate under supercritical conditions and total yield of C_2 olefins, including the target C_5-C_{11} fraction, were demonstrated.

A numerical code was developed by the **Group of Aerosol Catalysis** (headed by Dr. Valerii N. Snytnikov) for solution of the set with the Liuville-Vlasov non-stationary equation and the Poisson three-dimensional equation to simulate dynamics of coarse particles. The code was used for studying regimes of catalyst granules motion in a self-consistent gravitational field. The dispersion range of the starting function of particle velocity distribution was determined, in which the particles assemble in large stable agglomerates. The results obtained are of interest to scientists who deal with development of chemical technologies of aerosol catalysis and investigation of the natural chemical reactor of organic compounds synthesis at the protoplanetary disk.

The studies by the **Group of Stereoselective Catalysis** (headed by Dr. Oxana A. Kholdeeva) were focused on catalytic properties of mesoporous mesophase silica materials containing titanium ions (IV) (Ti-MMM) in alkene epoxidation and thioether sulfoxidation with hydrogen peroxide. The structural ordering of the heterogeneous matrix and the high level of titanium dispersing therein were established to be the key factors determining the catalytic activity of Ti-MMM in cyclohexene oxidation, the structural perfection of the catalyst being less important for effective oxidation of sulfides. Oxidation of the model substrate, benzyl phenyl sulfide, with hydrogen peroxide in the presence of Ti-MMM and Ti-substituted heteropolyanions was found to result in the formation of the same product set that argued the common mechanism for both reactions. The data obtained support the non-chain radical mechanism of the sulfide oxidation involving the formation of the cation-radical $RRS^{+\bullet}$. The formal kinetics of thioether oxidation with H_2O_2 was studied in the presence of the model catalyst, $TBA_7H_3P_2W_{22}Ti_2O_{79}$ dimer, in MeCN medium. When concentrated hydrogen peroxide was used, the limiting stage was found to be the formation of an active hydroperoxocomplex. In the case of diluted hydrogen peroxide, the dimer readily dissociated to monomers to give the hydroperoxocomplex, which in turn reacted slowly with the sulfide. Catalytic properties of Mn(III) and Co(II) complexes with (S,S)- and (R,R)-N,N -*bis*(3,5-di-*tert*-butylsalycylidene)-1,2-cyclohexanediamines were studied in thioether oxidation by molecular oxygen in the presence of *iso*-butyraldehyde.

Systematic studies of the **Group of Biocatalysis** (headed by Dr. Galina A. Kovalenko) were focused on adsorption of biologically active substances and non-growing bacterial cells (Bacillus subtilis, Eschericia coli, Rhodococcus sp.) on inorganic supports with textural parameters and surface physico-chemical properties varied over wide ranges. The results obtained allowed some general features of immobilization of the biological objects on the solid surfaces to be elucidated. The comparative studies made it possible to establish that a high adsorptive capacity is characteristic of the adsorbents based on catalytic filamentous carbon (CFC-1 and CFC-2) among the granulated carbon-containing supports (SUMS-type and Sibunit). The following conclusions were allowed by thorough studies of the adsorptive properties of CFC with respect to substances of the biological origin.

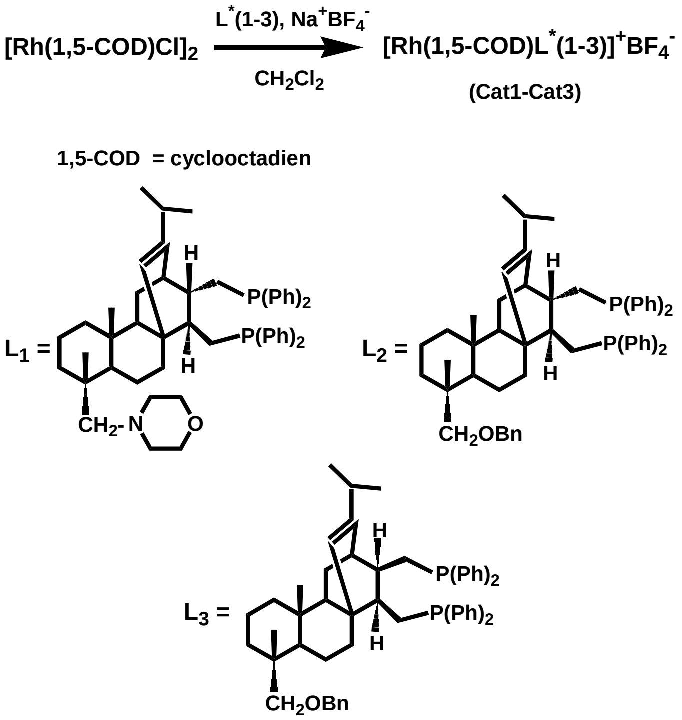
Analysis of experimental data on the adsorptivity of CFC with respect to aminoacids (L-tyrosine), proteins (albumin), enzyme (glucoamylase) and non-growing bacterial cells showed the difference in the adsorptive properties not to depend on the differences in the chemical properties of the CFC-1 and CFC-2 surfaces.

At the same time, the key factor that determines adsorption of aminoacids (L-tyrosine) and protein molecules (albumin, glucoamylase) on the surface of CFC-1 and CFC-2 under study is the area of accessible surface of the support depending on the porous structure, i.e. availability of pores suitable in size provides the effective and strong adsorption as well as the highest level of stabilization of the enzymatic activity.

The key factors affecting adsorption of the bacterial cells are both area and roughness of the accessible surface of the supports, determined by three independent methods, including the comparative and fractal methods. The experiments demonstrated that the amount and strength of adsorption of bacteria cells on CFC increased with an increase in the surface roughness, i.e. the thickness of the 'carbon coat'.

Biocatalytic properties of propane-assimilating bacteria of the Rhodococcus sp. strain (the strain was donated from the unique regional alkanotrophic microorganisms collection, Perm, of the Ural Branch of the Russian Academy of Sciences) were studied to show that the microorganisms reveal intracellular monooxygenase activity. Thus, processes of direct selective biooxidation of various organic substrates, including epoxidation of propylene into propylene oxide, can be achieved.

The **Group of Catalytic Synthesis of Biologically Active Compounds** (headed by Prof. Aleksandr G. Tolstikov) first synthesized three bidentate phosphorus-containing chiral ligands L_1-L_3, as well as catalysts Cat1-Cat3 based thereon using derivatives of maleopymaric and fumaropymaric acids. The structure of the new compounds was verified by the data of NMR spectroscopic studies and elemental analysis.



Scheme. *Synthesis of cationic Rh(I)-complexes with new chiral bis-phosphines of decahydro-3,10a-ethenophenanthrene raw.*

The synthesized chiral catalysts were used for hydrogenation of N-acylaminocinnamic acids into corresponding optically active aminoacids, (S)-phenylalanine and (S)-3,4-dihydroxyphenylalanine; the latter was hydrolyzed to produce a scalemic sample of laevodope, which is the known physiologically active chemical.

To follow-up the activity on commercialization of medical glue Sulfacrilate, technical data for the process were developed and submitted to a potential manufacturer.

Regularities of electrochemical oxidation of methane into syngas were thoroughly studied by the **Laboratory of Catalytic Processes in Fuel Cells** (headed by Prof. Vladimir A. Sobyanin) using a number of metal electrode-catalysts (Ni, Pt, Au, Ag) in a reactor with a solid oxygen-conducting electrolyte (SOE):

CH_4, electrode-catalyst |SOE| air electrode.

The electrodes based on systems, which were active to traditional catalytic oxidation of methane into syngas, were also shown to reveal the highest electrochemical activity. Hydrogen and carbon oxides are primary products of the electrochemical oxidation of methane. Conditions were chosen to provide stability of the electrode-catalysts, including carbonization tolerance, and the yield of syngas as high as 65-90%.

XPS, UV ES and LEED techniques were used for continuing studies of the processes of interaction of hydrocarbons and the surfaces of the closest planes Pt(111), (110) and (100). Interaction of methane and ethylene with the Pt(111) plane at 570-1200 °C was studied in detail. It was demonstrated that ethylene, unlike methane, does not produce graphite-like carbon structures. The carbon produced from methane was established to reveal much higher reactivity to oxygen than carbon produced from ethylene. Comparison of the results obtained with Pt(111) to the data for Pt(110) and (100) allowed the conclusion that the processes of interaction of CH_4 and C_2H_4 with Pt are structure sensitive.

DEPARTMENT OF CATALYTIC METHODS FOR ENVIRONMENTAL PROTECTION

HEAD OF THE DEPARTMENT PROF. ZINFER R. ISMAGILOV

Laboratory of Catalytic Heat Generators
Head: Prof. Zinfer R. Ismagilov

Group of Monolith Honeycomb Supports and Catalysts
Head: Prof. Rimma A. Shkrabina

Group of Direct Catalytic Hydrogen Sulfide Oxidation
Head: Dr. Mikhail A. Kerzhentsev

Laboratory of Catalytic Conversion of Solid Fuels and Wastes
Head: Prof. Aleksandr D. Simonov

Department of Catalytic Methods for Environmental Protection concentrates on fundamental research, catalyst and process development in a variety of fields of environmental catalysis: catalytic combustion, abatement of atmospheric pollutants from stationary and automotive sources, treatment of hazardous wastes, etc. It is composed of 2 laboratories and 2 groups.

The **Laboratory of Catalytic Heat Generators** (headed by Prof. Zinfer R. Ismagilov) has been engaged in the following research projects.

- IR spectroscopy was used for studying the nature of sulfate complexes formed upon adsorption of hydrogen sulfide on the surface of oxide catalysts. The mechanism of direct partial oxidation of hydrogen sulfide over oxide catalysts was suggested which involves formation of sulfate-sulfite complexes at the initial stage, which then react with hydrogen sulfide from the gas phase or with physically adsorbed hydrogen sulfide to produce elementary sulfur and water.
- The phase composition and activity of Mn-Al-O catalysts were studied in a model reaction of methane oxidation. The catalysts were prepared using γ-alumina; they also comprised a phase of χ-Al_2O_3 and were modified by adding Mg, La and Ce oxides. The presence of χ-Al_2O_3 phase in the initial support was shown to promote a deeper interaction of alumina with the introduced manganese ions and modifiers. It provides a higher thermostability and activity of the catalysts

under study compared to the commercial Mn-Al-O catalyst ICT-12-40. For this reason, these catalysts can be recommended for high temperature (up to 1300 °C) oxidation processes.

- The said compositions deposited as washcoats onto supports of complex geometrical shapes (honeycomb material or monoliths) were also found to reveal high thermostability and activity to oxidation of methane.
- Adhesive properties of Ni-containing catalysts supported on washcoated high-porous foam materials (HPFM) were studied in the reaction of steam reforming under hydrothermal conditions. The Ni catalysts supported on CeO_2-containing washcoating layer were shown to be as active as the commercial GIAP-18 catalysts, whereas the concentration of the active component was 1%, which is one tenth of that of the commercial sample.
- Pt, Pd-containing catalysts, perovskites, hexaaluminates on metal foam materials were developed. Plasma spraying technique was used to deposit on the metal surface a gradient layer with subsequent deposition of active components on it. Catalysts developed were successfully tested in catalytic heat exchangers for combined methane combustion and methane steam reforming.
- Based on the results obtained by a systematic investigation of the regularities of the formation of the phase composition and porous structure of different types of alumina treated in a plasma jet outflow the technique of the preparation of spherical γ-alumina encapsulated in α-alumina is worked out. Encapsulated spherical γ-alumina can be used for the preparation of different types of catalysts with improved characteristics.

The research interests of the **Group of Monolith Honeycomb Supports and Catalysts** (headed by Prof. Rimma A. Shkrabina) focus on the synthesis and characterization of poison-resistant and stable monolith copper-exchanged zeolite catalysts for selective reduction of nitrogen oxides with hydrocarbons.

Preparation conditions, optimization of the composition and properties of copper-exchanged zeolite catalysts were studied using bulky copper-exchanged zeolites. The data obtained for bulk catalysts were used to optimize preparation conditions and composition of washcoated catalysts containing copper-exchanged zeolite in the washcoat. The washcoat comprising $Ce\{Cu[80\%H\text{-}ZSM\text{-}5+10\%TiO_2+10\%\ \alpha\text{-}Al_2O_3]\}$ was shown to provide a stable activity of the catalyst and the resistance to poisons (steam and sulfur-containing compounds).

Synergistic effect was observed for copper-containing zeolite catalysts comprised of titanium and cerium oxides, *i.e.* the catalyst activity was stable in the presence of both steam and sulfur-containing compounds in the reaction medium. The catalysts modified by titanium and cerium oxides are also stable under conditions of multicycle testing in the poisoning-regeneration mode.

In the recent years much attention is paid to the problem of decontamination of wastes containing components of rocket propellants. The **Group of Direct Catalytic Hydrogen Sulfide Oxidation** (headed by Mikhail A. Kerzhentsev) has been involved in the investigation of oxidation of the vapor of 1,1-dimethylhydrazine (UDMH) - the principal constituent of the liquid propellants, a highly toxic compound - over solid catalysts. Activity and selectivity to N_2 and

NO_x of a series of catalysts in the reaction of UDMH oxidation were studied in an integral flow reactor in a temperature range 200-400 °C.

The product composition and kinetics of UMDH oxidation over catalyst $Cu_xMg_{1-x}Cr_2O_4/\gamma\text{-}Al_2O_3$ developed for the fluidized bed combustion of fuels and wastes were studied using a gradientless vibro fluidized catalyst bed reactor. A substantial increase in the conversion to CO_2 was found to start at 200 °C, and practically full oxidation of UDMH to the complete oxidation products (CO_2, H_2O and N_2) was observed at above 300 °C. In the temperature range between 200 and 300 °C, chromatographic studies showed, along with the complete oxidation products, as many as 14 peaks assigned to various intermediate compounds formed from UDMH. Based on the presence of these compounds among the reaction products, a probable mechanism of UDMH oxidation based on adsorption of UDMH and its oxidation on the catalyst surface to the gaseous reaction products was suggested and supported by IR studies.

Additional studies using gas chromatographic and IR spectroscopic techniques are in progress to prove and define this mechanism.

The **Laboratory of Catalytic Conversion of Solid Fuels and Wastes** (headed by Prof. Aleksandr D. Simonov) has investigated the kinetics of oxidation of graphitized carbon in the fluidized bed of catalyst IC-12-73 at the temperature range of 500-800 °C and oxygen concentration of 0.5-21 vol %. The reaction order with respect to oxygen was shown to vary from 0 to 1 depending on the process conditions (temperature and oxygen concentration), the observed activation energy being varied with the range of 20 to 30 kCal/mol. Reactivities of solid fuels of different metamorphism levels were studied in the oxidation in a fluidized bed of catalyst
IC-12-70 at 700 °C. As the metamorphism increases, the level of solid fuel combustion efficiency was shown to decrease in the following series: sludge lignin > peat > coal > anthracite. A mobile demonstration installation for catalytic combustion of fuels and wastes (liquid and solid) of up to 80 kCal/h capacity was assembled.

DEPARTMENT OF CATALYTIC PROCESS ENGINEERING

HEAD OF THE DEPARTMENT PROF. A.S. NOSKOV

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

Group of Zeolites and Zeolite Based Catalysts
Head: Prof. Gennadii V. Echevskii

Group of Petrochemical Synthesis
Head: Dr. Vyacheslav N. Romannikov

Laboratory of Kinetics of Catalytic Processes
Head: Dr. Sergei I. Reshetnikov

Group of Mathematical Methods for Catalytic and Adsorption Processes Modeling
Head: Dr. Natalia A. Chumakova

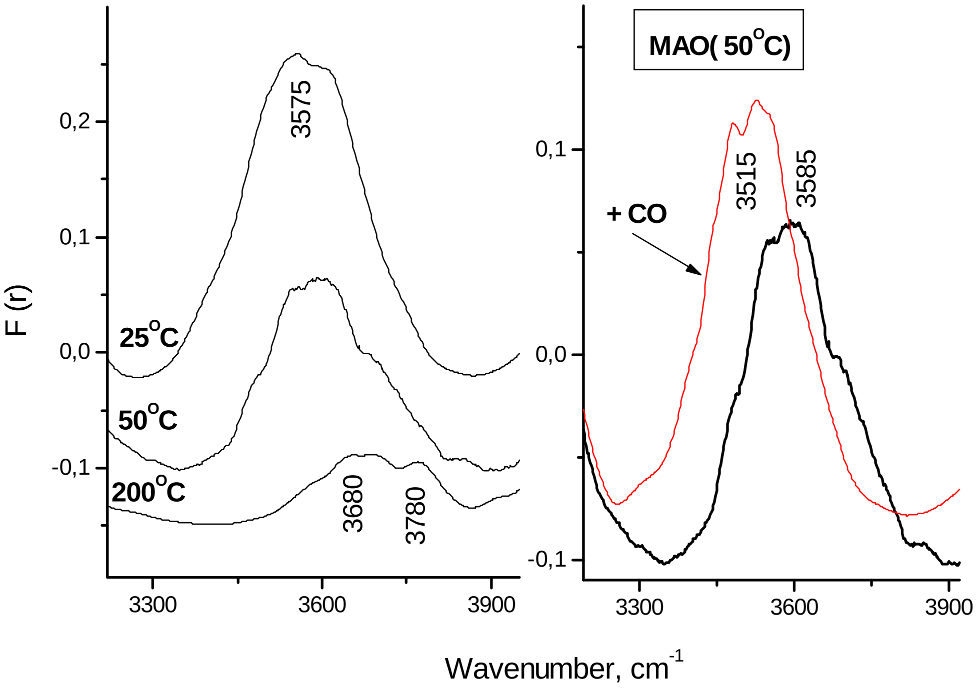
Laboratory of Dynamics of Catalytic Processes
Head: Dr. Andrey N. Zagoruiko

Laboratory of Industrial Catalytic Processes
Head: Il’ya A. Zolotarskii

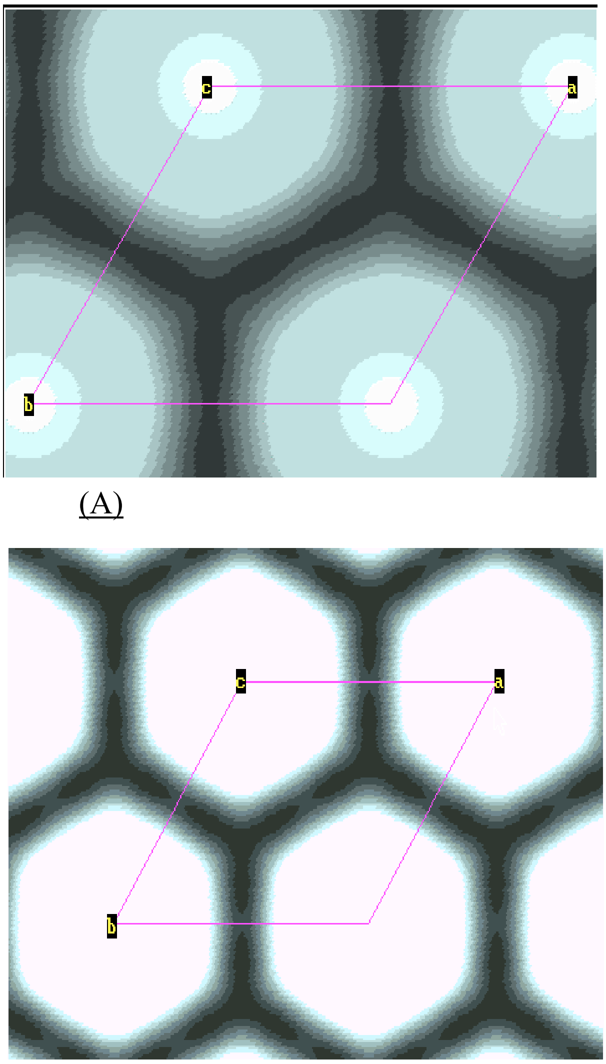
Laboratory of Unsteady-State Catalytic Methods for Gas Purification
Head: Prof. Aleksandr S. Noskov

Spectroscopic studies of the structure of solid polymethylalumoxane (MAO) has been an important interest for the **Laboratory of Zeolites and Acid-Base Catalysis** (headed by Prof. Eugenii A. Paukshtis).

Samples of solid MAO calcined at 20-280 °C were studied using IR DR spectroscopic technique at 800-7000 cm^{-1}. The presence of a water molecule inside the cage-structure of MAO was shown (ν_{OH} 3575-3585 cm^{-1}). According to quantum calculations, insertion of the water molecule inside a MAO globule provided the structure stability. Low temperature adsorption of CO resulted in formation of a weak hydrogen bond with the OH-group of water (a shift of a.b. at ν_{OH} 3585 to 3515 cm^{-1} is observed). It was found that elimination of water upon heating to 150 °C did not result in destruction of the MAO structure, the reaction of protolysis between hydroxyl groups and methyl groups of MAO to evolve CH_4 being observed. Destruction of the MAO structure was observed at above 150 °C, in this case OH-groups with ν_{OH} at 3680 and 3780 cm^{-1} (typical of Al_2O_3) were formed. Overtones of the structural oscillations were analyzed to show that supporting MAO on SiO_2 did not result in the structure destruction. Low temperature adsorption of CO (-50 °C) was used for studying acid properties of MAO and MAO/SiO_2. Presumably, this is the presence of a water molecule in the MAO structure which provides the high Lewis acidity.



Researches in the field of synthesis of mesoporous mesophase materials (MMM) fulfilled by the **Group of Petrochemical Synthesis** (headed by Dr. Vyacheslav N. Romannikov) allowed both the criteria for evaluation of the MMM structure perfection and the conditions of formation of highly-ordered materials with hexagonal arrangement to be revealed. The Rietveld's technique in combination of continuous electron density presentation was used for thorough structural analysis of such materials (for SiO_2-MMM as an example). The obtained electron density maps made it possible to visualize the real structure of the MMM and to formulate assumptions on a number of important features of such a structure, in particular, on the hexagonally shaped mesopores and on the blockwise structure of silicate walls.



(A)

(B)

Fig. *Electron density maps for the as-synthesized (comprising surfactant cations, A) and calcined (comprising SiO_2 only, B) samples of highly-ordered SiO_2-MMM. The structural features allowing the assumption on both hexagonally shaped mesopores and blockwise structure of the silicate walls are clearly seen in the maps (built-up with trefoil fragments separated by "gaps" exhibiting lowered electron density*)

The **Laboratory of Kinetic of Catalytic Processes** (headed by Dr. Sergei I. Reshetnikov) develops theoretical and experimental methods to study catalytic processes taking into account unsteady state of the catalyst. In 1999 it proceeded in studying the kinetic of interaction of the reagents with the V-Ti catalysts in reaction of toluene oxidation. Mathematical model was proposed to show the influence of unsteady state oxidation in reactions of partial oxidation based on the conceptual model, including two types of active centers. The main factor influencing the selectivity of the reaction was shown to be slow by-site processes of mutual transformation.

The **Group of Mathematical Methods for Catalytic and Adsorption Processes Modeling** (headed by Dr. Natalia A. Chumakova) maid a success in the following aspects.

The problem of numerical study of a 1D heat wave propagation model was considered in the case of two consequent exothermic reactions in a catalytic fixed bed as an example. A modern efficient algorithm based on the orthogonal factorization method and Newton's method is developed, some recommendations on the construction of initial approximation are given, and influence of key physical and chemical parameters on the catalytic heat wave properties is studied. New computing program is rather efficient and general, and allows studying different unsteady processes with heat wave propagation phenomena.

New software for numerical simulation of steady state catalytic process in two-stage ammonia oxidation performance in the system “Pt-containing gauzes+non-platinum honeycomb catalyst” was developed. The mathematical model takes into account the local coefficients of heat and mass transfer in both subsystems (jointly with the Laboratory of Industrial Catalytic Processes headed by I.A. Zolotarskii and the Laboratory of Unsteady-State Catalytic Methods for Gas Purification headed by Prof. A.S. Noskov).

The research activities of the **Laboratory of Dynamics of Catalytic Processes** (headed by Dr. Andrey N. Zagoruiko) were concentrated in two main areas:

- An experimental installation for studies of dynamic regimes of oxidation of ammonia and organic compounds was designed and assembled. The installation allows relaxation modes of the reactions to be studied. It was assembled using special materials to prevent adsorption of components of the reaction mixture (mainly water and ammonia) on the surface of tubes and the other units. The installation is in line with a system for chromatographic analysis of the mixture composition with computer processing of detector signals.
- Dynamic modes of complete oxidation reactions over aluminum-magnesium catalyst IC-12-40 (with oxidation of carbon monoxide and butane as examples) were studied. In both cases, accumulation of intermediate oxidation products on the catalyst surface was observed. The accumulation even proceeded at high temperatures (ca. 300 °C), and adsorption products in the form of CO_2 were evolved upon the further heating of the catalyst. Processing of the experimental dynamic kinetic curved was started.

Cooperative work of the **Laboratory of Industrial Catalytic Processes** (headed by Il'ya A. Zolotarskii) with the Laboratory of Catalysts for Deep Oxidation headed by Prof. V.A. Sadykov and the Department of Applied Catalysis Problems allowed to expand the reference list of honeycomb oxide catalyst IC-42-1 used at the second stage of ammonia oxidation in nitric acid plants. In 1999, the number of enterprises exploiting catalyst IC-42-1 increased from 2 to 5. The first installation based on IC-42-1 for production of nitric acid started operating in the USA. The use of the BIC-42-1 catalyst allows 25% saving of platinum for oxidation of ammonia.

In cooperation of the Laboratory of Industrial Catalytic Processes with the Laboratory of Catalysts for Deep Oxidation a process was developed for production of syngas through selective oxidation of natural gas at millisecond contact times. The process is based on unique honeycomb catalysts. The process piloting and scaling-up were carried out. Preparation to assembling the first industrial installation is in progress at the Norilsk Mining and Smelting Complex. The new process as compared to the known processes allows the capitals costs to be 5-10 times decreased and operational costs by 30-50% decreased. Due to the low cost price of the syngas, the process is promising for the use in chemical, metallurgical and electronic industries.

The **Laboratory of Unsteady-State Catalytic Methods for Gas Purification** (headed by Prof. Aleksandr S. Noskov) has been concerned with the following general problems.

- Low-loaded ruthenium catalysts for synthesis of ammonia were developed in cooperation with the Laboratory of Catalytic Methods for Atmosphere Protection headed by Prof. Pavel G. Tsyryul'nikov (Omsk Division of the Boreskov Institute of Catalysis). The catalysts allow the process to be achieved at 10-50 atm and 300-375 °C. The nature of the precursor of the active component was shown to have a defining effect on the catalyst activity. Cesium was discovered to be the optimal promoter. Experimental studies allowed the optimal conditions for synthesis of ammonia over ruthenium catalysts to be chosen: pressure 30 atm, temperature 350 °C, ammonia yield 14.8 vol %. The technology for synthesis of the catalysts was developed at the laboratory scale. The optimal conditions of the catalyst activation (gas phase composition, activation temperature and exposure time at individual stages) were found. The technology was also developed for preparation of the active component precursor (starting ruthenium complex) that makes it possible to give up the expensive imported reactant and to diminish the ruthenium loss during supporting the active component.
- A supported manganese-bismuth oxide catalyst for selective oxidation of ammonia into nitrogen suboxide to provide higher than 90% yield of the target product was developed in cooperation with the Laboratory of Dynamics of Catalytic Processes headed by Dr. A.N. Zagoruiko and the Laboratory of Industrial Catalytic Processes headed by I.A. Zolotarskii. Dynamics of the catalyst activity was studied depending on the composition of the reaction medium. Application of methods of mathematical simulation allowed the technological processes for synthesis of N_2O in a tube reactor and in a fluidized catalyst bed to be developed. The results of the theoretical consideration were fully supported by pilot testing of the processes undertaken in the Boreskov Institute of Catalysis and in Solutia (USA). Optimal process conditions were determined. For the tube reactor, the outlet concentrations of the reactants (NH_3 and O_2) must be not higher than 7-8 vol %, and the process in fluidized catalyst bed can be achieved at the concentrations below 50 vol %. Thus, fundamentals of catalytic synthesis of nitrogen suboxide using the inexpensive and abundant raw material, ammonia, were developed to create the source of raw materials for commercial processes of partial oxidation of hydrocarbons by nitrogen suboxide.

DEPARTMENT OF PHYSICOCHEMICAL METHODS FOR CATALYSTS INVESTIGATION

HEAD OF THE DEPARTMENT PROF. DIMITRII I. KOCHUBEY

Laboratory of Quantum Chemistry
Head: Prof. Georgii M. Zhidomirov

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

Laboratory of Metal Catalysts
Head: Prof. Valerii I. Savchenko

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

Laboratory of Adsorption
Head: Prof. Valerii F. Yudanov

Laboratory of the Texture Studies
Head: Prof. Vladimir B. Fenelonov

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

Laboratory of Analytical Chemistry
Head: Prof. Vladislav V. Malakhov

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

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

Group of Low Temperature Catalysis by Metals
Head: Dr. Vladimir V. Gorodetskii

Group of the Mechanisms of Radical-Catalytic Reactions
Head: Dr. Vladimir A. Rogov

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

The following works have been carried out in the **Laboratory of Quantum Chemistry** (headed by Prof. Georgii M. Zhidomirov) during past year:

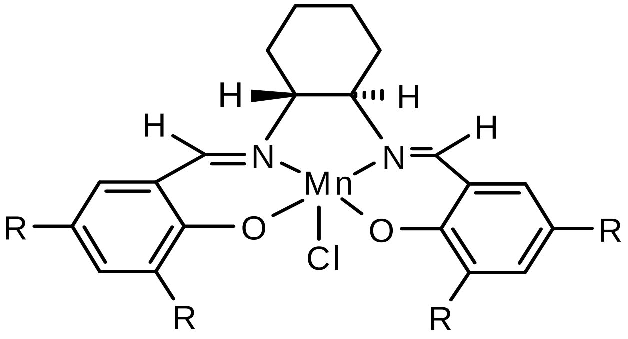
- *In situ* EPR technique was applied to study iron states in FeZSM-5 zeolites. A set of tests has been suggested which allowed to "display" the unobservable iron states in FeZSM-5 zeolites and to study their reaction ability.
- The final formulation of the Hartree-Fock method for calculation molecular structures with open shells has been proposed in general approach, applicable for the molecules of arbitrary (high) symmetry. Invariant expansions for the interelectron interaction integrals and energies of spectroscopic states have been obtained.
- *Ab initio* DFT method was used to analyze electronic structure and reaction ability of polymethylalumoxane $(\text{-Al}(CH_3)O)_n$ - new unique cocatalyst of homogeneous catalytic systems for olefins polymerization. The DFT-computations have shown that the acidity of Lewis sites in the MAO increases with the increase of molecular weight. For $n \leq 6$ the cyclic structure of MAO is the most energy stable. For n=1-6 the "double-cage" structure became more stable than cyclic one, while for $n \geq 9$ - the "triple-cage" structure.
- An approach for calculation of the electron states of stepped crystal faces in the frames of the method of modified equations of strong bonding has been developed.
- In addition to two variants of the formation of binuclear iron-containing structures in zeolites (1 - extraframework oxide-hydroxide structures, and 2 - structures based on the cation position formed by an Fe ion in a framework position), an *ab initio* calculation of a number of neutral and

charged model binuclear structures corresponding to the localization of Fe ions in neighbor cation positions of the zeolite has been performed. A cluster model of such site including a fragment of the zeolite lattice has been constructed.

- The effect of point defects on the silver surface on the stabilization of quasi-molecular oxygen adsorption forms has been studied in the frames of the cluster HF/DFT method. It has been shown that a quasi-ozonide oxygen structure can be stabilized at a vacancy defect.
- A computer program for calculation of electron-exited states in transition metal compounds by the configuration interaction method with single and double excitations has been developed.
- Diffusion restrictions in reactions taking place on model supported catalysts prepared by the electron lithography technique have been analyzed. The possible effect of the transformations of catalytic particles caused by the adsorption of reagents has been studied. Kinetic models describing the storage of oxygen in CeOx in supported Pt-Pd-Rh catalysts used for neutralization of exhaust gases have been developed. The investigation of the effect of lateral interactions between adsorbed particles on the kinetics of elementary processes in an adsorption layer has been continued.

Among pioneering results of the **Laboratory of Investigations of Mechanisms of Catalytic Reactions** (headed by Prof. Eugenii P. Talsi) are registering of the EPR signal of complex Mn^{III}Salen which arises from the forbidden transition $|-2\rangle \rightarrow |+2\rangle$, g=8, T=77 K, and ^{1}H NMR and EPR characterization of manganese complexes formed in catalytic systems **1**+PhIO and **1**+*m*-chloroperbenzoic acid (*m*-CPBA).

Oxo complex of manganese (V) $[(Salen)Mn^{V}{=}O]^+$ and acylperoxo complex (Salen)Mn^{III}(OOCOAr) were shown to be the active species of catalytic systems **1**+PhIO and **1** + *m*-CPBA, respectively.



1 R = t-Bu

It was shown also that parameters of quadrupole interaction tensors and of chemical shift, simultaneously determined from static and MAS spectra of central transition of quadrupole nuclei with semi-integer spins, combined with SATRAS and MQ-MAS data were used for withdrawing the most complete (for the present moment) set of parameters from ^{51}V NMR spectra of VO_x/TiO_2 catalysts. The interaction with the support was discovered to produce strongly coordinated VO_x characterized by a high magnitude of the quadrupole constant (10-16 MHz). These data are in a good agreement with the results of computer simulation of the V_2O_5/TiO_2 surface.

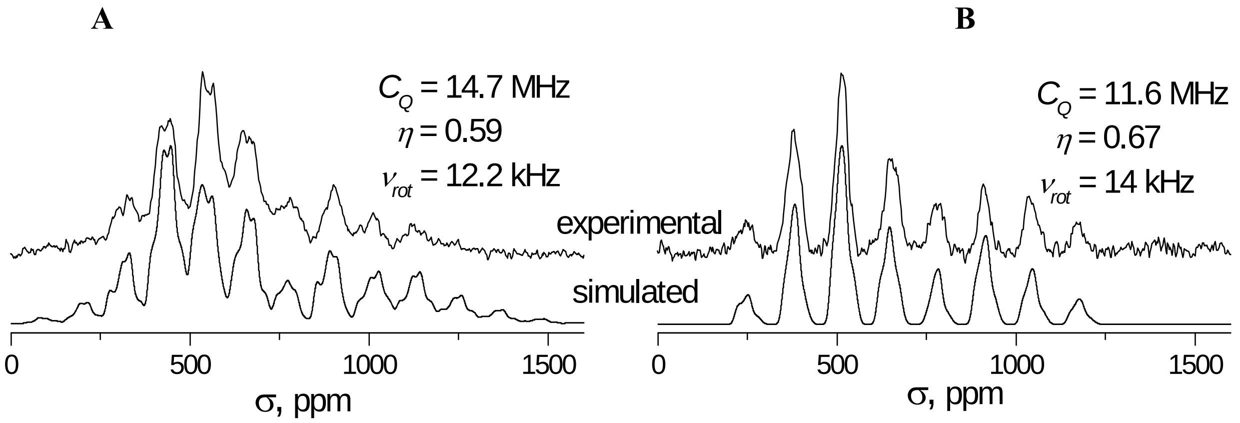


Fig. *105.2 MHz ^{51}V NMR spectra of strongly coordinated VO_x sites formed in vanadium-containing catalysts*

^{35}Cl, ^{133}Cs NMR and magnetic susceptibility studies of the state and process of hydrolysis of aqueous $K_2[RuCl_5H_2O]$ solutions were carried out.

The Monte-Carlo method was successfully used by the **Laboratory of Metal Catalysts** for reactions of CO oxidation over Pt(100) with the model involving the (1×1) – (hex) phase transition to study the effect of the surface O_{ads} and CO_{ads} diffusion on the velocity of the O_{ads} and CO_{ads} wave movement and on the species allocation in the reaction zone. The width of the reaction zone was determined which agreed with the pertinent experimental data. The velocity of the reaction front expansion and the nature of the species allocation within the reaction zone were compared for the three-stage scheme and the scheme based on the (1×1)–(hex) phase transition. The calculations allowed the conclusion on the morphology of the adsorbed layer in the course of the reaction to be made.

ODE (ordinary differential equations) method was used to treat the influence of the intermediate species migration between different surface fragments on the catalytic activity distribution function of linearly inhomogeneous surface fragments. The diffusion was shown to result in a considerable variation in the reaction rate.

A number of low-temperature catalysts for CO oxidation were studied using physical simulation. Conditions of the low-temperature activity were reliably established for the Pd/Fe_2O_3 system. The reaction mechanism, which involves adsorption of oxygen on reduced sites of iron oxide, adsorption of carbon monoxide on palladium and reaction CO_{ads}+O_{ads} of the region of the interphase metal-oxide boundary, probably due to diffusion of adparticles through the boundary into another phase, was suggested.

The mechanism of nucleation and growth of p(2x2) and c(2x2) adsorption structures upon chemisorption of oxygen on the surface of (100) metals was established. Relationship between structural transformations in the adsorption layer and the adsorption rate and heat was discovered.

The following works have been carried out by the **Laboratory of Structural Methods** (headed by Prof. Sergey V. Tsybulya) during the past year:

A new program for simulation of X-ray diffraction patterns of polycrystalline materials with different kinds of imperfections has been developed. These calculation are performed on the base of the model of one-dimensional (1D) disordered crystal being the statistical sequence of biperiodic layers. The sequence of layers is specified with the use of order-disorder parameters and some probability coefficients. Such defects as small sizes of coherently scattering domains, microstrains and stacking faults are taken into account. Simulated diffraction pattern is compared and fitted for best correspondence with the experimental one.

Defect structure of γ-Al_2O_3 prepared by thermal decomposition of well-crystallized boehmite (γ-AlOOH) has been studied by HREM. It was found that the intrinsic feature of γ–alumina structure is a presence of almost hexagonal closed loops formed due to the ordering of cation vacancies over octahedral on (110) and (111) planes. These defects are relatively stable; they are preserved, though being changed in shape, in the γ–alumina sample upon its further calcination until the appearance of traces of δ–alumina phase.

Tilt induced changes in HRTEM images obtained near [110] zone of cubic centrosymmetric Si and noncentrosymmetric SiC were studied by the use of multislice image simulations. The contrast of Si images was shown to change symmetrically with tilt with low brightness variations while SiC demonstrates strong anisotropy along [001] direction and strong variations of contrast. It was shown that the contrast of 6H-SiC could be treated to some extent as a sequence of independent twinned cubic modules. Limits of this representation were studied and the role of forbidden reflections in the image formation was clarified. A method was demonstrated to determine the polarity of the SiC crystal utilizing the anisotropic tilt dependence of contrast.

An improved method was suggested for determination of pore size in mesoporous mesophase materials (MMM) of the MCM-41 family in the **Laboratory for Catalyst Texture Testing** (headed by Prof. Vladimir B. Fenelonov). The method is based on the hexagonal mesopore model and the use of integrated adsorption and XRD data. Computations based on this method produce the results agreeing with independent measurements and calculations using full-profile diffraction X-ray analysis.

Next methods were applied by the **Laboratory of Analytic Chemistry** (headed by Prof. Vladislav V. Malakhov) to study composition of catalysts and reaction products:

Methods of detection and identification

The standard-free stoichiographic method of differential dissolution was used for qualitative and quantitative phase analysis of various catalysts and products formed at different stages of the catalyst preparation and the use, *viz.* co-precipitation, mechanochemical activation, drying, thermal treatment, redox transformations, modification of the basic catalyst composition, *etc.* Among the systems under study were V-Ti-O, Cu-Cr-O, Cu-Al-O, Zr-S-Si-O, Cu-Zn-Al-O, Fe-Al-Si-O, La-Al-Si-O, V-Mo-Al-Fe-O, *etc.*

The differential dissolution method, in its preparative version, was first used for precision correction of phase composition of heterogeneous catalysts to study the nature of their catalytic action (system V-Ti-O for selective oxidation), as well as to determine composition of catalysts using XRD, NMR techniques and of single crystals HTSC (system LaSrCuO) using electron microscopic technique.

Gas chromatography

Conditions were studied and optimized for gas chromatographic separation of small amounts (below 200 ppm) of ammonia in mixtures of hydrogen (up to 75 vol. %) and nitrogen (up to 25 vol. %), the products of catalytic synthesis of ammonia, as well as separation of microimpurities of *n*-propane and *n*-butane in water using modified porous polymer sorbents.

A device for capillary chromatographic detection of organic microimpurities sorbed on solid catalysts was designed and fabricated. The thermodesorption-cryofocusing principle was used. The device was equipped into a chromatomass spectrometer VG 70-70. A high efficiency of the device was demonstrated for detecting microquantities of chemical compounds of different kinds sorbed on the surface of zeolite catalysts.

The technology was accomplished for preparation of capillary columns with fixed siloxane liquid phases, thermostable (up to 420 °C) silarylene polymers, as well as adsorption columns with alumina. The technology makes is possible to prepare an optimal set of columns to provide analysis of mixtures of organic compounds comprising 1 to 60 carbon atoms.

The **Laboratory for Catalyst Activity Testing** (headed by Dr. Nikolai N. Bobrov) is concerned with the development of modern physico-chemical methods of investigation:

- A method and the device for obtaining single-parameter dependence of catalytic activity on catalyst parameters and process conditions in flow circulation reactors in order to improve the productivity and comprehension of the catalyst activity testing and to diminish the test cost.
- An improved procedure for oxidation of methane into formaldehyde by oxygen in a flow circulation reactor with hardening allowed the process selectivity to formaldehyde to reach 100% at 650 °C (for the case of vanadium catalysts). The procedure is the basis of a new method for selection of more effective catalysts for this process.
- Methods and devices for heat desorption dynamic measuring of the quantity of nitrogen adsorbed at 77 K which allowed determination of specific BET and STSA surface areas and, concurrently, adsorption and desorption branches of the nitrogen adsorption isotherms. Thus, the range of application of dynamic adsorption methods can be expanded, and the cost of adsorption measurements can be diminished due to the substitution of dynamic devices for the expensive static ones.

The statistical lattice model of a supported catalytic particle was developed in the **Center for Catalyst Characterization and Testing** (headed by Bair S. Bal'zhinimaev). The model takes into account variations in the shape and the surface morphology of the particle upon contacting the reaction medium. Different temperature-dependent equilibrium shapes of the supported particle are observed depending on the metal-metal and metal-support bond energies. Qualitative and quantitative differences of kinetics of a catalytic reaction proceeding over such a particle from the case of the infinite smooth surface were shown. If the adsorbate-metal interaction is strong enough, considerable adsorption-induced changes in the surface morphology may occur.

A complex of physical and chemical methods was used to study properties and structure of silica and boron-silica glass fiber supports. It has been found that sever alkali leaching of glasses produces matrix, which is similar to SiO_2 by chemical composition, but essentially differing by properties from conventional silicas. Its structure and properties are mostly adequately described by a pseudo-intercalation model of layered matter including alternating layers of 3-4 silica-oxygen tetrahedrons, separated by narrow (less than 5 Å) cavities containing many OH-groups (~ 5000 meq./g or 2 OH/Si). These hydroxyl groups differ from those typical for the usual globular silicas. Despite the small size of interlayer cavities, intercalation of comparatively large cations into the matrix bulk is possible. Introducing cations Pt, Pd and others into the glass fibers the samples were obtained showing high activity in oxidation of hydrocarbons, selective hydrogenation of olefins, DeNOx processes, etc.

A new analysis method, designed to study the dynamics of isotope label transfer in heterogeneous catalyst reactions takes into account the hydrodynamic peculiarities of process occurrence in various type reactors.

Revealed was qualitative and quantitative relationship between the type of reaction mechanism and particular features of isotope response curves. Isotope transfer parameters were studied regarding the effect of hydrodynamic regime in reactors. Model systems analysis allows one to suggest the most probable scheme of ethylene oxidation and NO reduction by methane by the data of isotope-dynamic experiments.

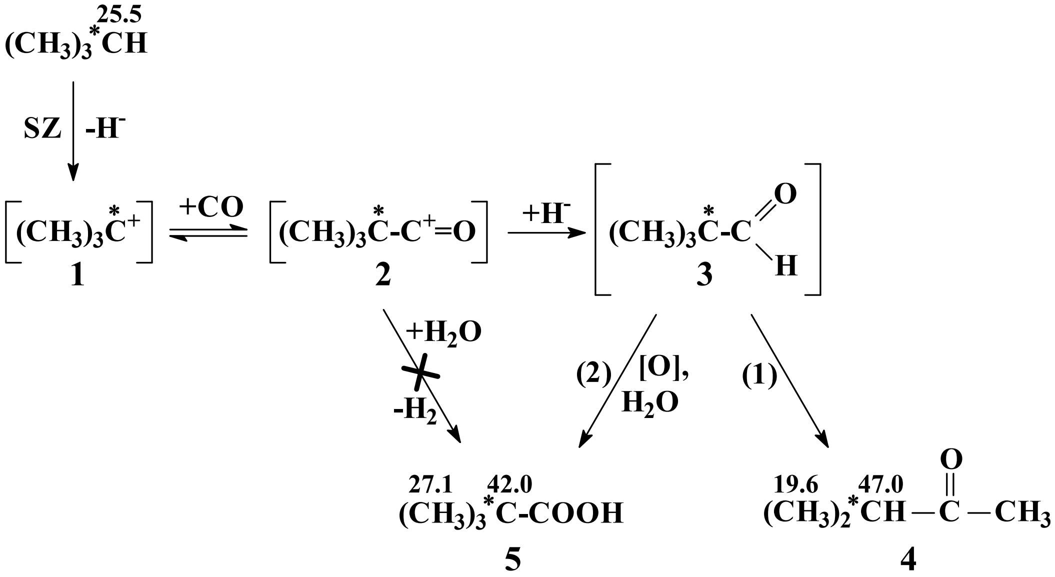
Research of the **Group of Low-Temperature Catalysis by Metals** (headed by Dr. Vladimir V. Gorodetskii) has been centered on the following topics:

- Disappearance potential spectroscopy (DAPS) was first used to study electronic properties of the surface of Pt(100) single crystal and the dynamics of variations in these properties as affected by adsorption of H_2, O_2, CO, NO. The conjugate electron excitation was discovered upon interaction of primary electrons with the metal surface, which allows the chemical composition of the adsorbed layer to be analyzed. The new excitation channel involves concurrent generation of electron vacancy at the frame level of the metal and threshold ionization of valent electrons of the adsorbed layer.
- TPR studies at 270-300 K discovered that a small amount of NO (ca.0.05%) added to hydrogen at the Pt(100)-*hex* plane gave rise to a sharp increase in $\Theta_{H_{ads}}$. Interaction of amino species formed on the Pt(100)-1×1 surface with NO was studied. $NH_{2,ads}$ was shown to react with NO at $T \geq 260$ K: an atomic nitrogen layer N_{ads} is accumulated on the surface. The reaction between $NH_{2,ads}$ and NO was shown to be intermediated by imido-species NH_{ads}. TP-reaction in the mixed layer saturated with NO_{ads} and $NH_{2,ads}$ proceeds like a surface explosion at $T \approx 370$ K and produces nitrogen and water. The amino-species were established to react with hydrogen at the temperature range of 350 to 470 K to form ammonia.
- Mechanisms of oscillations in the reaction of CO oxidation, one with the “phase transition” (Pt) and the “oxide” one (Pd), were compared. Reversible transitions into different stages (low active, *hex*, and high active, 1×1, surface phases) were found for the Pt(100) planes under the oscillation conditions. It was discovered that the low activity (*hex*) was caused by both low

magnitude of S_{O_2} and the island nature of CO adsorption preventing dissociation of O_{2ads} molecules. As to the active phase (1×1) with high S_{O_2}, statistically allocated molecules of CO_{ads} do not hinder dissociation of O_{2ads}. Monte-Carlo simulation of the dynamic processes (oscillations, waves) at the Pt(100) plane revealed that, in accordance with FEM and FIM data, the maximal rate of formation of CO_2 molecules fell at a narrow *reaction zone* at the boundary between layers of O_{ads} and CO_{ads}.

- FEM studies on a Pd-tip demonstrated that the oscillations involve periodical formation and consumption of *subsurface* oxygen, $O_{ads} \rightleftharpoons O_{sub}$, which induces changes in catalytic properties of the metal. There is the anisotropic wave propagation along the direction from (100) to (110) planes. At oscillations, (100) planes are always covered with a CO_{ads} layer, and (110), (210), (310) planes with O_{ads}.

In situ high resolution solid-state ^{13}C NMR and *ex situ* liquid-state ^{13}C NMR techniques, as well as GC-MS analysis were used by the **Group of NMR Spectroscopy for Catalytic Hydrocarbon Conversion** (headed by Dr. Alexander G. Stepanov) to show that isobutane undergoes carbonylation by carbon monoxide over sulfated zirconia. In the absence of water at 70 °C, there occurs the selective formation of methyl-*iso*-propylketone at 30% conversion of isobutane. Trimethylacetic acid is the main reaction product in the presence of water. The observed carbonylation reaction is illustrated by the following Scheme:



Tert-Butyl carbenium ion **1**, which is formed upon elimination of a hydride ion from the alkane, interacts with carbon monoxide to produce oxo-carbenium ion **2**. Cation **2** accepts the hydride ion eliminated before to form pivalic aldehyde **3**. Rearrangement of aldehyde **3** by route (1) produces methyl-*iso*-propyl ketone **4**. In the presence of water, the fast process of oxidation of **3** by sulfated zirconia (route 2) results in formation of acid **5**. The observed reactions demonstrate potentialities of sulfated zirconia as a solid acid catalyst for synthesis of aldehydes, ketones and carboxylic acids from alkanes and carbon monoxide.

OMSK DIVISION OF THE BORESKOV INSTITUTE OF CATALYSIS

EXECUTIVE DIRECTOR VASILII S. ALFEEV

SCIENTIFIC MANAGER PROF. VALERII K. DUPLYAKIN

SCIENTIFIC-RESEARCH SUBDIVISIONS

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Head: Prof. Valerii K. Duplyakin

Group of Carbon Materials
Head: Dr. Georgii V. Plaksin

Laboratory of Catalytic Methods for Atmosphere Protection
Head: Prof. Pavel G. Tsyrul'nikov

Laboratory of Catalytic Processes
Head: Dr. Aleksandr S. Belyi

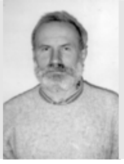
Laboratory of Kinetics and Modeling of Petrochemical Processes
Head: Prof. Nikolai M. Ostrovskii

Group of Zeolite-Containing Catalytst for Petrochemistry and Petroleum Refining
Head: Dr. Vladimir P. Doronin

SUBDIVISION OF PHYSICOCHEMICAL METHODS OF INVESTIGATION

Group of Adsorption
Head: Dr. Vladimir A. Drozdov

Group of X-Ray and Electron Microscopy Technique
Head: Dr. Aleksandr I. Nizovskii



Group of Spectral Methods
Head: Dr. Valentin P. Talsi

Analytical Group
Head: Tatiana V. Kireeva

DEPARTMENT OF EXPERIMENTAL TECHNOLOGY

HEAD: DR. ALEKSANDR I. ORUZHEINIKOV

DEPARTMENT OF APPLIED CATALYSIS

HEAD: KONSTANTIN V. KOLMOGOROV

SCIENTIFIC-RESEARCH SUBDIVISIONS

Members of the **Laboratory of Deep Petroleum Refining** (headed by Prof. Valerii K. Duplyakin), including the **Group of Carbon Materials** (headed by Dr. Georgii V. Plaksin) are active under main subjects:

- Systematic approach to the designing of catalysts of acidic action:

  - Supported oxides and sulfate-oxide composites (catalyst and the process of isobutane alcylation by butylenes)

  - Solid phosphorous acid on carbon supports (catalyst for butylenes oligomerization).

- Catalytic process and catalyst for olefins skeletal isomerization and oligomerization (jointly with the Laboratory of Kinetics and Modeling of Petrochemical Processes headed by Prof. N.M. Ostrovskii and Group of Zeolite-Containing Catalysts for Petrochemistry and Petroleum Refining headed by Dr. V.P. Doronin).

- Development of new materials based on carbon and carbon containing composites including natural raw material.

- Design of the technology for carbon molecular sieves production and processes of gas separation over sieves.

While developing the technology of integrated processing of natural raw materials (sapropels and peat sapropels) of deposits of Omsk Region in cooperation with Vega-2000 Co. (Omsk), a new sorbent Sibsorbent-1 was synthesized for recovering oil and oil products from water surface. The sorbent was successfully tested during All-Russian Exercises for Breakdown Elimination at Oil-Trunk Pipelines (Sibnefteprovod Co.) held in Tyumen in August 1999. At present, comparative studies of the sorbent are in progress in labs of Sibnefteprovod Co.

The research program of the **Laboratory of Catalytic Methods for Atmosphere Protection (**headed by Prof. Pavel G. Tsyrul’nikov) included:

- Development of catalysts for low temperature synthesis of ammonia over carbon support “Sibunit”.

- Study of the nature of the high-temperature dispergation.

- Design of the catalyst “Cu/Sibunit” for methanol dehydrogenation to methylformiat.

The nature of the thermoactivation effect was studied. The effect was discovered earlier as a sharp increase in the catalytic activity to complete oxidation (reburning) of aluminomanganese catalysts pre-calcined at extremely high temperatures (9500-10000 °C).

The thermoactivations effects were discovered to be characteristic of numerous catalytic systems, including those containing platinoids, at different temperature ranges. Based on the data obtained, a new approach to synthesis of catalysts was suggested.

A new catalytic composition 'cesium-ruthenium on Sibunit' was developed in cooperation with the Department of Applied Catalysis Problems of the Boreskov Institute of Catalysis. This is the catalyst of new generation for low-temperature synthesis of ammonia; it operates at 30-50 atm instead of 300 atm. The activity of the synthesized catalyst samples was superior to that of the catalysts known from the patent literature. A pilot batch of the catalyst was supplied to the industrial plant for testing.

The **Laboratory of Catalytic Processes** (headed by Dr. Aleksandr S. Belyi) made a success in development of new generation of catalysts for oil hydrocarbon reforming and design of catalytic process for motor fuels production with the use of natural raw materials.

The technology for synthesis of the catalyst for the basic process of oil processing, reforming, to produce high-octane unleaded gasolines was improved. Commercialization of the catalyst at the oil processing market is in progress. The catalysts of the PR family provide stable manufacturing of gasoline components with octane numbers not lower than 95. It was for the first time in Russian oil processing industry, when the long lifetime of these domestic reforming catalysts was demonstrated. The experts consider them as the superior reforming catalysts that are competitive to the catalysts produced by the world leaders in the field (UOP, Procatalys, etc.).

The research directions of the **Laboratory of Kinetics and Modeling of Petrochemical Processes** (headed by Prof. Nikolai M. Ostrovskii) include:

- The theory and kinetics of catalysts deactivation
- Catalyst pellet design
- Kinetic methods for catalyst testing
- Reaction kinetics over new catalysts
- Chemical reactor modeling and optimization
- Development of computer programs.

The mechanism of deactivation of ionic platinum species by coke was suggested. Coke is formed as a monolayer over ionic platinum, which is in the form of fine clusters on the surface. The coke formation is accompanied by the self-regeneration under the action of hydrogen and by migration of coke precursors to the support. The mechanism also involves formation of multilayered coke on the support; the model of this process was developed before. A general kinetic equation for the catalyst deactivation according to the nonlinear mechanism of the surface binary interaction was derived based on the model.

Variations in the catalyst activity to aromatization of octane over an aluminoplatinum catalyst comprising more than 60% of ionic platinum illustrated the application of the mechanism and model of the deactivation.

The **Group of Zeolite-Containing Catalysts for Petrochemistry and Petroleum Refining** (headed by Dr. Vladimir P. Doronin) is concentrated on the development and improvement of:

- Catalysts for catalytic cracking of petroleum fractions;
- Catalysts for the processes of diesel fuels hydrodeparaffinezation;
- Catalysts and supports based on natural clays and their intercalates.

New compositions of the microspherical catalyst for cracking of vacuum gas oil were developed to improve the yield of gasoline and octane number, as well as to provide recycling of secondary feedstocks (coking gas oils, deasphaltizates, extracts of oil processing, *etc*.). Technology for synthesis of new types of catalysts was developed and commercialized. The efficiency of these catalysts was verified at operation of industrial cracking installations.

Joint work of the Laboratory of Deep Petroleum Refining, the Laboratory of Kinetics and Modeling of Petrochemical Processes, and the Group of Zeolite-Containing Catalysts for Petrochemistry and Petroleum Refining allowed to develop a catalyst for skeleton isomerization of *n*-butylenes and the catalytic process ISOLEN for the follow-up esterification of the isomers by methanol into methyl-*tert*-butyl ester (MTBE), an octane-increasing additive to gasolines. The following results were obtained:

- A unique (unused in the world practice before) catalytic composition was developed which comprises high dispersed niobium oxide supported on alumina.
- The industrial version of the catalyst and the technology for the catalyst manufacturing were developed.
- Catalytic and life tests of the prototype of the industrial catalyst were performed to demonstrate the advantages against the Western analogues.
- Thermodynamic and kinetic studies of the main and side reactions became the basis of the ISOLEN process.
- The technological mode of the reactor unit was optimized and the technical data for the process were developed.

The technology is to be achieved at the large scale in 2000 to increase the annual production of MTBE from 40 to 60 t that means production of extra 300000 t/y of ecologically friendly high-octane automotive gasolines (AI-93, AI-95, AI-98).

SUBDIVISION OF PHYSICOCHEMICAL METHODS OF INVESTIGATION

The **Group of Adsorption** (headed by Dr. Vladimir A. Drozdov) is engaged in systematic studies of physico-chemical principals of texture design for modern catalysts and adsorbents used for the processes of petroleum refining, petrochemistry and environment protection.

Texture and adsorptive properties of composites based on oxide systems and activated clays, modified zeolites and microporous carbon-carbonaceous materials from plant raw are investigated intensively. The regularities of microstructure formation of carbonaceous molecular sieves, obtained from plant raw are studied.

Application and development of numerical methods to obtain quantitative information about structural inhomogeneity of microporous objects of different composition and structure (carbon materials, zeolites, activated and intercalated clays) is among other directions of activities in the Group.

The **Group of Spectral Methods** (headed by Dr. Valentin P. Talsi) is engaged in NMR-spectroscopy of solutions and solid substances (Bruker AC 200P spectrometer) and IR spectroscopy study of catalyst surface.

The **Analytical Group** (headed by Tatiana V. Kireeva) is focused on X-ray fluorescence analysis of solid substances (VRA-30 spectrometer), atomic absorption analysis (AAS-30 spectrophotometer) and traditional chemical and physico-chemical methods.

The Group is well equipped with modern physical devices, which allow one to perform the complete characterization of catalysts and supports, natural and technique water, diesel fuels, some biological objects, etc.

The experimental facilities of the **Group of X-Ray and Electron Microscopy Technique** (headed by Dr. Aleksandr I. Nizovskii) are:

X-ray analysis (diffractometers DRON-3, HZG-4/A);

Electron microscopy (electron microscope BS-350).

ST. PETERSBURG DIVISION
OF THE BORESKOV INSTITUTE OF CATALYSIS

DIRECTOR AND SCIENTIFIC MANAGER
PROF. SERGEY S. IVANCHEV

VICE-DIRECTOR DR. VALERY P. TULMANKOV

SCIENTIFIC-RESEARCH SUBDIVISIONS

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

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

Group of Catalysis for Modification of Polymeric Systems
Head: Dr. Alla M. Mesh

Group of Physico-Chemical Characterization Methods
Head: Dr. Saul Ya. Khaikin

St. Petersburg Division of the Boreskov Institute of Catalysis was founded in the beginning of 1999 in order to intensify R&D activities in the field of commercial processes for the synthesis of complex chemical products, polymers and polymeric composites using catalytic techniques, and to accelerate the commercialization of research results in the European region of Russia.

Research results

- Emulsion polymerization mechanism studies afforded revealing the approaches to the control over latex particle morphology and suggesting a new process for hollow particle latex synthesis.
- Peculiarities of ethylene polymerization and co-polymerization with higher α-olefins are studied using catalytic systems based on a series of metallocenes and metal-siloxanes.
- Kinetic features and mechanism of graft polymerization of some monomers onto polypropylene are studied.

RESEARCH ACTIVITY

Quantum-Chemical Studies

A DFT QUANTUM-CHEMICAL STUDY OF THE STRUCTURES AND ACTIVE SITES OF POLYMETHYLALUMOXANE

I.I. Zakharov, V.A. Zakharov, G.M. Zhidomirov

Macromol. Theory Simul., 8 (1999) pp. 272-278.

The electronic structure and geometry of the polymethylalumoxane (MAO) $[-Al(CH_3)O-]_n$ with different size (n=4-12) have been studied using quantum-chemical DFT calculations. It has been found: 1) Starting from n=6, three-dimensional oxo-bridged (cage) structure of MAO is more stable than the cycle structure. 2) Both for cage structure and for cycle structure the Lewis acidity of Al atoms characterized by their net positive charge amplifies with increasing of MAO size (n value). 3) Trimethylaluminium (TMA) reacts with the cage structure of MAO with cleavage of Al-O dative bond and formation of acidic tri-coordinated Al^v and basic di-coordinated O^v atoms in MAO molecule. Two molecules $AlMe_3$ are associated with acidic Al^v and basic O^v centers. As the MAO increases in size, the acidity of Al^v centers amplifies and distance Al^v- ($AlMe_3$) shortens; on the contrary, interaction of $AlMe_3$ with O^v centers weakens and distance O^v-($AlMe_3$) increases with increasing of n value. The total heat of Al_2Me_6 interaction with MAO (sum interaction of Al^v-($AlMe_3$) and O^v-($AlMe_3$)) noticeably decreases as the size of MAO increases (from 50.9 kcal/mol for n=4 to 20.2 kcal/mol for n=12). It is proposed acidic Al^v and basic O^v centers formed in cage structure of MAO interact with zirconocene yielding «cation-like» zirconium active centers.

A DFT QUANTUM-CHEMICAL STUDY OF THE STRUCTURES AND REACTIVE SITES OF POLYMETHYLALUMOXANE

I.I. Zakharov, V.A. Zakharov, G.M. Zhidomirov

Metalloorganic Catalysts for Synthesis and Polymerization, Ed. by W. Kaminsky, Springer-Verlag, Berlin, 1999, pp. 128-135.

DFT quantum-chemical calculations have been performed to elucidate the geometrical and electronic structure of methylalumoxane $(-Al(Me)O-)_n$ with different size (n=6, 8, 12). The three-dimensional oxo-bridged (cage) structures of methylalumoxane (MAO) have been analyzed. It has been found the cage structure consisting of three layers of $[-Al(CH)_3O-]_4$ units is the most stable for MAO with n=12. Trimethylaluminium (TMA) reacts with MAO with cleavage of Al-O dative bond and formation of acidic tricoordinated Al and basic dicoordinated O atoms in MAO molecule. Two molecules of $AlMe_3$ are associated with these sites. The total heat of TMA interaction with MAO depends on the n value and MAO structure. The reactive sites of MAO are proposed on the base of data obtained.

OXIDATIVE ADDITION OF DIHYDROGEN AS THE KEY STEP OF THE ACTIVE CENTER FORMATION IN THE HDS SULFIDE BIMETALLIC CATALYSTS: *AB INITIO* MO/MP2 STUDY

I.I. Zakharov, A.N. Startsev, G.M. Zhidomirov, V.N. Parmon

J. Molec. Catal. A: Chemical, 137(1-3) (1999) pp. 101-111.

The electronic structure of Ni in the sulfide bimetallic species (SBMS), which is the active component of the sulfide HDS catalysts, is studied with the *ab initio* molecular orbital calculations. Earlier it have been shown that the d^8 Ni(II) electronic state in the SBMS composition can not be active in HDS reaction because of the lack of possibility to coordinate S-containing molecule. Therefore this paper deals with study of possibility to stabilize d^6 electron configuration with the formal Ni(IV) oxidation state. With this in mind the reaction of oxidative addition of dihydrogen to square-planar complex $Ni(II)Cl_2(PH_3)_2$ has been studied, which allowed to predict a stabilization of the octahedral complex $Ni(IV)H_2Cl_2(PH_3)_2$ with d^6 configuration. This allows to assume a possibility of an oxidative adsorption of dihydrogen to the Ni atom entering the SBMS composition. *Ab initio* calculations have shown that such type of oxidative addition is thermodynamically favorable resulting in stabilization of the Ni(IV) d^6 electronic state. Consequently, the dihydrogen molecule is assumed to dissociate on the Ni atom resulting in formation of “surface” H_s and “occluded” H_o hydrogen, which is located under Ni atom in the center of the trigonal sulfur prism. The structure of the active centers is optimized and stretching modes of the hydrogen atoms are calculated, which appear to be close to the literature data. The H_2S adsorption on the active center was also investigated and there was shown that the hydrogen disulfide molecule benefits to stabilization of the active Ni(IV) d^6 state. The conclusion is drawn that the deciding factor in the formation of the active centers of sulfide HDS catalysts is the “occluded” hydrogen.

A LINEAR REPRESENTATION OF THE TIGHT-BINDING WAVE AND GREEN FUNCTIONS OF DEFECT CRYSTALS BY PERFECT CRYSTAL FUNCTIONS

V.M. Tapilin

Phys. Low-Dim. Struct., 5/6 (1999) pp. 189-193.

The coefficients of the tight-binding wave function of a perturbed crystal were represented as a linear combination of contributions of the unperturbed crystal wave and Green functions. The similar representation was used for the tight-binding Green function. The sets of equations determining values of the contributions were developed. These sets of equations are compared with the Lippmann-Schwinger and Dayson equations.

MOLECULAR MODELS OF CATALYTICALLY ACTIVE SITES IN ZEOLITES. QUANTUM CHEMICAL APPROACH

**G.M. Zhidomirov, A.L. Yakovlev, M.A. Milov,
N.A. Kachurovskaya, I.V. Yudanov**

Catal. Today, 51(3-4) (1999) pp. 397-410.

A brief review of quantum chemical studies of different active sites in zeolites is presented. Various factors that significantly affect the strength of Brönsted acid sites in zeolites are discussed. An interaction of zeolite protons with entrapped metal particles is considered as a reason of electron-deficiency of metal clusters in zeolite cavities on the Pd and Pt species as an example. Probable precursors of Lewis acid sites (LAS) and reliable molecular models of the LAS in zeolites are discussed on the basis of quantum chemical analysis. Transition metal ions can be catalytically active in the lattice or extra-lattice zeolite positions and the two possibilities are considered for selective oxidation site in titanium silicalite and FeZSM-5 zeolite catalysts, respectively.

QUANTUM CHEMICAL STUDY OF NITROUS OXIDE ADSORPTION AND DECOMPOSITION ON LEWIS ACID SITES

A.L. Yakovlev, G.M. Zhidomirov

Catal. Lett., 91 (1999) pp. 91-95.

Density Functional calculations demonstrate that ordinary Lewis sites containing three- and five-coordinated Al are unlikely to decompose N_2O, since the formation of a weak Al-O bond does not compensate the N-O bond rupture. Ground state of the cluster-oxygen adsorption complexes is triplet. The hypothetical site $Al(OH)_4AlO$ can be reactive towards the N_2O decomposition with the heat -17.8 kcal/mol and activation barrier 19.7 kcal/mol.

SUPPRESSION OF RADICAL-CATIONIC BENZENE OLIGOMERIZATION ON SULFATED ZIRCONIA

A.F. Bedilo, A.M. Volodin

React. Kinet. & Catal. Lett., 67(1) (1999)
pp. 197-203.

The effect of the catalyst activation conditions on transformations of benzene radical cations on sulfated zirconia has been studied by *in situ* ESR spectroscopy. After the catalyst activation at 300 °C there was no oligomerization of the radical cations to biphenyl and heavier products, which is observed after the catalyst calcination at 500 °C. It has been suggested that the oligomerization is suppressed by the presence of strong Brönsted sites on the surface.

DENSITY- AND DENSITY-MATRIX-BASED COUPLED KOHN-SHAM METHODS FOR DYNAMIC POLARIZABILITIES AND EXCITATION ENERGIES OF MOLECULES

**A. Goerling*, H.H. Heinze*, S.Ph. Ruzankin,
M. Staufer*, N. Rösch*** (*Technical University of Munich, Garching, Germany)

J. Chem. Phys., 110 (1999) pp. 2785-2799.

Basis set methods for calculating dynamic polarizabilities and excitation energies via coupled Kohn-Sham equations within time-dependent density functional theory are introduced. The methods can be employed after solving the ground state Kohn-Sham equations with a fitting function approach. Successful applications of the methods to test molecules are presented. Coupled Kohn-Sham methods based on the linear response of the Kohn-Sham density matrix are derived from the standard coupled Kohn-Sham equation based on the linear response of the electron density and the relations between the two types of coupled Kohn-Sham equations are investigated. The choice of norm functions associated with basis set representations of the coupled Kohn-Sham equations is discussed and shown to be a critical point of basis set approaches to time-dependent density functional theory.

ADSORPTION OF TRANSITION METAL ATOMS ON OXYGEN VACANCIES AND REGULAR SITES OF THE MgO(001) SURFACE

A.V. Matveev, K.M. Neyman*, I.V. Yudanov,
N. Rösch* (*Technical University of Munich, Garching, Germany)

Surf. Sci., 426(1) (1999) pp. 123-139.

Adsorption of Cu, Ni, Ag, and Pd atoms on F_s and F_s^+ oxygen vacancy sites as well as on regular O^{2-} centers of the MgO(001) surface has been studied by means of gradient-corrected density functional using cluster models embedded in a matrix of model potentials and point charges. Scalar relativistic effects have been taken into account for adsorbed Ag and Pd species. The electronic structure, geometric parameters, and binding energies of adsorption complexes have been calculated and analyzed with reference to the electronic properties of the vacancy sites and the metal atoms in question. For all adsorbates considered, adsorption is found to be stronger on F_s sites by 1-2.4 eV compared with regular O^{2-} sites, with Pd and Ni forming the most stable complexes. On the F_s^+ site the single valence electron of Cu and Ag atoms couples with an unpaired electron of the vacancy forming a covalent bond. As a result the adsorption energy of these atoms on F_s^+ is by more than 1 eV stronger than on the F_s sites; on the other hand, the adsorption energies of Ni and Pd are reduced on F_s^+ by 0.5 eV and 1.3 eV respectively. The whole series of M/F_s^+ complexes is characterized by rather uniform values of adsorbate-substrate distances (1.5-1.7Å) and adsorption energies (2.2-2.6 eV).

ACTIVITY OF PEROXO AND HYDROPEROXO COMPLEXES OF Ti(IV) IN OLEFIN EPOXIDATION: A DENSITY FUNCTIONAL MODEL STUDY OF ENERGETICS AND MECHANISM

I.V. Yudanov, P. Gisdakis*, C. Di Valentin*,
N. Rösch*(*Technical University of Munich, Garching, Germany)

Eur. J. Inorg. Chem., 12 (1999) pp. 2135-2145.

Epoxidation of olefins by Ti(IV) peroxo and hydroperoxo (alkylperoxo) complexes was investigated using a hybrid DFT method (B3LYP). Reaction energies and activation barriers for direct oxygen transfer to ethylene as model olefin were computed for various model complexes to compare the epoxidation activity of $Ti(\eta^2\text{-}O_2)$ and TiOOR (R = H, CH_3) moieties. The activity of complexes with a $Ti(O_2)$ peroxo group is shown to be essentially quenched when the coordination sphere of the complex is saturated by strong base (σ-donor) ligands. At variance, the activity of a TiOOH functional group depends only weakly on the saturation of the coordination sphere of the Ti center. Substitution of methyl for hydrogen in a TiOOH group is found to slightly increase the activation barrier of epoxidation. The computational results give preference to reaction paths that involve TiOOR species. The factors governing the activity of $Ti(O_2)$ and TiOOR groups, in particular the effects of donor ligands, are discussed on the basis of a molecular orbital analysis.

DENSITY FUNCTIONAL STUDY OF SO_2 ADSORPTION IN HY ZEOLITES

V.A. Nasluzov* , A.M. Shor* , F. Nörtemann,**
M. Staufer, I.V. Yudanov, N. Rösch**** (*Institute of Chemistry and Chemical Technology, Krasnoyarsk, Russia; **Technical University of Munich, Garching, Germany)

J. Molec. Struct. (Theochem), 466(1-3) (1999) pp. 235-244.

The interaction of SO_2 molecules with active sites of HY zeolite was studied by means of density functional model cluster calculations employing a generalized gradient approximation (GGA) of the exchange-correlation functional. A fragment of the zeolite framework which contains an acid bridging hydroxyl group and an adjacent basic oxygen center was modeled by the cluster $H_3SiO(H)AlOSiH_3$. The equilibrium geometry structures were determined for various donor-acceptor and hydrogen-bonded conformers of SO_2/HY adsorption complexes. These two adsorption interactions are similarly weak with the hydrogen-bonded form being more stable by about 2 kcal/mol. In this most stable conformer, the interaction of the sulfur atom with the adjacent oxygen center leads to additional stabilization. The assignment of the SO_2/HY complexes to hydrogen bonded species is confirmed by a comparison of experimental and calculated adsorption induced shifts of SO_2 and OH vibrational frequencies.

TRIGONAL-BIPYRAMIDAL LEWIS BASE ADDUCTS OF METHYLTRIOXORHENIUM(VII) AND THEIR BISPEROXO CONGENERS: CHARACTERIZATION, APPLICATION IN CATALYTIC EPOXIDATION, AND DENSITY FUNCTIONAL MECHANISTIC STUDY

F.E. Kuhn*, A.M. Santos*, P.W. Roesky, E. Herdtweck*, W. Scherer*, P. Gisdakis*, I.V. Yudanov, C. Di Valentin*, N. Rösch***
(*Technical University of Munich, Garching, Germany; Karlsruhe University, Karlsruhe, Germany)

Chemistry-A European J., 5(12) (1999) pp. 3603-3615.

Methyltrioxorhenium(VII) (MTO) forms trigonal-bipyramidal adducts with pyridines and related Lewis bases. These complexes have been isolated and fully characterized, and two single-crystal X-ray structures are reported. The complexes react with H_2O_2 to form mono- and bisperoxo complexes, which were examined *in situ* by ^{1}H and ^{17}O NMR spectroscopy. A clear increase in electron deficiency at the Re center can be observed from the MTO complexes to the bisperoxo complexes in all cases examined. The activity of the bisperoxo complexes in olefin epoxidation depends on the Lewis bases, the redox stability of the ligands, and the excess of Lewis base used. Density functional calculations show that when the ligand is pyridine or pyrazole there are significantly stabilized intermediates and moderate energies of the transition states in olefin epoxidation. This ultimately causes an acceleration of the epoxidation reactions. In contrast, the catalytic performance is reduced when the ligand was a nonaromatic nitrogen base. The frontier orbital interaction between the olefin HOMO π(C-C) and orbitals with σ^*(O-O) character in the LUMO group of the Re-peroxo moiety controls the olefin epoxidation.

CLUSTER QUANTUM CHEMICAL STUDY OF TRIAMINOTOLUENE INTERACTION WITH A MODEL CLAY SURFACE

N.U. Zhanpeisov[1,2], J.W. Adams[3], S.L. Larson[3], C.A. Weiss[3], B.Zh. Zhanpeisova[1], D. Leszczynska[4], J. Leszczynski[1] ([1]Jackson State University, Jackson, USA; [2]Boreskov Institute of Catalysis, Novosibirsk, Russia; [3]U.S. Army Engineer Waterways Experimental Station, Vicksburg, USA; [4]Florida State University, Tallahassee, USA)

Struct. Chem., 10(4) (1999) pp. 285-294.

The paper presents the results of an *ab initio* cluster quantum chemical study at the HF/6-31G level for the triaminotoluene (TAT) molecule interaction with a model clay surface, in particular, a kaoline-type clay mineral. The latter is characterized by a layer structure that contains three different structure units corresponding to alumina, silica, and an intersection of alumina-silica. According to the obtained results, the physical adsorption of TAT took place both on alumina and silica structure units. In going from silica to alumina-silica units, the two-center adsorption of TAT will result in strong adsorption via formation of a TATH* species stabilized by two strong H bonds. Different channels of interaction of TAT with kaoline-type clay surfaces (i.e., one-, two-, and three-center adsorption of TAT, an aromatic six-member ring opening of TAT) and its destruction via breaking the methyl-aromatic or amino-aromatic ring bonds are also discussed.

THEORETICAL QUANTUM CHEMICAL STUDY OF TAUTOMERISM AND PROTON TRANSFER IN 6,8-DITHIOGUANINE

N.U. Zhanpeisov[1,2], W. W. Cox[2], J. Leszczynski[2]
([1]Boreskov Institute of Catalysis, Novosibirsk, Russia; [2]Jackson State University, Jackson, USA)

J. Phys. Chem. A, 103 (1999) pp. 4564-4571.

Ab initio quantum chemical calculations were performed to study the tautomeric rearrangements in the 6.8-dithioguanine. Molecular geometries of all the possible 35 tautomeric structures have been fully optimized without imposing any constraints at the HF/3-21G level. For the seven most favorable structures, full geometry optimizations were performed at the higher level of theory using the 6-31G** basis set. The effects of electron correlation were further accounted for at the second-order Moller-Plesset perturbation theory level with the frozen-core approximation. The proton-transfer reactions were considered between the normal and selected rare tautomeric forms in the gas phase and also for the water assisted proton transfer. It was shown that at all applied levels of theory the standard 6,8-dithioguanine (with protons at the N1, N7 and N9 sites and on its amino groups) is the global minimum on the potential energy surface in the gas phase. For the monohydrated complexes of dithioguanine, the complex **1**$\cdot H_2O$(N1H) is the most stable one and is characterized by the highest interaction energy. The relative stability of monohydrated complexes of normal dithioguanine which interacts with the water through N9H and N7H groups follows stability of **1**$\cdot H_2O$(N1H). Water-assisted proton-transfer reactions considerably decreases the energy barrier as compared to the ability of gas phase processes to do the same.

SPECIFIC SOLVATION EFFECTS ON THE STRUCTURES AND PROPERTIES OF NEUTRAL AND ONE-ELECTRON OXIDIZED FORMAMIDINE-FORMAMIDE COMPLEXES. A THEORETICAL *AB INITIO* STUDY

N.U. Zhanpeisov[1,2], **J. Leszczynski**[2] ([1]Boreskov Institute of Catalysis, Novosibirsk, Russia; [2]Jackson State University, Jackson, USA)

J. Phys. Chem. A, 103 (1999) pp. 8317-8327.

Ab initio quantum chemical calculations were performed for the neutral and one-electron oxidized formamidine-formamide model systems in the gas phase and in a water solution. Full geometry optimizations without any constraints on the planarity of these complexes were carried out at the HF/6-31G* level. For the neutral dimers, the solvent effects were modeled by explicit inclusion of four, six, and nine water molecules, which creates the first, intermediate, and second hydration spheres around these dimers. For one-electron oxidized systems the effects of the first hydration shell water molecules were accounted for. Single point calculations were also performed at the correlated MP2/6-31G*//HF/6-31G* level. The interaction and solvation energies were corrected for the basis set superposition error. It was shown that the relative stability of the neutral model formamidine-formamide complexes is quite opposite to that of the analogous adenine-uracil base pairs: the double proton transferred FF2 dimer becomes more stable than the zwitterionic FF3 dimer. An increase in the number of water molecules from the first to the second hydration shell results in an overestimated stability for the FF3 zwitterionic structure. For a one-electron oxidation process, the FF3$^{(+)}$ cation-radical dimer is the most stable dimer while the double-proton-transfer process becomes the least favorable process in both the gas phase and in a water solution.

SPECIFIC SOLVATION EFFECTS ON THE STRUCTURES AND PROPERTIES OF WATSON–CRICK AND REVERSE WATSON–CRICK ISOCYTOSINE–CYTOSINE AND GUANINE–CYTOSINE BASE PAIRS: A THEORETICAL *AB INITIO* STUDY

N.U. Zhanpeisov[1,2], **J. Leszczynski**[2] ([1]Boreskov Institute of Catalysis, Novosibirsk, Russia; [2]Jackson State University, Jackson, USA)

J. Molec. Struct. (Theochem), 487(1-2) (1999) pp. 107-115.

Ab initio quantum chemical studies were performed for the standard and most favorable reverse Watson–Crick isocytosine–cytosine (iCC) and guanine–cytosine (GC) complexes in the gas phase and in a water solution. Full geometry optimizations at the Hartree–Fock (HF) level with the 6-31G(d) basis set without any constraints on the planarity of these complexes were carried out. The water solution was modeled by explicit inclusion of a different number of water molecules, which creates the first hydration shell around these base pairs. Single point calculations were also performed at the correlated MP2/6-31G(d) level. The interaction and solvation energies were corrected for the basis set superposition error. It was shown that both the base pairs considered, possessed similar molecular properties in the gas phase. The presence of the N9-H group in guanine causes changes in the structure of the first hydration shell around the RWC GC base pair compared to the RWC iCC pair.

COMBINED KINETIC AND THERMODYNAMIC ANALYSIS OF CATALYTIC REACTIONS COUPLED VIA A COMMON INTERMEDIATE: ONSAGER EQUATIONS FOR COUPLED CHEMICAL REACTIONS FAR FROM EQUILIBRIUM

V.N. Parmon, A.G. Okunev

Kinetics & Catalysis, 40(1) (1999) pp. 1-6.

It was found that the presence of a common intermediate in a system with several parallel catalytic processes could substantially affect the selectivity and even reverse the direction of chemical reactions because of thermodynamic coupling of the catalytic processes.

The mutual effect of coupled processes can be described by the modified Onsager equations in which the differences of the thermodynamic heads (that exponentially depend on the chemical potentials) of the reactants and the products of catalytic reactions play a role of thermodynamic forces. As a particular example, kinetic and thermodynamic criteria were derived whose fulfillment provides the absence of catalyst coking in the course of carbon dioxide conversion of methane.

CATALYSIS AND NON-EQUILIBRIUM THERMODYNAMICS: MODERN *IN SITU* STUDIES AND NEW THEORETICAL APPROACHES

V.N. Parmon

Catal. Today, 51(3-4) (1999) pp. 435-456.

The paper discusses some modern approaches, which consider the state of operating catalysts from the point of view of non-equilibrium thermodynamics. Both theoretical speculations as well as experimental data of some *in situ* studies are considered. An emphasis is put on the *stable* non-equilibrium states of catalysts.

DERIVATION OF THE CLASSICAL KELVIN (THOMSON) FORMULA FOR EQUILIBRIUM SATURATED VAPOR PRESSURE OVER A DROP OF A LIQUID

V.N. Parmon

Russ. J. Phys. Chem., 73(1) (1999) pp. 7-11.

An increase in the chemical potential of a condensed phase inside a disperse particle caused by capillary ("Laplace") pressure due to surface tension forces produces effects similar to those obtained in the traditional Kelvin (Thomson) theory, which calculates saturated vapor pressure over a disperse particle through excess surface energy only, without introducing corrections for chemical potential changes. If the standard "force" definition of surface tension coefficient σ is used (this definition refers to values measured in capillary experiments and not related to any specific particle geometry), more rigorous calculations of saturated vapor pressure over a spherical particle give the dependence $p=p_0 \exp(10\sigma V_1/3rRT)$ in place of the traditional formula $p=p_0 \exp(2\sigma V_1/rRT)$. The traditional form of the Kelvin (Thomson) equation remains unchanged if the thermodynamic rather than force definition of the surface tension coefficient is used. The thermodynamic definition, recommended by IUPAC, relates this coefficient to a change in the free energy of the whole substance inside a disperse particle and takes into account particle geometry.

SCALING COULOMB INTERACTION IN CALCULATIONS ON ELECTRON SPECTRA OF TRANSITION METAL COMPLEXES

I.L. Zilberberg, M.A. Milov, G.M. Zhidomirov

J. Struct. Chem., 40(1) (1999) pp. 3-12.

A simple procedure for scaling two-electron integrals in *ab initio* calculations of the transition metal complexes excited states was suggested. The method is based on the fact that the Slater-type functions being scaled the one-centered two-electron integrals depend linearly on the scaling factor. This results in the linear dependence of the d-d transitions energies on the scale of the Coulomb interaction, allowing one to control effectively the calculation results varying the Slater exponent. In order to test the suggested procedure *ab initio* calculations of the lowest excited states in complexes CrF_6^{3-}, MnF_6^{2-} and VF_6^{3-} were performed using CI and CASSCF methods. For the transition elements the basis of effective Slater functions, fitted from the optical spectra of their atoms and ions, was used. It was shown that in the STO-6G basis with the effective exponents, the experimental transitions might be reproduced in the accuracy of 2000 cm^{-1} even using a small active space determined by orbitals localized on the central atom of the complexes.

EXCITED STATES OF CHROMATE ION: CALCULATION BY SEMIEMPIRICAL NDDO/MC METHOD

I.L. Zilberberg, G.M. Zhidomirov

J. Struct. Chem., 40(2) (1999) pp. 228-233.

A new semiempirical method was developed for calculating excited states of transition metal complexes. The method is based on application of (1) the configurational interaction method, (2) the semiempirical NDDO/MC method to obtain the ground state, (3) a set of valent Slater-type *spd*-orbitals, which were deliberately fitted from optical spectra of transition elements, along with the corresponding core integrals. The method was tested by calculating electron-excited states of chromate ions. There was obtained a good agreement with the experimental energies of vertical transitions as well as with the results of *ab initio* calculations.

FORMS OF CHEMISORBED OXYGEN ON Ag(111) SURFACE: SEMIEMPIRICAL INVESTIGATION BY THE NDDO/MC METHOD

I.L. Zilberberg, M.A. Milov, G.M. Zhidomirov

J. Struct. Chem., 40(3) (1999) pp. 422-430.

Atomic and molecular adsorption of oxygen on Ag(111) face was calculated using the semiempirical NDDO/MC method. The Ag_{38} cluster with top (active) 16-atom rhombic face was used. In order to take into account the metallicity of silver the self-consistent alignment of cluster's HOMO to the experimental Fermi level was used. Two surface and three subsurface stable positions of atomic oxygen adsorption were found. As resulted from the calculations, molecular oxygen adsorption is not energetically favorable, though it corresponds to the local minimum of the potential energy surface. The role of subsurface oxygen in activation of oxygen atoms on the surface was discussed.

ATOMIC AND MOLECULAR OXYGEN SPECIES ON Ag(331). THEORETICAL DFT ANALYSIS

V.I. Avdeev, G.M. Zhidomirov

J. Struct. Chem., 40 (3)(1999) pp. 413-421.

Oxygen adsorption on the Ag(331) plane was analyzed using the cluster approximation of the density functional theory (DFT). Adsorption sites (AS) for bridge-like (S2) and three-centered (S3) coordination of oxygen were identified on the stepped plane of Ag(331); Ag-O bond energies on these sites were calculated. The strength of the Ag-O bond ranges from 50 to 65 kcal/mol for the atomic adsorption depending on the kind of AS. The heat of molecular adsorption $\Delta H=5$ kcal/mol for AS of the S2(L1-L2) type. The molecule is oriented in parallel to the Ag(110) plane between terraces with R(O-O)=1.34 Å. Calculations showed triplet as the ground state of the $O_2/Ag_2O(331)$ system but the spin density was partly delocalized on the silver atoms so as the spin density on oxygen $\rho_s(O)=0.46$ ($\rho_s=1.0$ for a free O_2 molecule). The energy of singlet state was 9 kcal/mol higher of that of the ground state.

ADSORBED NH_x SPECIES ON Pt(111) AND Pt(100) SURFACES STUDIED BY THE SEMIEMPIRICAL METHOD OF INTERACTING BONDS

A.R. Cholach, N.N. Bulgakov

Catal. Lett., 58(4) (1999) pp. 183-187.

The properties of the adsorbed NH_x species (x=0, 1, 2, 3) on platinum (111) and (100)-(1×1) single-crystal planes are studied by the semi-empirical method of interacting bonds. Both surfaces reveal similar features. The adsorbed species NH and NH_2 are stable on the surface, and stable $NH_{3(ads)}$ species con not form. The $NH_{2(ads)}$ species is favorable in adsorbed hydrogen excess, but lack of the latter results in NH_{ads} becoming dominant. Both NH and NH_2 species are expected to diffuse easily over the surface due to the small difference between their bond strengths to various adsorption sites.

Monte-Carlo Simulation to Study Physico-Chemical Processes

MONTE-CARLO SIMULATIONS OF THE KINETICS OF CATALYTIC REACTIONS ON NANOMETER-SIZED PARTICLES, WITH DIFFUSION OVER FACET BOUNDARIES

H. Persson*, P. Thormahlen*, V.P. Zhdanov,
B. Kasemo* (*Chalmers University of Technology, Gëteborg, Sweden)

J. Vac. Sci. Techn. A, 17 (1999) pp. 1721-1726.

The kinetics of heterogeneous reactions occurring on supported nm catalyst particles is simulated. The attention is focused on the interplay of the reaction kinetics on different facets and edges.

SIMULATIONS OF THE KINETICS OF RAPID REACTIONS ON SUPPORTED CATALYST PARTICLES

H. Persson*, P. Thormahlen*, V.P. Zhdanov,
B. Kasemo* (*Chalmers University of Technology, Gëteborg, Sweden)

Catal. Today, 53 (1999) pp. 273-288.

A brief review of simulations of reaction kinetics on nm catalyst particles is presented.

MONTE CARLO SIMULATION OF OSCILLATIONS IN THE NO-H_2 REACTION ON Pt(100)

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

Appl. Catal. A: General, 187(1) (1999) pp. 61-71.

The Monte Carlo simulation of phase separation during kinetic oscillations in catalytic reactions accompanied by adsorbate-induced surface restructuring is presented. As an example, the NO-H_2 reaction on Pt(100) is analyzed. The lattice-gas model employed to describe surface restructuring and the reaction steps takes into account substrate-substrate, substrate-adsorbate and adsorbate-adsorbate lateral interactions. Using a reduced generic mechanism of the reaction, the type of spatio-temporal patterns are shown which might be observed on the nm scale.

SIMULATION OF SURFACE RESTRUCTURING AND OSCILLATIONS IN CO-NO REACTION ON Pt(100)

V.P. Zhdanov

J. Chem. Phys., 110 (1999) pp. 8748-8753.

Kinetic oscillations occurring in the CO-NO reaction on Pt(100) at UHV conditions and relatively high temperatures are accompanied by adsorbate-induced surface restructuring. Employing the Monte Carlo technique, the type of spatio-temporal patterns is shown which might be observed in this system on the nm scale. The model used to describe surface restructuring is based on the lattice-gas approximation and predicts the formation of restructured islands even at low adsorbate coverages. Simulations are executed with qualitatively realistic ratio between the rates of different steps involved into the game.

CHEMICALLY-INDUCED DIFFUSION-LIMITED INTERFACE GROWTH

V.P. Zhdanov

Phys. Rev. E, 59 (1999) pp. 3714-3716.

Employing a lattice-gas model, the Monte Carlo kinetics of heterogeneous reaction resulting in the growth of a new phase on the top of the solid in the case when the process is limited by reactant diffusion via the film is studied. For the simplest set of particle-particle interactions and Metropolis diffusion dynamics, the model proposed predicts the power-law growth of the film thickness with the exponent of 0.3. Such low values of the growth exponent are usually attributed to the reactions involving grain-boundary diffusion. It has been shown that the growth slowdown might result from the formation of a thin dense layer just on the bottom of the newly formed phase. The model introduced is rather flexible. Choosing other types of the particle-particle interactions or diffusion dynamics, one can easily get diverse regimes of the growth.

SURFACE RESTRUCTURING, KINETIC OSCILLATIONS, AND CHAOS IN HETEROGENEOUS CATALYTIC REACTIONS

V.P. Zhdanov

Phys. Rev. E, 59 (1999) pp. 6292-6305.

Comprehensive Monte Carlo simulations of isothermal kinetic oscillations and chaos in catalytic reactions accompanied by adsorbate-induced surface restructuring is presented. An analysis is based on the lattice-gas model describing surface restructuring in terms of the statistical theory of first-order phase transitions. As an example, the kinetics of the NO-H_2 reaction on the Pt(100) surface is treated. A proposed reduced mechanism of this reaction includes NO adsorption, desorption, and decomposition occurring on the restructured patches of the surface (the decomposition products are rapidly removed from the surface via N_2 desorption and H_2O formation and desorption). Calculations are performed with qualitatively realistic ratio between the rates of different elementary steps. In particular, NO diffusion is several orders of magnitude faster compared to the other steps. On the nm scale, the model predicts formation of restructured islands with atomically-sharp boundaries. The shape of islands is found to change dramatically with varying the reaction conditions. Despite phase separation on the surface, the transition from almost harmonic oscillations (with relatively small separate islands) to chaos (with merging islands) is demonstrated to occur via the standard Feigenbaum scenario. Near the critical point, the dependence of the amplitude of oscillations on the governing parameter is shown to be close to that predicted for the Hopf supercritical bifurcation.

SIMULATION OF KINETIC OSCILLATIONS IN CATALYTIC REACTIONS ACCOMPANIED BY OXIDE FORMATION

V.P. Zhdanov

Surf. Rev. Lett., 6 (1999) pp. 347-353.

One of the generic mechanisms of oscillations in heterogeneous catalytic reactions with participation of oxygen is based on slow oxidation and reduction of the metal surface. The Monte Carlo simulation of spatio-temporal patterns corresponding to this mechanism is presented. As an example, the 2A+B2->2AB reaction mimicking CO (or H_2) oxidation on Pt is analyzed. Calculations, taking into account the nonideality of the kinetics of oxidation and reduction of the substrate, are executed with qualitatively realistic ratio of the rates of elementary steps. The results obtained indicate that the reaction scheme under consideration possesses of ability of spatial self-organization even if cooperative effects in nucleation, growth and decay of oxide islands are neglected. In the latter case, the islands are however small and rather disordered. With the cooperative effects, the size of islands becomes larger but not dramatically. Very strong tendency to form oxide islands is found to suppress oscillations.

SIMULATION OF KINETIC OSCILLATIONS IN CATALYTIC REACTIONS ACCOMPANIED BY ADSORBATE-INDUCED SURFACE RESTRUCTURING

V.P. Zhdanov

Surf. Sci., 426(3) (1999) pp. 345-357.

The Monte Carlo simulations of phase separation on the nm scale during kinetic oscillations in catalytic reactions accompanied by adsorbate-induced surface restructuring is presented. As an example, the 2A+B2->2AB reaction mimicking CO oxidation on noble metals is analyzed. The lattice-gas model employed to describe surface restructuring and the reaction steps takes into account substrate-substrate, substrate-adsorbate and adsorbate-adsorbate lateral interactions and predicts the formation of restructured islands even at low A coverages (as in the case of CO adsorption on Pt(100)).

SUBSTRATE-MEDIATED PHOTOINDUCED CHEMICAL REACTIONS ON ULTRATHIN METAL FILMS

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

Surf. Sci., 432(1-2) (1999) L599-L603.

Photostimulated rate processes (e.g., desorption, dissociation, or chemical reactions) on metal surfaces with UV and visible photons occur in most cases via excitation of hot electrons in the metal. It was shown that the cross-section of such processes can be considerably enhanced by replacing the bulk metal by an ultrathin metal film (with the thickness of 10-30 Å) deposited on the surface of a semiconductor with a suitable band gap. The mechanism analyzed includes generation of hot electrons (or holes) primarily in the semiconductor, diffusion of these electrons toward the metal-vacuum interface, and attachment to the adsorbate.

NONTRADITIONAL MODELS OF OSTWALD RIPENING ON SOLID SURFACES: FROM PHYSICS TO BIOLOGY

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

Surf. Sci., 437(3) (1999) pp. 307-316.

The Monte Carlo simulations of Ostwald ripening of (i) submonolayer islands on a heterogeneous surface, (ii) lipid bilayer islands, and (iii) 3D supported nm crystallites on a uniform surface is presented. With increasing the dimension of a model (from (i) to (iii)), the growth of the average size characterizing phase separation is found to become slower. In particular, the growth law exponent falls from the classical Lifshitz-Slyozov (LS) value, x=1/3, obtained for the mono- and bilayer islands, down to much lower values, x=1/8, associated with the nm crystallites. The latter finding is in good agreement with the results of numerous experimental studies of sintering of supported nm crystallites employed in heterogeneous catalysis.

NANOFABRICATION OF MODEL CATALYSTS AND SIMULATIONS OF THEIR REACTION KINETICS

S. Johansson*, K. Wong*, V.P. Zhdanov,
B. Kasemo* (*Chalmers University of Technology, Gëteborg, Sweden)

J. Vac. Sci. Techn. A, 17 (1999) pp. 297-302.

The methods employed to fabricate model supported nm catalysts, including wetness impregnation, vacuum vapor deposition, electron-beam lithography, spin-coating, and vesicle-mediated deposition are briefly reviewed. Recent simulations of the kinetics of heterogeneous reactions occurring on supported catalyst particles are discussed as well.

NUCLEATION AND GROWTH OF p(2x2) AND c(2x2) ADSORPTION STRUCTURES DURING OXYGEN ADSORPTION ON THE (100) SURFACE OF METALS AT LOW TEMPERATURES

A.N. Salanov, V.N. Bibin

Surf. Sci., 441(2-3) (1999) pp. 399-409.

The nucleation and growth of p(2x2) and c(2x2) adsorption structures during dissociative chemisorption of oxygen on a metal surface with a square lattice of adsorption sites has been studied by Monte Carlo simulation at low temperature (300 K) when the surface diffusion of chemisorbed atoms is slow (i.e. under non-equilibrium conditions). An adsorption model taking into account both direct and indirect adsorption pathways, lateral interactions between chemisorbed particles and their immobility was used. The p(2x2) islands nucleate due to direct dissociative chemisorption of O_2 molecules on 3NN (third-nearest neighbor) adsorption sites occurring via occupation of NN sites by the oxygen atoms followed by hopping of one of the atoms to a 3NN site. The p(2x2) islands grow due to the indirect adsorption occurring via trapping of O_2 molecules into precursor states followed by the migration above the adsorption island and the chemisorption on similar sites at the edges of the adsorption islands. The c(2x2) islands are mostly formed by merger of antiphase p(2x2) islands spatially not coherent with respect to each other in both directions, and grow also due to the indirect adsorption. Antiphase boundaries are formed by merger of the antiphase p(2x2) islands spatially not coherent with respect to each other in one direction.

MONTE CARLO METHODS FOR SIMULATING THE CATALYTIC OXIDATIVE DEHYDROGENATION OF PROPANE OVER VMgO CATALYST

Y. Boudeville*, M. Kolb*, A. Pantazidis*, C. Marquez-Alvarez*, C. Mirodatos*, V.I. Elokhin
(*Institut de Recherches sur la Catalyse, Villeurbanne Cedex, France)

Chem. Engin. Sci., 54(20) (1999) pp. 4295-4304.

The oxidative dehydrogenation of propane (ODHP) has been studied by non-steady-state kinetic experiments and by various experimental characterization techniques under conditions close to the reaction conditions. The reaction proceeds via Mars-van Krevelen mechanism. The work reports on Monte Carlo simulation of the ODHP over VMgO catalysts. The dynamic behavior of the reaction has been explored by handling new Monte Carlo models with a catalytic reaction graph, 2D pattern recognition of adsorbed molecules, 3D oxygen bulk diffusion and the description of the selective and non-selective routes of the ODHP process.

MECHANISM OF LOW-TEMPERATURE CO OXIDATION ON A MODEL Pd/Fe_2O_3 CATALYST

A.V. Kalinkin, V.I. Savchenko, A.V. Pashis

Catal. Lett., 59 (1999) pp. 115-119.

Model Pd/Fe_2O_3 catalyst prepared by the vacuum technique has been studied in the carbon monoxide oxidation in the temperature range of 300-550 K at reagent pressures P(CO)=16 Torr, P(O_2)=4 Torr. It has been shown that the activity of the fresh catalysts is determined by palladium. According to the XPS data, the reduction with carbon monoxide results in the formation of Fe^{2+} (formally Fe_3O_4) and appearance of the catalytic activity in this reaction at low temperatures (350 K). High low-temperature activity of the catalyst is supposed to be connected with the reaction between oxygen adsorbed on the reduced sites of the support (Fe^{2+}) and CO adsorbed on palladium (CO_{ads}) at the metal-oxide interface.

SIMULATION OF THE REACTION FRONT PROPAGATION DURING CO OXIDATION ON Pt(100) UNDER UNSTEADY-STATE CONDITIONS

N.I. Efremova, V.I. Savchenko

React. Kinet. & Catal. Lett., 67(2) (1999) pp. 311-317.

The effects of the CO_{ads} surface diffusion on the reaction front propagation and the particle distribution in the reaction zone during the CO oxidation on Pt (100) have been compared with the employment of the Monte Carlo method for a model taking into account the (1x1) $\Leftrightarrow$ (hex) transformation and for a 3-stage reaction scheme.

Catalysis on Zeolites

DINITROGEN FORMATION OVER LOW-EXCHANGED Cu-ZSM-5 IN THE SELECTIVE REDUCTION OF NO BY PROPANE

E.V. Rebrov, A.V. Simakov, N.N. Sazonova, E.S. Stoyanov

Catal. Lett., 58(2-3) (1999) pp. 107-118.

The role of gaseous NO and propane has been studied over low-exchanged Cu-ZSM-5 zeolite employing TPD, FTIR and pulse technique with alternate introduction of NO or propane onto the catalyst surface. The rate of the N_2 formation is directly proportional to the content of gaseous NO and the surface coverage with 2-nitrosopropane. There was no formation of N_2 during interaction of gaseous propane with NO adsorbates. However, 2-nitrosopropane and its isomer acetone oxime were also formed in this reaction.

PROPENE SURFACE SPECIES AND THEIR ROLE IN NO REDUCTION OVER Cu-ZSM-5 IN THE EXCESS OF OXYGEN

V.A. Matyshak*, A.A. Ukharskii*, A.N. Il'ichev*, V.A. Sadykov, V.N. Korchak* (*Semenov Institute of Chemical Physics, Moscow, Russia)

Kinetics & Catalysis, 40(1) (1999) pp. 105-111.

The nature and reactivity of surface complexes under the conditions of NO reduction by propene over Cu-ZSM-5 in the excess of oxygen are studied *in situ* by IR spectroscopy. The π - and π-allyl complexes are formed during the interaction of C_3H_6 or $C_3H_6 + O_2$ with the zeolite surface at low temperatures, whereas coke is formed at higher temperatures. Complexes with organic nitro compounds are observed in the presence of NO at relatively low temperatures, and nitrito complexes are found under the reaction conditions (300 °C). NO reduction by propene over Cu-ZSM-5 in the excess of O_2 occurs via two routes. One involves the formation of coke on the surface followed by the interaction of coke with NO to yield the reaction products. In this process, coke by itself serves as a reducing agent. In this reaction, copper ions increase the rate of the coke formation and change the ratio between the amounts of "soft" and "hard" coke. The other route involves the reaction between propene and the Cu^{2+}–O–N=O complex formed on copper ions followed by the formation of reaction products. This process is analogous to that observed earlier for NO_x reduction by propane in these systems.

EFFECT OF REACTION MEDIUM AND TEMPERATURE ON PHASE COMPOSITION OF ACTIVE COMPONENT IN ZEOLITE-CONTAINING PALLADIUM CATALYST FOR CO OXIDATION

V.Z. Radkevich*, M.F. Savchits*, B.N. Novgorodov, D.F. Kochubei*, Y.G. Egizarov* (*Institute of Physicoorganic Chemistry, Minsk, Belarus)

Russ. J. Appl. Chem., 71(10) (1998) pp. 1766-1770.

The effect of reaction medium (1% CO in air) and temperature (100-200 °C) on active-phase formation in zeolite-containing palladium catalyst chemisorption properties of metal, and activity of the system in CO oxidation was studied.

ON THE OXYGEN EFFECT IN NITRIC OXIDE REDUCTION BY METHANE OVER Co/ZSM-5

L.G. Pinaeva, E.M. Sadovskaya, A.P. Suknev, V.B. Goncharov, V.A. Sadykov, B.S. Bal'zhinimaev, T. Decamp*, C. Mirodatos* (*Institut de Recherches sur la Catalyse, Villeurbanne, France)

Chem. Eng. Sci., 54(20) (1999) pp. 4327-4335.

The catalytic reduction of NO by CH_4 over Co/ZSM-5 zeolite is studied by means of transient *in situ* DRIFT, SSITK and TAP analysis. Co ions located at interface of Co clusters and zeolite are found to react with NO in the presence of oxygen to form anchored NO_2^{d+} species stabilized under reaction conditions. These species form the main active sites for activating methane molecule. Two ways of CO_2 formation from the same intermediate including fragments of both NO_x and partially dehydrogenated CH_4 molecule are proposed in the mechanistic scheme of the reaction.

Studies on Silver Catalysts for Ethylene Epoxidation

DYNAMICS OF ISOTOPIC LABEL TRANSFER IN CATALYTIC REACTIONS

E.M. Sadovskaya, D.A. Bulushev, B.S. Bal'zhinimaev

Kinetics & Catalysis, 40(1) (1999) pp. 54-61.

Dynamics of isotopic label transfer in open catalytic systems is studied in the general form. The advantages and limitations of steady-state isotopic transient kinetic analysis are compared to those of the kinetic relaxation method. The applicability of the isotopic relaxation method to the discrimination of the reaction mechanisms is discussed. This method can also be applied to the determination of the composition of adsorption layer and kinetic parameters taking into account gas dynamics in a catalytic reactor. The mechanism of isotopic label transfer in ethylene epoxidation over silver catalyst is elucidated. The surface coverage by various forms of adsorbed oxygen and the values of rate constants of the steps of ethylene oxide and carbon dioxide formation are estimated.

ETHYLENE EPOXIDATION OVER SILVER CATALYSTS

B.S. Bal'zhinimaev

Kinetics & Catalysis, 40 (6) (1999) pp. 795-810.

Physical and kinetic methods were used to study the structural, electron, and catalytic properties of silver catalysts for ethylene epoxidation: bulk silver (Ag(111) and foil), silver powder, and supported silver catalysts (Ag-Al_2O_3, Ag/SiO_2, and Ag/C). The nature of size effects, the mechanism for the formation of active states of adsorbed oxygen, and the mechanism of ethylene epoxidation were determined. Based on these data, several unusual phenomena are explained and reasons for the unique catalytic activity of silver in ethylene epoxidation are discussed.

THE CONCEPT OF QUASIMOLECULAR ELECTROPHILIC OXYGEN IN ETHYLENE EPOXIDATION OVER SILVER

A.I. Boronin, V.I. Avdeev, S.V. Koshcheev, K.T. Murzakhmetov, S.F. Ruzankin, G.M. Zhidomirov

Kinetics & Catalysis., 40(5) (1999) pp. 653-672.

The ethylene-epoxidizing form of oxygen (O_{ep}) adsorbed on Ag(111) and Ag(110) single crystals and polycrystalline silver foil was examined by X-ray and UV photoelectron spectroscopy (XPS and UPS). It was shown that O_{ep} has a quasimolecular nature and exhibits high thermal stability (T > 700 K). The quantum-chemical study of associative forms of oxygen on the defects of the silver surface was carried out by the methods of density functional theory (DFT) in a cluster approximation. It was found that the associative (molecular) ozone-like species of oxygen on the surface of silver with cationic vacancies (V) is more stable than atomic oxygen (the energy difference is 44 kcal/mol). The identification of emission bands in UV photoelectron spectra performed on the basis of theoretical calculations of the ozone-like structure supported the quasimolecular nature of O_{ep}. The mechanisms known for ethylene epoxidation were analyzed. A new mechanism implying the participation of quasimolecular electrophilic oxygen O_{ep} in epoxidation was proposed. This mechanism describes the major regularities of epoxidation observed in the experiments on a regular basis.

MODELING OF OXYGEN ADSORPTION ON SILVER

E.A. Ivanov, A.I. Boronin, S.V. Koshcheev, G.M. Zhidomirov

React. Kinet. & Catal. Lett., 66(2) (1999) pp. 265-272.

Different adsorption forms of oxygen on silver are discussed. Four main types of oxygen forming at different temperatures and oxygen pressures have been distinguished. A kinetic model describing the formation and transformations of the oxygen forms and taking into account the surface amorphization has been proposed. Numerical modeling of stationary concentrations using this model gives evidence for a temperature window ΔT=500-800 K, where a quasi-molecular oxygen state (E=530.5 eV, T_{des}=800-900 K) can exist at high oxygen pressures.

XPS, UPS, TPD AND TPR STUDIES OF OXYGEN SPECIES ACTIVE IN SILVER-CATALYZED ETHYLENE EPOXIDATION

V.I. Bukhtiyarov, V.V. Kaichev, E.A. Podgornov, I.P. Prosvirin

Catal. Lett., 57(4) (1999) pp. 233-239.

The covalent oxygen chemisorbed on silver has been characterized by XPS, UPS, TPD and TPR. It has been shown that this oxygen species active in ethylene epoxidation is characterized by full isotope scrambling in TPD spectra of O_2 and the absence of UPS lines located below the silver-4d zone. Both the results testify its atomic origin.

OXYGEN ADSORPTION ON Ag(111): X-RAY PHOTOELECTRON SPECTROSCOPY (XPS), ANGULAR DEPENDENT X-RAY PHOTOELECTRON SPECTROSCOPY (ADXPS) AND TEMPERATURE-PROGAMMED DESORPTION (TPD) STUDIES

V.I. Bukhtiyarov, V.V. Kaichev, I.P. Prosvirin

J. Chem. Phys., 111(5) (1999) pp. 2169-2175.

The O_2 adsorption on Ag(111) single crystal in the range of 300-500 K has been studied by XPS, ADXPS, and TPD. At room temperature, the O1s line observed at 530.0 eV goes down to 528.2 eV when the sample is heated to 420 K. The comparison of XPS and TPD data indicates that both lines can be assigned to chemisorbed atomic oxygen. The depth concentration profiles calculated on the basis of the angular-dependent XPS data show that the line at 530.0 eV is responsible for oxygen adsorbed at the surface, as opposed to that at 528,2 eV which is assigned to oxygen between the top and second silver layers. The formation of surface silver oxide is concluded in the latter case.

Development and Application of Physicochemical Methods for Catalysts Investigation

IR STUDIES OF THE TRANSFORMATION OF NITROGEN-CONTAINING ORGANIC INTERMEDIATES DURING SELECTIVE REDUCTION OF NITROGEN OXIDES BY HYDROCARBONS

S.A. Beloshapkin, V.A. Matyshak*, E.A. Paukshtis, V.A. Sadykov, A.N. Il'yichev*, A.A. Ukharskii*, V.V. Lunin** (*Semenov Institute of Chemical Physics, Moscow, Russia; **Lomonosov Moscow State University, Moscow, Russia)

React. Kinet. & Catal. Lett., 66(2) (1999) pp. 297-304.

Thermal transformations of nitromethane and deuterated acetonitrile adsorbed on the surface of H-ZSM-5, Cu-ZSM-5, Co-ZSM-5 has been studied by IR spectroscopy. The nature of cation has been found to greatly affect the transformation pathways of these species as possible intermediates in the NO_x selective reduction by hydrocarbons, thus explaining different selectivity of these catalysts.

IR DIFFUSE-REFLECTANCE SPECTROSCOPIC STUDY OF BENZONITRILE, CO, AND NO INTERACTION WITH VANADIUM-MAGNESIUM CATALYSTS FOR ETHYLENE POLYMERIZATION

M.A. Mats'ko, E.A. Paukshtis, T.B. Mikenas, A.P. Sobolev, V.A. Zakharov

Kinetics & Catalysis, 40(4) (1999) pp. 547-551.

The adsorption of benzonitrile, CO, and NO on vanadium-magnesium catalysts (VMC) of ethylene polymerization was studied by IR diffuse-reflectance spectroscopy. It was shown that carbon oxide and benzonitrile interact with both the Lewis acid sites of magnesium chloride and the coordinatively unsaturated V^{4+} ions in VMC, and the absorption bands of magnesium chloride overlap with the absorption bands of VMC. The complexes of CO and benzonitrile with V^{5+} ions were not found in the $VOCl_3/MgCl_2$ system. The coordinatively unsaturated V^{4+} ions in VMC can be identified using NO as a probe molecule (the absorption bands at 1776, 1840, and 1920 cm^{-1}). NO does not interact with magnesium chloride used as a support in this system.

IR SPECTROSCOPIC STUDY OF SILICA GEL MODIFIED BY TRIETHYLALUMINUM UNDER VARIOUS CONDITIONS

V.N. Panchenko, N.V. Semikolenova, I.G. Danilova, E.A. Paukshtis, V.A. Zakharov

Kinetics & Catalysis, 40(4) (1999) pp. 556-561.

The surface organoaluminum compounds formed during repeated treatments of silica gel with triethylaluminum (TEA) and dioxygen (method A) and with TEA and water followed by heating in air and in a vacuum (method B) are studied by FTIR spectroscopy. The modification of silica gel using the methods A and B results in the formation of novel surface hydroxyl groups, which are characterized by absorption bands at 3615 and 3690 cm^{-1}. According to the IR-spectroscopic data on CO adsorbed at low temperature, these OH groups are close in their acidity to OH groups of typical aluminosilicates. When using CO as a probe molecule adsorbed at room temperature and at the temperature of liquid nitrogen, the supports prepared by method A contain Lewis acid sites of two types: strong (2228 cm^{-1}) and weak (2188 cm^{-1}), and the supports prepared by method B also contain Lewis acid sites of a moderate strength (2210 cm^{-1}). The concentrations of Lewis acid sites of various types are determined, and data on the influence of the modification procedure and the number of treatments on the concentrations of various Lewis acid sites are obtained.

IRS STUDY OF ETHYLENE POLYMERIZATION CATALYSTS SiO_2/MAO/ZIRCONOCENE

V.N. Panchenko, N.V. Semikolenova, I.G. Danilova, E.A. Paukshtis, V.A. Zakharov

J. Molec. Catal. A: Chemical, 142(1) (1999) pp. 27-37.

IR spectroscopy has been used to study the interaction of silica with two methylaluminoxane (MAO) samples differed by trimethylaluminum (TMA) content and with TMA. MAO and TMA have been shown to react with silica in a different way. Whereas TMA interacts with terminal hydroxyl groups of silica via the protolysis reaction, MAO mainly adsorbs on the surface hydroxyl groups of silica without noticeable protolytical reaction with them. When silica is treated with commercial grade MAO with significant TMA content, the silica surface hydroxyl groups mainly interact with TMA and MAO adsorbs on the surface of SiO_2/TMA sample. Lewis acid sites (LAS) of silica, modified with TMA and MAO samples differed by TMA content, have been investigated by IR spectroscopy (CO adsorption as probe molecule at 77 K). Two types of LAS were found on the surface of silica modified with MAO and TMA: LAS of moderate strength (ν_{CO}=2204-2212 cm^{-1}) and weak LAS (ν_{CO}=2194 cm^{-1}). The concentration of these acidic sites was estimated. By anchoring of Cp_2ZrCl_2 on silica, modified with TMA and MAO, the corresponding catalysts $SiO_2/TMA/Cp_2ZrCl_2$ and $SiO_2/MAO/Cp_2ZrCl_2$ were prepared and tested at ethylene polymerization. Some correlation between the amount and strength of surface LAS of supports, catalysts composition and their activity are discussed. It is proposed that the surface active species are formed at zirconocene interaction with the most strong LAS.

STEPWISE FORMATION OF PROTON HYDRATES $H^+\cdot NH_2O\cdot p$TBP$\cdot Cl^-$ IN TBP SOLUTIONS OF HCl: COMPOSITION, STRUCTURE AND PECULIARITIES OF IR SPECTRA

E.S. Stoyanov

Phys. Chem. Chem. Phys., 1 (1999) pp. 2961-2966.

Stepwise formation of several $H^+\cdot NH_2O\cdot p$TBP proton hydrates in tributyl phosphate (TBP) solutions of HCl has been studied by IR spectroscopy. As the water content in solutions increases, sequential formation of four compounds $(H_3O^+\text{-}Cl^-\cdot TBP)_n$ (**I**), $(H_5O_2^+\cdot Cl^-\cdot TBP)_m$ (**II**), $H_5O_2^+\cdot Cl^-\cdot H_2O\cdot TBP)_p$ (**III**) and $(H_5O_2^+\cdot Cl^-\cdot 2H_2O\cdot TBP)$ (**IV**) has been found. A generic connection between the structures of **I-IV** and particular features of their IR spectra has been established. The proton monohydrate in **I** should not be considered as a hydroxonium ion H_3O^+, but rather as a molecular fragment of a proton disolvate of the $B_1\text{-}H^+\text{-}B_2$ type, where $B_1=H_2O$ and $B_2=Cl^-$. As a stronger proton acceptor in comparison with $FeCl_4^-$ and ClO_4^- ions, the Cl^- anion has a direct contact with the $H_5O_2^+$ cation in **II-IV**. As a result, only H_2O molecules of the first co-ordination sphere of the $H_5O_2^+$ distributed cation are spectroscopically distinguishable from the more distant H_2O molecules of the surroundings. It has been shown that the main features of the IR spectra of the $H_5O_2^+$ cation, including the so-called continuous background absorption (CBA), are due to its intrinsic properties and to the influence of molecules of the first co-ordination sphere that are bound to it. Water molecules of the second and following hydration spheres of the contact ion pair $H_5O_2^+\cdot Cl^-$ do not feel the proton charge and do not affect CBA to a noticeable extent.

MOLECULAR STRUCTURE OF POLYETHYLENE PRODUCED WITH SUPPORTED VANADIUM-MAGNESIUM CATALYST

L.G. Echevskaya, V.A. Zakharov, A.V. Golovin, T.B. Mikenas

Macromol. Chem. Phys., 200 (1999) pp. 119-123.

Molecular structure of polyethylene (PE) produced with supported titanium-magnesium (TMC) and vanadium-magnesium (VMC) catalysts has been studied by IR and ^{13}C NMR spectroscopic methods. It has been shown that PE produced with VMC in the presence of hydrogen differs by a lower content of double bonds and higher branching compared with PE obtained with TMC. Furthermore, branching is observed both in the heptane-soluble low molecular weight fraction and in the high molecular weight fraction of PE. ^{13}C NMR studies of the low molecular weight fraction of PE showed the presence of methyl branches. The content of methyl branches has been estimated for the polymer molecules of different mass. Intramolecular isomerization of the growing polymer chains involving hydrogen seems to be the possible reason for the methyl branches formation.

HIGH-RESOLUTION SOLID-STATE NMR SPECTROSCOPY IN THE STUDIES OF CONVERSIONS OF HYDROCARBONS AND ALCOHOLS ON ZEOLITES

A.G. Stepanov

Russ. Chem. Rev., 68(7) (1999) pp. 563-580.

The review surveys advances in high-resolution solid-state ^1H and ^{13}C NMR spectroscopy applied to studies of conversions of hydrocarbons and alcohols on zeolite catalysts of an acidic nature. The possibilities of NMR spectroscopy in the studies of mechanisms of chemical reactions and analysis of compounds formed *in situ* are considered.

The bibliography includes 134 references.

ACTIVATION OF SMALL ALKANES ON SOLID ACIDS. AN H/D EXCHANGE STUDY BY LIQUID AND SOLID STATE NMR: THE ACTIVATION ENERGY AND INHIBITING EFFECT OF CARBON MONOXIDE

J. Sommer*, D. Habermacher*, R. Jost*, A. Sassi*, A.G. Stepanov, M.V. Luzgin, D. Freude, H. Ernst**, J. Martens***** (*Universite Louis Pasteur, Strasbourg, France; **Universität Leipzig, Leipzig, Germany; ***Katholieke Universiteit Leuven, Heverlee, Belgium)

J. Catal., 181(2) (1999) pp. 265-270.

The regioselective hydrogen/deuterium exchange taking place between isobutane and acidic OH groups of strong solid acids has been investigated both by *in situ* solid state ^{1}H MAS NMR with perdeuteroisobutane and H-ZSM-5 and by liquid ^{1}H and ^{2}H NMR with isobutane on various D_2O exchanged solid acids. The activation energy of the process was estimated from the variable temperature *in situ* ^{1}H MAS NMR kinetic experiments. A drastic inhibition of the hydrogen exchange was observed in all cases when carbon monoxide was present which is rationalized by the interaction of CO with carbocationic reaction intermediates.

^{13}C AND ^{1}H NMR SPECTROSCOPIC CHARACTERIZATION OF TITANIUM(IV) ALKYLPEROXO COMPLEXES $Ti(OOtBu)_n(OiPr)_{4-n}$ WITH n=1, 2, 3, 4

D.E. Babushkin, E.P. Talsi

React. Kinet. & Catal. Lett., 67(2) (1999) pp. 359-364.

Using ^{13}C and ^{1}H NMR spectroscopy, titanium(IV) alkylperoxo complexes $Ti(OOtBu)_n(OiPr)_{4-n}$ with n=1, 2, 3 and 4 were characterized in the reaction of $Ti(OiPr)_4$ with tBuOOH in CH_2Cl_2 and $CDCl_3$.

CHARACTERIZATION OF V_2O_5-TiO_2 CATALYSTS PREPARED BY MILLING BY ESR AND SOLID STATE ^{1}H AND ^{51}V NMR

O.B. Lapina, A.A. Shubin, A.V. Nosov, E. Bosch*, J. Spengler*, H. Knözinger* (*Institut für Physikalische Chemie, Universität München, München, Germany)

J. Phys. Chem., 103(36) (1999) pp. 7599-7606.

The interaction between V_2O_5 and TiO_2 under milling in a ball mill (an alternative procedure of catalysts preparation) was characterized by ^{1}H, ^{51}V MAS and ^{51}V static (wide line) NMR supplemented by simulations of ^{51}V NMR spectra. Additionally, ESR and magnetic susceptibility measurements were carried out for the characterization of the paramagnetic V^{4+} and V^{3+} sites. It has been shown that after milling, two different types of octahedrally coordinated vanadium (V^{5+}) species (V^{5+}(I) and V^{5+}(II)) strongly bonded to TiO_2 are formed. At the same time, the appearance of V^{3+} ions and an increase of their concentration is observed during milling-calcination processes, along with the formation of at least three different types of paramagnetic V^{4+} species corresponding to (i) V^{4+} centers in O-deficient V_2O_{5-x}; (ii) VO^{2+} vanadyl species (V^{4+}(I)) with the vanadium centers in octahedral symmetry with axial distortion; (iii) V^{4+}(II) species with vanadium centers in octahedral symmetry, but with different bond lengths and strengths as compared to V^{4+}(I). Relative amounts of different V^{4+} and V^{5+} species depend on the milling time, the presence of H_2O in the system, and the subsequent calcination procedure (temperature and calcination time). Thus, V^{5+}(I) species formed predominantly during milling, whereas V^{5+}(II) species formed after thermal treatment. For the structural characterization of these species, complete set of the quadrupole and chemical shielding tensor parameters, including relative tensor orientations, have been estimated. This allows us to conclude that octahedral environment of vanadium in V^{5+}(II) species is less distorted than in V^{5+}(I) and in both cases the distortion is less axial than in V_2O_5. Combined NMR, ESR and magnetic susceptibility measurements indicate that all vanadium species (V^{3+}, V^{4+}, and V^{5+}) are isolated from each other on the TiO_2 support.

CHARACTERISATION OF STRONGLY BONDED V(V) SPECIES IN VO_X/TiO_2 CATALYST BY STATIC AND MAS SOLID STATE ^{51}V NMR SPECTROSCOPY

A.A. Shubin, O.B. Lapina, V.M. Bondareva

Chem. Phys. Lett., 302(3-4) (1999) pp. 341-346.

^{51}V static and MAS NMR spectroscopy of central transition is shown to be an effective method for the characterization of strongly bonded V(V) species in VO_X/TiO_2 catalysts. Simultaneous determination of quadrupole and CSA tensors parameters (i.e. C_Q, η_Q, δ_σ, η_σ) from both static and MAS NMR spectra of central transition permits to extract all NMR parameters with a reasonable accuracy. For the first time large ^{51}V quadrupolar constant (14-16 MHz) has been obtained for strongly bonded V(V) species in supported vanadia catalyst, whereas CSA tensor principal components were found to be very close to those for bulk vanadium(V) oxide.

EFFECT OF MILLING OF V_2O_5 ON THE LOCAL ENVIRONMENT OF VANADIUM AS STUDIED BY SOLID STATE ^{51}V NMR

A.A. Shubin, O.B. Lapina, E. Bosch*, J. Spengler*, H. Knözinger* (*Institut für Physikalische Chemie, Universität München, München, Germany)

J. Phys. Chem., 103(16) (1999) pp. 3138-3144.

The local environment of the vanadium nucleus in V_2O_5 after milling in a ball mill was characterized by the combination of static (wide line) and MAS ^{51}V NMR techniques together with theoretical simulations of NMR spectra. An important information on the quadrupole and chemical shielding tensors, including their relative orientation and the distribution of magnetic resonance parameters, is discussed for the vanadium nucleus in V_2O_5 after milling. Special attention was given to the formation of paramagnetic V^{3+} and V^{4+} ions and their influence on ^{51}V NMR spectra of diamagnetic V^{5+} in milled samples. It was shown that paramagnetic V^{3+} ions are responsible for the loss (up to about 70%) of the intensity in ^{51}V NMR spectra. There is no significant influence of paramagnetic V^{4+} on the local environment of V^{5+} in large agglomerates of V_2O_5 presumably because the V^{4+} is located in small patches of V_6O_{13} - like shear structures. V^{4+} and V^{3+} ions are most likely distributed inhomogeneously.

HIGH-TEMPERATURE MULTINUCLEAR MAGNETIC RESONANCE STUDIES OF VANADIA CATALYSTS FOR SO_2 OXIDATION

O.B. Lapina, V.V. Terskikh, A.A. Shubin, K.M. Eriksen*, R. Fehrmann* (*Technical University of Denmark, Lyngby, Denmark)

Colloids and Surfaces A: Physicochem. & Engin. Aspects, 58(1-2) (1999) pp. 255-271.

Multinuclear ^{23}Na, ^{39}K, ^{133}Cs, ^{17}O, ^{51}V NMR studies of the V_2O_5-$M_2S_2O_7$ (M=Na, K, Cs) systems in the temperature range 20-650 °C have been performed for vanadium oxide mole fractions, $X(V_2O_5)$ in the range 0–0.5. At ambient temperature the melt - quenched glassy samples exhibit a three-dimensional network of vanadium oxo sulfate complexes. Octahedral coordination of vanadium atoms is found in the glassy samples at all compositions studied, in accordance with ^{51}V NMR spectra. Alkali cations are distributed randomly within an anion network. At high vanadium concentration the structure of vanadium sites in the glasses is very similar to those found in $Cs_4(VO)_2O(SO_4)_4$, whereas for small vanadium contents the vanadium sites are separated by additional sulfate ligands. Heating to the glass-transition temperature, T_g, and above, leads to jumps of the alkali cations between different sites. The mobility of pyrosulfate groups is accompanied by dissociation to SO_4^{2-} and SO_3. At elevated temperature the mobility of SO_3 molecules is sufficient to participate in chemical exchange with the sulfate groups of the network. Addition/splitting mechanism involving SO_3 has been proposed to be responsible for random fluctuations of the ^{51}V nuclear quadrupole tensor at given vanadium network sites with characteristic correlation time τ_c. For $10^{-8} < \tau_c < 10^{-6}$s the ^{51}V NMR line became unobservable. For Cs-containing samples increase of the temperature is accompanied by fast crystallization. In this case cooperative motion of the anion network, caused by bond breaking and bond formation, dominates at temperatures around T_g. The NMR spectra of alkali metals were found to be very characteristic for the structure of the network formed in melts between V_2O_5 and $M_2S_2O_7$. ^{17}O, ^{23}Na, ^{39}K, ^{133}Cs spectra recorded at 500 °C point to the formation of different species and rapid exchange between them. A change of the local vanadium environment in melts takes place at $X(V_2O_5) \sim 0.1$ and 0.3 most probably due to the formation of dimeric and polymeric V(V) complexes, possibly $(VO)_2O(SO_4)_4^{4-}$ and $(VO_2SO_4)_n^{n-}$. Correlation time of ^{51}V quadrupole tensor fluctuations for samples with $X(V_2O_5) \sim 0.1$-0.5 is higher than 10^{-8} s, which makes ^{51}V NMR spectra unobservable in the region 400-500°C, whereas for more dilute samples, τ_c is determined mainly by the size of the vanadium-sulfate species making ^{51}V spectra of these samples observable. The dependence of ^{51}V chemical shift on the vanadium concentration indicates a change of coordination number in the system V_2O_5-$M_2S_2O_7$ from tetrahedral in pure V_2O_5 to octahedral in dilute samples. The structure of supported catalysts is very similar to the structure of bulk melts (V_2O_5-$M_2S_2O_7$), the main difference revealed is lower mobility of all structural units (such as metal cations, SO_4^{2-} and SO_3) for the supported melts.

PROGRESS ON THE MECHANISTIC UNDERSTANDING OF SO_2 OXIDATION CATALYSTS

O.B. Lapina, B.S. Bal'zhinimaev, S. Boghosian*, K.M. Eriksen, R. Fehrmann**** (*University of Patras and Institute of Chemical Engineering and High Temperature Chemical Processes, Patras, Greece; **Technical University of Denmark, Lyngby, Denmark)

Catal. Today, 51 (1999) pp. 469-479.

For almost a century vanadium oxide based catalysts have been the dominant materials in industrial processes for sulfuric acid production. A vast body of information leading to fundamental knowledge on the catalytic process was obtained by Academician G.K. Boreskov [Catalysis in Sulfuric Acid Production, Goskhimizdat, Moscow, 1954 (in Russian)]. In recent years these catalysts have also been used to clean flue gases and other SO^{2-} containing industrial off-gases. In spite of the importance and long utilization of these industrial processes, the catalytic active species and the reaction mechanism have been virtually unknown until recent years.

It is now recognized that the working catalyst is well described by the molten salt/gas system $M_2S_2O_7$-$MHSO_4$-V_2O_5/SiO_2-O_2-SO_3-H_2O-CO_2-N_2 (M=Na, K, Cs) at 400-600 °C and that vanadium complexes play a key role in the catalytic reaction mechanism.

Multiinstrumental investigations that combine the efforts of four groups from four different countries has been carried out on the model system as well as on working industrial catalysts. Detailed information has been obtained on the complex and on the redox chemistry of vanadium. Based on this, a deeper understanding of the reaction mechanism has been achieved.

^{129}Xe NMR STUDY OF XENON ADSORBED ON $V_2O_5/TiO_2/SiO_2$ CATALYSTS

V.V. Terskikh, M. Siedl*, H. Knözinger* (*Institut für Physikalische Chemie, Universität München, München, Germany)

Colloids and Surfaces A: Physicochem. & Engin. Aspects, 158(1-2) (1999) pp. 249-254.

^{129}Xe NMR spectroscopy was used to study xenon adsorption on $V_2O_5/TiO_2/SiO_2$ catalysts with varying ratio of supported vanadia and titania components. These catalysts were chosen because of their strong electron-accepting (Lewis) acidity. Xenon atoms despite their large polarizability exhibit weak basic properties. The specific interactions of adsorbed xenon atoms with the strongest Lewis acidic sites were detected with ^{129}Xe NMR. It was demonstrated that a possibility of such interactions should be taken properly into account when studying porous solids by the adsorption of gaseous xenon.

^{27}Al NMR MAS STUDY OF THE SURFACE ALUMINIUM COMPLEXES FORMED IN REACTION OF ORGANOALUMINIUM COMPOUNDS WITH SUPPORTED $TiCl_4$ /$MgCl_2$ CATALYST

A.G. Potapov, V.V. Terskikh, V.A. Zakharov, G.D. Bukatov

J. Molec. Catal. A: Chemical, 145 (1999) pp. 147-152.

^{27}Al NMR MAS method has been used to study the surface aluminum compounds forming during the treatment of supported $TiCl_4/MgCl_2$ catalyst with organoaluminum compounds (OAC) of various composition ($AlEt_3$, $AlOct_3$, $AlEt_2Cl$). Dialkylaluminium chloride has been found to be the main surface compound in the case of trialkylaluminium. Three surface species of dialkylaluminium chloride have been identified: one of them corresponds to 5-coordinated aluminum; the other two correspond to 6-coordinated aluminum with different alkyl-to-chlorine ratio. The relative amounts of surface species depend on the conditions of OAC reaction with catalysts and OAC composition. After polymerization of ethylene or propylene on trioctylaluminum-treated catalysts (polymer yield ca. 1 g/1 g catalyst), the signals of 5-coordinated aluminum disappear from the ^{27}Al NMR spectra of the catalysts.

^{207}Pb NMR STUDY OF NOVEL Pb-Pb CHEMICAL BONDING IN LEAD MONOXIDES, α-PbO AND β-PbO

S.P. Gabuda*, S.G. Kozlova*, V.V. Terskikh, C. Dybowski, G. Neue***, D. Perry*****
(*Institute of Inorganic Chemistry, Novosibirsk, Russia; **University of Delaware, Newark, Poland)

Chem. Phys. Lett., 305(5-6) (1999) pp. 353-358.

α-PbO and β-PbO have been studied with ^{207}Pb NMR MAS spectroscopy in the solid state. The

^{207}Pb NMR chemical-shift tensor in α-PbO is axial, with principal values $\delta_{\perp} = 3030$, $\delta_{||} = -270$ and $\delta_{iso} = 1930$ ppm. In β-PbO, the ^{207}Pb NMR powder spectrum is approximately represented by a single non-axial tensor with principal values δ^{11}=2820, δ_{22}=2760, δ_{33}=-1000,

δ_{iso}=1525 ppm and η=0.024, although there appears to be an overlap of two very similar patters. Using normal-coordinate analysis, the ^{207}Pb magnetic shielding tensor is represented as a sum of contributions from separate Pb-O and Pb-Pb interactions. It is shown that Pb-O and Pb-Pb contributions are of the same order of magnitude. A potential underlying relativistic reason for the abnormal Pb-Pb interaction is revealed.

Ti(IV) STATE IN CONCENTRATED HYDROCHLORIC ACID SOLUTIONS AS STUDIED BY MULTINUCLEAR MAGNETIC RESONANCE

M.A. Fedotov, G.A. Zenkovets, V.Yu. Gavrilov

Russ. J. Inorg. Chem., 44(6) (1999) pp. 911-914.

The state of Ti(IV) in hydrochloric acid solutions was studied by ^{2}H, ^{17}O, ^{35}Cl, and ^{49}Ti NMR. In solutions, titanium is primarily incorporated into the $TiOCl_4(H_2O)_x$ complexes (x=0, 1), which represent the monomer or low-nuclearity oligomers, including the dimers with *trans-* and *cis-*arranged oxygen atoms and bridging chloro ligands.

NUCLEAR MAGNETIC RESONANCE IN ANALYTICAL CHEMISTRY OF INORGANIC SUBSTANCES IN SOLUTION

M.A. Fedotov

J. Analyt. Chem., 54(1) (1999) pp. 15-18.

The potentialities of nuclear magnetic resonance (NMP) for the chemical analysis of liquid samples are considered. The distinguishing features of NMR and its advantages and limitations are discussed. Ways for overcoming the limitations of NMR are proposed and examples of analysis demonstrating the advantages of NMR over other methods of chemical analysis are presented.

^{17}O AND ^{103}Rh NMR STUDY OF RHODIUM(III) AQUO AND AQUO-SULFATO COMPLEXES IN AQUEOUS AND SULFATE MEDIA

M.A. Fedotov, V.A. Shipachev*, L.M. Levchenko*
(*Institute of Inorganic Chemistry, Novosibirsk, Russia)

Russ. J. Coord. Chem., 25(1) (1999) pp. 31-35.

Solutions of Rh(III) aquo complexes obtained by different methods were studied by the ^{103}Rh and ^{17}O NMR methods. In combination with the electronic absorption spectra of these solutions, their ^{103}Rh and ^{17}O NMR spectra indicate the presence of an admixture of polynuclear complexes, which increases upon concentration. It is shown that, in the presence of H_2SO_4, polymerization reactions occur in parallel with the substitution of HSO_4^- ions for the water molecules in the Rh(III) aquo ion; the number of coordinated water molecules regularly decreases as SO_4^{2-} is added.

HETEROPOLY ACIDS IN DILUTE SOLUTIONS BY ^{31}P NMR SPECTROSCOPY

G.M. Maksimov

Russ. J. Inorg. Chem., 43(9) (1998) pp. 1454-1456.

^{31}P NMR spectra were recorded from 0.01 to 0.0003 M solutions of six phosphorus-containing heteropolyacids (HPAs) in water and organic solvents. The HPAs studied are not transformed in the organic solvents examined. In water solutions, $H_5PW_{11}TiO_{40}$ and $H_6P_2Mo_{18}O_{62}$ HPAs are also stable in the range of concentrations studied. The other HPAs experience partial or complete destruction depending on dilution. $H_6P_2W_{18}O_{62}$ is degraded by a dissociative mechanism; $H_3PW_{12}O_{40}$, by an alkaline-hydrolysis mechanism; and $H_3PMo_{12}O_{40}$ and $H_6P_2W_{21}O_{71}$ degradation follows a combination mechanism.

NMR STUDY OF TRANSFORMATIONS OF MONOCHLORDIMETHYL ETHER IN THE PRESENCE OF TIN(IV) CHLORIDE

V.P. Talsi, S.V. Ignashin

Russ. J Appl. Chem., 72(10) (1999) pp. 1832-1835.

^{1}H and ^{13}C NMR were used to study solutions of Tin(IV) chloride in commercial monochlordimethyl ether. Comparison of NMR spectra of these solutions with those of similar solutions of $TiCl_4$ used in production of anion exchangers allowed to get more specific information on the side reactions of the components of chloromethylating systems, affecting the characteristics of ion-exchange resins.

^{1}H NMR STUDY OF TRANSFORMATIONS OF MONOCHLORDIMETHYLIC ETHER IN THE PRESENCE OF ZINC CHLORIDE

V.P. Talsi, S.V. Ignashin

Russ. J. Appl. Chem., 72(10) **(**1999) pp. 1836-1838.

^{1}H NMR method was used to study solvolytic reactions occurring in commercial monochlordimethyl ether in the solution of $ZnCl_2$. The reason is discussed for the high selectivity of $ZnCl_2$ in comparison with titanium(IV) chloride as the chloromethylation catalyst in- production of ion-exchange resins.

INTRINSIC MICROPOROSITY AND GAS TRANSPORT IN POLYPHENYLENE OXIDE POLYMERS

O.M. Il'initch, V.B. Fenelonov, A.A. Lapkin*,
L.G. Okkel', V.V. Terskikh, K.I. Zamaraev
(*University of Bath, Bath, UK)

Micropor. & Mesopor. Mater., 31 (1999) pp. 97-110.

Glassy polymers of the polyphenylene oxide series (PPOs) were investigated using the low-temperature nitrogen adsorption and ^{129}Xe NMR techniques. The experimental data are indicative of a developed system of interconnected microcavities existing in the polymers. The intrinsic microporosity of PPOs is most probably formed by a continuous three-dimensional network of molecular-sized interstices between the rigid-chain macromolecules. These supposedly constitute the free volume of the polymers. The micropores are likely to be of the 'throat and cavity' type, where a cavity may possess several throats. Effective diameters of the throats were estimated to be approximately 0.4 nm at 77 K. It is believed that transport of gas molecules occurs through these micropores. Variations in gas permeability and sorption characteristics, which are dependent on the previous history of the polymer, were investigated and interrelations between these features analyzed. Crystallinity vs. gas permeability relationships for PPO membranes was studied. It is concluded that crystalline and amorphous phases of polyphenylene oxides have similar gas permeabilities for the experimental conditions employed. Analysis of the experimental data shows that it is justified to look upon polyphenylene oxides as polymeric analogues of solid microporous adsorbents.

TRANSFORMATIONS OF HEXANITROIRIDATE(III) ION IN CHLORIDE AND HYDROCHLORIC ACID SOLUTIONS

A.B. Venediktov*, M.A. Fedotov, S.V. Korenev*
(*Institute of Inorganic Chemistry, Novosibirsk, Russia)

Russ. J. Coord. Chem., 25(4) (1999) pp. 266-270.

^{15}N NMR and electronic spectroscopy were used to study transformations of a hexanitroiridate(III) ion in neutral chloride and hydrochloric acid solutions at 100 ^{o}C or at boiling. In neutral solutions, the nitrate ions are replaced by Cl^- to form tetranitro, trinitro, and dinitro derivatives, among which *trans*-$[Ir(NO_2)_4Cl_2]^{3-}$ and *fac*-$[Ir(NO_2)_3Cl_3]^{3-}$ are the most kinetically stable. Quantitative transformation of $[Ir(NO_2)_6]^{3-}$ into hexachloro complexes in hydrochloric acid (6–12 M) solutions takes from 40 to 60 h. The conversion of $[IrNO_2Cl_5]^{3-}$ into hexachloroiridate ion is the rate-limiting step of the process. The reaction with hydrochloric acid in the presence of urea results in fast and quantitative transformation of $[Ir(NO_2)_6]^{3-}$ into hexachloroiridate ions without the accumulation of the nitrate ions in solution.

DETECTION OF EPR SPECTRA IN S=2 STATES OF Mn^{III}(SALEN) COMPLEXES

K.P. Bryliakov, D.E. Babushkin, E.P. Talsi

Mendeleev Commun., 1 (1999) pp. 29-32.

The first detection of EPR signals of Mn^{III}(Salen) complexes (R,R)-(-)-*N,N'-bis*(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexanediaminomanganese(III) cloride **(1)** and *N,N'*-Bis(salicylidene) ethylenediaminomanganese(III) cloride (**2**) is described. These signals were used for the characterization of intermediates in catalytic epoxidation in Jacobsen's catalytic system (Mn^{III}Salen + PhIO).

THE METALLOCENE/METHYLALUMINOXANE CATALYSTS FORMATION: EPR SPIN PROBE STUDY OF LEWIS ACIDIC SITES OF METHYLALUMINOXANE

E.P. Talsi, N.V. Semikolenova, V.N. Panchenko,
A.P. Sobolev, D.E. Babushkin, A.A. Shubin,
V.A. Zakharov

J. Molec. Catal. A: Chemical, 139(2-3) (1999) pp. 131-137.

Using stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) as a spin probe, Lewis acidic sites of methylalumoxane (MAO) were monitored. It was found, that MAO contains at least two types of acidic sites. TEMPO, coordinated to the first ones, exhibited triplet of sextets in EPR spectrum with hyperfine structure from nitrogen (a_N=19.6 G) and aluminum (a_{Al}=1.74 G). TEMPO, bound to the second type of acidic sites, displays broadened triplet (a_N=19.6 G). The amount of the acidic sites observed was estimated to be ca. 1 per 30-100 aluminum atoms of MAO. The acidic sites exhibiting triplet of sextets in the EPR spectrum could be attributed to coordinately unsaturated aluminum in $MeAlO_2$ environment, and those, exhibiting broadened triplet - to aluminum atoms in Me_2AlO environment.

ESR STUDY OF RADICAL GENERATION IN THE COURSE OF CATALYTIC PYROLYSIS OF HYDROCARBONS

N.A. Vasilieva, V.K. Ermolaev, S.Yu. Kuz'mitskaya

Kinetics & Catalysis, 40(1) (1999) pp. 100-104.

The possibility of alkyl radical generation on the heterogeneous catalysts for hydrocarbon pyrolysis is studied using radical freezing in the resonator of an ESR spectrometer. The pyrolysis of *n*-butane and *n*-undecane on the magnesium oxide samples with a defect structure is investigated. The higher the catalyst activity during pyrolysis, the higher its ability to generate additional ethyl radicals into the gas phase. The results provide the experimental evidence for the concept of the catalysis sphere based on the radical–chain theory of the heterogeneous–homogeneous reactions of the catalytic pyrolysis of hydrocarbons.

ESR DETECTION OF COPPER ION CLUSTERS IN THE Cu-Zn-Al OXIDE CATALYSTS FOR METHANOL SYNTHESIS

A.A. Altynnikov, V.F. Anufrienko, A.Ya. Rozovskii*, G.I. Lin*, E.V. Lunina, V.A. Sadykov** (*Topchiev Institute of Petrochemical Synthesis, Moscow, Russia; **Moscow Lomonosov State University, Moscow, Russia)

Kinetics & Catalysis, 40(1) (1999) pp. 117-120.

It was found by ESR spectroscopy that the treatment of the Cu–Zn–Al oxide catalysts for methanol synthesis with pyridine did not produce isolated pyridinate complexes. In this case, three types of copper clusters were formed; two of them were assigned to the ordered Jahn–Teller clusters. It was suggested that the cluster structures consist of the Cu^{2+}–O–M–O–Cu^{2+} oxide fragments (where M is the Al^{3+}, Zn^{2+}, and Cu^{2+} ion), which were not decomposed upon treatment with pyridine.

ESR STUDY OF THE STABILIZATION OF V^{4+} IONS IN TiO_2 (ANATASE)

A.A. Altynnikov, G.A. Zenkovets, V.F. Anufrienko

React. Kinet. & Catal. Lett., 66(1) (1999) pp. 85-90.

ESR data on vanadium-titanium oxide heated at 300-550 °C indicate that V^{4+} ions are stabilized in the substitution sites of TiO_2 (anatase).

ESR STUDY OF REDUCED VANADIUM-TITANIUM OXIDE CATALYSTS

A.A. Altynnikov, G.A. Zenkovets, V.F. Anufrienko

React. Kinet. & Catal. Lett., 67(2) (1999) pp. 273-279.

Reduction of vanadium-titanium oxide catalysts with hydrogen in the temperature range of 150-450 °C results in the increase of the content of V^{4+} ions in substitution positions of TiO_2 with the anatase structure. The temperature increase up to 250 °C results in the growth of the spectral intensity of V^{4+} associates in substitution positions of anatase. At higher treatment temperatures their intensity decreases due to the formation of VO_2 fragments in anatase. At 400 °C and higher temperatures a solid solution of V^{4+} ions in rutile is formed.

AN EFFECTS OF RESTRICTED AVERAGING IN ESR SPECTRA OF HIGHLY ORIENTED PARAMAGNETIC CENTERS

O.N. Mart'yanov, V.F. Yudanov

J. Struct. Chem., 40(6) (1999) pp. 1085-1090.

A model system Fe^{3+} – natrolite was used for experimental study of the process of generation of noise-like magnetic resonance spectra observed before for polycrystal samples of zeolites and for a number of other fine dispersed systems. The experimental data showed that the observed noise-like spectra are non-averaged set of lines produced by randomly oriented microcrystals. Physical conditions of the emergence of noise-like spectra were formulated, and methods were suggested for extracting previously inaccessible information.

INTRINSIC NOISELIKE SPECTRA OF THE MICROWAVE CAVITY OF AN ELECTRON-SPIN-RESONANCE SPECTROMETER

O.N. Mart'yanov, V.F. Yudanov

Instrum. & Experim. Techn., 1 (1999) pp. 69-71.

Noiselike spectra of the microwave cavity of an electron-spin-resonance (ESR) spectrometer are investigated. A hypothesis about the ferromagnetic origin of the observed absorption based on available experimental data is suggested. It is shown that the presence of noiselike spectra of the cavity walls limits the sensitivity of modern ESR spectrometers.

RESONANCE CAPTURE OF ELECTRONS AND ACIDITY OF SOME COMPOUNDS IN GAS PHASE

V.S. Shmakov*, I.I. Furley*, A.G. Tolstikov,
E.M. Vyrypaev* (*Institute of Organic Chemistry, Ufa, Russia)

Bashkirian Chemical J., 6(2-3) (1999) pp. 37-40.

The acidity of the molecules in the gas phase can be determined by the maximum of the curves of effective output of $(M\text{-}H)^-$ ions generated as a result of the resonance electron capture.

XPS OBSERVATION OF OH GROUPS INCORPORATED IN Ag (111) ELECTRODE

D.Yu. Zemlyanov, E.R. Savinova, A. Scheybal*,
K. Ddoblhofer*, R. Schlögl* (*Fritz-Haber-Institut der Max-Planck Gesellschaft, Berlin, Germany)

Surf. Sci., 418(2) (1998) pp. 441-456.

An Ag(111) single crystal electrode emersed from NaF + NaOH electrolyte (pH 11) under anodic polarization has been studied *ex situ* by means of X-ray photoelectron spectroscopy (XPS). “Underpotential” oxidation has been found at +0.2 and 0.0 V vs. Hg/HgO, that is by 0.2-0.4 V more negative than the reversible potential of the Ag_2O phase formation. The generation of a number of surface and bulk oxygen-containing species, including surface Ag_2O-like species, surface and bulk OH groups (OH_{ads} and OH_{bulk}, respectively), surface and bulk atomic oxygen, has been observed on the emersed electrode.

The present work provides the first direct evidence of the hydroxide incorporation in the bulk of an Ag(111) electrode in the course of underpotential oxidation. OH_{bulk} is characterized by a O 1s peak at approximately 532.8 eV, while surface OH_{ads} manifests itself as the peak at ca. 531.6 eV. The origin of the positive binding energy shift is discussed. Surface and bulk OH groups demonstrate substantially different thermal stability. Surface species desorb below 470 K, while dissolved OH groups exhibit high stability towards prolonged annealing in vacuum at temperatures up to 750 K; they remain in the near-surface region even after sputtering by Ar^+ and He^+ ions. The oxide-like species is characterized by the O 1s peak at 529.5 eV and decomposes after heating in vacuum at a temperature of about 470 K. The He(I) and He(II) UP spectra of the emersed electrode along with the XPS data provide evidence that the coverage with surface oxide is less than 1 ML. A tentative scheme of Ag(111) underpotential oxidation is discussed.

PLATINUM COLLOID SUPPORTED ON GRAPHITE: X-RAY PHOTOELECTRON SPECTROSCOPY STUDY

Sh.K. Shaikhutdinov, M. Schildenberger*,
M. Noeske*, G. Mestl** (*Universität Ulm, Ulm/Donau, Germany; **Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany)

React. Kinet. & Catal. Lett., 67(1) (1999) pp. 129-135.

Two states of platinum Pt^o and $Pt^{+\delta}$, with the binding energy of the $Pt(4f_{7/2})$ line at 71.4 ± 0.1 and 72.2 ± 0.3 eV, are revealed by XPS in colloidal platinum deposited onto graphite. The latter state is assigned to surface Pt atoms partially oxidized due to the interaction with water and/or oxygen-terminated sulfonate group in an organic shell. The colloid deposition is found to be temperature dependent with the activation energy of ~40 kJ/mol.

NEUTRON DIFFRACTION STUDY OF THE REDUCED COPPER CHROMITE STRUCTURE

L.M. Plyasova, I.Yu. Molina, T.A. Krieger,
T.M. Yurieva, L.P. Davydova, A.M. Balagurov

Surface, 11 (1999) pp. 28-39.

Neutron diffraction study of copper chromite activated by hydrogen at 270 °C during a few hours was performed. It was shown that under these conditions cation deficient spinel stabilized by OH groups was formed. The structural formula of this metastable phase, which decomposes onto Cu^o and $\alpha\text{-}Cr_2O_3$ under hydrogen flow if temperature is increased, was refined by using the Rietveld method.

STUDY OF THE INTERACTION PRODUCTS OF SOME N- AND O-CONTAINING COMPOUNDS WITH HIGHLY DISPERSED COPPER(II) HYDROXIDE

G.L. Elizarova, D.I. Kochubey, V.V. Kriventsov,
G.V. Odegova, L.G. Matvienko, V.N. Kolomiichuk,
V.N. Parmon

J. Colloid. & Interface Sci., 213(1) (1999) pp. 126-132.

Composition and structure of the surface compounds formed after interaction between $Cu(OH)_2$ supported on aerosil and bpy, py, PhOH, and H_2O_2 are studied. The EXAFS and electron spectroscopy methods show the main part of copper ions to remain in a hydroxide surrounding, whose structure does not change practically and does not depend on the nature of the extra ligands used. The colloidal $Cu(OH)_2$ stabilized by starch is found to reveal the same properties as the supported one, but differs by greater sizes of hydroxide particles.

THE STRUCTURE OF AMORPHOUS BULK AND SILICA-SUPPORTED COPPER(II) HYDROXIDES

V.V. Kriventsov, D.I. Kochubey, G.L. Elizarova, L.G. Matvienko, V.N. Parmon

J. Colloid. & Interface Sci., 215(1) (1999) pp. 23-27.

The data obtained show that at pH 7 copper(II) ions are adsorbed on a SiO_2 surface as polymeric species of hydroxide nature. The structure of these species is similar to that of the bulk amorphous copper hydroxide. The amorphous state of supported $Cu(OH)_2$ is caused by a small (ca. 11 Å) size of the surface particles. In contrast, the over stoichiometric water molecules seem to act as "amorphizers" of the bulk copper hydroxide. The structures of the bulk and dispersed amorphous copper(II) hydroxide were determined. The amorphous $Cu(OH)_2$ has a layered structure close to the structure of the crystalline hydroxide, but the layers in the amorphous hydroxide are shifted toward one another approximately for of the "c" period of the lattice.

CRYOGENIC EXAFS INVESTIGATIONS OF THE SHORT-RANGE STRUCTURAL ENVIRONMENT OF GALLIUM IN $PbO-Ga_2O_3$ GLASSES

J. Heo*, Y.G. Choi, V.A. Chernov** (*Pohang University of Science and Technology, Pohang, Kyungbuk, South Korea; **Electronics and Telecommunications Research Institute, Taejon, South Korea)

J. Non-Crystal. Solids, 256-257 (1999) pp. 119-123.

Gallium K-edge extended X-ray absorption fine structure (EXAFS) spectra of $PbO-Ga_2O_3$ glasses were recorded at liquid-nitrogen temperature (77 K) to understand the coordination scheme of gallium in these glasses. Four oxygens were found to be bonded to each Ga, forming GaO_4 tetrahedra with an average bond distance of 1.855±1.862 Å. Assuming a non-Gaussian distribution of Ga-O bond distances provided better results with a smaller *R*-factor compared to the Gaussian counterpart. Two-subshell fitting indicated that oxygens with Ga-O bond distance of ~1.87 Å are bonded to three cations, while the shorter Ga-O bonded oxygens are two-coordinated.

EXAFS SPECTROSCOPIC STUDY OF $PbO-Bi_2O_3-Ga_2O_3$ GLASSES

Y.G. Choi*, K.H. Kim*, V.A. Chernov, J. Heo**
(*Electronics and Telecommunications Research Institute, Taejon, South Korea; **Pohang University of Science and Technology, Pohang, Kyungbuk, South Korea)

J. Non-Crystal. Solids, 259 (1999) pp. 205-211.

Extended X-ray absorption fine structure (EXAFS) spectra for ternary heavy metal oxide glasses with compositions of $(1-x)(0.75PbO + 0.25Ga_2O_3) + xBi_2O_3$ where x increased from 0 to 0.4 in 0.1 increments, indicate the formation of GaO_4 tetrahedral unit with Ga-O bond length of ~1.87 Å in all glasses. Pb also forms both PbO_3 and PbO_4 polyhedra, but the average oxygen coordination number around lead decreases from 3.50 to 2.96 with decreasing PbO concentration. From the EXAFS data it was concluded that Bi forms BiO_5 and BiO_6 units as it does in the α-Bi_2O_3 crystal. Two distinct Bi-O distances of ~2.18 and ~ 2.46 Å were resolved. Formation of each type of the polyhedra results in shortage of total oxygen ions for forming two-fold coordinated oxygens and as a result, formation of three-coordinated oxygens becomes necessary.

Pb LIII-EDGE EXAFS AND XANES ANALYSES ON THE STRUCTURAL ENVIRONMENT OF LEAD IN $PbO-Ga_2O_3$ GLASSES

Y.G. Choi*, K.H. Kim*, V.A. Chernov, J. Heo**
(*Electronics and Telecommunications Research Institute, Taejon, South Korea; **Pohang University of Science and Technology, Pohang, Kyungbuk, South Korea)

J. Non-Crystal. Solids, 246 (1999) pp. 128-135.

Pb LIII-edge absorption spectra of $PbO-Ga_2O_3$ glasses were analyzed and the local environment of lead in glasses was proposed. A single-shell fitting of Pb LIII-edge EXAFS (extended X-ray absorption fine structure) spectra of three $PbO-Ga_2O_3$ glasses showed that the Pb-O bond distances were between 0.229 and 0.231 nm with the oxygen coordination numbers between 3.3 and 3.5. Comparison of the absorption peaks in the pre-edge region of the Pb LIII-edge XANES (X-ray absorption near edge structure) spectra between glasses and other reference crystals indicated that the Pb^{2+} ions form either PbO_3 or PbO_4 polyhedra. These polyhedra are connected through either two- or three-coordinated oxygen similar to the configuration in $PbSiO_3$ crystal.

DEVELOPMENT OF AEROGEL CHERENKOV COUNTERS WITH WAVELENGTH SHIFTERS AND PHOTOTUBES

M.Yu. Barnykov*, A.R. Buzykaev*, A.F. Danilyuk, S.F. Ganzhur*, I.I. Goldberg*, G.M. Kolachev*, S.A. Kononov*, E.A. Kravchenko*, V.I. Mikerov*, T.M. Muraviova*, G.D. Minakov*, A.P. Onuchin*, A.V. Sidorov*, V.A. Tayursky* (*Budker Institute of Nuclear Physics, Novosibirsk, Russia)

Nuclear Instrum. & Methods in Phys. Res. A, 419 (1998) pp. 584-589.

The paper is devoted to the development of Cherenkov counters based on the Aerogel, wavelength SHIfters and PHototubes (ASHIPH). The microchannel plate photomultipliers with multialkali photocathode are used. Data on the PMT multiplication gain in the magnetic field and noise are presented. Main parameters of wavelength shifters, aerogel SAN-96, and PTFE reflector are measured. The project of the ASHIPH system for the KEDR detector is developed. The counters will operate in 1.8~T magnetic field and will separate mesons in the momentum region of 0.6-1.5 GeV/c. As compared to the option of the direct light collection on the photomultiplier, this method gives a possibility to diminish the number of PMTs essentially. The possibility to increase a light collection in the ASHIPH detector owing to combination of 'blue' and 'green' shifters is discussed.

MEASUREMENT OF OPTICAL PARAMETERS OF THE AEROGEL

A.R. Buzykaev*, A.F. Danilyuk, S.F. Ganzhur*, E.A. Kravchenko*, A.P. Onuchin* (*Budker Institute of Nuclear Physics, Novosibirsk, Russia)

Nuclear Instrum. & Methods in Phys. Res. A, 433 (1999) pp. 396-400.

The work is devoted to the measurement of optical parameters of aerogel, which can be used as Cherenkov light radiator. The refractive index, the light scattering and absorption lengths, the variation of the refractive index inside an aerogel block were measured for the aerogel produced conjointly by the Institute of Catalysis and Institute of Nuclear Physics (Novosibirsk). The consideration on atomic and nuclear properties of aerogel is presented.

OXYGEN PRESSURE DEPENDENCE OF THE α-Fe_2O_3 (0001) SURFACE STRUCTURE

Sh.K. Shaikhutdinov, W. Weiss* (*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany)

Surf. Sci., 432(3) (1999) pp. L6270-L634.

The dependence of the α-Fe_2O_3 (0001) hematite surface structure on ambient oxygen gas pressure was investigated with scanning tunneling microscopy and low energy electron diffraction. For this, thin epitaxial α-Fe_2O_3 (0001) films grown onto a Pt(111) substrate were prepared in oxygen partial pressures between 10^{-6} and 1 mbar at temperature around 830 ^{o}C. In high pressures of 1 mbar an oxygen-terminated surface structure covers almost the whole sample surface. At pressures between 10^{-4} and 10^{-1} mbar comparable amounts of oxygen and iron-terminated surface areas coexist in neighboring domains. The lateral size of these domains decreases from values of 200-900 Å for pressures between 10^{-3} and 10^{-1} mbar to values around 30 Å at 10^{-4} mbar. At 10^{-5} mbar the oxygen-terminated surface areas completely vanish and an iron-terminated α-Fe_2O_3 (0001) surface structure is formed, which is partly covered by disordered patches with lateral sizes of 10-20 Å. Further decreasing the oxygen pressure to 10^{-6} mbar results in a partial reduction of the surface region and the formation of coexisting α-Fe_2O_3 (0001) and FeO_{1-x} (111) domains that are arranged in an ordered manner forming a superstructure known as ‘biphase structure’.

TEMPERATURE DEPENDENCE OF CHAIN INITIATION IN PYROLYSIS OF PROPANE STUDIED BY DIRECT MASS-SPECTROMETRIC DETECTION OF METHYL RADICALS

A.Yu. Gladky, V.K. Ermolaev, V.N. Parmon

React. Kinet. & Catal. Lett., 67(1) (1999) pp. 183-189.

Methyl radicals have been detected by direct mass-spectrometric detection of radicals in pyrolysis of propane under stationary conditions at 500 Pa in a flow quartz reactor. The process is shown to be homogeneously initiated, the surface of quartz not affecting the propane dissociation under the conditions employed.

MECHANISM OF THE ION DIMER FORMATION IN SECONDARY ION MASS SPECTROMETRY

V.P. Ivanov, S.N. Trukhan, A.I. Borodin

Intern. J. Mass Spectrom., 188 (1999) pp. 183-187.

The influence of temperature on the emission of the Ni_2^+ and Ni^+ secondary ions has been investigated in the temperature range from 350 to 1100 K using secondary ion mass spectrometry. The ferroparamagnetic phase transition at $T \cong 620$ K on nickel is found to strongly affect only the emission of Ni^+ but not the emission of Ni_2^+. The data show that the Ni_2^+ dimers form via the ion–molecule recombination reaction in the near surface region rather than by a direct emission of the bound molecules.

ADSORPTION OF SOME SMALL MOLECULES ON A Pd FIELD EMITTER

P.D. Cobden*, B.E. Nieuwenhuys*, V.V. Gorodetskii
(*Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands)

Appl. Catal. A: General, 188(1-2) (1999) pp. 69-77.

The adsorption of CO, H_2 and NO on Pd field emitters has been studied using Field Emission Microscopy (FEM). The results are compared with earlier studies on Rh and Pt tips. The isosteric heat of adsorption of CO was found to be ~154 kJ mol^{-1} in the limit of zero coverage, decreasing to 133 kJ mol^{-1} at coverage of 0.5. At 300 K, a saturated layer of CO caused a work function increase of 0.98 eV above that of the clean surface. The (110) and (311) areas of the tip experience greater increases in work function than the other planes present on the tip. The initial heat of adsorption of H_2 was found to be ~127 kJ mol^{-1}, decreasing to

~104 kJ mol^{-1} at a coverage of 0.5. The work function increased by adsorption of H_2 by a maximum of 0.21 eV. At 300 K, NO while increasing the work function by 0.46 eV retained the same pattern as the clean tip. Heating the tip above 400 K, with NO in the gas phase produced an increase in emission around the (311) and (310) planes, with the possible formation of subsurface oxygen. On introducing NO to Pd at 550 K, almost no change was seen in the work function. When H_2 was in the gas phase, a similar phenomenon already occurred at 450 K. Subsequent removal of the H_2 led to an increase in emission, which could be restored by simply adding H_2 again.

FIELD EMISSION MICROSCOPE STUDY OF THE INITIAL BEHAVIOUR OF THE PALLADIUM-HYDROGEN SYSTEM AT LOW TEMPERATURES

P.D. Cobden*, V.V. Gorodetskii, B.E. Nieuwenhuys*
(*Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands)

Surf. Sci., 432(1-2) (1999) pp. 61-68.

For the first time, the initial stages of the uptake of hydrogen by palladium metal have been studied on a microscopic scale. A novel technique for the production of stable, clean Pd tips of small radius (~2000 Å) has enabled field emission microscopy (FEM, resolution ~ 20 Å) to be successfully applied. Exposure of Pd to H_2 at low temperatures led to an increase in emission starting at highly open surface present on the tip. This has been interpreted as both the formation of subsurface H, and the formation of extruding PdH particles on top of the Pd tip. Growth of these particles proceeds in a *staccato* manner. Heating of the tip after saturation leads to a change in emission distribution over the tip, a *black wave* that engulfs the whole surface followed by an increase in emission, that is possibly related to a phase transition from β-PdH to a mixture of α- and β-PdH (the so-called β_{min} transition). When most of the hydrogen has been removed from the sample by heating in vacuum, Pd crystallites remain on the surface. They are fairly stable up to high temperatures of ~700 K at which they melt back into the bulk of the tip.

KINETIC OSCILLATIONS AND SURFACE WAVES IN CATALYTIC CO+O_2 REACTION ON Pt SURFACE: FIELD ELECTRON MICROSCOPE, FIELD ION MICROSCOPE AND HIGH RESOLUTION ELECTRON ENERGY LOSS STUDIES

V.V. Gorodetskii, W. Drachsel* (*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany)

Appl. Catal. A: General, 188(1-2) (1999) pp. 267-275.

Recent experimental work has shown that the field electron microscope (FEM) and the field ion microscope (FIM) can also serve as an *in situ* catalytic flow reactor. Platinum field emitter (model catalyst, grain diameter ~ 700 Å) expose different nano single-crystal planes with well-defined crystallographic orientations. Isothermal, non-linear dynamic processes of the CO+O_2 reaction on Pt have been studied as well as the formation of face–specific adsorption islands, mobility of reaction/diffusion fronts and creation of chemical waves. Analysis of Pt surface with a local atom resolution of 4-6 Å shows the availability of a sharp boundary between the mobile CO_{ads} and O_{ads} fronts. It has been found that the back phase transition of Pt surface (100) hex $\leftrightarrow$ 1×1 plays an initiating function in the generation of chemical waves along certain crystallographic orientations of Pt surface. The reaction zone maximum active in CO_2 formation, with a width of up to 40 Å, has been discovered between adsorbed CO_{ads} and O_{ads} beds. The adsorption of O_2 and the reaction of molecular O^{2-}_{2ads} state as well as an atomic O_{ads} state with CO on the Pt(100)-(hex) and the Pt(100)-(1×1) single crystal surface have been studied with HREELS and thermal desorption spectroscopy (TDS) techniques.

OSCILLATIONS OF THE NO-H_2 REACTION OVER Ir(110) IN ACTIVITY AND SELECTIVITY

C.A. de Wolf*, B.E. Nieuwenhuys*, M.M. Slinko, M.Yu. Smirnov** (*Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands; **Institute of Chemical Physics, Moscow, Russia)

Surf. Sci., 433/435 (1999) pp. 63-68.

Self-sustained isothermal oscillations in the NO-H_2 reaction were found on the Ir (100) surface. The rates of NH_3 on N_2 formation oscillate exactly out of phase. The high activity state during oscillations (high NO conversion) corresponds to a high rate of NH_3 formation while in the low activity state a high rate of N_2 formation has been observed.

The shape of the oscillations is very sensitive to changes in the H_2/NO ratio or temperature. Build-up of a stable N species might play an important role in the mechanism of the oscillations.

MECHANISM FOR ACTIVATION OF HYDROGEN AND HYDROGENATION OF ACETONE TO ISOPROPANOL AND OF CARBON OXIDES TO METHANOL OVER COPPER-CONTAINING OXIDE CATALYSTS

T.M. Yurieva

Catal. Today, 51(3-4) (1999) pp. 457-467**.**

The present paper summarizes the results of comprehensive studies by a set of methods of the processes of reduction of copper chromite and of solid solutions of copper ions in zinc oxide. The composition and structure of copper-containing oxide catalysts in hydrogen medium and the nature of activated hydrogen species were investigated. Quantitative data on the interaction between hydrogen and the oxide catalysts and on the interaction of molecules to be hydrogenated with the reduced state of the catalysts are presented. The mechanism for the synthesis of methanol from CO and CO_2 and for the hydrogenation of acetone to isopropanol is discussed.

COMPLEX METAL COMPOUNDS CONTAINING ETHYLENEDIAMINE AND DINITROAMINE ANION

L.V. Varand*, S.V. Larionov*, N.N. Kundo
(*Institute of Inorganic Chemistry, Novosibirsk, Russia)

Russ. J. General. Chem., 69(2) (1999) pp. 273-274.

Complex compounds of nickel (II), cobalt (III), copper (II), zinc (II) and cadmium (II) with ethylene diamine comprising dinitroamide anions were synthesized. The compounds were studied using magnetic susceptibility, electron microscopy and differential thermal analysis techniques.

COMPOSITION CHARACTERIZATION OF $Bi_2Sr_2CaCu_2O_x$ SINGLE CRYSTALS BY DIFFERENTIAL DISSOLUTION TECHNIQUE

I.G. Vasilyeva*, V.V. Malakhov, L.S. Dovlitova, H. Bach** (*Institute of Inorganic Chemistry, Novosibirsk, Russia; **Ruhr-University Bochum, Germany)

Mater. Res. Bull., 34(1) (1999) pp. 81-92.

A new method, differential dissolution (DD), was used to characterize the real stoichiometry of 2-3 mm^2 Bi-2212 samples, which locked like single crystals according to the optical microscopy. A shape of dissolution kinetic curves used as an indicator of the crystalline state has shown the crystals are not real single crystals but consist of thin single-crystal layers packed along the c axis. The stoichiogram values recorded as a function of time or crystal dissolution degree were used to determine the composition and thickness of each layer, as well the composition of interfaces. The results obtained by the DD method along with data of other techniques are discussed in terms of chemical inhomogeneity of Bi-2212 crystals grown by different methods.

Studies on Electrocatalytic Processes

METHANE CONVERSION TO SYNGAS OVER PT-BASED ELECTRODE IN A SOLID OXIDE FUEL CELL REACTOR

G.L. Semin, V.D. Belyaev, A.K. Demin*,
V.A. Sobyanin (*Institute of High Temperature Electrochemistry, Ekaterinburg, Russia)

Appl. Catal. A: General, 181(1) (1999) pp. 131-137.

Electrocatalytic oxidation of methane over Pt-based electrode-catalyst in a solid oxide fuel cell reactor

CH_4, Pt $|0.9ZrO_2 + 0.1Y_2O_3|$ Pt, air

was studied at 800 °C and atmospheric pressure. SEM and ESCA techniques were used to characterize the electrode-catalyst. It is found that Pt-based electrode is an active electrode-catalyst for partial oxidation of methane (in a diluent absence) to syngas, concentration ratio being $[H_2]/[CO]\approx 2$. Methane conversion and carbon monoxide selectivity attained 97 and 95%, respectively. Under these conditions reactor is operated in a fuel cell mode, and the electrode-catalyst is stable (to coking, too).

N_2O REDUCTION BY CO OVER Pt ELECTRODE IN A SOLID OXIDE ELECTROLYTE CELL

V.D. Belyaev, T.I. Politova, V.A. Sobyanin

Catal. Lett., 57(1-2) (1999) pp. 43-47.

The reduction of nitrous oxide by carbon monoxide in a cell with a solid oxygen-conducting electrolyte

$CO+N_2O$,Pt | $0.9ZrO_2 + 0.1Y_2O_3$ | Pt + PrO_2, air

was studied. Experiments were performed in the temperature range 410-670 ^{0}C. The reaction kinetics under open-circuit conditions and the effect of current passing through the cell on the reaction rate were found to depend on the gaseous composition. In particular: i) for a reaction mixture rich in N_2O, in contrast to the reaction mixture rich in CO, the temperature steady-state multiplicity of the reaction was observed under open-circuit conditions; ii) for the reaction mixture rich in CO, in contrast to the reaction mixture rich in N_2O, a slight non-Faradaic enhancement of the reaction rate upon cathodic current application was demonstrated.

EFFECTS OF MICROSTRUCTURE IN ETHYLENE GLICOL OXIDATION ON GRAPHITE SUPPORTED Pt ELECTRODES

N.P. Lebedeva, G.N. Kryukova, S.V. Tsybulya, E.R. Savinova

Electrochimica Acta, 44 (1998) pp. 1431-1440.

Activities of graphite supported and polycrystalline Pt in electrocatalytic oxidation of ethylene glycol in neutral unbuffered Na_2SO_4 solutions have been compared. Morphology and microstructure of supported Pt electrodes have been studied using scanning electron microscopy, high-resolution transmission electron microscopy and X-ray diffraction. Specific activity of Pt electrodes and sensitivity to poisoning has been found to depend strongly on their microstructure. Supported electrodes appear to be from 4 to 6 times less active than polycrystalline Pt in the potential region between 0.3 and 0.9 V vs. SHE but much more stable to self-poisoning. The electrode microstructure has much less effect on the activity at high (over 0.9 V vs. SHE) anodic potentials.

PARTIAL OXIDATION OF ETHANE IN A FUEL CELL-LIKE ELECTROCHEMICAL REACTOR IN THE GAS PHASE UNDER MILD CONDITIONS

A.O. Kuzmin, E.R. Savinova, V.N. Parmon

React. Kinet. & Catal. Lett., 66(1) (1999) pp. 147-153.

Partial oxidation of ethane with dioxygen in a gas-phase, fuel cell-like electrochemical reactor under mild conditions is reported. Ethane is shown to be selectively oxidized to ethanol and acetaldehyde on the carbon gas-diffusion cathode in the presence of transition metal ions (Fe^{2+}, Cu^{2+}). The reaction proceeds at ambient pressure and temperature in the range from 318 to 353 K.

PARTIAL OXIDATION OF ETHANE IN H_2/O_2 FUEL CELL UNDER MILD CONDITIONS

A.O. Kuzmin, E.R. Savinova, V.N. Parmon

React. Kinet. & Catal. Lett., 66(2) (1999) pp. 351-357.

The partial oxidation of ethane to ethanol and acetaldehyde in the H_2/O_2 fuel cell under mild conditions is reported. The reaction proceeds at the carbon gas-diffusion cathode in the presence of transition metal ions (Fe^{2+}, Cu^{2+}) at ambient pressure and temperature 343 K.

EFFECT OF TRANSITION METAL IONS ON PARTIAL ETHANE OXIDATION IN AN ELECTROCHEMICAL SYSTEM

A.O. Kuzmin, E.R. Savinova, V.N. Parmon

React. Kinet. & Catal. Lett., 66(2) (1999) pp. 359-366.

Transition metal ions (Fe^{2+} and Cu^{2+}) have been found to enhance the rate of ethane partial oxidation in a gas-liquid electrochemical reactor under mild conditions (363 K, atmospheric pressure). The effect is discussed in terms of a radical-chain mechanism involving OH radicals.

PARTIAL OXIDATION OF LIGHT PARAFFINS WITH HYDROGEN PEROXIDE IN THE PRESENCE OF PEROXOCOMPLEXES OF COPPER(II) HYDROXIDE

A.O. Kuzmin, G.L. Elizarova, L.G. Matvienko,
E.R. Savinova, V.N. Parmon

Mendeleev Commun., 6 (1998) pp. 210-212.

Methane, ethane and ethylene are oxidized by hydrogen peroxide in aqueous solutions at room temperature and atmospheric pressure in the presence of peroxocomplexes of copper(II) hydroxide; the reaction presumably proceeds by a non-radical mechanism.

EX-SITU XPS STUDY OF THE INTERFACE BETWEEN A Ag(111) ELECTRODE AND AN ALKALINE ELECTROLYTE.
1. INFLUENCE OF THE ELECTRODE POTENTIAL ON THE ADSORPTION OF OXYGEN SPECIES

E.R. Savinova, D.Yu. Zemlyanov, A. Scheybal*, Th. Schedel-Niedrig*, K. Doblhofer*, R. Schlögl* (*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany)

Langmuir, 15 (1999) pp. 6546-6551.

A Ag(111) single crystal electrode emersed from the NaF + NaOH electrolyte (pH 11) under the anodic polarization has been studied *ex-situ* by means of X-ray photoelectron spectroscopy (XPS). The oxidation of the electrode starts at -0.6 V vs. Hg/HgO (ca. 1 V negative to the reversible potential of Ag_2O phase formation) and manifests itself by the appearance of different surface and bulk oxygen-containing species. These are: surface OH groups (OH_{ads}), surface oxide-like species ($O^{\delta-}_{ads}$) and bulk OH groups (OH_{bulk}). The OH_{bulk} exhibit high thermal stability in vacuum but can be efficiently removed from the electrode via cathodic polarization.

EX-SITU XPS STUDY OF THE INTERFACE BETWEEN A Ag(111) ELECTRODE AND AN ALKALINE ELECTROLYTE.
2. STRUCTURE OF THE DOUBLE LAYER

E.R. Savinova, D.Yu. Zemlyanov, A. Scheybal*, R. Schlögl*, K. Doblhofer* (*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany)

Langmuir, 15 (1999) pp. 6552-6556.

A Ag(111) single crystal electrode emersed from alkaline NaF + NaOH electrolyte under various potentials has been studied *ex-situ* by means of X-ray photoelectron spectroscopy (XPS). Superequivalent specific adsorption of negatively charged hydroxide and oxide species has been observed at the potentials positive to the point of zero charge (E_{pzc}). The interfacial electroneutrality is provided by the coulombic attraction of Na^+ cations, which are retained in the emersed double layer. Upon heating the emersed electrode in UHV above 370 K the double layer disintegrates via the decomposition of the adsorbed hydroxide and surface oxide species and likely dissolution of sodium in the Ag(111) bulk. A model of the interface between a Ag(111) electrode and an alkaline electrolyte is discussed.

DETECTION OF 4-CARBOXYBENZALDEHYDE IN TEREPHTHALIC ACID USING VOLTAMMETRIC TECHNIQUE WITH RENEWABLE GRAPHITE ELECTRODE

N.F. Zakharchuk, N.S. Borisova, A.V. Romanenko

Chem. for Sustainable Devel., 7(1) (1999) pp. 35-38.

A method for detecting 4-carboxybenzaldehyde in terephthalic acid using a renewable graphite electrode as the main one was described. An evident advantage of such one against a dripping mercury electrode is health safety and a potentiality of improving the accuracy due to the differential mode of the electrode polarization.

Studies on Silica Gels

WHY AN APPARENT SURFACE DIMENSION OF SILICA GELS MAY BE ABNORMALLY HIGH

A.G. Okunev, Yu.I. Aristov

Langmuir, 15(15) (1999) pp. 5068-5072.

In the present paper some problems of the "surface resolution analysis" to characterize silica gels are addressed. The adsorption of organic adsorbates (fatty acids, aliphatic alcohols, and ketones) from CCl_4 solution on mesoporous silicas of various porosity was measured. A simple linear relationship is found between the monolayer thickness and the monolayer volume, which is valid even for the adsorbates of different homology series. A simple model to describe adsorption experiments quantitatively has been developed. The model shows that the curvature of silica mesopores may influence the packing of test molecules in the monolayer and leads to a decrease in the adsorbate monolayer capacity for large molecules, so that measured surface area is underestimated. The effect increases, when the ratio of adsorbed layer thickness h to pore radius R increases and may reach some tens of percent. The model explains why the apparent values of silica surface dimension may be abnormally high ($D_s > 3$).

KINETICS OF THE SiO_2 AEROGEL DISSOLUTION IN AQUEOUS NaOH SOLUTIONS: EXPERIMENT AND MODEL

A.G. Okunev, S.A. Shaurman, A.F. Danilyuk,
Yu.I. Aristov, G. Bergeret*, A. Renouprez*
(*Institut de Recherches sur la Catalyse, Villeurbanne, France)

J. Non-Cryst. Solids, 260(1-2) (1999) pp. 21-30.

The paper is devoted to the study of the kinetics of silica aerogel dissolution in 0.05 -0.79 M NaOH aqueous solutions at temperatures 15 – 56 ^{o}C. The aerogel samples are prepared via common one- and two-step procedures, and differ considerably in the primary particle size. Kinetic peculiarities of the process are studied under both reaction and diffusion controlled modes and kinetic parameters are established by experimental curve fitting. The dissolution activation energy is found to be equal to 82 ± 6 kJ/mol for all the aerogels. The dissolution kinetic curves appear to be S-shaped, so that the process rate passes through a maximum. The coincidence of SAXS and BET specific surface areas indicates that the aerogels have no closed porosity so the initial rate increase cannot be explained by the opening of closed pores. A new modification of the Iler dissolution kinetic model has been developed to describe the experimentally observed kinetic curves.

THE DISSOLUTION KINETICS OF SiO_2 AEROGELS IN AQUEOUS NaOH SOLUTIONS

A.G. Okunev, S.A. Shaurman, A.F. Danilyuk,
A.N. Shmakov, Yu.I. Aristov

Colloid J., 61(3) (1999) pp. 355-358.

The dissolution kinetics of SiO_2 aerogels was investigated by three complementary experimental techniques – the kinetic method, static light scattering and small-angle X-ray scattering. Four aerogel samples synthesized by the catalytic hydrolysis of alkoxides with the use of one- and two-stage procedures were investigated. The aerogels differed in their specific surface areas, densities and optical properties. Regularities of the dissolution of the aerogels in 0.05–0.4 M NaOH aqueous solutions were studied in the kinetic- and diffusion-controlled regimes over the temperature range 15-56 °C. In spite of the different conditions of aerogel synthesis, the activation energies of their dissolution measured in the kinetic regime were identical and equal to 82±6 kJ/moll. Once the critical degree of diffusion for the aerogels was reached, the *threshold* disintegration of their secondary structure occurred and silica clusters (SiO_2)cl consisting of primary particles appeared in the solution. *In situ* registration of scattering showed that the disintegration of the aerogels results in 10-300 nm fragments. A correlation between the shape of peaks in light-scattering curves of the aerogel dispersions and their optical properties was found.

MECHANISM OF STRUCTURAL ORDERING OF MONODISPERSE SPHERICAL SILICA PARTICLES IN CONCENTRATED ALCOHOL SUSPENSIONS

V.V. Serdobintseva*, D.V. Kalinin*, A.F. Danilyuk (*Institute of Mineralogy and Petrography, Novosibirsk, Russia)

React. Kinet. & Catal. Lett., 67(1) (1999) pp. 143-147.

Structural ordering of monodispersed spherical silica particles (MSSP) occurs in ammonia stabilized concentrated suspensions obtained by tetraethoxysilane (TEOS) hydrolysis in alcohol-aqueous solutions in the ammonia concentration range from 0.0001 to 0.0008 mol/L. MSSP interaction follows the DLFO (Deryagin, Landau, Ferway, and Overbeck) mechanism when electrostatic repulsive forces between the particles predominate, and the structural ordering requires straitened conditions, which are provided by suspension concentrating through MSSP gravitational precipitation.

SUPRAMOLECULAR CRYSTAL GROWTH IN CONCENTRATED SUSPENSIONS OF CHARGED MONODISPERSE SPHERICAL SILICA PARTICLES

V.V. Serdobintseva*, D.V. Kalinin*, A.F. Danilyuk, N.A. Rudina (*Institute of Mineralogy and Petrography, Novosibirsk, Russia)

React. Kinet. & Catal. Lett., 68(2) (1999) pp. 313-318

Concentrated suspensions of charged monodisperse spherical silica particles (MSSP), stabilized by alkalies or ammonia are able to crystallize at a degree of destabilization. Crystal structures with the particles fixed up at the distances from each other reveal an isotropic normal mechanism of continuous growth with rough phase boundary. Crystallization is determined by three parameters: concentration of particles, the thickness and density of ion atmosphere around the particles and temperature. Crystallization of MSSP suspensions is considered as a model of supramolecular crystallization in the field of synthesis of mesoporous structures.

KINETICS OF SUPRAMOLECULAR CRYSTALLIZATION OF CONCENTRATED SUSPENSIONS OF MONODISPERSED SPHERICAL SILICA PARTICLES

V.V. Serdobintseva*, A.F. Danilyuk, S.V. Vosel*, D.V. Kalinin* (*Institute of Mineralogy and Petrography, Novosibirsk, Russia)

React. Kinet. & Catal. Lett., 68(2) (1999) pp. 387-392.

The kinetics of the supramolecular crystallization of concentrated suspensions is three-dimensional and follows the Avrami-Erofeev equation: $A=1 -\exp[-(kt)^m]$, where m=4. The rate constant k is proportional to the probability of the appearance of a crystallization center in unit volume in unit time and the linear crystal growth rate, which is determined experimentally.

THE SYNTHESIS OF AEROGEL TILES WITH HIGH LIGHT SCATTERING LENGTH

A.F. Danilyuk, E.A. Kravchenko*, A.G. Okunev, A.P. Onuchin*, S.A. Shaurman (*Budker Institute of Nuclear Physics, Novosibirsk)

Nuclear Instrum. & Methods in Phys. Res. A, 433 (1999) pp. 406-407.

In this work the possibility of aerogel tiles production for RICH detectors is described. Monolithic blocks of silica aerogel are synthesized by two-step sol-gel processing of tetraetoxysilane $Si(OEt)_4$ followed by high temperature supercritical drying with organic solvent.

The important characteristic of aerogel is the light scattering length in its volume. In the wide range of refraction indexes the light scattering length is higher than ~4 cm at ~400 nm.

Catalysis by Metal Complexes

COMPLEXATION OF IRON(III) IONS WITH ARSENIC(III)-TUNGSTEN(VI)-HETEROPOLY ANIONS FROM DATA OF OPTICAL AND INFRARED SPECTROSCOPY AND THE DIFFERENTIATING DISSOLUTION METHOD

L.G. Detusheva, L.I. Kuznetsova, V.A. Likholobov, A.A. Vlasov, N.N. Boldyreva, S.G. Poryvaev, V.V. Malakhov

Russ. J. Coord. Chem., 25(8) (1999) pp. 569-575.

Reactions of the unsaturated heteropoly anions (HPAs) $[AsW_9O_{33}]^{9-}$ (AsW_9), $[As_2W_{19}O_{67}(H_2O)]^{14-}$ (As_2W_{19}), and $[As_2W_{20}O_{68}(H_2O)]^{10-}$ (As_2W_{20}) with the Fe^{3+} and Co^{2+} ions are examined. The lacunar As(III)-HPAs are shown to stabilize the superstoichiometric (per one HPA) number of Fe^{3+} ions in solutions at $pH \geq 6$. As_2W_{19} (pH 6) attaches up to 12 Fe^{3+} ions, whereas the number of attached Co^{2+} ions corresponds, under the same conditions, only to the number of “vacancies” in As_2W_{19} and As_2W_{20} lattices, i.e., to 2 and 1, respectively. AsW_9 (pH 7.5) forms an M-containing $As_2W_{18}M_3$ complex and, thus, additionally stabilizes ~3 Fe^{3+} or Co^{2+} ions. The complexes of lacunar HPAs with Fe^{3+} and Co^{2+} ions were isolated from solutions as solid salts containing Cs^+ cations. All cesium salts relate to the common structural type, As_2W_{21} HPA. The conclusion is drawn that superstoichiometric Fe^{3+} ions are present in Fe(III)-containing $As_2W_{18}Fe_3$ and $As_2W_{19}Fe_2$ HPAs in the form of oligomeric hydroxide species grafted into HPA.

POLYOXOMETALATES FOR THE STUDY OF ACTIVE SITES IN CATALYTIC TRANSFORMATIONS OF ORGANIC SUBSTANCES

L.I. Kuznetsova, G.M. Maksimov, V.A. Likholobov

Kinetics & Catalysis, 49(5) (1999) pp. 622-637.

The article reviews original studies of the catalytic properties of heteropoly compounds with various compositions and structures in the liquid-phase acidic, and oxidative reactions of organic substances. The methods for heteropoly compound synthesis using of electrodialysis, mechanochemistry, and reverse-osmotic membrane separation of ions are considered. New methods for the synthesis of soluble mono- and polynuclear complexes from transition metal ions (M) and $PW_{11}MO_{39}^{n-}$-based heteropoly compounds, and the preparation of metal colloids stabilized by isopoly and heteropoly compounds are proposed. The activity in acidic reactions is determined by the Brönsted acidity along with the structure of the heteropoly compound anion. The interaction between M and a heteropoly compound and the type of an additional ligand in the coordination sphere of M play a critical role in hydrocarbon oxidation by oxygen donors (H_2O_2, *t*-BuOOH, and O_2 /H_2 mixtures).

Bibliography: 135 references.

SUPPORTED AMMONIA SYNTHESIS CATALYSTS BASED ON POTASSIUM DERIVATIVES OF ANIONIC RUTHENIUM, OSMIUM AND IRON CARBONYL CLUSTERS

S.M. Yunusov*, E.S. Kalyuzhnaya*, H. Mahapatra, V.K. Puri**, V.A. Likholobov, S.B. Shur***

(*A.N. Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia, **Project and Development India Limited, Bihor, India)

J. Molec. Catal. A: Chemical, 139(2-3) (1999) pp. 219-225.

The first catalysts on carbon support exhibiting activity in ammonia synthesis in the absence of a specially added electron promoter have been found. The catalysts were prepared by deposing $K_2[Ru_4(CO)_{13}]$, $K_2[Os_3(CO)_{11}]$ and $K_2[Fe_2(CO)_8]$ from THF solutions on the original graphite-like active carbon ‘Sibunit’ followed by drying of the samples obtained at 20 °C in vacuum. The highest efficiency is displayed by the $K_2[Ru_4(CO)_{13}]$ catalyst which is active in ammonia synthesis starting from 250 °C (1 atm). On passing from $K_2[Ru_4(CO)_{13}]$ to $K_2[Os_3(CO)_{11}]$ and then to $K_2[Fe_2(CO)_8]$ the rate of ammonia synthesis lowers. The replacement of ‘Sibunit’ by usual commercial active carbon SKT results in sharp decrease in activity and stability of the catalysts. An introduction of metallic potassium into the catalysts on ‘Sibunit’ carbon accelerates strongly the process of ammonia synthesis. A study of the $K_2[Ru_4(CO)_{13}]$+K and $K_2[Fe_2(CO)_8]$+K catalysts has shown that at constant transition metal and carbon contents in the system, the activity of both catalysts passes through a maximum with an increase in potassium quantity, in the case of ruthenium the position of the maximum being reached at considerably less amounts of potassium in the sample than in the case of iron. The $K_2[Ru_4(CO)_{13}]$+K catalyst is much less active than the $K_2[Fe_2(CO)_8]$+K catalyst at 200 °C but considerably exceeds it in activity at higher temperatures (250-350 °C).

STRUCTURE OF METHYLALUMINOXANE AND THE MECHANISM OF ACTIVE CENTER FORMATION IN THE ZIRCONOCENE/METHYLALUMINOXANE CATALYTIC SYSTEM

V.A. Zakharov, E.P. Talzi, I.I. Zakharov, D.E. Babushkin, N.V. Semikolenova

Kinetics & Catalysis, 40(6) (1999) pp. 836-850.

New data on the structure of polymethylaluminoxane - Al(CH$_3$)O]$_n$ (MAO), the nature of its Lewis acidity, and the mechanism of formation of the active centers of the metallocene catalysts during interaction between MAO and Cp$_2$ZrMe$_2$ obtained by spectroscopy (^{27}Al, ^{17}O, ^{1}H, and ^{13}C NMR and spin probe ESR) and density functional theory (DFT) calculations are considered. A three-dimensional structure of MAO (a cage structure) with four-coordinated aluminum atoms and three-coordinated oxygen atoms is found to be the most probable. Experimental evidence for the presence of relatively weak Lewis acid sites in MAO (about 1 site per 50 atoms of Al) is obtained for the first time. The acidity of MAO depends on the size of a MAO molecule n, and it increases with increasing n. A scheme for the formation and structure of Lewis acid sites formed upon interaction between MAO and Al$_2$Me$_6$, which is always present in the MAO samples is proposed. Cationic intermediates formed in the MAO/Cp$_2$ZrMe$_2$ system at high molar ratios Al/Zr=200–4000 corresponding to real conditions of polymerization are characterized for the first time. A scheme of equilibria between them and the most probable precursors of the active centers in this system are proposed. A new mechanism for the formation of the [Cp$_2$ZrMe]$^+$[MAO Me]$^-$ ionic pair involving the abstraction and occlusion of a methyl ligand in the bulk of a MAO molecule is proposed on the basis of quantum-chemical calculations.

IRS STUDY OF ETHYLENE POLYMERIZATION CATALYSTS SiO$_2$/MAO/ZIRCONOCENE

V.A. Zakharov, V.N. Panchenko, N.V. Semikolenova, I.G. Danilova, E.A. Paukshtis

Polymer Bulletin, 43 (1999) pp. 87-92.

Lewis acidic sites (LAS) of silica, modified with TMA and MAO samples differed by TMA content have been characterized by IR spectroscopy (CO adsorption as probe molecule at 77 K). Two types of LAS were found on the surface of silica modified with MAO and TMA: M LAS of moderate strength (ν_{CO}=2204-2212 cm^{-1}) and weak LAS (ν_{CO}=2194 cm^{-1}). The concentration of these acidic sites has been estimated.

It was shown by IRS study Cp$_2$ZrMe$_2$ interacts both with W LAS and M LAS. Correlation between the amount of M LAS and the activity of ethylene polymerization has been found.

STRUCTURE AND PROPERTIES OF MONO- AND HETEROMETALLIC CADMIUM, ZINC, AND NICKEL COMPLEXES CONTAINING DIETHYLDITHIOCARBAMATE IONS AND ETHYLENEDIAMINE MOLECULES

S.M. Zemskova*, L.A. Glinskaya*, R.F. Klevtsova*, M.A. Fedotov, S.V. Larionov* (*Institute of Inorganic Chemistry, Novosibirsk, Russia)

J. Struct. Chem., 40(2) (1999) pp. 340-350.

Crystal structure of mono- and heterometal complexes [MEn$_3$]L$_2$ (M=Zn^{2+}, Ni^{2+}), [MEn$_3$][CdL$_3$]$_2$ (M=Cd^{2+}, Zn^{2+}, Ni^{2+}) comprising ethylenediamine (En) molecules and diethyldithiocarbamate ions (L=(C$_2$H$_5$)$_2$NCS) was studied. These are isostructural heterometal complexes built-up by discrete mononuclear ions. Central atom M in [MEn$_3$]$^{2+}$ cations being located on a double axis, there are two independent metallocycles among three MN$_2$C$_2$ of the cation [MEn$_3$]$^{2+}$. One of the two independent metallocycles is of gaush-configuration. Chelate angles N-M-N in the coordinated En molecules are 77.0 and 82.9° (M=Cd^{2+}); 80.0 and 80.5° (M=Zn^{2+}); 79.9 and 80.8° (M=Ni^{2+}). Nitrogen atoms are disposed as a distorted octahedron around M. Mean M-N bond lengths are 2.35, 2.19 and 2.14 Å for M=Cd^{2+}, Zn^{2+}, Ni^{2+}, respectively. All the atoms of the complex anion [CdL$_3$]$^-$ are at a common position, the central atom coordinates three bidentate cyclic L$^-$ ligand. Atoms S form a deformed trigonal prism, in which S…S distances in the vertical edges are almost equal in length ranging between 2.94(1) and 3.00(2) Å in all the complexes. ^{1}H, ^{14}N, ^{113}Cd NMR studies showed that ionic complexes [ZnEn$_3$]L$_2$ and [CdEn$_3$][CdL$_3$]$_2$, when dissolved, are transformed into multiligand complexes of non-electrolyte type.

Stereoselective Catalysis

ROLE OF PROTONS IN METHYL PHENYL SULFIDE OXIDATION WITH HYDROGEN PEROXIDE CATALYZED BY Ti(IV)-MONOSUBSTITUTED HETEROPOLYTUNGSTATES

O.A. Kholdeeva, G.M. Maksimov, R.I. Maksimovskaya, L.A. Kovaleva, M.A. Fedotov

React. Kinet. & Catal. Lett., 66(2) (1999)
pp. 311-317.

Using ^{31}P NMR and kinetic measurements the relationship between the composition of tetrabutylammonium (TBA) salts of Ti(IV)-monosubstituted heteropolytungstate, $PW_{11}TiO_{40}^{5-}$, and its catalytic activity in the oxidation of methyl phenyl sulfide (MPS) with hydrogen peroxide has been established. Acid TBA salts of $PW_{11}TiO_{40}^{5-}$ showed high catalytic activity, while the corresponding TBA salts, containing no protons, are poor catalysts for this reaction. The catalytic activity of TBA-PW_{11}Ti samples in the MPS oxidation by H_2O_2 correlates with the rates of their peroxo complex formation.

OXIDATION OF METHYL PHENYL SULFIDE WITH MOLECULAR OXYGEN IN THE PRESENCE OF ISOBUTYRALDEHYDE AND TRANSITION METAL MONOSUBSTITUTED HETEROPOLYTUNGSTATES

I.V. Khavrutskii, G.M. Maksimov, O.A. Kholdeeva

React. Kinet. & Catal. Lett., 66(2) (1999)
pp. 325-330.

Catalytic properties of transition metal substituted heteropolytungstates, $PW_{11}MO_{39}^{n-}$ (PW_{11}M) with M = Co(II), Cu(II), Pd(II), Ru(IV), Ti(IV), and V(V), in the oxidation of thioethers by the dioxygen/isobutyraldehyde system have been studied at ambient conditions using methyl phenyl sulfide (MPS) as a model substrate. MPS was found to be quantitatively oxidized to the corresponding sulfoxide and sulfone in the presence of PW_{11}M with M=Co^{II} and Ti^{IV}. The reaction proceeds via radical chain mechanism.

Selective Water Sorbents and Heat Accumulating Materials

NEW COMPOSITE SORBENTS FOR SOLAR-DRIVEN TECHNOLOGY OF FRESH WATER PRODUCTION FROM THE ATMOSPHERE

Yu.I. Aristov, M.M. Tokarev, L.G. Gordeeva,
V.N. Snytnikov, V.N. Parmon

Solar Energy, 66(2) (1999) pp. 165-168.

In this communication new selective water sorbents are presented developed at the Boreskov Institute of Catalysis and their application for fresh water production from the atmosphere is discussed. A general scheme of the water production is also presented and the particular solar-driven unit is suggested which may be recommended for desert areas with a hot and dry climate. The results of our lab-scale tests have demonstrated a feasibility of the fresh water production with the output of 3-5 tonnes of water per 10 tonnes of the dry sorbent per day.

SELECTIVE WATER SORBENTS FOR MULTIPLE APPLICATIONS.
8. SORPTION PROPERTIES OF $CaCl_2$ - SiO_2 SOL-GEL COMPOSITES

L.G. Gordeeva, J. Mrowiec-Bialon*, A.B. Jarzebski*, A. Lachowski*, J. Malinovski*, Yu.I. Aristov
(*Institute of Chemical Engineering, Gliwice, Poland)

React. Kinet. & Catal. Lett., 66(1) (1999) pp.113-120.

This paper presents sorption properties of $CaCl_2/SiO_2$ composites synthesized with a sol-gel approach. Desorption isobars measured at T=30-140 ^oC and vapor partial pressure 12.8-81.0 mbar clearly show a correlation between the sorbents porous structure and their sorption properties. The sample adsorptivities are found to exceed 1.2 kg H_2O/kg adsorbent (or 20-25 mol H_2O/mol of the salt). That is markedly higher than any reported before for silica-based materials. This results in the high energy storage capacity reaching 3,400 kJ/kg of the dry sorbent, as confirmed by direct calorimetric measurements. The isosteric desorption heat is found to decrease from 67±5 kJ/mol to 46±5 kJ/mol with increase in the surface coverage.

SELECTIVE WATER SORBENTS FOR MULTIPLE APPLICATIONS.
9. TEMPERATURE INDEPENDENT CURVES OF SORPTION FROM THEORY OF VOLUME FILLING OF MICROPORES

S.I. Prokopiev, Yu.I. Aristov

React. Kinet. & Catal. Lett., 67(2) (1999) pp. 345-352.

In this paper a new equation of Henry-like type for describing water activity as a function of temperature (260 – 600 K) and water mole fraction (0.3 – 0.8) in concentrated aqueous solutions of $CaCl_2$, LiBr, LiCl, LiI and $MgCl_2$ both in bulk and dispersed states is presented. The four-parameter equation allows both a precise description of literature data on the water activity and a correct prediction of the water sorption properties of concentrated electrolyte solutions confined to pores that is of high importance for analyzing different practical applications of selective water sorbents.

USE OF MODERN COMPOSITE MATERIALS OF THE CHEMICAL HEAT ACCUMULATOR TYPE FOR FIRE PROTECTION AND FIRE EXTINGUISHING

V.N. Parmon, O.P. Krivoruchko, Yu.I. Aristov

Prevention of Hazardous Fires and Explosions,
Eds. V.E. Zarko et al., 1999, Kluwer Academic Publishers, the Netherlands, pp. 34-48.

The Boreskov Institute of Catalysis has recently invented Chemical Heat Accumulators (now the name Selective Water Sorbents (SWS) is more widely used) which employ chemical and physical dehydration of water molecules tightly coupled to an appropriate lattice material. These storage media are able to absorb large amount of heat (more than 2000 kJ kg^{-1} of the dry material) that could make them promising for fire protection applications. These materials are now under extensive experimental studies and have been successfully tested in some commercial applications like air conditioning, seasonable energy storage, sorption heat pumps, refrigeration machines, efficient fire-retarding powders, etc.

In this communication, some basic physico-chemical properties of the SWS materials as well as examples of their application to fire protection and fire extinguishing are presented and discussed.

CHEMITHERMAL PROCESSES IN FUTURE NUCLEAR POWER ENGINEERING: MITH OR REALITY. 1. ADAM - EVA

Yu.I. Aristov, S.I. Prokopiev, Yu.Yu. Tanashev, L.G. Gordeeva, V.N. Parmon

Energy: Economcs, Tehnics, Ecology, 1 (1999) pp. 9-13.

This paper opens the discussion on the application of chemical methods of energy accumulation for transformation of nuclear energy to chemical one and addresses to everybody interested or specialized in this field. The ADAM-EVA method suggested in literature and realized in the pilot plant scale is analyzed.

CHEMITHERMAL PROCESSES IN FUTURE NUCLEAR POWER ENGINEERING: MITH OR REALITY. 2. ICAR

Yu.I. Aristov, S.I. Prokopiev, Yu.Yu. Tanashev, L.G. Gordeeva, V.N. Parmon

Energy: Economcs, Tehnics, Ecology, 2 (1999) pp. 17–23.

Continuation of the discussion started in the part 1 is focused on the alternative ICAR method that has recently been suggested in the Boreskov Institute of Catalysis. The chemical principles of the method are described together with the obstacles for its practical application.

SiO_2-LiBr NANOCOMPOSITE SOL-GEL ADSORBENTS OF WATER VAPOR: PREPARATION AND PROPERTIES

J. Mrowiec-Bialon*, A.I. Lachowski*, A.B. Jarzebskii*, L.G. Gordeeva, Yu.I. Aristov
(*Institute of Chemical Engineering, Gliwice, Poland)

J. Colloid & Interface Sci., 218 (1999) pp. 500-503.

Water vapor adsorption on SiO_2-LiBr sol-gel materials strongly depends on bromide content. Adsorption capacities exhibited by these materials at higher relative pressures can be as high as 0.8 kg of water/kg of adsorbent. These adsobents can be regenerated by heating at 473 K and reused. However, a gradual decay of adsorption properties occurs during repeated adsorption-desorption cycles. Thus, this family of adsorbents seems to be less attractive than the corresponding SiO_2-$CaCl_2$ composites.

Nature, Mechanism and Physicochemical Essence of the Low-Waste, Environmentally Friendly Methods of Catalyst Preparation

ABOUT MESOPORE SURFACE AREA AND SIZE CALCULATIONS FOR HEXAGONAL MESOPHASES (TYPES OF MCM-41, FSM-16, etc.)

V.B. Fenelonov, V.N. Romannikov, A.Yu. Derevyankin

Micropor. & Mesopor. Mater., 28 (1999) pp. 57-72.

The paper is devoted to the geometry of mesoporous mesophase systems (MMSs) of the MCM-41 or FSM-16 texture types. The interrelations among surface areas inside and outside the mesoporous blocks of the MMS, of the size and the volume of mesopores are discussed. The equations for calculating these texture characteristics are derived. These equations are based on the adsorption data and X-ray diffraction studies, and are applied for considerations of the silica and zirconia hexagonal MMS texture. The approach was used for a critical review of the results published by other authors for similar systems.

PHYSICO-CHEMICAL FEATURES OF THE FORMATION OF SILICEOUS POROUS MESOPHASES.
1. GENERAL IDEAS ON THE MECHANISM

V.N. Romannikov, V.B. Fenelonov, A.V. Nosov, A.Yu. Derevyankin, S.V. Tsybulya, G.N. Kryukova

Russ. Chem. Bull., 10 (1999) pp. 1845-1851.

The formation of the mesoporous mesophase materials via sedimentation of soluble forms of silica of the surface of cationic cetyltrimethylammonium micelles is studied. The main physico-chemical factors influencing the formation of siliceous mesoporous materials are revealed and discussed. These factors permit the explanation of the changes observed in structural and textural characteristics of the materials.

PHYSICO-CHEMICAL FEATURES OF THE FORMATION OF SILICEOUS POROUS MESOPHASES.
2. THE EFFECT OF THE SIZE OF SURFACTANT MOLECULES

V.N. Romannikov, V.B. Fenelonov,
A.Yu. Derevyankin

Russ. Chem. Bull., 10 (1999) pp. 1852-1856.

The formation of the siliceous mesoporous mesophase materials (Si-MMM) via sedimentation of soluble forms of silica on the surface of alkyltrimethylammonium bromide C_nTMABr was investigated. Surfactants with alkyl chain length n=12, 14, 16, 18 were used. It was shown that the alkyl chain length increment does not influence significantly on the main stages and mechanisms of formation, but leads to increasing mesopore size and volume keeping pore surface and wall thickness near constant.

SUPPORT AND CATALYST FOR THE ALKYLATION OF BENZENE BY ETHYLENE PROCESS

R.A. Shkrabina, Z.R. Ismagilov, N.A. Koryabkina, Yu.K. Vorobiev

Euro-Asian J. of Chem. Techn., 1 (1999) pp. 57-64.

A method for preparation of a spherical alumina support with preset porous structure for a catalyst of benzene alkylation with ethylene has been developed. The process of the support manufacture has been adjusted in a pilot installation, and an industrial installation for production of alumina support for the alkylation catalyst has been designed and built at the Shevchenko Plastics Plant (Aktau, Kazakhstan).

THERMOCHEMICAL ACTIVATION OF PSEUDOBOEHMITE

E.A. Taraban, B.P. Zolotovskii, R.A. Buyanov

Chem. for Sustainable Devel., 7(6) (1999)
pp. 729-733.

It has been elucidated that thermochemical activation of pseudoboehmite does not lead to formation of the product with increased reaction ability in contrast to three hydroxide. Pseudoboehmite transfers into one of intermediate states in the course of thermochemical activation, the one that the solid phase passes under the usual conditions of dehydrogenation. The peculiarities of the thermochemical activation and the properties of the product formed are conditioned by structural features of initial hydroxide.

THE THREE-DIMENSIONAL MICROPOROUS STRUCTURE OF ALUMINA SYNTHESIZED THROUGH THE ALUMINUM HYDROTHERMAL OXIDATION ROUTE

S.F. Tikhov, V.B. Fenelonov, V.I. Zaikovskii,
Yu.V. Potapova, V.A. Sadykov

Micropor. & Mesopor. Mater., 33(1-3) (1999)
pp. 137-142.

The structural properties and porosity of a γ-alumina sample prepared by the hydrothermal treatment of powdered aluminum were investigated using techniques of nitrogen adsorption, mercury porosimetry, and electron microscopy. The information available from each technique is used to present a more complete picture of the three-dimensional pore structure of this sample, in terms of size, shape, distribution, crystallographic orientation and accessibility of pores.

APPLICATION OF PLASMA SPRAYING IN THE PREPARATION OF METAL-SUPPORTED CATALYSTS

Z.R. Ismagilov, O.Yu. Podyacheva,
O.P. Solonenko*, V.V. Pushkarev, V.I. Kuzmin*,
V.A. Ushakov, N.A. Rudina
(*Institute of Theoretical and Applied Mechanics,
Novosibirsk, Russia)

Catal. Today, 51 (1999) pp. 411-417.

Catalysts supported on metals are widely used today, but room still remains for further improvement of catalyst characteristics. The subject of this paper is the application of a plasma spraying for the deposition of alumina coatings on metal substrates of different geometry (plates, foams) for subsequent synthesis of catalysts. The alumina layer sprayed successfully solves two different problems: (i) it serves as a washcoat on which a catalyst is synthesized, and (ii) it protects the metal surface from oxidation at high temperatures.

NEW TECHNOLOGY FOR PRODUCTION OF SPHERICAL ALUMINA SUPPORTS FOR FLUIDIZED BED COMBUSTION

Z.R. Ismagilov, R.A. Shkrabina, N.A. Koryabkina

Catal. Today, 47 (1999) pp. 51-71.

Fluidized bed catalytic combustion has proved to be very promising for industrial application. The milestone problem is the development of support and catalyst with a high mechanical and thermal stability. New technology for production of alumina supports with desired spherical shape, texture and structure has been developed. In this paper several pathways to produce aluminum hydroxide of a pseudoboehmite structure including conventional and new technologies are discussed. Properties of spherical granules depend on the method of granulation and most attention has been paid to development and optimization of hydrocarbon-ammonia molding to produce uniform alumina spheres. Several methods to estimate mechanical strength of spherical aluminas are applied to evaluate mechanical durability of prepared catalysts in a fluidized bed. Optimization of high quality spheres production focused on study of the effect of initial hydroxide properties and molding conditions on properties of the final product. Modification of spherical alumina with oxides of Mg, Ce, La and Si proved to be effective to substantially improve the mechanical and thermal stability. This effect is most pronounced when pairs of these dopes are introduced simultaneously.

ALUMINA SUPPORTS: PREPARATION, PROPERTIES AND APPLICATION IN CATALYTIC PROCESSES FOR ENVIRONMENTAL PROTECTION

Z.R. Ismagilov, R.A. Shkrabina, N.A. Koryabkina

Analytic Review, «Ecology», SB RAS, Novosibirsk, Issue 50, 1999, 81 pp.

Basic methods (traditional and novel) to produce aluminum oxides and hydroxides are reviewed. Methods to regulate properties of aluminum oxides and hydroxides, effect of methods of preparation, granulation and thermal treatment on such characteristics as texture, specific surface area, phase composition, mechanical strength and thermal and mechanical stability are discussed. Main attention is paid to the methods of preparation and studies the properties of spherical aluminum oxide – support for the catalysts to be used in flow or fluidized beds. The main principle of chemical modification - introduction of various additives to aluminum hydroxide/oxide - is considered to be an effective method to control properties of the aluminum oxide systems.

GENESIS AND PROPERTIES OF HIGHLY DISPERSED FRAMEWORK ZIRCONIUM PHOSPHATES - ACID CATALYSTS OF HEXANE ISOMERIZATION

S.N. Pavlova, V.A. Sadykov, G.V. Zabolotnaya, D.I. Kochubey, R.I. Maksimovskaya, V.I. Zaikovskii, V.V. Kriventsov, E.B. Burgina, S.V. Tsybulya, A.M. Volodin, E.A. Paukshtis, V.N. Kolomiichuk, M.V. Chaikina*, N.N. Kuznetsova, V.V. Lunin**, D. Agrawal***, R. Roy***** (*Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; **Moscow Lomonosov State University, Moscow, Russia; ***The Pennsylvania State University, University Park, PA)

Phosph. Research Bull., 10 (1999) pp. 400-405.

Highly dispersed framework NZP-type zirconium phosphates were synthesized via both sol-gel method (SG) and mechanochemical activation (MA) of solid precursors followed by their hydrothermal treatment (HTT) in the presence of surfactants. Genesis of samples real structure and its effect on the surface properties and activity in hexane isomerization were studied.

HIGH-SURFACE AREA FRAMEWORK ZIRCONIUM PHOSPHATES AS CATALYSTS OF HEXANE ISOMERIZATION AND DEHYDROAROMATIZATION: SYNTHESIS AND PROPERTIES

V.A. Sadykov, S.N. Pavlova, G.V. Zabolotnaya, D.I. Kochubey, R.I. Maksimovskaya, V.I. Zaikovskii, V.V. Kriventsov, S.V. Tsybulya, E.B. Burgina, E.A. Paukshtis, A.M. Volodin, V.B. Fenelonov, N.N. Kuznetsova*, V.V. Lunin*, M.V. Chaikina, D. Agrawal***, R. Roy*****
(*Moscow Lomonosov State University, Moscow, Russia; **Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; ***The Pennsylvania State University, University Park, PA)

Mater. Res. Soc. Symp. Proc., 459 (1999) pp. 255-260.

Mechanochemical activation of solid inorganic precursors and sol-gel routes followed by hydrothermal treatment in the presence of surfactants were used to synthesize highly dispersed NZP-type complex zirconium phosphates. Genesis of samples real structure and its impact on the surface properties and catalytic performance in the reactions of hexane isomerization and dehydroaromatization has been studied.

SYNTHESIS OF HIGH-SURFACE-AREA COMPLEX ZIRCONIUM PHOSPHATES VIA MECHANOCHEMICAL ACTIVATION ROUTE

V.A. Sadykov, S.N. Pavlova, G.V. Zabolotnaya, R.I. Maksimovskaya, S.V. Tsubulya, E.B. Burgina, V.I. Zaikovskii, G.S. Litvak, M.V. Chaikina*,
V.V. Lunin, N.N. Kuznetsova**, R. Roy***,**
D. Agrawal*** (*Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia; **Moscow Lomonosov State University, Moscow, Russia; ***The Pennsylvania State University, University Park, PA)

Mater. Res. Innov., 2(6) (1999) pp. 328-337.

High-power ball mill activation of the mixture of hydrated zirconium salts (oxonitrates, oxochlorides) with ammonium phosphates followed by hydrothermal treatment at temperatures not exceeding 200 °C at a nearly neutral pH was found to yield crystalline dispersed phase of cubic ammonium zirconium phosphate $NH_4Zr_2(PO_4)_3$ along with admixtures of zirconium pyrophosphate and disordered orthorhombic compounds of the zirconium orthophosphate type. Addition of soluble lanthanum salts into the starting mixture and presence of such surfactant as polyethylene oxide during hydrothermal treatment allowed to suppress formation of zirconium pyrophosphate. In the same conditions and at the same Zr/P ratio equal to 2/3, hydrothermal treatment of gels obtained by reacting mixed zirconium and lanthanum nitrates solutions with ammonium phosphates yields no crystalline products, and only treatment in acid media generates a phase of the α-$ZrPO_4(OH)$ type coexisting with the $NH_4Zr_2(PO_4)_3$ phase if polyethylene oxide is present. X-ray powder diffraction, transmission electron microscopy, ^{31} MAS-NMR, FTIRS and thermal analysis were applied to elucidate factors affecting crystallization of the complex zirconium phosphates in the hydrothermal conditions. The most essential factor appears to be generation of some nuclei of zirconium phosphates under high pressures developed in the course of mixed solids mechanical activation. These nuclei are embedded into the matrix of such well-crystallized solid products as ammonium nitrate or chloride, which affect the atomic arrangement of the former species. Hence, metastable cubic or orthorhombic structure of the phases obtained via mechanical activation route can be assigned in part to the nuclei-matrix orientation relationship. Due to easily scaled-up synthesis procedure, these results appear to be very promising for manufacturing of dispersed framework zirconium phosphates as acid catalysts or fast proton conductors.

MATRIX EFFECT IN SYNTHESIS OF HIGHLY DISPERSED COMPLEX FRAMEWORK ZIRCONIUM PHOSPHATES WITH THE USE OF MECHANICAL ACTIVATION

S.N. Pavlova, V.A. Sadykov, G.V. Zabolotnaya,
M.V. Chaikina*, R.I. Maksimovskaya,
S.V. Tsybulya, E.B. Burgina, V.I. Zaikovskii,
G.S. Litvak, N.N. Kuznetsova, V.V. Lunin****
(*Institute of Solid State Chemistry, Novosibirsk, Russia; **Moscow Lomonosov State University, Moscow, Russia)

Doklady Chemistry, 364(2) (1999) pp. 12-14.

Numerous physicochemical techniques were used for studying the structure and phase composition of framed zirconium phosphates synthesized by hydrothermal treatment of amorphous precursors followed by calcination. The precursors were prepared using the sol-gel method and mechanical activation of solids. Effects of the solid salt matrix and surfactants on the course of synthesis of crystal framed zirconium phosphates through mechanical activation and hydrothermal treatment were first discovered.

Fe-CONTAINING SUPPORTED CATALYSTS IN REACTION OF H_2S OXIDATION WITH OXYGEN

G.A. Bukhtiyarova, N.S. Sakaeva, V.A. Varnek*,
E.B. Burgina, L.M. Plyasova, V.I. Bukhtiyarov,
V.V. Kaichev, B.P. Zolotovskii (*Institute of Inorganic Chemistry, Novosibirsk, Russia)

Chem. for Sustainable Devel., 7(4) (1999) pp. 359-374.

Influence of the nature of salt precursors on the behavior of iron-containing catalysts, which were prepared by impregnating KSK-1 silica with solutions of Fe(III) nitrate or Fe(II) sulfate, in the reaction of oxidation of hydrogen sulfide by oxygen was investigated. Surface iron compounds formed during the reaction were identified using various techniques. Catalytic properties and the nature of these compounds were compared. The comparative studies elucidated that iron disulfide is an active component of the reaction of hydrogen sulfide oxidation into sulfurous anhydride, while catalysts comprising iron sulfates and oxides oxidize selectively hydrogen sulfide to sulfur.

Thus, supported iron-containing systems can change the route of the reaction of hydrogen sulfide oxidation depending on the nature of surface iron compounds formed under the action of the reaction medium that make them promising objects to develop catalysts for selective and complete oxidation of hydrogen sulfide.

CATALYTIC ACTIVITY OF POWDER AND MONOLITH PEROVSKITES IN METHANE COMBUSTION

P. Ciambelli*, V. Palma*, S.F. Tikhov, V.A. Sadykov,
L.A. Isupova, L. Lisi** (*University of Salerno, Fisciano, Italy; **Research Institute on Combustion IRC-CNR, Napoli, Italy)

Catal. Today, 47(1-4) (1999) pp. 199-207.

Honeycomb monolith perovskite catalysts were prepared from ultradispersed powders of mixed oxides of rare-earth metals (La-Ce or Dy-Y) and transition metals (Ni, Fe, Mn) by mechanochemical method. A plasmochemical method was used to obtain La-Ni containing monoliths. The catalytic activity of powders and monoliths was compared in the catalytic combustion of methane. The intrinsic catalytic properties of the active components (apparent kinetic constant and energy of activation) were not significantly affected by the manufacturing procedure of monoliths in a large range of temperatures. Best performance was exhibited by La-Ni oxides containing monoliths, which possess the highest pore volume and fraction of macropores.

MONOLITH HONEYCOMB MIXED OXIDE CATALYSTS FOR METHANE OXIDATION

L.A. Isupova, G.M. Alikina, O.I. Snegurenko,
V.A. Sadykov, S.V. Tsybulya

Appl. Catal. B: Environmental, 21 (1999) pp. 171-181.

Kinetics data on methane oxidation were obtained for perovskite monolith catalysts. Influences of perovskite chemical composition, binder composition and calcination temperature were studied.

HONEYCOMB CATALYSTS FOR CLEAN-UP OF DIESEL EXHAUSTS BASED UPON ANODIC-SPARK OXIDIZED ALUMINUM FOIL

S.F. Tikhov, G.V. Chernykh, V.A. Sadykov,
A.N. Salanov, G.M. Alikina, S.V. Tsybulya,
V.F. Lysov* (*Institute of Applied Physics, Novosibirsk, Russia)

Catal. Today, 53(4) (1999) pp. 639-646.

Highly efficient technology of aluminum foil anodic spark oxidation in the water-based electrolytes has been applied to form strongly adhering protective alumina layer at the surface. Basic stages of the oxidation were studied by SEM and XRD. Secondary supports, promoters and modifiers including rare-earth oxides were used to increase the thermal stability up to 900 ^{0}C. These composite materials were assembled as thin wall honeycomb supports loaded with a number of active components. The catalysts were tested in the reactions of CO and CH_x oxidation, NO_x selective reduction by hydrocarbons and demonstrated a high performance and a low pressure drop at high space velocities. City diesel buses field tests of converters equipped with those catalysts demonstrated their high and stable performance in clean-up of exhausts from SOF, CO, gaseous hydrocarbons and NO_x.

THE INFLUENCE OF HETEROGENEOUS DOPANT POROUS STRUCTURE ON THE PROPERTIES OF PROTONIC SOLID ELECTROLYTE IN $CsHSO_4$-SiO_2 SYSTEM

V.G. Ponomareva*, G.V. Lavrova*, L.G. Simonova
(*Institute of Solid State Chemistry, Novosibirsk, Russia)

Solid State Ionics, 118 (1999) pp. 317-323.

Transport, thermal and structural properties of $(1\text{-}x)CsHSO_4\text{-}xSiO_2$ (where x=0-0,9) composite solid electrolytes have been studied by complex impedance, DSC and X-ray diffraction methods. The used highly dispersed silica are different in their specific surface area (13-580 m^2/g), pore size (R=14-1000 Å) and pore size distribution. It was shown that the low-temperature phase conductivity of composites is ca 2-2.5 orders of magnitude higher than that of the individual $CsHSO_4$. Composite properties depend on content and pore size of SiO_2. The low-temperature phase conductivity is maximum at x=0.5-0.7. The optimum pore size of heterogeneous dopant is in a range of 35-100 Å, where the most composite conductivity increase takes place and thermodynamic and structural properties change markedly ("dimensional effect"). For composites based on these silicas the enthalpies of $CsHSO_4$ superionic phase transition and melting considerably decrease. As x increases the ionic component becomes partially or completely amorphous. The $CsHSO_4$ dispersion most likely proceeds in composites based on silica, the pore size of which is 170 Å.

EFFECT OF SiO_2 MORPHOLOGY AND PORES SIZE ON THE PROTON NANOCOMPOSITE ELECTROLYTES PROPERTIES

V.G. Ponomareva*, G.V. Lavrova*, L.G. Simonova
(*Institute of Solid State Chemistry, Novosibirsk, Russia)

Solid State Ionics, 119 (1999) pp. 295-299.

The composite solid electrolytes $(1\text{-}x)MeHSO_4\text{-}xSiO_2$, (where Me=Cs, Rb, x=0-0.8) have been studied by complex impedance, DSC and X-ray diffraction methods. The used SiO_2 varied in specific surface areas (13-580 m^2 g^{-1}), pores size (R=14-1000 Å) and pores size distribution. The low-temperature conductivity of the composites was shown to exceed by 1-3 orders of magnitude that of the individual salts. It depended on SiO_2 content, silica pores size and their distribution. There is optimum silica pores size in a range of 35-100 Å, where the most composite conductivity increase takes place; the ionic component becomes either partially or completely amorphous with x increasing ("dimensional effect"). The $MeHSO_4$ dispergation mainly proceeds in composites with R=170 Å. The $MeHSO_4$ state does not change when SiO_2 pores size is 1000 Å. In systems with R=14 Å both $MeHSO_4$ low-temperature phase and amorphous state are observed.

SO_4^{2-}/TiO_2 (ANATASE): SOME PECULIARITIES OF THE STRUCTURE FORMATION DURING THERMAL TREATMENT

G.A. Zenkovets, S.V. Tsybulya, E.B. Burgina, G.N. Kryukova

Kinetics & Catalysis, 40(4) (1999) pp. 562-566.

Specific features of the formation of the titanium dioxide structure doped by sulfate ions are studied. Sulfate ions and water molecules enter the anatase structure to form the fragments of the titanyl sulfate type. This results in a significant decrease in the lattice parameter c, the disturbance of the cation distribution, and the appearance of microdistortions in the structure.

NEW TECHNOLOGIES FOR HPAs AND HPAs BASED CATALYSTS

G.M. Maksimov, V.V. Molchanov, V.V. Goidin

Chem. Industry., 10 (1998) pp. 599-601.

New methods of HPAs synthesis – electrochemical (electrodialysis) and with the use of mechanochemical activation of oxides are presented. The first method is good for the synthesis of W-containing HPAs, in particular, W-P HPAs. Mechanochemical activation is effective at synthesis of Mo- or Mo-V-heteropoly acids. Both methods are characterized by high productiveness, complete use of expensive initial materials, absence of waste products and low power inputs.

PHYSICOCHEMICAL PROPERTIES OF THE $V_2O_5\text{-}H_3PO_4\text{-}SiO_2$ SYSTEM

T.N. Yakovleva*, R.S. Dulina*, D.V. Tarasova*, R.I. Maksimovskaya, M.M. Soderzhinova*
(*Karpov Research Institute of Physical Chemistry, Moscow, Russia

Russ. J. Inorg. Chem., 44(2) (1999) pp. 231-236.

The influence of the component ratio on the physicochemical properties of $V_2O_5–H_3PO_4–SiO_2$ mixtures was studied. It was shown that coarse-grained vanadium(V) phosphate dihydrate is formed when vanadium(V) oxide, phosphoric acid, and silica gel are stirred together. During heat treatment, the silica gel reacts with free phosphoric acid, keeping vanadyl metaphosphate from forming. The grain size of the solid products is controlled mainly by phase constitution.

PROPERTIES OF BARIUM AND LANTHANUM HEXAALUMINATES PREPARED BY SOLID-STATE REACTION AND SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

O.V. Andryushkova*, V.A. Ushakov, O.A. Kirichenko*, M.A. Korchagin*, V.A. Poluboyarov* (*Institute of Solid State Chemistry, Novosibirsk, Russia)

Inorganic Mater., 34(8) (1998) pp. 832-837.

The catalytic activity, specific surface area, and electron paramagnetic resonance of substituted barium hexaaluminates prepared via mechanical activation are studied. Unsubstituted barium and lanthanum hexaaluminates are characterized by X-ray diffraction. Self-propagating high-temperature synthesis is shown to be a promising technique for preparing melted barium hexaaluminate. Electron-microscopic examination of melted and fracture surfaces reveals microstructural features that are believed to be responsible for the high strength of the material.

SYNTHESIS AND PROPERTIES OF IRIDIUM(III) TRINITROTRIAQUO COMPLEX AND ITS DERIVATIVES

S.V. Korenev*, A.B. Venediktov*, V.I. Malkova*, M.A. Fedotov (*Institute of Inorganic Chemistry, Novosibirsk, Russia)

Russ. J. Coord. Chem., 25(9) (1999) pp. 650-652.

Simple methods for preparing hitherto unknown iridium(III) trinitrotriaquo and iridium(III) trinitrotrichloro complexes were developed. The purity of the compounds was proved by high-resolution (^{15}N, ^{14}N) NMR, electronic absorption, and IR spectroscopies; solid substances were characterized by elemental analysis. The quantitative data on the acidity of *fac*-$[Ir(NO_2)_3(H_2O)_3]$ are presented. The changes in the ^{15}N NMR chemical shifts of the iridium(III) trinitrotriaquo complex are discussed as functions of pH.

INCREASE OF EFFICIENCY OF TITANIUM OXIDE CATALYSTS FOR SULFUR RECOVERY BY THE CLAUS METHOD

G.A. Bukhtiyarova, N.S. Sakaeva, B.P. Zolotovskii, V.I. Murin*, R.A. Buyanov (*VNIIGas, Moscow Region, Russia)

Chem. for Sustainable Devel., 7(2) (1999) pp. 119-127.

The efficiency of catalysts for the Claus process of sulfur recovery from acid gases of oil and gas purification, waste gases of non-ferrous metallurgy was shown to depend on the activity for Claus reactions and hydrolysis of COS, CS_2, including those in the presence of oxygen in the reaction mixture, on the stability to deactivation caused by the formation of surface sulfates. It was established that introduction of V and Mg compounds into the titanium oxide catalyst Ti-Ca allows a new polyfunctional catalyst for the Claus process to be obtained, high protective behavior and enhanced stability to deactivation during the Claus reactions and COS hydrolysis in the presence of oxygen being characteristic of this catalyst. Thus, the new catalyst can be used for effective sulfur recovery from technological gases comprising oxygen in a considerable proportion.

NEW CATALYSTS AND APPROACHES TO INCREASE EFFICIENCY OF PURIFICATION OF MONOMERS FROM ADMIXTURES OF ACETYLENIC AND DIENE HYDROCARBONS BY HYDROGENATION

V.V. Molchanov, R.A. Buyanov

Chem. Industry, 4 (1999) pp. 265-269.

Catalytic systems unknown before, among which are hydrides of magnesium intermetallides and metal-filamentous carbon systems, were shown to be effective for selective hydrogenation. New methods for improving the hydrogenation selectivity were suggested based on the study of hydrogenation mechanisms, *viz.* the role of hydrogen species in the catalytic action.

PLATINUM SUPPORTED CATALYSTS PREPARED FROM METAL CARBONYL CLUSTERS FOR HYDROCARBON CONVERSION

P.E. Kolosov*, N.B. Shitova, M.D. Smolikov, V.A. Drozdov, E.M. Moroz (*Omsk State University, Omsk, Russia)

Mater. Res. Soc. Symp. Proceed., 549 (1999) pp. 243-248.

The investigation of surface Pt/alumina, Pt/carbon (Sibunit) and Pt/SiO_2 species prepared by anchoring of Pt carbonyl clusters of various nuclearity as precursors for high dispersive and thermostable platinum supported catalysts for hydrocarbons conversion, using RDF (radial distribution functions) and chemisorption methods, has shown strong metal-support interaction with formation of Pt/alumina phase with highly dispersed (practically monoatomic) and homogeneously distributed Pt atoms onto alumina surface. The catalytic properties were studied in methane oxidation and cyclohexane dehydrogenation reactions.

ARTIFICIAL RIBONUCLEASES: SYNTHESIS AND RNA CLEAVING PROPERTIES OF CATIONIC CONJUGATES BEARING IMIDAZOLE RESIDUES

D.A. Konevetz* , I.E. Beck, N.G. Beloglazova*, I.V. Sulimenkov, V.N. Sil'nikov*, M.A. Zenkova*, G.V. Shishkin*, V.V. Vlassov*** (*Institute of Bioorganic Chemistry, Novosibirsk, Russia; **Institute of Energy Problems in Chemical Physics, Chernogolovka, Russia)

Tetrahedron, 55(2) (1999) pp. 503-512.

Small mimics of the ribonuclease active centre were synthesized by conjugating imidazole residues to a dicationic compound. These compounds were shown to cleave RNA under physiological conditions. The compounds provide new probes for the investigation of RNA structure in solution and potential catalytic RNA cleaving groups for antisense oligonucleotide derivatives.

NANOPARTICLES OF Ti AND Zr IN ORGANOSILICON POLYMER CERAMIC PRECURSORS

S.P. Gubin*, E.M. Moroz, A.I. Boronin, V.V. Kriventsov, D.A. Zyuzin, N.A. Popova, E.K. Florina**, A.M. Tsirlin**** (*N.S. Kurnakov Institute of General and Inorganic Chemistry, Moscow, Russia; **Institute of Chemistry and Technology of Organoelement Compounds, Moscow, Russia)

Mendeleev Commun., 2 (1999) pp. 59-61.

A procedure was developed for introducing Ti and Zr nanoparticles into organosilicon polymer ceramic precursors; all of the particles were found to be multiphase and to contain the metals, metal carbides, and metal oxides associated with the polymer matrix.

Carbon and Carbon Containing Materials. Synthesis and Processes with their Participation

^{129}Xe NMR STUDY OF CARBONACEOUS MATERIALS: EFFECT OF SURFACE CHEMISTRY AND NANOTEXTURE

P.A. Simonov, S.V. Filimonova, G.N. Kryukova, E.M. Moroz, V.A. Likholobov, T. Kuretzky*, H.P. Boehm*

Carbon, 37 (1999) pp. 591-600.

Some aspects of the relationship between the physicochemical state of microcrystalline carbons and the ^{129}Xe NMR parameters of adsorbed xenon have been investigated. No correlation between the values of the ^{129}Xe chemical shift (δ_0) and the substructural characteristics of the carbons (interlayer spacing, crystallite size, content of ordered or amorphous carbon of the samples), micropore volume and specific surface area was revealed. The δ_0 values do increase linearly with the surface concentrations of “strong” adsorption sites for H_2PdCl_4, and chemisorbed heteroatoms (O, Cl) as well. HREM studies of carbon surface microstructure revealed δ_0 to be nanotexture-dependent. The lowest δ_0 value (~14 ppm) was detected for a graphitizied carbon black, the surface of which consists primarily of exposed basal planes of carbon crystallites, and the highest δ_0 value (~100 ppm) for a carbon sample with exposed edge faces. Medium δ_0 values (50±10 ppm) were found for carbons the surface of which is roughened up by steps formed by carbon layers of different size.

COBALT CATALYSTS OF METHANE DECOMPOSITION: ACCUMULATION OF THE FILAMENTOUS CARBON

L.B. Avdeeva, D.I. Kochubey, Sh.K. Shaikhutdinov

Appl. Catal. A: General, 177(1) (1999) pp. 43-51.

Cobalt catalysts are tested in methane decomposition reaction at 475-600 ^{o}C and pressure ~ 1 bar to evaluate their catalytic properties in non-oxidative methane conversion via an accumulation of carbon. Catalyst preparation method, a nature of a support and temperature regimes are found to strongly influence this process. The best performances are found with the coprecipitated 60-75 wt % Co-alumina catalysts at 500 ^{o}C. XRD, EXAFS, TEM investigations indicate a close similarity between the Co and Ni catalysts previously studied. However, in contrast to nickel, the carbon filaments with a hollow-like core morphology are produced on the Co catalysts. Data further point that an accumulation of the filamentous carbon is a promising route to utilize methane as a main component of the natural gas.

The obtained results showed that using such bimetallic systems permits to carry out liquid phase hydrodechlorination of hexachlorobenzene under mild conditions. Methods of catalysts preparing effect on their activity and selectivity.

NEW NICKEL CATALYSTS FOR THE FORMATION OF FILAMENTOUS CARBON IN THE REACTION OF METHANE DECOMPOSITION

M.A. Ermakova, D.Yu. Ermakov, G.G. Kuvshinov, L.M. Plyasova

J. Catal., 187(1) (1999) pp. 77-84.

A method for intentional synthesis of metal catalysts, specifically nickel catalysts for methane decomposition, was developed. The method was based on impregnation of a porous metal oxide with the precursor of a textural promoter followed by reduction of the latter. The desired texture of NiO was provided by pre-calcining it at a certain temperature within the range of 300 to 900 °C. A family of nickel-based catalytic systems with various concentrations of the active component, metal particle size, and stability to deactivation in the course of synthesis of filamentous carbon was prepared. The yield of carbon and mechanical strength of carbon particles growing on the catalyst during methane decomposition were found to increase with the concentration of nickel in the catalyst to reach their maxima at 90-96% of nickel. The highest yield of carbon (375-384 g of carbon per g of nickel) was observed for the catalyst with particles of 10-40 nm average diameter. The effect of textural promoters (SiO_2, Al_2O_3, MgO, TiO_2 and ZrO_2) on the catalyst performance was studied, the highest carbon yield was obtained with SiO_2.

XRD STUDIES OF EVOLUTION OF CATALYTIC NICKEL NANOPARTICLES DURING SYNTHESIS OF FILAMENTOUS CARBON FROM METHANE

M.A. Ermakova, D.Yu. Ermakov, L.M. Plyasova, G.G. Kuvshinov

Catal. Lett., 62(2-4) (1999) pp. 93-97.

XRD technique was used for studying a series of high-loaded (90%) nickel catalysts with silica as a textural promoter. These were catalysts for direct cracking of methane at 550 °C. A relation between the initial average size of active catalyst particles, carbon yield and average methane conversion was demonstrated. Genesis of these catalysts was studied including oxide precursors, reduced catalysts prior to the reaction, as well as catalysts upon their contacting the reaction medium for various periods of time from 15 minutes to 2 hours. The active catalyst particles were shown to merge or disperse at the outset of the reaction depending on their initial size. Anyway, the close average sizes ranging from 30 to 40 nm were observed by the end of the first reaction hour for all the catalytic systems providing the carbon yield of 300 to 385 g per g Ni. The catalytic system was shown to self-organize in the course of direct methane cracking, *i.e.* the catalyst particles transform in response to the reaction conditions. If the size of nickel particles cannot vary, these catalysts are inefficient for the given process.

MECHANISM OF POROUS FILAMENTOUS CARBON GRANULE FORMATION ON CATALYTIC HYDROCARBON DECOMPOSITION

G.G. Kuvshinov, Yu.I. Mogilnykh, D.G. Kuvshinov, D.Yu. Ermakov, M.A. Ermakova, N.A. Salanov, N.A. Rudina

Carbon, 37(8) (1999) pp. 1239-1246.

The growth of catalytic filamentary carbon granules formed on methane decomposition over Ni catalysts has been studied. As a result, a hundred-fold increase in the particle volume can be obtained. It was established that as Ni concentration in the initial catalyst increases, the solidity of catalytic filamentary carbon (CFC) aggregates, formed on methane decomposition, increases. In the course of CFC formation on the finely-disperse catalyst of high nickel content, the inner structure of the growing granule transforms from the dense agglomerate of nickel particles into a dense carbon filament packing with rather large single internal cavities (cracks). On the granule surface there is a layer whose filament packing remains loose. The physical model of granule formation has been proposed.

FILAMENTARY CARBON AS A CATALYST FOR DIRECT HYDROGEN SULFIDE OXIDATION TO SULFUR

G.G. Kuvshinov, Yu.I. Mogilnykh, M.Yu. Lebedev

Chem. Industry, 1 (1999) pp. 26-33.

Potentiality of catalytic filamentous carbon (CFC) as a catalyst for direct oxidation of hydrogen sulfide into sulfur was investigated. CFC was demonstrated to compete with active carbons and metal oxide catalysts at a considerable excess of oxygen in the inlet gas. The activity and selectivity of the process depending of the state of nickel particles involved in the catalytic filamentous carbon and on the textural parameters of the carbon were studied.

SYMMETRICAL SPIRAL FORMS OF FILAMENTOUS CARBON FORMED FROM BUTADIENE-1,3 ON THE Ni-Cu/MgO CATALYST: REGULARITIES AND MECHANISM OF GROWTH

V.I. Zaikovskii, V.V. Chesnokov, R.A. Buyanov

Kinetics & Catalysis, 40(4) (1999) pp. 552-555.

High resolution electron microscopy (HREM) was used to study the regularities of formation of symmetrical spiral forms of filamentous carbon from butadiene-1,3 on a Ni–Cu/MgO catalyst at 450 °C. Mirror-symmetrical carbon filaments coiled in spirals were shown to grow from one particle of the Ni–Cu alloy. A microphase of metastable carbide Ni_3C was formed on the front side of the particle during filament growth, and the crystalline particle of the Ni–Cu alloy included a series of twinning planes (111) parallel to the mirror-symmetrical plane of the crystal that separated twin blocks with the fcc structure. A mechanism of growth of the symmetrical spiral forms of filamentous carbon is proposed.

SOLAR THERMAL DECOMPOSITION OF HYDROCARBONS AND CARBON MONOXIDE FOR THE PRODUCTION OF CATALYTIC FILAMENTOUS CARBON

A. Meier*, V.A. Kirillov, G.G. Kuvshinov,
Yu.I. Mogilnykh, A. Reller*, A. Steinfeld*,
A. Weidenkaff* (*Switzerland, PSI)

Chem. Eng. Sci., 54 (1) (1999) pp. 3341-3348.

Concentrated solar radiation is used as the clean source of process heat for the production of catalytic filamentous carbon (CFC) by thermal decomposition of gaseous hydrocarbons (CH_4 and C_4H_{10}) and by CO disproportionation in the presence of small metal catalyst particles. Depending on the catalyst, two different types of CFC, namely nanotubes and nanofibers, are obtained in solar experiments. Nanotubes are formed mainly using Co/MgO catalyst for CO and CH_4+N_2; nanofibers are formed mainly on Ni/Al_2O_3 catalysts for CH_4, CH_4+N_2 and C_4H_{10}. Laboratory experiments confirm these findings. Typically, the following properties were determined by BET and X-ray diffraction for CFC samples formed under both solar and laboratory experimental conditions: the surface area is about 50-170 m^2/g, the pore volume is in the range of 0.4-0.8 cm^3/g, the micropore volume is between 0.002 and 0.008 cm^3/g, and the average pore diameter ranges between 10 and 40 nm. From these properties and from the inspection of high-resolution transmission electron micrographs it was concluded that CFC with well-defined morphology could be produced using concentrated solar radiation.

STUDY OF THERMOCATALYTIC DECOMPOSITION OF POLYETHYLENE AND POLYVINYL ALCOHOL IN THE PRESENCE OF AN UNSTEADY-STATE Fe-CONTAINING CATALYST

N.I. Maksimova, O.P. Krivoruchko

Chem. Eng. Sci., 54(20) (1999) pp. 4351-4357.

The thermal decomposition of low-density polyethylene (LDPE) and polyvinyl alcohol (PVA) in nitrogen flow at a temperature range of 573-873 K was investigated in the presence of Fe-containing catalysts. In this temperature range decomposition of these polymers with formation of gaseous (C_1-C_4), liquid (C_5-C_{30}), and solid (carbon, carbide, graphite) products is observed. During this process, α-FeO(OH) used as a precursor of the catalyst is reduced to iron oxides and metal, and, therefore, it is in unsteady state. The unsteady state of catalyst allows one to affect on all stages of polymer decomposition. Gas chromatography-mass spectroscopy (GCMS) and X-ray diffractometry (XRD) show that the presence of the Fe-containing catalyst greatly affects both liquid and solid products of thermal decomposition of LDPE and PVA.

PREPARATION OF NANOSCALE THIN-WALLED CARBON TUBULES FROM A POLYETHYLENE PRECURSOR

N.I. Maksimova, O.P. Krivoruchko, A.L. Chuvilin, L.M. Plyasova

Carbon, 37(10) (1999) pp.1657-1661.

A method for producing thin-walled carbon tubules from a polyethylene precursor in the presence of a Fe catalyst uniformly distributed in the bulk of the polymer is presented. The mechanism of their formation involves the decomposition of the polyethylene precursor on the catalyst particles at 600 ^{o}C leading to the formation of disordered carbon shells covering the catalyst particles, and sequential removal of the catalyst particles through defects in the carbon shells in temperature range 600-750 ^{o}C. The structure of the tubules obtained was not damaged during the purification by the treatment in an acid solution, which allows one to obtain pure samples of thin-walled carbon tubules. Apparently, this method opens the way for further chemical decoration and modification of thin-walled carbon tubules leading to the preparation of carbon materials with novel physical and chemical characteristics.

STRUCTURAL INVESTIGATIONS OF CLOSE-PACKED SINGLE-WALL CARBON NANOTUBE MATERIAL

E.D. Obraztsova*, V.Yu. Yurov*, V.M. Shevluga*, R.E. Baranovsky*, V.A. Nalimova, V.L. Kuznetsov, V.I. Zaikovskii** (*General Physics Institute, Moscow, Russia, **Moscow Lomonosov State University, Moscow, Russia)

NanoStructured Mater., 11 (1999) pp. 295-306.

A structure of recently produced 100% single-wall carbon nanotube material with a paper-like quality (permitting to measure the parameters of the individual tubes *in situ*) has been investigated thoroughly by a set of techniques being informative for nanoscale objects; a high resolution transmission electronic microscopy, scanning tunneling microscopy with an atomic resolution and Raman scattering.

THEORETICAL STUDY OF THE FORMATION OF CLOSED CURVED GRAPHITE-LIKE STRUCTURES DURING ANNEALING OF DIAMOND SURFACE

V.L. Kuznetsov, I.L. Zilberberg, Yu.V. Butenko, A.L. Chuvilin, B. Segall* (*Case Western Reverse University, Cleveland, Ohio)

J. Appl. Phys., 86(2) (1999) pp. 863-870.

In recent high resolution transmission electron microscopic studies it have been found that high temperature vacuum annealing (1200-1800 K) of ultradispersed (2-5 nm) and micron size diamond produces fullerene-like graphitic species, namely, onion-like carbon and closed curved graphite structures (multilayer nanotubes and nanofolds), respectively. The theoretical studies were undertaken to help in the understanding of the experimental data for these systems. (1) Calculations of cluster models by a standard semiempirical method (MNDO a software package) are used to explain the preferential exfoliation of {111} planes over other low index diamond planes. (2) The same approach suggests the likelihood that the graphitization is initiated by a significant thermal displacement of a single carbon atom at temperatures close to the Debye temperature. (3) At the diamond-graphite interface the formation of two curved graphitic sheets from three diamond {111} planes have been observed. It was suggested that the evolution of this interface proceeds by a “zipper”-like migration mechanism with the carbon atoms of the middle diamond layer being distributed equally between the two growing graphitic sheets. (4) The observed mosaic packaging of closed curved graphite structures during the diamond surface graphitization is suggested to be a self-assembling process. This process is explained in terms of the “stretching” of a bowed graphite hexagonal network. The stretch is due to the fact that, if relaxed, the network would be smaller than the initially transformed hexagonal diamond (111), and to the increased separation between the separated sheet and the surface. The initial phase of the process is studied quantitatively using a molecular mechanics simulation.

STRUCTURAL MEASUREMENTS FOR SINGLE-WALL CARBON NANOTUBES BY RAMAN SCATTERING TECHNIQUE

E.D. Obraztsova*, J.-M. Bonard, V.L. Kuznetsov, V.I. Zaikovskii, S.M. Pimenov*, A.S. Pozarov*, S.V. Terekhov*, V.I. Konov*, A.N. Obraztsov***, A.P. Volkov***** (*General Physics Institute, Moscow, Russia; **Insitute de Physique Experimentale, Lausanne, Switzerland; ***Moscow Lomonosov State University, Moscow, Russia)

NanoStructured Mater., 12 (1999) pp. 567-572.

The single-wall carbon nanotubes grown by different techniques have been investigated by Raman scattering and high resolution transmission electron microscopy (HRTEM). The tube diameter values and the tube distribution over diameter have been estimated from the position and shape of the low-frequency band in the Raman spectrum containing the “breathing” modes. The diameter-dependent enhancement of the Raman signals form the different nanotube fractions occurred not only due to optical resonance with the laser excitation energy, but also due to thermo-induced resonance. The low-field electron emission from the single-wall carbon nanotube material has been measured. The threshold fields were 0.75-2 V/μm, the emission current reached the value 15 mA/cm^2 at fields of 20 V/μm.

ROLE OF THE CURVATURE OF ATOMIC LAYERS IN ELECTRON FIELD EMISSION FROM GRAPHITIC NANOSTRUCTURED CARBON

A.N. Obraztsov*, A.P. Volkov*, I.Yu. Pavlovsky*, A.L. Chuvilin, N.A. Rudina, V.L. Kuznetsov
(*Moscow Lomonosov State University, Moscow, Russia)

JETP Lett., 69(5) (1999) pp. 411-417.

Layers of oriented carbon nanotubes and nanometer-size plate-shaped graphite crystallites are obtained by a CVD method in a glow discharge plasma. A structural-morphological investigation of a carbon material consisting of nanotubes and nanocrystallites is performed, and the field emission properties of the material are also investigated. It is shown that electron field emission is observed at electric fields equal to or greater than 1.5 V/μm. The low fields giving rise to electron emission can be explained by a decrease in the work function as a result of the curvature of atomic layers of graphitic carbon.

RAMAN IDENTIFICATION OF ONION-LIKE CARBON

E.D. Obraztsova*, M. Fujii, S. Hayashi**, V.L. Kuznetsov, Yu.V. Butenko, A.L. Chuvilin**
(*General Physics Institute, Moscow, Russia; **Kobe University, Rokko, Nada, Kobe, Japan)

Carbon, 36(5-6) (1998) pp. 821-826.

A specific Raman spectrum of carbon spherical shells (onions) synthesized by annealing-induced (T=1800 K) chipping off the outer carbon layers from 5-nm size diamond particles has been observed. It shows a clearly seen band at 1572 cm^{-1}. Its downshift from the position 1582 cm^{-1} (known for a pure graphite) is interpreted as an influence of shell curvature. The summary contribution of the shells constituting the 5-nm diameter onion is estimated. A narrowness (FWHM=15 cm^{-1}) of the first order Raman band of onions together with a dominance of the peak at 2712 cm^{-1} (FWHM=65 cm^{-1}) in their second order spectrum point to a high degree of structural perfection of a graphite network in shells.

Catalysis for Synthesis Sulfur-Organic Compounds

REACTION OF DODECANOL-1 WITH H_2S ON ACID CATALYSTS

A.V. Mashkina, L.G. Sakhaltueva

React. Kinet. Catal. Lett., 66 (1) (1999) pp. 133-140.

The reaction of dodecanol-1 with H_2S has been studied at 275 °C and 0.1 MPa on acid catalysts. The effect of their composition on the direction and rate of conversion has been elucidated. The proton-donor catalysts accelerate only alcohol dehydration, whereas in the presence of catalysts containing Lewis acid sites dodecanol-1 react with H_2S yielding dodecanethiol-1. The reaction rate increases with increasing concentration and strength of Lewis acid sites.

ACTIVITY OF TRANSITION METAL SULFIDES IN HYDROGENATION OF THIOLENE-1,1-DIOXIDES

A.V. Mashkina, T.S. Sukhareva

React. Kinet. Catal. Lett., 67(1) (1999) pp. 103-110.

The activity and selectivity of sulfides of group VI-VIII metals in the liquid-phase hydrogenation of thiolene-1,1-dioxides to thiolane-1,1-dioxide were studied at elevated hydrogen pressure. The generation of thiolane-1,1-dioxide is accompanied by the substrate decomposition. These processes follow absolutely independent routes. The specific activity of Ni sulfide was four and 60-80 times lower than that of Pt, Re, Co and W sulfides, and Rh and Pd sulfides, respectively. Assumed that the reaction rate is limited by the interaction of dissolved thiolene-1,1-dioxide with adsorbed hydrogen, and the reaction proceeds at high surface coverage with hydrogen.

INVESTIGATIONS IF THE FIELD OF CATALYTIC SYNTHESIS OF ORGANIC SULFUR COMPOUNDS

A.V. Mashkina

Chem. for Sustainable Devel., 7(6) (1999) pp. 703-712.

Results obtained in the field of catalytic synthesis of organic sulfur compounds from sulfuric constituents of oil, gas and products of processing of natural raw materials were summarized. Sulfolane and 4-methylthiazol were synthesized using sulfur dioxide, alkanethiols, dimethyl sulfide, thiolane using hydrogen sulfide. Dialkyl sulfides were synthesized based on lower alkanethiol constituents of natural gas. Dialkyl sulfides were transformed to thiolsulfinates, thiolsulfonates, sulfacids and thiols. Individual and oil sulfides were oxidized into sulfoxides. Thiophenes were synthesized through heterocyclization of various organosulfur compounds; reactions of dehydrogenation, dealkylation and hydrogenation of these thiophenes were studied.

Heteropoly Acids in Catalysis

P-Mo-V HETEROPOLY ACIDS AS CATALYSTS FOR 2,6-DIALKYLPHENOLS OXIDATION TO THE CORRESPONDING 2,6-DIALKYL-1,4-BENZOQUINONES BY MOLECULAR OXYGEN

I.G. Kolesnik, E.G. Zhizhina, K.I. Matveev

React. Kinet. & Catal. Letters, 68(2) (1999) pp. 339-346.

A new method for preparation of 2,6-dialkyl-1,4-benzoquinones by oxidation of 2,6-dimethyl-(DMP) and 2,6-ditertbutylphenols (DTP) by dioxygen in a two-phase “water-organic” system in the presence of P-Mo-V heteropoly acids was proposed. The DMP and DTP are oxidized to the corresponding quinones at 313÷343 K in the presence of different organic solvents. The best solvent is trichloroethylene for DMP oxidation, and one is toluene for DTP oxidation. The selectivity of DMP oxidation reaches 85%, and one of DTP oxidation is 77%.

MECHANISM OF FORMIC ACID DECOMPOSITION ON P-Mo HETEROPOLY ACID

G.Ya. Popova, I.I. Zakharov, T.V. Andrushkevich

React. Kinet. & Catal. Lett., 66(2) (1999) pp. 251-256.

Hydrated (undecomposed) form of heteropolyacid $H_3PMo_{12}O_{40}/SiO_2$ exhibits a higher activity in the formic acid decomposition than the corresponding dehydrated sample. The formic acid decomposition takes place on strong Brönsted acid sites of the heteropoly acid. *Ab initio* SCF MO LCAO method was used for the calculation of the electronic state of two surface complexes of HCOOH molecule (S1 and S2) coordinated to a proton H^+. The S1 complex is formed by proton addition to the carbonyl oxygen, whereas the S2 complex is formed by proton addition to the oxygen atom of the C-O-H fragment of HCOOH. The selective weakening of the C-O bond and localization of the positive charge on the (O=C-H) fragment in the protonated complex S2 are favorable for the decomposition of formic acid to CO and H_2O.

PALLADIUM(II) COMPLEXES WITH PYRIDINEDICARBOXYLIC AND 2,4,6-PYRIDINETRICARBOXYLIC ACIDS

V.F. Odyakov

Russ. J. Inorg. Chem., 44(2) (1999) pp. 178-182.

The palladium(II) chelate $Pd(Hpdc)_2{\bullet}yH_2O$ with 2,4-, 2,5-, and 2,6-pyridinedicarboxylic acids ($Hpdc^-$) as bidentate ligands (**I**–**III**, respectively) were obtained in the solid state. In addition, the complex $(H_2O)Pd(dipic)$ (**IV**) with 2,6-pyridinedicarboxylic acid ($dipic^{2-}$) as a tridentate ligand was synthesized. Complex **IV** enters into the composition of stable homogenous catalysts of olefin oxidation. The mixed-ligand BPd(dipic) complexes, where B is pyridine (py) (**V**), quinoline (**VI**), or nicotinic and isonicotinic acids (**VII** and **VIII**, respectively), as well as the anionic complex $[ClPd(dipic)]^-$ (**IX**) were also obtained. The chelate $Pd(H_2tmes)_2 \cdot 3H_2O$ (**X**) and the mixed-ligand $(py)Pd(Htmes) \cdot 1.5H_2O$ complex (**XI**), in which 2,4,6-pyridinetricarboxylic acid acts as the bidentate (H_2tmes^-) and tridentate ($Htmes^{2-}$) ligand, respectively, were synthesized.

THERMOCHEMICAL STUDY OF THE REDUCTION AND OXIDATION OF MOLYBDOVANADOPHOSPHORIC HETEROPOLY ACIDS IN AQUEOUS SOLUTIONS

E.G. Zhizhina, Yu.D. Pankrat’ev, V.F. Odyakov, K.I. Matveev

Russ. J. Inorg. Chem., 44(4) (1999) pp. 506-510.

The differential enthalpy ($-\Delta_r H_{4j}$) of the reduction of 0.2 M aqueous solutions of heteropoly acids $H_{3+x}PV_xMo_{12\,x}O_{40}$ (HPA-x, $1 \le x \le 3$) by hydrazine hydrate (HH) at 343 K was investigated as a function of x and of the degree of reduction $m=[V^{IV})]/[HPA\text{-}x]$. For all of the HPA-$x$ solutions studied, the initial $-\Delta_r H_{4j}$ value (at $m \sim 0$) approximated 436±14 kJ per mole of HH. For an HPA-3 solution at $m \approx 0.65$, a maximum in $-\Delta_r H_{4j}$ was observed (≈ 483 kJ per mole of HH) due to the interaction of the VO_2^+ and VO^{2+} cations in the inner coordination sphere of the HPA-3 ion. This maximum is similar to that observed in the reduction of an 0.1 M solution of VO_2ClO_4 in 4 M $HClO_4$. In the case of reduction of HPA-1, HPA-2, or salts of HPA-3, no $\Delta_r H_{4j}$ maxima were observed, because the content of VO_2^+ in the ICS of the corresponding heteropoly anion is too low. The $-\Delta_r H_{4j}$ values for solutions of HPA-3 salts depend only on the pH but not on the nature of the cation. The enthalpies of oxidation of solutions of the reduced forms of the HPA-x by dioxygen ($-\Delta_r H_{2j}$) were calculated. The sequence of oxidation of various V^{IV} species in solutions of the reduced HPA-x is opposite to the sequence of reduction of various forms of V^V in the initial solutions of HPA-*x*.

THERMOCHEMICAL STUDY OF REDUCTION AND OXIDATION REACTIONS OF MOLYBDOVANADOPHOSPHORIC HETEROPOLY ACIDS IN AQUEOUS SOLUTIONS

E.G. Zhizhina, V.F. Odyakov, K.I. Matveev

Euro. J. Inorg. Chem., 6 *(*1999) pp. 1009-1014.

Reduction and oxidation of aqueous solutions of heteropoly acids $H_{3+x}PV_xMo_{12-x}O_{40}$ (HPA-*x*, where $1 \le x \le 6$) and their salts are reversible reactions. Differential enthalpies of reduction of their 0.2 M solutions by hydrazine hydrate, $-\Delta_r H_{4j}$, were measured at 343 K. The $-\Delta_r H_{4j}$ values depend on *x* and *m*, where m=[V^{IV}]/[HPA-*x*]. At m~0, the initial $-\Delta_r H_{4j}$ is 436 ± 14 kJ mol^{-1} HH for all HPA-*x*. For HPA-*x* with $3 \le x \le 6$, the curves $-\Delta_r H_{4j} = f(m_j)$ have maxima associated with formation and reduction of the outer-sphere cation $V^V V^{IV} O_3^{3+}$, that are similar to maximum observed on reduction of 0.1 M VO_2ClO_4 in 4 M $HClO_4$. No maxima are observed for the reduction of HPA-1, HPA-2, and salts of HPA-3. For HPA-3 salts, $-\Delta_r H_{4j} = f(m_j)$ depends primarily on the pH of the salt solution, rather than on the nature of the cation. The sequences of the reduction of different V^V forms in initial HPA-*x* solutions, and ones of oxidation of different V^{IV} forms in reduced H_mHPA-*x* solutions are discussed.

Catalysis and Biotechnology

ADSORPTION AND ANTIFIBRINOLYTIC ACTIVITY OF ε-AMINOCAPROIC ACID ON CARBON-CONTAINING ENTEROSORBENTS

G.A. Kovalenko, E.V. Kuznetsova, M.P. Vanina

Chemical-Pharmaceutical J., 32(11) (1999) pp. 39-42.

Study on adsorption of ε-aminocaproic acid (low-molecular weight inhibitor of fibrinolysis) on carbon-containing enterosorbents of SUMS, SKN, Carbactine types was carried out to develop medicine for stomatology. Due to polymolecular character of adsorption amount of adsorbed ε-aminocaproic acid exceeded 1g per 1 g of enterosorbent. Preliminary clinical testing of medicine based on ε-aminocaproic acid adsorbed on enterosorbents showed high efficiency in medical treatment of gingivitis and parodontitis.

CARBONACEOUS MATERIALS AS ADSORBENTS FOR BIOLOGICALLY ACTIVE SUBSTANCES AND BACTERIAL CELLS

G.A. Kovalenko, V.A. Semikolenov,
E.V. Kuznetsova, G.V. Plaksin, N.A. Rudina

Colloid J., 61(6) (1999) pp. 729-736.

Regularities of the adsorption of biological objects (proteins, enzymes, and nonproliferating bacterial cells) on new porous carbonaceous materials differing in the structure of the porous matrix and the microstructure of the surface were studied. The character of the distribution of the immobilized cells of microorganisms on the surface of carbonaceous adsorbents was studied by scanning electron microscopy.

UV SPECTROSCOPIC DETERMINATION OF CONCENTRATIONS OF ACID AND BASIC SITES ON THE SURFACE OF SUPPORTS AND ADSORBENTS

G.A. Kovalenko, M.P. Vanina

Factory Laboratory, 9 (1999) pp. 43-46.

A rapid and comparatively simple method for UV spectroscopic determination of concentrations of acid and basic sites of different strength was described. The method is based on direct titration of the surface by weak acids and bases with various pKa. The concentration of surface sites was determined from the adsorption level of the pertinent titrant at the range of formation of the monolayer coat (plateau in the adsorption isotherms); it was expressed as μmol/m^2. The method was checked with supports prepared from alumina and titanium oxide with different textural parameters and chemical nature.

METHANE HYDROXYLATION AND PROPYLENE EPOXIDATION BY RESTING CELLS OF *METHYLOCOCCUS CAPSULATUS IMV 3021*

G.A. Kovalenko, V.M. Lenskaya

Appl. Biochem. & Microbiol., 34(4) (1998) pp. 321-325.

Studies on kinetics of direct biooxidation of methane into methanol and propylene into epoxypropane were carried out in suspensions of resting cells of methanotroph *Methylococcus capsulatus IMV 3021.* To increase the yields of the desired oxy-products in cell suspensions, optimal conditions (temperature, pH, concentrations of exogenic co-factors for methane monooxygenase, and the concentrations of inhibitors of further methanol oxidation) were selected. Apparent kinetic constants were determined.

IMMOBILIZATION OF METHANOTROPHIC BACTERIA *METHYLOCOCCUS CAPSULATUS* ON INORGANIC SUPPORTS

G.A. Kovalenko, V.M. Lenskaya, G.B. Barannik, N.A. Kulikovskaya

Appl. Biochem. & Microbiol., 34(6) (1998) pp. 573-577.

Various methods of immobilization of methanotrophic cells *Methylococcus capsulatus IMV 3021* on inorganic granulated or honeycomb monolithic supports based on oxides of aluminum, titanium, and iron were studied. Bacteria incorporated into silica gel and injection into pores of granulated inorganic supports (“immuring”) retained about 50% of the initial biocatalytic activity and continuously oxidized the substrate studied (propylene) for dozens of hours. These cells displayed considerably higher activity and stability in comparison to methanotrophs immobilized on the surface of supports by adsorption.

New Results in Studying Photocatalytic and Related Processes

COMPOSITION OF THE ADSORBED LAYER ON THE SURFACE OF MAGNESIA IN THE PRESENCE OF ATMOSPHERIC AIR

V.S. Zakharenko, V.N. Parmon

Russ. J. Phys. Chem., 73(1) (1999) pp. 117-120.

The surface of adsorbents and catalysts (including photoadsorbents and photocatalysts) before their industrial or research use is usually treated with various cleaning and conditioning procedures at high temperatures. On the contrary, at natural atmospheric conditions, solid aerosol particles do not undergo any pretreatment. So, the surface of the aerosol particles resembles the surface of catalysts prepared under “mild” conditions and exposed to a long stay in the air. In this case, the chemical composition and state of the interface between the gas phase and aerosol particle bulk is determined by the composition of the surrounding atmosphere and the ability of the main components of the aerosol to adsorb the gas phase components of the atmosphere.

When a surface of magnesia exposed to air for a long time is irradiated with a $\lambda<400$ nm light, NO and N_2 are released into the gas phase at a constant ratio of 2:1. This is be explained by the photodecomposition of N_2O adsorbed on the MgO surface. The spectral dependence of the effective quantum yield for the photoformation of $2NO/N_2$ mixture is determined; at 365 nm, the absolute quantum yield of the reaction is 0.025. The absorptance of magnesia at this wave length is 0.04. It is established that the spectrum of formation of the $2NO/N_2$ mixture is similar to the absorption spectrum of magnesia.

REMEDIATION OF THE EARTH'S ATMOSPHERE THROUGH PHOTOINITIATED DESTRUCTION OF FREENESS ON THE ALKALINE EARTH’S OXIDE COMPONENTS OF TROPOSPHERIC AEROSOLS

V.S. Zakharenko, V.N. Parmon,

Colloids and Surfaces A: Physicochem. & Engin. Aspects, 151 (1999) pp. 367-376.

Interaction of some freons with the ambient air-exposed surface of magnesium oxide and calcium hydroxycarbonate in darkness and under mild UV radiation, corresponding to solar light in the troposphere, can result in efficient irreversible destructive adsorption of some freons. The above photoadsorption activity appears to be related with the optical absorption, detected at wavelengths ranging within 300-400 nm and caused presumably by surface carbonates or some other surface compounds. The irreversible adsorption is observed for H-containing freons like CF_3CH_2F and CHF_2Cl while for hydrogen-free ozone-depleting freons like CF_2Cl_2 any adsorption is not detected. It was suggested that at the photostimulated adsorption, fluorine and chlorine atoms substitute oxygen atoms in the magnesium oxide lattice and hydroxyl groups of calcium hydroxycarbonates.

CATALYST APPLICATION IN SOLAR THERMOCHEMISTRY

V.A. Kirillov

Solar Energy, 66(5) (1999) pp. 143-149.

In this report, a comprehensive survey on the current state of catalyst application in the field of solar energy transformation and storage is presented. Corresponding catalyzed solar chemical processes include the pyrolysis of carbonaceous compounds for the production of hydrogen, the production of filamentous carbon as well as the synthesis of unsaturated hydrocarbon compounds by rapid direct heating of methane and quenching of the reaction products.

STUDY OF TiO_2 DEACTIVATION DURING GASEOUS ACETONE PHOTOCATALYTIC OXIDATION

A.V. Vorontsov, E.N. Kurkin*, E.N. Savinov
(*Institute on New Chemical Problems,
Chernogolovka, Moscow Region, Russia)

J. Catal., 186(2) (1999) pp. 318-324.

The kinetics of the deep photocatalytic oxidation of acetone was studied. Special attention was paid to the thermal deactivation process. The rate of the reaction reaches a peak at about 100 °C. With increasing concentration of water vapor the peak shifts towards higher temperature, whereas with increasing acetone concentration the peak shifts towards lower temperature. An increase in water vapor concentration slightly decreases the rate of oxidation at 40 °C and increases it at temperatures above the rate maximum. The presence of two types of acetone adsorption sites was deduced from two C=O bands of adsorbed acetone at 1683 and 1710 cm^{-1} and can explain the dependence of the rate on acetone concentration. The rate of oxidation increases at temperatures below the peak, mainly because of the increase in the rate coefficient at the sites of the first type. This behavior has been ascribed to the thermal oxidation of an intermediate of the photocatalytic process. Abrupt drop in rate at temperatures above the peak is due to the partial oxidation products of acetone thermal oxidation that modifies the TiO_2 surface.

INFLUENCE OF A FORM OF PHOTODEPOSITED PLATINUM ON TITANIA UPON ITS PHOTOCATALYTIC ACTIVITY IN CO AND ACETONE OXIDATION

A.V. Vorontsov, E.N. Savinov, J. Zhensheng*
(*Henan University, Kaifeng, China)

J. Photochem. & Photobiol. A: Chemistry,
125(1-3) (1999) pp. 113-117.

Specimens of titania with platinum in various oxidation states deposited by a photocatalytic method, as well as mixture of PtO_2+TiO_2, and PtO_2 have been studied by means of XPS, TEM and UV-VIS diffuse reflectance spectroscopy. Activities of the specimens in thermal and photocatalytic complete oxidation of gaseous acetone and CO by atmospheric oxygen at 400 ^oC have been evaluated using a flow-circulating reactor. Photocatalytic activity increases with lowering of Pt oxidation state. Possible reasons of this behavior are discussed.

THE SURFACE EFFECTS ON REGULARITIES OF ELECTRON TRANSFER IN CdS AND CdS/Cu_xS COLLOIDS AS STUDIED BY THE PHOTOLUMINESCENCE QUENCHING

D.V. Bavykin*, E.N. Savinov, V.N. Parmon
(*Novosibirsk State University, Novosibirsk, Russia)

Langmuir, 15(140 (1999) pp. 4722-4727.

CdS colloids of different sizes were prepared using two different methods: either with an excess of S^{2-} ions, or with an excess of Cd^{2+} ions. The shape of the luminescence spectra and regularities of luminescence quenching have been studied for both colloids. It has been found that positively charged electron acceptor molecules (bication of methylviologen) quench effectively the luminescence of the colloids with the S^{2-} ions excess and practically do not quench luminescence of the colloids with the Cd^{2+} ions excess. Vice versa, negatively charged electron acceptor molecules (anions of heteropolyacids) quench effectively the luminescence of the colloids with excessive Cd^{2+} ions and do not quench the luminescence of the colloids with excessive S^{2-} ions. The observed phenomenon can be explained easily by taking into account the necessity of adsorption of the quencher molecules on the surface of semiconductor particles in the electron transfer process. It has also been observed that for the both types of the colloids the efficiency of the luminescence quenching is related with the luminescence wavelength. The regularities of the luminescence quenching have been studied for the CdS colloids of different size coated with Cu_xS as well. It was observed that addition of copper ions increases the efficiency of luminescence quenching by methylviologen (MV^{2+}) and tungstophosphoric heteropolyacid (PW_{12}). Moreover, the shape of the luminescence spectra of these coated colloids depends on the excitation wavelength, the increase of excitation wavelength resulting in the shift of luminescence spectra to the ‘red’ region.

CONTROL OF THE SIZE AND PHOTOCHEMICAL PROPERTIES OF Q-CdS PARTICLES, ATTACHED TO THE INNER AND/OR OUTER SURFACE OF LECITHIN VESICLE BILAYER MEMBRANE BY THE NATURE OF ITS PRECURSORS

O.V. Vassil’tsova, A.L. Chuvilin, V.N. Parmon

J. Photochem. & Photobiol. A: Chemical, 125 (1999)
pp. 127-134.

Cadmium sulfide nanoparticles have been *in situ* generated on the inner and/or outer surfaces of monolamellar lecithin vesicles. Chemical agents, strongly chelating or bounding the Cd^{2+} cations, are shown to influence dramatically the size of CdS nanoparticles as well as their optical, luminescence and photochemical properties. The more stable is a Cd^{2+}-containing complex created by these chelating agents, the smaller are the CdS particles formed. In case of $CdCl_2$ and $Cd(NO_3)_2$ as the CdS precursors inside the vesicles, a steady rise in size of growing CdS nanoparticles is observed, while in case of $K_2[CdEDTA]$ the accumulation of mass of growing occurs without a change in the nanoparticle size. The size of CdS particles and their initial growth rate depend also on pH of the vesicle suspension, modification of the lipid membrane, being, however, independent of the $CdCl_2$ concentration, if $CdCl_2$ is the CdS precursor. In the presence of a sacrificial electron donor (S^{2-} or EDTA), the bandgap irradiation of the lipid-vesicle-supported CdS particles yields charge separation and electron transfer to lipophilic cetylviologen bications, $C_{16}V^{2+}$, imbedded into the lipid bilayer. The initial quantum yield of $C_{16}V^{2+}$ formation depends on the topology of vesicular systems and CdS localization on the inner or outer surface of the lecithin membrane. Presence of EDTA anions enhances sufficiently the initial quantum yield of vectorial electron phototransfer from CdS nanoparticles to cetylviologen.

ORGANIZED PHOTOCATALYTIC SYSTEMS BASED ON LIPID VESICLES AND SEMICONDUCTOR NANOPARTICLES

O.V. Vassil'tsova*, V.N. Parmon

Kinetics & Catalysis, 40(1) (1999) pp. 62-70.

Photochemical properties of cadmium sulfide semiconductor nanoparticles fixed on the outer or inner surface of lipid vesicle membranes and the specific features of their formation are considered. Basic factors determining the size of CdS nanoparticles, which are formed *in situ* in lipid vesicle systems, and the prospects of using for their use to increase the efficiency of photochemical charge separation at the vesicle cavity–membrane interface are discussed. The methods are found for efficient, purposeful transmembrane electron phototransfer catalyzed by semiconductor nanoparticles in lipid vesicles. Preliminary experiments were carried out to create the electron transport chain based on CdS/Cu_xS nanoheterostructures. New electron carriers, menadione and SiW_{12} heteropoly anions were used for electron transfer through lipid membranes. It is shown that heteropoly anions immobilized on the vesicle surface provide efficient conjugation of electron transport chains. This enables in the creation of an active photocatalytic system for the reduction of water into hydrogen.

Catalysts for Oil Refinery. Synthesis, Physicochemical and Catalytic Properties

MOLECULAR ASPECTS OF CATALYSIS BY SULFIDES

A.N. Startsev

Kinetics & Catalysis, 40(6) (1999) pp. 811-818.

The paper presents a review of the comprehensive studies on the molecular structure of the active component of sulfide catalysts for the hydrorefining of oil fractions and the molecular mechanism of their action. An alternative approach to catalysis by sulfides is developed based on the experimental findings and the quantum-chemical studies. The notion on the oxidative addition and occlusion of hydrogen in the active component of sulfide hydrodesulfurization catalysts was examined and justified. The concerted mechanism of thiophene hydrogenolysis over sulfide bimetallic catalysts of different chemical compositions received further support.

SULFIDE CATALYSTS FOR HYDRODESULFURIZATION OF OIL FRACTIONS: FORM ACTIVE COMPONENT COMPOSITION TO ITS MOLECULAR DESIGN

A.N. Startsev

Chem. for Sustainable Devel., 7(4) (1999) pp. 433-442.

The recent achievements in the studying of the structure and catalytic properties of the active component of the sulfide desulfurization catalysts are analyzed. The molecular structure of the active component and electronic structure of the metals forming it are examined. The determinative role of occluded hydrogen in the generation of unusually high oxidation level for Ni (IV) and Co (III) – active centers of the given catalysts is revealed. The concert mechanism for the hydrogenolysis of C–S bond with the participation of sulfide catalysts of various composition is proved. The opportunity of purposeful synthesis of highly effective catalysts for deep hydropurification of oil fraction is considered.

Catalysts for Detoxication of Industrial Gases

SINGLE-STAGE CATALYTIC METHODS FOR ACID GASES PURIFICATION FROM HYDROGEN SULFIDE

Z.R. Ismagilov, M.A. Kerzhentsev, S.R. Khairulin, V.V. Kuznetsov

Chem. for Sustainable Devel., 7(4) (1999) pp. 375-396.

One-stage catalytic methods for purification of acid gases from hydrogen sulfide, physicochemical features of the reaction of direct heterogeneous catalytic oxidation of hydrogen sulfide to elemental sulfur and principal types of catalysts used for this reaction are discussed. Experimental data obtained for oxidation of hydrogen sulfide over oxide catalysts are presented. Catalyst $MgCr_2O_4/\gamma\text{-}Al_2O_3$ is shown to reveal a high activity and selectivity to this reaction at the temperature range of 200-300 °C. Introduction of hydrocarbons into the mixture of hydrogen sulfide with air does not cause the catalyst destruction under the process conditions and catalyst deactivation. Adsorption of hydrogen sulfide on the surface of oxide catalysts $\gamma\text{-}Al_2O_3$, $Fe_2O_3/\gamma\text{-}Al_2O_3$ and $MgCr_2O_4/\gamma\text{-}Al_2O_3$ was studied using IR spectroscopy with Fourier transformation; the mechanism of hydrogen sulfide oxidation was suggested. The results obtained during the research allowed a one-stage technology to be developed for purification of gases with high concentration of hydrogen sulfide (>5%). The technology is based on oxidation of hydrogen sulfide into elemental sulfur in a fluidized bed of catalyst $MgCr_2O_4/\gamma\text{-}Al_2O_3$. The process was successfully tested for purification of real gases containing hydrogen sulfide in pilot units.

CATALYTIC PURIFICATION OF GEOTHERMAL STEAM FROM HYDROGEN SULFIDE

S.R. Khairulin, Z.R. Ismagilov, M.A. Kerzhentsev

Chem. for Sustainable Devel., 7(4) (1999) pp. 443-449.

Geothermal steam is a prospective source for generation of heat and electric energy. However, exploring and development of geothermal steam fields causes the problem of environmental contamination by hydrogen sulfide, which is a constituent of the steam. The paper deals with analysis of up-to-date methods for purification of geothermal steam. A method based on direct oxidation of hydrogen sulfide into elemental sulfur in a reactor with BIC's proprietary honeycomb catalyst is described. Thorough laboratory studies allowed the industrial technology to be developed and a pilot installation to be assembled. The life tests supported the efficiency of the technical solutions: the level of steam purification reached 99.9%. A deliberately designed catalyst retained its structural and mechanical properties and a high activity after 2500 hours of its continuous operation.

DEVELOPMENT OF CATALYTIC TECHNOLOGIES FOR PURIFICATION OF GASES FROM HYDROGEN SULFIDE BASED ON DIRECT SELECTIVE CATALYTIC OXIDATION OF H_2S TO ELEMENTAL SULFUR

Z.R. Ismagilov, S.R. Khairulin, M.A. Kerzhentsev, A.M. Mazgarov*, A.F. Vildanov* (*All-Russian Institute of Hydrocarbon, Ufa, Russia)

Euro-Asian J. Chem. Techn., 1 (1999) pp. 49-56.

In the Boreskov Institute of Catalysis in cooperation with specialists of All-Russian Institute of Hydrocarbons novel methods of purification of fossil fuels based on oxidation of hydrogen sulfide to elemental sulfur have been developed. In this paper the results of laboratory and pilot plant testing of the technologies are presented.

ON THE NATURE OF FACTORS DETERMINING REACTIVITY OF STRONGLY BOUND SURFACE SPECIES AS INTERMEDIATES IN HETEROGENEOUS CATALYTIC REDOX REACTIONS

V.A. Sadykov, A.Ya. Rozovskii*, V.V. Lunin, G.I. Lin*, G.M. Alikina, G.A. Bukhtiyarova, B.P. Zolotovskii, S.A. Beloshapkin** (*Topchiev Institute of Petrochemical Synthesis, Moscow, Russia; **Lomonosov Moscow State University, Moscow, Russia)

React. Kinet. & Catal. Lett., 66(2) (1999) pp. 337-341.

The rate-limiting stage of heterogeneous catalytic redox reactions with participation of strongly bound surface species, such as nitrates, carbonates and sulfites, is the interaction of these heteroatomic oxidants with the reducing agents. It appears to be mainly determined by their bonding strength with the surface, being independent of the nature of the central atom (carbon, sulfur, nitrogen) and the energy of its bond with oxygen.

REMOVAL OF 1,1-DIMETHYLHYDRAZINE FORM AQUEOUS SOLUTIONS BY CATALYTIC OXIDATION WITH HYDROGEN PEROXIDE

O.P. Pestunova, G.L. Elizarova, V.N. Parmon

Russ. J. Appl. Chem., 72(7) (1999) pp. 1209-1213.

The catalytic oxidation of 1,1-dimethylhydrazine water solutions at pH 7-11 and 298 K is described. The supported hydroxides of some transition metals as the catalysts and H_2O_2 as oxidant are used. The Cu-containing samples are found to be the most active catalysts. H_2O_2 is shown to be the more effective oxidant than air. The main product of the reaction under study is formazane.

Catalytic Technologies for Combustion

CATALYTIC COMBUSTION OF LEAN METHANE-AIR MIXTURES

V.A. Sazonov, Z.R. Ismagilov, N.A. Prokudina

Catal. Today, 47(1-4) (1999) pp. 149-153.

Catalytic combustion of lean methane-air mixtures was studied on supported iron oxide and platinum monolith catalysts. Flameless catalytic combustion was investigated in the temperature range 600-900 °C, GHSV up to 10000 h^{-1}, and methane concentration in initial gas mixture 1-9 vol. %. It was shown that under certain process conditions complete combustion of methane at ~4.5 vol. % inlet methane concentration occurs.

FLUIDIZED BED CATALYTIC COMBUSTION

Z.R. Ismagilov, M.A. Kerzhentsev

Catal. Today, 47(1-4) (1999) pp.339-346.

The principles and applications of fluidized bed catalytic combustion are described. The experience and current activities of the Boreskov Institute of Catalysis in the development of fluidized bed catalytic combustion of various fuels and organic wastes are briefly reviewed. Prospects for new applications of this technique are discussed.

CATALYTIC HEAT-EXTRACTION UNITS

V.N. Parmon, A.D. Simonov

Energy, 4 (1999) pp. 18-24.

The results of employing catalytic heat-extraction units KTU-02 (up to 0.2 Gcal/h capacity) were summarized. The units were manufactured at Arsenal-2 Company (Novosibirsk) based on advances of the Boreskov Institute of Catalysis in the field of fuel oxidation in a fluidized catalyst bed.

Liquid Phase Catalytic Technologies

METHODS OF LOW-CONCENTRATED INDUSTRIAL GASES DESULFURIZATION

Z.P. Pai

Chem. for Sustainable Devel., 7(4) (1999) pp. 411-431.

Problems of desulfurization of various kinds of industrial sulfur-containing gases were analyzed. Parameters of technologies used for purification of waste gases of the Claus process containing hydrogen sulfide and sulfur recycling were compared. Chemical features of the liquid-phase mode of the Claus process were considered with the LPD-process (liquid-phase desulfurization, developed at the Boreskov Institute of Catalysis) as an example. Various applications of modifications of the LPD technology developed for purification and processing of industrial gases comprising SO_2, H_2S and concomitant impurities (COS, NH_3, HCN, NO_x, As_2O_3, *etc.*) were discussed. The principal flow charts were presented. Potentialities of diversification of ecologically friendly products of utilization of toxic impurities were demonstrated.

HEXACHLOROBENZENE HYDRODECHLORINATION IN THE PRESENCE OF BIMETALLIC CATALYSTS

V.I. Simagina, A.J. Renouprez*, G. Bergeret*, M. Gemenez*, I.V. Stoyanova, V.A. Likholobov
(*Institut de Recherches sur la Catalyse, Villeurbanne, France)

Organohalogen Compounds, 40-44 (1999) pp. 341-344.

The goal of this study was getting and investigation of effective and inexpensive catalysts, permitting to carry out liquid-phase hydrodechlorination under mild reaction conditions. This problem was decided at employment of bimetallic catalysts consist of compounds of nickel or copper and palladium (nickel, copper - basic components), supported on carbon material «Sibunit». For increasing the reaction rate hexachlorobenzene hydrodechlorination was carried out in a two-phase system (aqueous KOH and organic solvent) with using onium salts as Phase-Transfer catalyst.

LOW-TEMPERATURE CATALYTIC OXIDATION OF HYDROGEN SULFIDE BY OXYGEN IN SOLUTIONS AND GAS PHASE AND PROSPECTS OF THE PRACTICAL APPLICATION FOR DESULFURIZATION PROCESSES

O.N. Kovalenko, N.N. Kundo

Chem. for Sustainable Devel., 7(4) (1999) pp. 397-409.

The problem of gas- and liquid-phase catalytic oxidation of hydrogen sulfide by oxygen was discussed. Analysis of the pertinent experimental data allowed general regularities to be revealed for the mechanism of hydrogen sulfide oxidation in solutions and at the surface of solid catalysts. It involves acid-base processes of hydrogen sulfide dissociation and reduction of oxidized sulfur species, and redox processes based on electron transfer. Two potential pathways, *viz.* polysulfide one and direct oxidation of hydrosulfide ions by oxygen, were demonstrated. The observed oscillation processes and critical phenomena were accounted for by the transition of one of the processes to another under the action of the reaction parameters. The activity of the catalysts was shown to depend on two factors: oxygen activation at the surface of transition metal oxides and adsorption of sulfur compounds in the form of polysulfide ions or other kinds of species comprising the S_n chain on basic sites of the catalyst. The use of low temperature catalytic processes of oxidation of H_2S by oxygen for fine purification of gases from hydrogen sulfide was demonstrated to allow undesirable side processes with components of gases under processing to be avoided. Experimental data supported the conclusion on availability of fine purification of Claus waste gases by means of oxidation of H_2S by oxygen at the temperatures below the dew point, sulfur being adsorbed on the catalyst surface and then removed by flowing hot inert gas.

COBALT PHTHALOCYANINE DERIVATIVES SUPPORTED ON TiO_2 BY SOL-GEL PROCESSING.
2. ACTIVITY IN SULFIDE AND ETHANETHIOL OXIDATION

T.L. Stuchinskaya, N.N. Kundo, L.V. Gogina[a]
U. Schubert*, A. Lorenz*, V. Maizlish** (*Institut fur Anorganische Chemie, Technische Universitat Wien, Wien, Austria; **Ivanovo State Academy of Chemistry and Technology, Ivanovo, Russia)

J. Molec. Catal., A: Chemical, 140(3) (1999) pp. 235-240.

One of the most effective catalysts for HS-oxidation(desulfurization) is cobalt phthalocyanine (CoPc). Traditionally, this insoluble material has been used as a heterogeneous catalyst. Water-soluble forms have been obtained by sulfonation; the di-substituted product is useful and the tetrasulfonate is particularly active. Various methods have been examined to heterogenise CoPc or its derivatives, but difficulty has been found in obtaining materials sufficiently stable (to leaching) or in maintaining the catalytic activity.

It has been shown that the sulphonyl groups can be used for an efficient immobilization of the normally soluble catalysts in a porous, inert matrix. Reaction of SO_2X-substituted CoPc (X=Cl or OH) with titanium alkoxides, $Ti(OR)_4$, gives the $SO_3Ti(OR)_3$-substituted form. Sol-gel condensation of this with more titanium alkoxide gives solid, porous materials containing about 1.3 wt % of the active catalyst firmly bound to a TiO_2 matrix. The new materials obtained by sol-gel processing were investigated for sulfide and mercaptoethanol liquid-phase oxidation.

Preliminary investigations have been made into the effect of conditions of preparation on the morphology. In a modification of sol-gel procedure, the solution containing both substituted CoPc and alkoxides can be used to coat the surface of inert carriers, followed by hydrolysis and condensation at the solid surface. This material shows good stability in aqueous sulfide systems, has higher activity than the corresponding homogenous catalyst, and can be recovered and re-used without loss of activity.

CATALYTIC COMBUSTION OF SULFUR-CONTAINING WASTE GASES: PROSPECTIVE APPLICATION

N.N. Kundo

Chem. for Sustainable Devel., 7(3) (1999) pp. 259-267.

Waste gases of cellulose and fuel industries, metallurgical and chemical plants often comprise toxic sulfur compounds. Catalytic combustion is inappropriate for detoxification of the sulfuric wastes due to poisoning of the catalyst by the formed surface sulfides and sulfates. Therefore, the sulfuric wastes are neutralized by means of burning at about 1000 °C. The studies in the field demonstrated a potentiality of designing sulfur-resistant catalysts to allow complete oxidation of organic and sulfuric compounds to CO_2 and SO_2 at 300-500 °C followed by the technological sulfur recycling. The highest activity and poisoning resistance was observed with binary oxides of transition metals, specifically copper chromite. Development of the wasteless technology for the catalyst preparation from copper bichromate made it possible to experiment with the catalytic purification of waste gases containing H_2S, SO_2 and the other sulfur compounds.

INTENSIFICATION OF CATALYTIC OXIDATIVE REMOVAL OF HYDROGEN SULFIDE FROM SOLUTIONS IN THE PRESENCE OF TETRASULFONATE OF COBALT PHTHALOCYANINE IN A BABBLE-CENTRIFUGAL REACTOR

S.G. Zavarukhin, G.G. Kuvshinov, L.V. Gogina, N.N. Kundo

Chem. Industry., 2 (1999) pp. 90-94.

The efficiency of bubble-centrifugal reactor (BCR) for catalytic oxidative removal of hydrogen sulfide from solutions in the presence of TSCP has been studied. A solution of sodium sulfide was used for modeling the hydrogen sulfide containing solution in the experiments. The established volumetric flow rate of the oxidation of Na_2S in CBR at 0.05 mol/l of Na_2S was ca. 16 mol/l·h that is dozens and hundreds times of the corresponding parameter obtained for a laboratory agitated reactor and pilot-babble reactor.

PRESSURE LOSS IN CENTRIFUGAL BUBBLING APPARATUSES

S.G. Zavarukhin, G.G. Kuvshinov, M.A. Kuznetsov, N.P. Smirnov

Thermophysics & Aeromechanics, 6(1) (1999) pp. 89-98.

The present paper proposes the ascertained dependence for calculating the hydraulic resistance of bubble-centrifugal apparatuses (BCA) and gives experimental data on the resistance of BCA with various swirlers up to 410 mm in diameter and 210 mm in height. A technique for calculating a gas content in the layer and recommendations for choice of a swirler conicity are proposed.

ADSORPTIVE CLARIFICATION OF INTAKE SOLUTION FOR OXIDATIVE SULFUR-CYANIC GAS PURIFICATION

N.V. Dementieva*, V.G. Nazarov*, V.D. Glyachenko*, O.G. Unterberger*, N.N. Kundo, G.A. Faddeenkova (*Institute of Coal Chemistry, Ekaterinburg, Russia)

Coke and Chemistry, 2 (1999) pp. 23-27.

Technology for adsorptive clarification of solutions spent for oxidative sulfur-cyanic purification of coke gas from the phthalocyanine catalyst (cobalt tetra- and disulfonate) was developed. It was established that the granulated sorbent prepared from brown coal is preferable among the carbon adsorbents under study.

AN EFFECT OF ELECTRON BEAM ON AQUEOUS SOLUTIONS OF CHROMIUM (VI) SALTS

N.N. Kundo, G.I. Anisiforov, N.N. Boldyreva, V.A. Ivanchenko*, O.P. Slyudkin*, I.V. Mishakov*, P.V. Poplaukhin*, R.A. Salimov, N.K. Kuksanov**, S.E. Petrov**, S.N. Fadeev** (***Novosibirsk State University, Novosibirsk, Russia; **Budker Institute of Nuclear Physics, Novosibirsk, Russia)

Chem. for Sustainable Devel., 7(5) (1999) pp. 491-496.

The process of reduction of chromium (VI) salts in aqueous solutions under the action of electron beam was discussed. Experimental studies were focused on exposure of Cr(VI) salt solutions, both containing sulfur-based reductants and free of them, to the electron beam. The thiosulfate ion was shown to be the most effective reductant upon exposure of the solutions to the electron beam. High radiation doses (30 Mrad) were needed for reductant-free detoxication of the aqueous solutions of Cr(IV) salts. A model was suggested to describe the reaction kinetic in solutions.

DECOMPOSITION OF NITROGEN-CONTAINING SUBSTANCES IN WASTEWATER BY ELECTRON BEAM IRRADIATION

N.N. Kundo, V.A. Ivanchenko*, N.K. Kuksanov, S.E. Petrov**, G.I. Anisiforov, N.N. Boldyreva, A.V. Ivanchenko**** (*Novosibirsk State University, Novosibirsk, Russia; **Institute of Nuclear Physics, Novosibirsk, Russia)

Russ. J. Appl. Chem., 72(7) (1999)
pp. 1214-1216.

Aqueous solutions containing ammonia and 1,1-dimethylhydrazine together with an oxidizing agent, hydrogen peroxide can be neutralized under the action of electron beam. The degree of substance decomposition was studied in relation to irradiation dose and concentrations of hydrogen peroxide and starting substances.

THE INFLUENCE OF SULFUR-CONTAINING REDUCTANTS ON PROCESSES OF CHROMIUM (VI) ELIMINATION FROM AQUEOUS SOLUTIONS

N.N. Kundo, V.A. Ivanchenko*, I.V. Mishakov*, P.V. Poplaukhin* (*Novosibirsk State University, Novosibirsk, Russia)

Chem. for Sustainable Devel., 7(5)(1999)
pp. 485-490.

Comparative efficiency of reduction of chromium (IV) by various reductants (sodium sulfite, sodium sulfide, sodium thiosulfate, as well as iron (II)) was analyzed. Thermodynamic calculations showed practicability of all the four reductants, among which sulfite had to be the most active. Experimental studies demonstrated that iron (II) was the most appropriate reductant. The role of protonation of the reacting ions in the processes of chromium (IV) reduction was discussed. Optimal conditions of chromium (II) reduction by sulfur-containing reductants and iron (II) to satisfy the sanitary code of detoxication of wastewater and other kinds of waste products were recommended.

Mathematical Simulation of Processes and Reactors. Chemical Engineering

ANALYSIS OF AUTOOSCILLATIONS DURING CO OXIDATION ON NON-UNIFORM SURFACE CONSISTING OF TWO TYPES OF SITES COUPLED BY CO_{ads} DIFFUSION

S.I. Fadeev*, V.I. Savchenko, A.Yu. Berezin* (*Sobolev Institute of Mathematics, Novosibirsk, Russia)

React. Kinet. & Catal. Lett., 67(1) (1999)
pp. 155-161.

Areas of occurrence and character of autooscillations during CO oxidation on a non-uniform surface consisting of different sites M_1 and M_2, the reaction on which is kinetically connected by the diffusion of adsorbed CO (CO_{ads}), has been analyzed using numerical integration of an independent system and search of stationary solutions by the homotopy method.

NEW CATALYSTS AND CATALYTIC PROCESSES TO PRODUCE HYDROGEN AND SYNGAS FROM NATURAL GAS AND OTHER LIGHT HYDROCARBONS

V.N. Parmon, G.G. Kuvshinov, V.A. Sadykov, V.A. Sobyanin

Stud. Surf. Sci. & Catal., Natural Gas Conv. V,
119 (1998) pp. 677-683.

The paper discusses new honeycomb catalysts for natural gas oxidation to syngas, a recently developed processes of moderate-temperature (450-650 ^{o}C) catalytic pyrolysis of natural gas and/or light hydrocarbons into hydrogen and variable carbonaceous materials, as well as partial oxidation of natural gas into syngas in high temperature solid oxide fuel-cell-like systems. The advantages of the new processes against conventional ones lie, e.g., in ability to produce hydrogen completely free of carbon monoxide, as well as to cogenerate hydrogen or syngas with other valuable materials, chemicals or even electricity.

CONTROL OF THE SELECTIVITY IN PARTIAL OXIDATION OF HYDROCARBONS

E.A. Ivanov, S.I. Reshetnikov, A.A. Ivanov

React. Kinet. & Catal. Lett., 66(1) (1999) pp. 47-54.

A simple kinetic model for the partial oxidation of hydrocarbons on two types of sites was used to study the factors influencing on the reaction selectivity to the desired product. It is shown that it is possible to increase the selectivity significantly by regulating the ratio of the surface concentrations of partial and deep oxidation sites by a periodic temperature treatment.

MULTIPLICITY OF REGIMES IN A DUAL-REACTOR SYSTEM FOR PARTIAL OXIDATION OF HYDROCARBONS WITH THE CATALYST UNSTEADY STATE

E.A. Ivanov, S.I. Reshetnikov

React. Kinet. & Catal. Lett., 67(1) (1999) pp. 213-220.

A mathematical modeling of a dual-reactor system based on a kinetic scheme with two types of sites (accounting for deep and partial oxidation) has been performed. It has been shown that it is possible to regulate the state of a catalyst in the reaction zone by varying the rate of the catalyst circulation between the reactors, thus significantly increasing the reaction selectivity. A region of multiplicity of the process stationary regimes has been found. This region becomes smaller with the increase of the catalyst circulation rate.

SPATIAL REGULATION OF THE CATALYST ACTIVITY ENHANCEMENT FOR CATALYTIC REACTIONS WITH STOP-EFFECT

S.I. Reshetnikov, E.A. Ivanov

React. Kinet. & Catal. Lett., 68(2) (1999) pp. 393-398.

A kinetic model taking into account two types of active sites has been used for analysis of factors influencing the rate of a catalytic reaction. It has been shown that the reaction rate can be significantly increased by performing a reaction with the "stop-effect" in a dual-reactor system due to the catalyst circulation between the reactors, one of which is passed with an inert gas.

PERSPECTIVES IN DEVELOPMENT OF CATALYTIC PROCESS AT MILLENIUM EDGE

M.G. Slin'ko*, A.S. Noskov (*Karpov Institute of Physical Chemistry, Moscow, Russia)

Chem. Industry, 1 (1999) pp. 1-11.

Reviewed are modern tendencies in the design of technologies for catalytic processes, such as, process performance at millisecond residence times, process performance in many functional reactors, design of catalysts providing favorable conditions with respect to thermodynamics, process performance under subcritical and critical conditions, ultra pure combustion of natural gas, design of mobile catalytic plants for local heat supply. All these technologies are introduced into practice on industrial scale.

Discussed are priority fields in catalysis at the verge of century XXI related to activation of small molecules such as methane, nitrogen, etc., and to the synthesis of valuable products from methanol.

MATHEMATICAL MODELING OF UNSTEADY STATE OPERATION TAKING INTO ACCOUNT ADSORPTION AND CHEMISORPTION PROCESSES ON THE CATALYST PELLET

N.V. Vernikovskaya, A.N. Zagoruiko,
N.A. Chumakova, A.S. Noskov

Chem. Eng. Sci., 54(20) (1999) pp. 4639-4643.

In the paper the dynamics of hydrocarbons deep oxidation in the catalyst pellet with account of intraparticle diffusion limitations under alternating adsorption stage and oxidation one is studied by means of mathematical modeling. As an example the isopropyl benzene oxidation by oxygen on Cu/Cr/Al oxide catalyst is considered. It is shown that intraparticle diffusion limitation significantly influence both adsorption and oxidation performance. The modeling results demonstrate the existence of the optimal catalyst pellet size, providing the maximum purification efficiency in the adsorption-catalytic process of VOC abatement.

SO_2 OXIDATION METHOD. MATHEMATICAL MODELING TAKING INTO ACCOUNT DYNAMIC PROPERTIES OF THE CATALYST

N.V. Vernikovskaya, A.N. Zagoruiko, A.S. Noskov

Chem. Eng. Sci., 54(20) (1999) pp. 4475-4482.

Mathematical modeling of a new sulfur dioxide oxidation method in sulfuric acid production has been carried out. The method is based on the use of the nonstationary state of the catalyst surface, in particular, the absorption properties of active component of vanadia catalysts in relation to SO_2. The idea of the process is that the catalyst bed undergoes periodic cycling of the feed between air flow and a reaction gas mixture, containing SO_2. The directions of air and gas mixture flow are opposite.

The unsteady state kinetic model of SO_2 oxidation over vanadium catalyst is used to describe dynamics of the catalyst state. The influence of different parameters on SO_2 conversion and overall process performance is investigated. According to the modeling results, this method provides a decrease the SO_2 outlet content in the waste gases down to 50 ppm and thereby avoids the need for tail gas cleanup. The process may be easily applied to the second stage of a conventional DC/DA (double contact/double absorption) sulfuric acid plants.

NON-STATIONARY KINETIC MODEL FOR DEEP OXIDATION OF AROMATIC HYDROCARBONS ON OXIDE CATALYSTS

A.N. Zagoruiko

React. Kinet. & Catal. Lett., 66(1) (1999) pp. 63-70.

A non-stationary kinetic model for deep oxidation of aromatic hydrocarbons based on the fragmentation theory approach is proposed. The model is simple and provides qualitative adequacy and good quantitative description of experimental results.

A MULTIFUNCTIONAL REACTOR WITH A REGULAR CATALYST PACKING FOR FISCHER-TROPSCH SYNTHESIS

V.D. Meshcheryakov, V.A. Kirillov, N.A. Kuzin

Chem. Eng. Sci., 54(10) (1999) pp. 1565-1570.

A multifunctional reactor for carrying out Fischer-Tropsch synthesis is being developed. This is a gas-lift reactor with monolith type catalyst packing. A mathematical model of the reactor has been developed. The behavior of the reactor has been analyzed in wide range of design variables and operational conditions using literature correlations for the parameters included in the model. The computations show that it is possible to achieve better performance in this reactor than in conventional slurry reactor at the same catalyst loading.

NUMERICAL ANALYSIS OF FISCHER-TROPSCH PROCESSES IN REACTORS WITH A SLURRIED CATALYST BED

V.A. Kirillov, V.M. Khanaev, V.D. Meshcheryakov, S. I. Fadeev*, R.G. Luk'yanova* (*Sobolev Institute of Mathematics, Novosibirsk, Russia)

Theor. Found. of Chem. Engin., 33(3) (1999) pp. 270-278.

A mathematical model of Fischer–Tropsch synthesis in a slurry reactor is presented, and model parameters are estimated. The synthesis reaction is shown to proceed in the transition region. The effect of the catalyst weight, presaturation of the liquid by synthesis-gas components, phase velocities, and reactor dimensions on the efficiency of synthesis gas conversion is studied.

A STACKED CATALYST PACKING REACTOR FOR SUPEREXOTHERMAL PROCESSES IN GAS-LIQUID-SOLID THREE-DIMENSIONAL SYSTEMS

V.D. Meshcheryakov, V.A. Kirillov, N.A. Kuzin

Theor. Found. of Chem. Engin., 33(5) (1999) pp. 508-516.

The concept of using catalyst units in reactors for super exothermal processes in gas–liquid–solid systems was put forward. The lift-gas technique was employed for recirculating the liquid phase through a catalyst bed and a heat exchanger. The suggested procedure is demonstrated with the production of hydrocarbons from synthesis gas (Fischer–Tropsch synthesis) and is compared with industrial methods. It is shown that the suggested reactor offers a high degree of utilization of the reaction volume and high synthesis gas conversion per cycle, and allows easy control of temperature conditions.

MATHEMATICAL MODELLING OF CATALYTIC PROCESSES WITH PERIODIC OPERATION

E.A. Ivanov, S.I. Reshetnikov, S.I. Fadeev*
(*Sobolev Institute of Mathematics, Novosibirsk, Russia)

Siberian J. of Indust. Mathem., 2 (1999) pp. 94-105.

For a two-route reaction proceeding over different active sites with one of them blocked at high temperature, separation of the process into two stages allows the selectivity to be enhanced. The achievement of these stages as separated in time or in place makes it possible to choose optimal conditions for each of the zones. Varying the time of contact with the catalyst permits the process selectivity to be controlled and the yield of the target product to be increased. The method for calculation and studying the stationary and periodical solutions based on the general approach, *viz.* solution extension by a parameter is suggested.

SELF-HEATING OF MODEL PLASMA IN THE METHOD OF PARTICLES

V.A. Vshivkov*, D.V. Romanov, V.N. Snytnikov** (*Institute of Computational Technologies, Novosibirsk, Russia; **Novosibirsk State University, Novosibirsk, Russia)

Computational Techn., 4(3) (1999) pp. 62-72.

The influence of spontaneous self-force, a special error in the field of approximation in the method of large particles, on the spontaneous heating of collisionless plasma is considered. It has been shown that for NGP, PIC and other algorithms of the method of particles self-force does not decrease in space grid step. A new VSP class of grid nuclei has been studied free from the above-mentioned drawback and comparing well with PIC algorithm with respect to the consumption of computer resources.

ADSORPTION-CONTACT DRYING OF RIGID MATERIALS

A.D. Simonov, N.A. Yazykov, V.N. Parmon

Chem. for Sustainable Devel., 7(5) (1999) pp. 565-574.

The mechanism of moisture transfer upon adsorption-contact drying has been studied. It has been shown that at the moisture content in the donor material more then $U_{кр}$ the moisture transfer occurred both in the form of liquid through the contact area, filled with the capillary-condensed liquid phase, and in the form of gas. If the moisture content is lower $U_{кр}$ the moisture transfer occurred only in the form of gas. The equations have been proposed for estimation of $U_{кр}$, an effective profile of contact area and number of contacts between granules, and also an expression for kinetics of drying of non-deformed materials.

KINETICS OF PARTIAL OXIDATION OF PROPYLENE OVER INDUSTRIAL GRANULE OF MULTICOMPONENT CATALYST

E.M. Al'kaeva, T.V. Andrushkevich, N.A. Chumakova, O.A. Malinovskaya* (*Ben-Gurion University of the Negev, Israel)

Chem. Industry, 9 (1999) pp. 3-6.

Mathematical simulation of the reaction rates for partial oxidation of propylene into acrolein was performed based on the experimental data obtained for granules of a multicomponent catalyst containing oxide compounds of Mo, Bi, Co, Ni, Fe, K and Si. The developed computational method allows changes in the catalytic properties to be predicted depending on the shape and size of the granules.

Catalysis for Energy Conversion

SIMULATION AND EVALUATION OF PHASE DIAGRAMS

A. Yermakova, V.I. Anikeev

Theor. Found. of Chem. Engin., 33(10) (1999) pp 56-63.

A mathematical model for evaluating phase diagrams that is based on the Redlich–Kwong–Soave equation of state and is formulated in the form of nonlinear algebraic equations is suggested. The solution to the model equations and solution multiplicity are studied. Singular points due to phase inversion are revealed. Recommendations for selecting optimum approximations are given, and the examples of the evaluation are demonstrated.

PHASE DIAGRAMS OF COMPLEX MIXTURES UNDER SUPERCRITICAL CONDITIONS

A. Yermakova, V.I. Anikeev

Russ. J. Phys. Chem., 73(1) (1999) pp. 132-134.

Phase equilibria in binary mixtures in the subcritical and supercritical ranges of parameters and also gas–gas equilibria were studied. Phase diagrams are calculated by the homotopy method using the pressure as the parameter in the homotopy function. The Redlich–Kwong–Soave (RKS) equation with modified coefficients of two-particle interaction is used as a unified thermodynamic model for calculating phase states. Calculated pressure–composition diagrams for nitrogen–ammonia and nitrogen–*n*-heptane mixtures are compared to their respective experimental diagrams.

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