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# BORESKOV INSTITUTE OF CATALYSIS

SIBERIAN BRANCH OF RUSSIAN ACADEMY OF SCIENCES

# ANNUAL REVIEW '98

# ANNUAL REVIEW
## of Activities in Fundamental Areas
## 1998

**BORESKOV INSTITUTE OF CATALYSIS**
**SIBERIAN BRANCH OF RUSSIAN ACADEMY OF SIENCES**

**Novosibirsk**

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Dear Colleagues,

This is a real pleasure for me to present already the fifth issue of annual reviews of the Boreskov Institute of Catalysis in the main fields of its academic and R&D activity covering the year 1998.

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 remains 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 due to 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 appeared to be able to survive as a high quality specialized organization. Moreover, the intensity and quality of the research and engineering activity at the Institute became even higher. Hope, the readers will feel it themselves, when comparing the material of this and previous issues of the Annual Review.

The year 1998 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 to be possible only due to a very high professional value of the Institute among the industries both in our country 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 exceeded in 1998 the value of 50 %. Also, since the mid 1990-ths there was established a really strategic partnership with some world leading industrial companies.

Also, the year 1998 was the year of 40th anniversary of the Boreskov Institute of Catalysis created in 1958 by academician Georgii K. Boreskov. 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.

Year 1998 was of principle importance for the Institute, since from this year the Institute operated 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 this year the Institute succeeded also to reestablish 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.

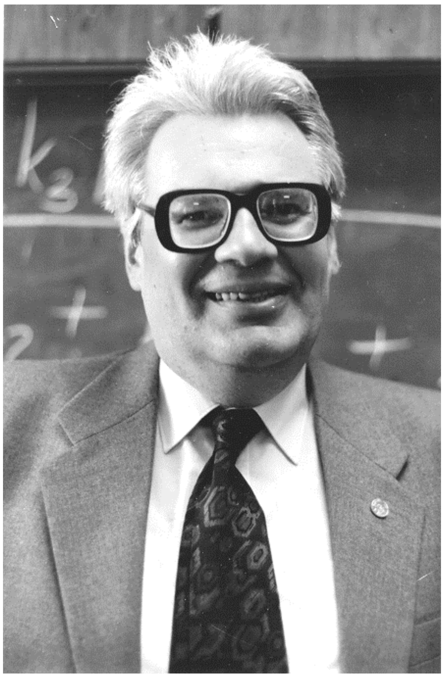
Since 1998 the Institute is united with some other R&D chemical institutions of the Russian academy of sciences in the frame of a new R&D association: the United Institute of Catalysis headed by the director of the Boreskov Institute of Catalysis. Now the United Institute of Catalysis (UOC) includes the Boreskov Institute of Catalysis with its Omsk and St. Petersburg Divisions, the Institute of Technical Carbon in Omsk as well as Scientific-Engineering Center "Zeosit" in Novosibirsk and Volgograd Scientific-Engineering Center on Volga River. The facilities of the UOC include now three powerful pilot plants capable to provide manufacturing the first industrial batches of various catalysts and specialty chemicals.

The year 1998 was already the forth year of activity of the third generation of the directorate of the Institute headed by Prof. Valentin N. Parmon. It became much younger also the staff of both the Board of Directors as well as the Scientific Council of the Institute. Indeed, these changes are very serious, since now the main research and administrative management in the Institute belongs to much younger generation. However, the new management recognizes 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 the many sides of the current Institute's capacity in basic research on catalysis, catalyst and catalytic technologies. As to the activity of the Institute in the applied areas, which is now much more active than before, under preparation now is a special issue of the Institute's reviews.

March, 1999 Valentin N. Parmon

# ACADEMICIAN KIRILL ILYICH ZAMARAEV (1939-1996)



May 20, 1999 is a memorial date for international community of scientists. This day is the 60th anniversary of Academician Kirill Ilyich Zamaraev, the Director of the Boreskov Institute of Catalysis (1984-1995), President of the International Union of Pure and Applied Chemistry (1994-1995), a wonderful person, an eminent physical chemist and statesman, talented teacher, great scientist in the area of catalysis and chemical kinetics.

Kirill I. Zamaraev was born in Moscow, Russia, on May 20, 1939 in the family of a famous soviet chemical engineer. He began his professional education at the Moscow Mendeleev Institute of Chemical Technology, then moved to the Moscow Physical-Technical Institute (MPhTI) in order to improve his knowledge of chemical physics. In both these universities his rank as a student was number one.

He received a BSc degree from the MPhTI in 1963 and was awarded a PhD in chemical physics in 1966 and a D.Sc. in physical chemistry in 1972 by the N. Semenov Institute of Chemical Physics (ICP) in Moscow (title of his doctoral thesis was “ESR study of transition metal complexes structure and reactivity”). In 1966-1976 he made his research as a junior research fellow, a senior research fellow and then a head of a laboratory at ICP where he performed a wide set of important basic research in the fields of elementary kinetics of electron spin exchange and electron tunneling transfer on large distances, as well as of ESR and NMR application to the studies of metallocomplex catalysts. At the same time he worked as an assistant professor at MPhTI. Since the beginning of 70th K. Zamaraev was drawn by academician N. Semenov into the studies on photocatalytic conversion of solar energy. In 1974-1975 he has been the first soviet long-term visiting researcher to the Cornel and Stanford Universities as well as the University of Chicago under a Program of scientific exchange in chemistry between the USSR and the USA.

In 1976 Professor Zamaraev has been elected as the corresponding member of the Academy of Sciences of the USSR and invited by academician G.K. Boreskov to join the Institute of Catalysis, Novosibirsk, 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 Boreskov Institute of Catalysis, and since that time he was the real leader of all research and development activity of this huge (more than 1000 people in staff) Institute.

Since 1986 till 1992 Professor Zamaraev held a position of the General Director of the large R&D association known as “MNTK “Katalyzator” Group”. Since 1985 he was the Chairman of the Scientific Council on Catalysis and its Industrial Applications of USSR (now of the Russian Federation), being the leader of the community of specialists in catalysis of the Russian Academy of Sciences. Since 1977 he was a Full Professor of the Novosibirsk State University having the chair in physical chemistry.

During the last changes in the former Soviet Union Professor Zamaraev was in charge of serious transformations of the Russian science on the way of its adaptation to the society with the market economy. He participated as a leading person at the formation of a large set of Federal Research Centers of Russia, which contain now, together with the Russian Academy of Sciences, the main scientific potential of Russia.

In 1994 the Boreskov Institute of Catalysis has obtained the status of the Federal Research Center also. In 1995, according to his own will, Kirill Zamaraev has left position of the Director of the Boreskov Institute of Catalysis, remaining the R&D Director of the Institute. The background of this decision was his sincere desire to spend more time on doing deep fundamental science.

Professor Zamaraev has been honored by the Russian Academy of Sciences and international community of chemists on several occasions. In 1987 he was elected a Full Member of the Academy of Sciences of the USSR (now Russia), in 1990 – a Member of the Academia European and a Foreign Fellow of the Indian National Science Academy, in 1995 – a Foreign Fellow of the Korean Academy of Science and Technology. In 1994 he was awarded by the Silver medal of the Royal Chemical Society of Great Britain as a centenary lecturer, in 1994 – by Karpinsky medal of the Chemical Society of Germany.

Since 60th Professor Zamaraev was a member of the International Union of Pure and Applied Chemistry. In 1987-1989 he was the President of the IUPAC Physical Chemistry Division, in 1990-1993 he organized the work of Editorial Advisory Board for Monographs on Chemistry for 21st Century, was a member of the IUPAC Executive Committee and Bureau. In 1994-1995 he held the position of the President of the IUPAC. In January 1996 he became the IUPAC Past-President.

Professor Zamaraev participated in the work of numerous scientific journals - Russian as well as international. He was the Editor-in-Chief of the *Reaction Kinetics and Catalysis Letters,* Regional Editor of the *Journal of Molecular Catalysis,* Member of the Editorial Boards of the journals *Catalysis Reviews, Catalysis Today, Catalysis Letters, Topics in Catalysis, Chemistry – A European Journal, Mendeleev Communications, Chemistry for Sustainable Development* and some other journals.

Professor Zamaraev is known for his mechanistic studies of catalysis at the molecular-atomic scale, and in particular for in situ characterization with the use of radiospectroscopy methods, i.e., electron spin resonance (ESR) and nuclear magnetic resonance (NMR). At the initial stage of his work Professor Zamaraev studied by ESR the structure of the transition metal complexes in solution and made a considerable contribution to the strategy of interpretation of complex EPR spectra of powder samples and reliable determination of EPR parameters.

He had discovered and kinetically characterized numerous electron tunneling reactions on large distances. He has performed pioneering experimental studies of reactions of electron tunneling between donor-acceptor pairs frozen in neutral matrices. He has demonstrated the possibility of electron tunneling on the distances of 15-30 Å and explored in detail the kinetics of this phenomenon in the time range from $10^{-6}$ to $10^{5}$ s. His fundamental studies of electron spin exchange in solution are also well known.

He was one of the pioneers who used the modern multinuclear solid state NMR for studies of the structure and the active sites on the catalyst's surfaces and intermediates of catalytic reactions in solutions and on solid surfaces.

He paid great attention to the study of chemistry in the second coordination sphere of metal complexes and the role of interfere interactions in the mechanisms of catalytic reactions. He was among the first to study of catalytic reactions in the gas phase by ion cyclotron resonance (ICR).

The works of Professor Zamaraev in photocatalysis and design of catalytic converters of solar energy utilization, as well as on the role of photocatalytic phenomena in the global chemistry of atmosphere, are the contribution to the XXI century science and technology. The approaches developed by Professor Zamaraev towards catalysis research helped to obtain unique results that were important for catalysis fundamentals and applications.

He published 3 monographs and over 300 articles in Russian and foreign journals.

Kirill Ilyich was a man of great heartfelt generosity, honesty, decency and kindness. He was a perceptive connoisseur of music and poetry. He really enjoyed the rare moments of contact with nature and he even celebrated his 50-th anniversary with his friends climbing and hiking at the mountains.

Kirill I. Zamaraev left us unfairly early. This is not only Russian science that has missed one of their front figures but this is the tremendous loss to the international catalysis and chemistry community. Kirill I. Zamaraev is missed by his many friends and colleagues.

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

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.

## STRUCTURE OF THE INSTITUTE

The list of personnel of the Institute amounts now up to 800 people in Novosibirsk and about 80 in Omsk, among them about 350 researchers of high qualification, presenting the unique society of specialists in all spectra of catalysts problems. They are 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 Institute incorporates 7 scientific-research departments, Department of Applied Catalysis Problems, International Center for Catalyst Characterization and Testing, and Information Center. The structure of the Institute includes also scientific-supportive units, manufacturing facilities, administration and services.

**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.

**The Information Center of the Institute** was established to serve the computational needs of the Institute. It has developed an information system “Catalysis”, which includes updated databases, such as the bibliography and the actual state of the art, related to research and applied works in the field of catalysts, commercial catalysis and catalytic processes developed in foreign countries and countries of the former USSR.

WWW-server of the Institute contains constantly renewed sections a) research stuff publications, b) patents, c) Catalytic Bulletin, d) Scientific Conferences.

The center is also engaged in automation of instrumentation of BIC. The unique information accumulated will be the base for creation of database on catalyst characteristics.

# STRUCTURE OF THE INSTITUTE

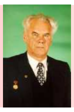
**Directorate:**
G.M. Matveev, B.S. Bal'zhinimaev,
V.I. Bukhtiyarov, B.I. Ermakov, S.P. Kil'dyashev,
A.S. Noskov, V.A. Likholobov, V.N. Parmon,
V.A. Sobyanin

**DIRECTOR**

**Directorate**

**Scientific Council**

## Research Departments



DEPARTMENT OF HETEROGENEOUS CATALYSIS
7 laboratories and 3 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 and 1 group Head: Prof. V.A. Kirillov

DEPARTMENT OF NONTRADITIONAL CATALYTIC PROCESSES AND TECHNOLOGIES
3 laboratories and 6 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

**Scientific-Supportive Units**

**Manufacturing Facilities**

**Administration and Services**

**The International 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.

## 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 Novosibirsk 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.*

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.*

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 this school 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.*

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.*

## 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.

# 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

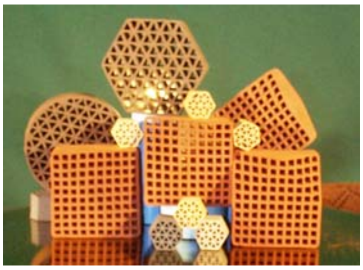
1990 - Russia

FORMALDEHYDE PRODUCTION FROM METHANOL OVER OXIDE CATALYST

1972 - Russia
1982 - Czech Republic, Bulgaria

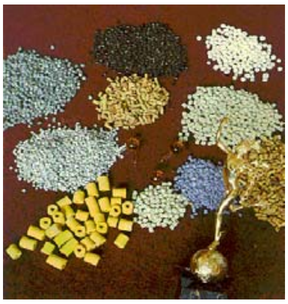
DEHYDROGENATION CATALYSTS FOR ELASTOMERS PRODUCTION

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

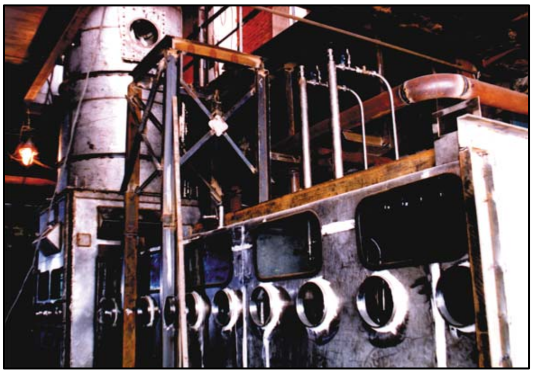
1992- Russia

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

# INSTRUMENT FACILITIES

The Institute engages the leading position in the world in the improvement and design of new physicochemical methods for catalyst study. 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.

## Elemental analysis

### *Bulk composition*

Atomic emission spectrometry with the preparation of samples in inductively bound plasma
Atomic absorption spectroscopy
X-ray fluorescence analysis of macro- and microprobes

### *Surface*

X-ray photoelectron spectroscopy (XPS)
Secondary ion mass-spectrometry (SIMS)

### *Phase analysis*

X-ray diffraction, including *in situ* diffraction
Phase analysis by differential dissolution
Thermally programmed reduction
EXAFS spectroscopy
X-ray diffusion scattering

### *Morphology*

Transmission electron microscopy
High resolution transmission electron microscopy
Scanning electron microscopy
Scanning tunneling microscopy
X-ray small-angle scattering

## Porometry

Mercury porometry
BET surface area measurement

## Spectral methods

NMR spectroscopy on different nuclei, including high-temperature and *in situ*
ESR spectroscopy, including *in situ*
UV-VIS diffuse reflectance spectroscopy
UV-VIS fluorescence

IR spectroscopy, including *in situ*
Near IR spectroscopy

## Methods for analysis of reaction products

Chromatography-mass-spectrometry
Gas, gas-liquid and liquid chromatography on packed, capillary and polycapillary columns, development of new techniques

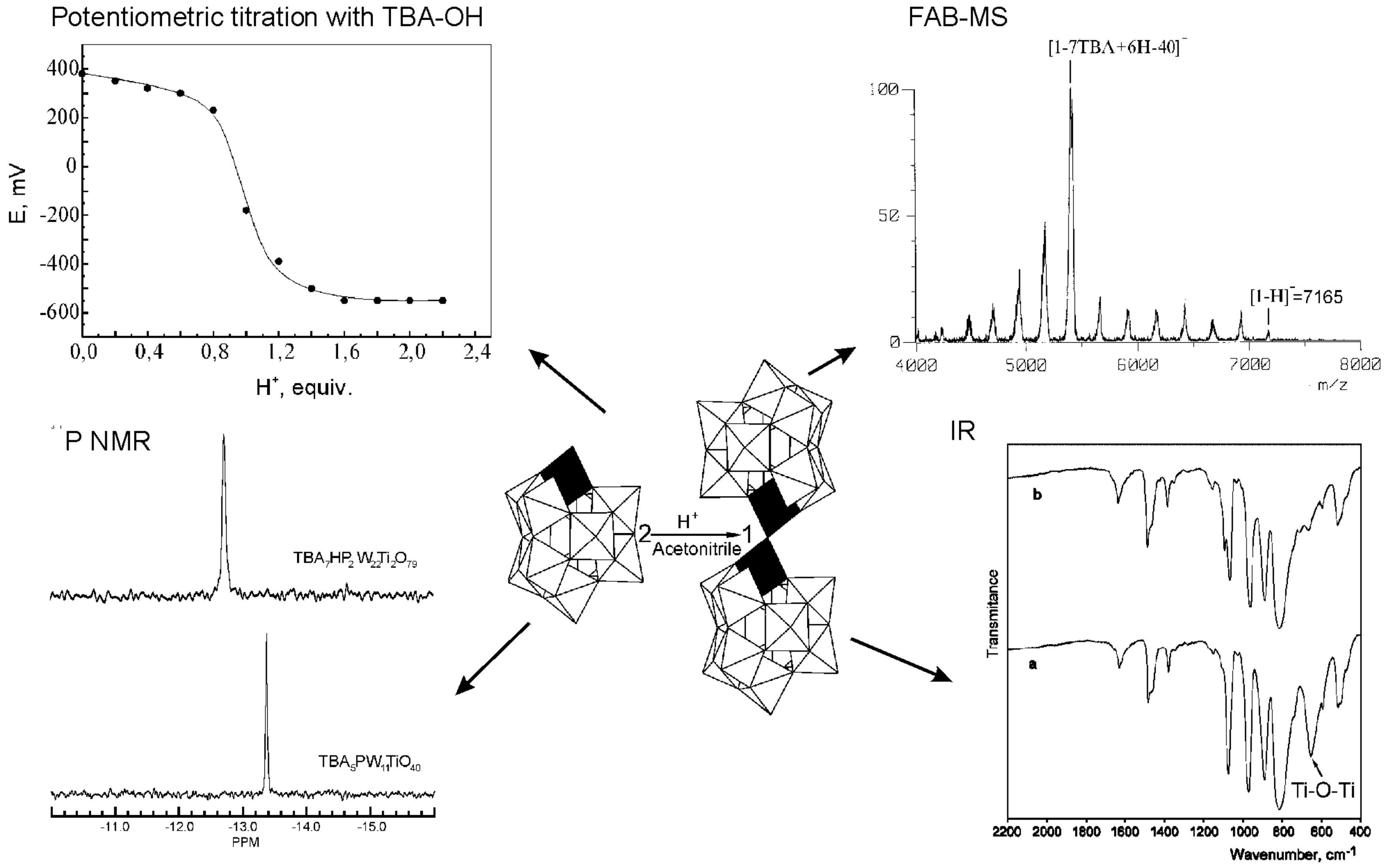
## Special techniques

Determination of the surface acidity using IR spectroscopy of probe molecules
Microcalorimetry
DTA/DTGA methods
Radioisotope techniques for analysis of reaction kinetics
Mass-spectrometric detection of free radicals.

## MAIN ACHIEVEMENTS IN 1998

### Titanium-substituted heteropolytungstates have been studied as model catalysts for selective oxidation of organic compounds with hydrogen peroxide.

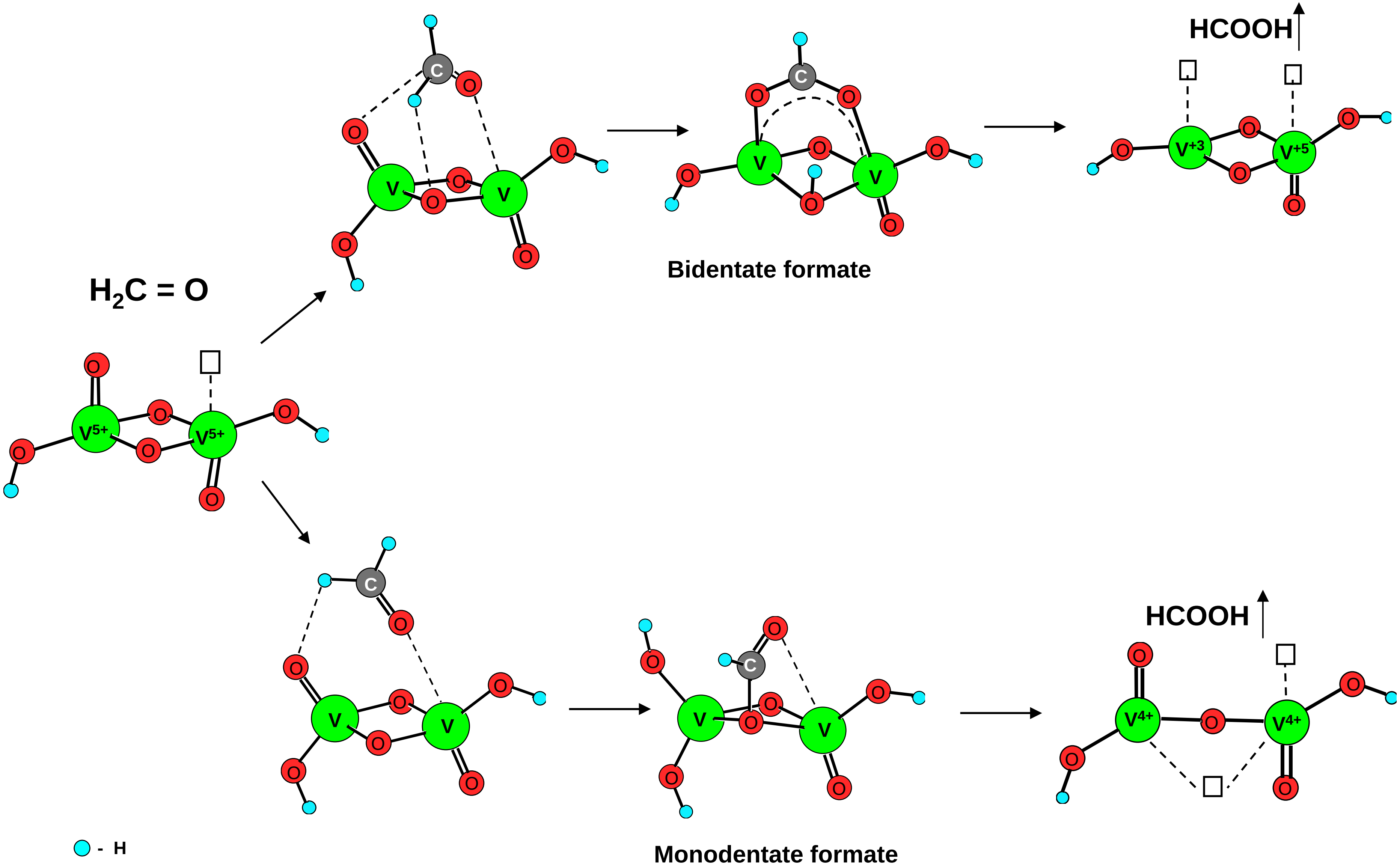
Heteropolyanions (HPA) substituted with transition metal ions $PW_{11}MO_{39}^{n-}$ ($PW_{11}M$) can be considered as models of catalytic sites distributed homogeneously in a heterogeneous matrix. Ti (IV)-substituted HPA are of special interest as they can be used as homogeneous models for investigation of the mechanisms of catalytic action of practically important heterogeneous catalysts - Ti-containing micro- and mesoporous materials, such as TS-1, Ti-MCM-41, etc. The present study has demonstrated practical applicability of such approach. It has been found that in MeCN there are 4 forms of monosubstituted Ti-HPA, namely, earlier unknown dimer $(PW_{11}Ti)_2OH$ (**1**), its deprotonated form $(PW_{11}Ti)_2O$ and two monomers $PW_{11}TiO$ (**2**) and $PW_{11}TiOH$ (**3**). The ratio between the forms depends on the concentrations of $H^+$ and $H_2O$. Dimer **1** has been isolated as a TBA salt $(Bu_4N)_7[\{PW_{11}O_{39}Ti\}_2OH]$ and characterized by the elemental analysis, potentiometric titration, IR, NMR ($^{31}P$, $^{17}O$, $^{183}W$) and FAB-MS. The catalytic activity of Ti-HPA in the oxidation of thioesters with $H_2O_2$ correlates with their activity in the formation of peroxocomplexes and decreases in the row **3** > **1** > **2**. The $H_2O_2$ addition to **1** and **3** results in the formation of the same peroxocomplex, most likely, $PW_{11}TiOOH$ (**I**). The interaction of **2** with $H_2O_2$ in MeCN leads to a slow formation of inactive peroxocomplex $PW_{11}TiO_2$ (**II**). The activity of **I** with respect to organic sulfides under stoichiometric conditions has been proved by $^{31}P$ NMR and optical spectroscopy. This is the first example demonstrating the reactivity of a titanium peroxocomplex to an organic substrate in a stoichiometric reaction.


Potentiometric titration with TBA-OH
E, mV
400
200
0
-200
-400
-600
0,0
0,4
0,8
1,2
1,6
2,0
2,4
H+, equiv.
FAB-MS
[1-7TBA+6H-40]⁻
100
50
0
4000
5000
6000
7000
8000
m/z
[1-H]⁻=7165
31P NMR
TBA7HP2W22Ti2O79
TBA5PW11TiO40
-11.0
-12.0
-13.0
-14.0
-15.0
PPM
2
H+
Acetonitrile
1
IR
b
a
Transmitance
Ti-O-Ti
2200
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber, cm-1

**The mechanism of formaldehyde oxidation to formic acid and structure of the active sites of highly selective V-Ti oxide catalyst have been studied for the first time by pulse methods and in situ FTIR in combination with ab initio quantum chemical computations by MO/HF method.**

Two possible pathways have been found for the formation of formic acid: from monodentate formate (MF) via a redox mechanism with the participation of oxygen from the catalyst and from bidentate formate (BF) via an associative mechanism with the participation of the gas phase oxygen at the formate decomposition stage. $V_2O_5OH_2$ cluster was chosen as a model of the active site (AS). The computation of this model and the energetic profile for both pathways has shown that MF is formed during the interaction of formaldehyde with a bridge oxygen atom, whereas BF results from the formaldehyde interaction with a vanadyl oxygen atom. The energies of the MF and BF intermediates formed are not very different. However, their decomposition with the formation of formic acid requires significantly different energetic expenses due to different oxidation states of vanadium in the AS. $V^{3+}$ is formed after the BF decomposition, while the MF decomposition results in the formation of $V^{4+}$. This makes the formic acid formation from BF energetically more favorable. This is confirmed by the experimental fact that the BF decomposition is faster by an order of magnitude than that of MF. The lower oxidation state of the AS ($V^{3+}$) in the case of the BF decomposition favors its faster reoxidation, which seems to account for the associative mechanism at the acid desorption stage.

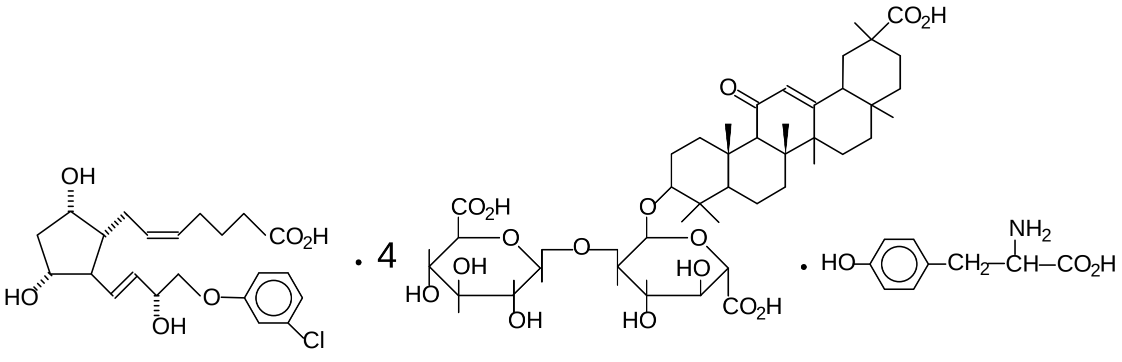
The determined mechanism of the selective transformations of formaldehyde opens the possibility of purposeful construction of the AS composition with respect to the strength of the surface formates and serves as a basis for the development of effective catalysts for the synthesis of formic acid from formaldehyde.


H2C = O
V5+
V5+
O
C
V
Bidentate formate
HCOOH
V+3
V+5
Monodentate formate
HCOOH
V4+
V4+
- H

### Methods for synthesis of novel promising substances for medical chemistry with variable biological activity (fungicide, growth simulating, antimicrobial, etc.) have been developed.

Studies on the search of substances with antihypoxic activity have been performed in the frames of SB RAS scientific and technical program "Integration". With the use of sulfur-containing alkaloids of landscape plant Diptichocarpus strictus, substituted hydantoins containing fragments of these alkaloid molecules in the side chain have been synthesized. For models of acute hypoxic normobaric hypoxia, hydantoins synthesized have been shown to have antihypoxic activity comparable to that of certified medical substances gutimine and bimethyl.

A new prostatic gland medicine "Kaltiram" has been patented (Russian patent). The development of the medicine was based on an original idea envisaging the introduction of a nontoxic biogenic amino acid and additives of vegetable origin into the composition with cloprostenol. According to the results of biological tests, "Klatiram" is effective for synchronization of the sexual desire of agricultural animals and synchronization of pig farrows.

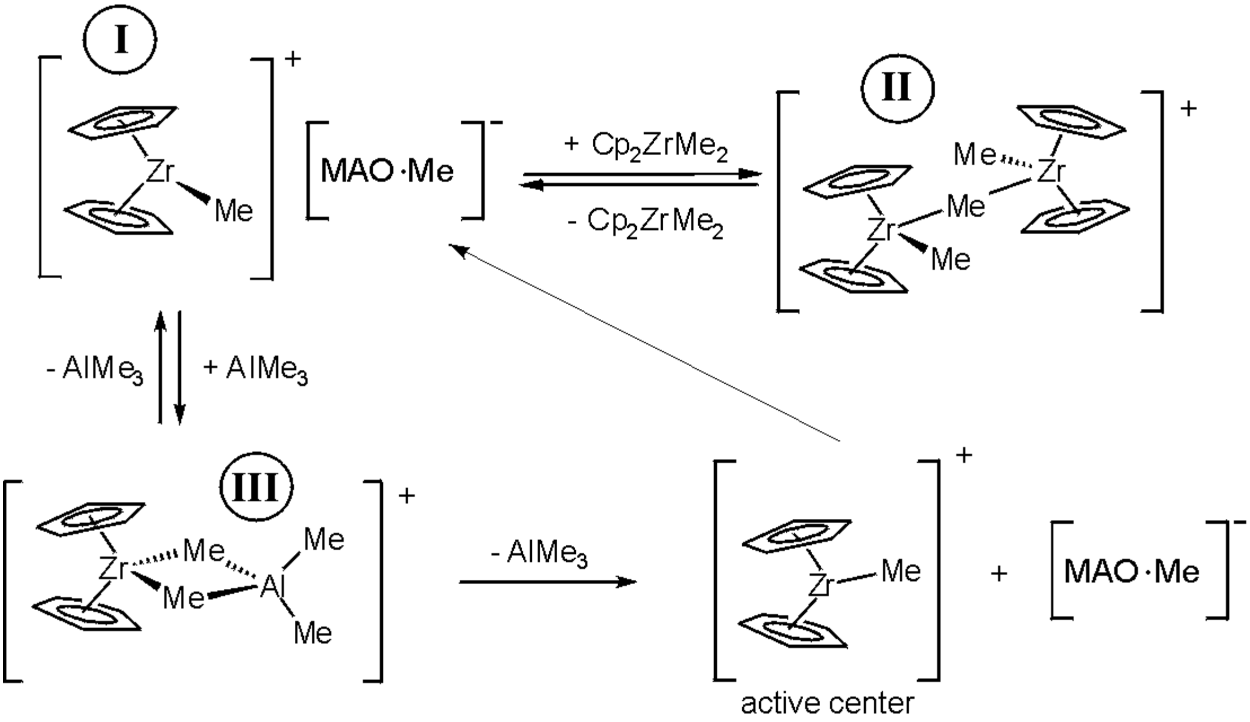


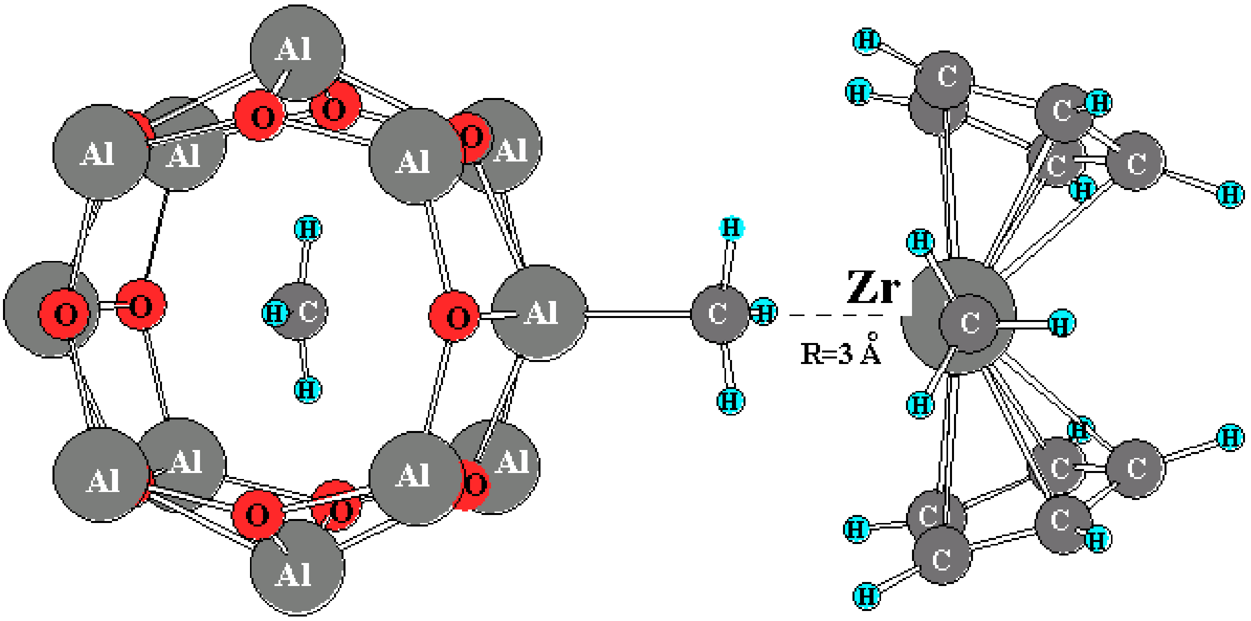
(Molecular complex: cloprostenol - glycerrisine acid - L-tyrosine)

### The composition of polymethylalumoxane (MAO), which is an activator of metallocene catalysts for polymerization of olefins, and mechanism of the formation of active sites during the MAO interaction with zirconocene have been studied by NMR, ESR and quantum-chemical DFT method.

NMR studies on $^{13}C$, $^{1}H$, $^{27}Al$ and $^{17}O$ nuclei and quantum-chemical DFT computations have shown that the most probable structure of MAO ($[-Al(CH_3)O-]_n$) is a three dimensional structure with oxygen bridges ("cage" structure) consisting of three layers of $[-Al(CH_3)O-]_m$ subunits with m = 3, 4. ESR studies with the application of nitroxyl radicals as spin probes have revealed the presence of several types of Lewis acid sites in MAO. DFT computations have shown that the acid sites in MAO are formed by breaking Al-O dative bonds in MAO due to the reaction with trimethylaluminum, which is always present in MAO.

The formation of the catalyst in the MAO/$(C_2H_5)_2Zr(CH_3)_2$ system at molar ratios Al/Zr = 200-400 corresponding to the polymerization conditions have been studied for the first time by $^{13}C$ NMR. A number of cation intermediates acting as precursors of active sites have been discovered and characterized, and a scheme of the formation of active sites in these systems has been suggested. The possibility of the formation of an ion pair in the $Cp_2Zr(CH_3)_2$/MAO system due to the abruption and occluding of a $[CH_3]^-$ ligand into the bulk of MAO with n ≥ 12 has been shown for the first time with the use of DFT studies. The electronic structure of the ion pair $[(MAO)_{12}CH_3]^- \ [(C_5H_5)ZrCH_3]^-$, which is a precursor of the polymerization active site, has been computed.





### Copper and iron hydroxides have been found to be effective catalysts for partial oxidation of light hydrocarbons in aqueous solutions under mild conditions (room temperature and atmospheric pressure) simulating the function of monooxygenases.

Bulk, colloid and $SiO_2$-supported copper and iron hydroxides have been found to be active in the $H_2O_2$ decomposition in aqueous solutions with neutral pH. During the reaction $Cu(OH)_2$ quickly forms peroxocomplexes with the composition $Cu:H_2O_2 = 1:1$ and 2:1, whereas iron (III) hydroxide forms a peroxocomplex that oxidizes Fe (III) to Fe (IV). The formation of peroxocomplexes of catalytically active hydroxides has been observed for the first time due to the application and spectrophotometric investigation of transparent solutions of colloid copper and iron hydroxides stabilized with starch. The formation of peroxocomplexes as intermediates results in the change of the $H_2O_2$ decomposition pathway. In contrast to the majority of other Cu and Fe compounds, in this case it follows a molecular mechanism rather than a radical Fenton-type one. Copper and iron hydroxides have been found to catalyze partial oxidation of various light hydrocarbons, such as methane, ethane, ethylene, with hydrogen peroxide in aqueous solutions even at room temperature and atmospheric pressure. The oxidation of methane and ethylene results in the formation of formic acid, whereas ethane oxidation leads to the formation of acetaldehyde. It has been found that the kinetics of the formation of intermediates formed in the $H_2O_2$ decomposition is significantly altered in the presence of oxidizable hydrocarbons. This may indicate that the same intermediates are formed during the $H_2O_2$ decomposition and the oxidation of substrates. Evidently, observed properties of hydroxides are, at least partly, equivalent to the principal function of the most important natural enzymes of the methanemonooxygenase type, which have not been simulated artificially so far.

### Adsorption immobilization of biologically active substances on carbon supports has been studied and medicaments with prolonged local action have been developed on its basis.

Principles for the development of medicaments with prolonged action have been formulated on the basis of studies on the immobilization of biologically active substances (BAS). First, high adsorption capacity of the support with respect to the biologically active substance is required. Second, the biological activity of BAS must be completely preserved after the immobilization on the support. Third, the strength of the BAS bonding with the surface must provide its partial desorption during a long period of time, the concentration of desorbed BAS in the therapeutic zone being sufficient for the demonstration of the healing effect. In such case, a local deposit of the medicine is formed in the therapeutic zone. This forms the basis for medicines of prolonged action. Based on detailed investigations of the adsorption properties of carbon enterosorbents SUMS, Carbactinum and Polyphepanum with respect to such antiseptics as furacilline, chlorohexidine and vitamin E, methods have been developed for preparation of medicaments with prolonged action and local therapeutic effect, including medicaments for complex treatment of paradont diseases in stomatology, and reaction conditions have been optimized.

# 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.

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 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 with the Institute of Energy Conversion and Storage, TAE-CNR, Messina was continued in the frame of the agreement between Russian Academy of Sciences (RAS) and National Council on the Scientific Research of Italy according to the program "**Catalysis for Solving the Energy Problem**".

### FRANCE

According to the agreement between RAS and CNRS BIC collaborates with the University of Paris on the project **"NMR Investigations of Mesoporous Systems".**

### INDIA

Complex ILTP program of scientific-technical cooperation, project **"Catalysis"**.

### YUGOSLAVIA

The agreement between Interacademic Board on Catalysis of the Serbian Academy of Sciences and Arts and the Boreskov Institute of Catalysis in the field of fundamentals of catalyst preparation and catalytic processes was signed.

## COOPERATION WITH FOREIGN ORGANIZATIONS IN THE FRAMEWORK OF BILATERAL AGREEMENTS

### GERMANY

### Fritz Haber Institute, Berlin

Started in 1994 XPS and UPS in situ studies on the structure of silver electrode/electrolyte boundary, namely, studies of adsorbed oxygen species on the Ag(111)/water electrolyte boundary in dependence of potential were continued.

Investigation of model catalysts surface structure by scanning electron microscopy technique is conducted.

### THE NETHERLANDS

The cooperations with the research institutions of The Netherlands are:

- ◊ **“Creation of Membrane-Catalytic Process for Fat Acids Eterification”,** Agricaltural-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.

### DENMARK

Studies on active component of vanadium catalysts for $SO_2$ oxidation are continued jointly with Technical University of Denmark, Lyngby, Denmark.

### SWITZERLAND

Jointly with the Institute of Chemical Engineering (EPFL), Lausanne, Switzerland BIC participates in the work on the project “**Unsteady State Catalysis as a Novel Approach to Design Chemical Reactors and Processes”.**

## 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.

In 1998 the group of computer modeling (Novosibirsk, Russia) has studied the action of individual components in $CH_4$+$N_2$ mixture in model micropores of active carbons by the GCEMC method.

In modeling the behavior of fluids in large micropores, one faces the same problems as in modeling on the open faces [1, 2]. But the algorithm presented in [2] seems to be complicated as well as the time required for performance. A more simple and elegant solution consists in dividing the model volume into three parts as a zone of “pure” adsorbate $V_a$, a zone of “pure” gas $V_g$ and an “intermediate” zone of the density drop $V_{ag}$ in going from an adsorbate to gas.

The theory of such “zone” approach have been developed and experimentally tested using a model adsorption of one-center molecules of nitrogen on the graphite surface at 78 K. Four types of molecules with the Lennard-Jones (LD) parameters $\varepsilon/k$=95.01 K and $\sigma_1$=0.3572, $\sigma_2$=0.3698, $\sigma_3$=0.385, $\sigma_4$=0.399 nm were tested.

It is evident that “zone” approach includes the dependence of the simulated results on the ratio between gas and the adsorbed phase. Unfortunately, “one-center” LD models of the $N_2$ molecule do not permit one to describe well the experimental data related to the nitrogen adsorption on the graphitized blocks. The reason is that the actual nitrogen molecules possess a quadruple moment whose long range is an order of magnitude higher than that of the LD potential. The latter changes qualitatively the ability of $N_2$ vapor for adsorption and condensation at high relative pressures. A two-atom model of the $N_2$ molecule, “X1”, possessing an effective model quadruple, provides better description of the experimental data.

Therefore, the zone approach was extended for two-atom molecules. The expressions for tradition probabilities, addition attempts, destruction or transition of molecules will contain a cosine of molecule axis slope to the adsorbed surface. The “two-atom” version of the zone approach GCEMC was successfully tested on nitrogen adsorption on the graphite surface. It was also studied how $N_2$ acts on adsorption in micropores of various sizes at different temperatures. For similar conditions, the behavior of the LD methane was studied.

References

1. D.K. Efremov, A.A. Shubin. Preprints of Intern. Symp. “Adsorption and Liquid Chromatography of Macromolecules” (Eds. Pojakov N.C., Eltekov Yu.A.), 1994, Moscow, “PAIMS”, pp. 4-5 (in Russian).
2. A.A. Shubin, D.K. Efremov. Dokl. Akad. Nauk, 342 (1995) pp. 345-349 (in Russian).

## 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.

The dynamics of hydrocarbon deep oxidation in the catalyst pellet with account of the intraparticle diffusion limitation under alternating adsorption stage and oxidation stage was studied by means of mathematical modeling. The results demonstrate the existence of an optimal catalyst pellet size providing the maximum purification efficiency in the adsorption-catalytic process of VOC abatement.

For the SCR process on a single catalyst particle it has been shown that under the programmed increase of the system temperature the particle diffusion limitation affects substantially all dynamic characteristics of the process, thus changing the process selectivity. In the case it is preferable to use spherical catalyst grains in the reactor.

The relation between the autowave solution of the model in the moving coordinate system on a whole 1-dimensional space and the solution of the boundary value problem (BVP) on a bonded interval of a fixed length has been studied numerically for the past year. In the first case a unique autowave solution was obtained, while in the second case the BVP had a one-parameter family of solutions.

The algorithm developed earlier at the Sobolev Institute of Mathematics SB RAS was adapted and used for the problem study.

### III. Dynamic Behaviour of Hydrocarbons Entrapped in Zeolite Pores

Project Coordinator*:*

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

Participants:

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

The dynamics of linear alkane - *n*-octane, adsorbed in zeolite H-ZSM-5 was investigated using $^2$H NMR, QENS and $^1$H pulse NMR. It has been found that at the loading 1.8 molecules per u.c. adsorbed *n*-octane molecules are located exclusively in the straight channels and diffuse along the direction of the straight channels with 1D-diffusion coefficient $D \sim 2.4\cdot10^{-11}$ m$^2$/s at 300 K. In the course of translational movement along the straight channels some self-consistent "rotational" motions of all $CH_n$- (n=2, 3) groups of hydrocarbon skeleton in the molecule take place, which are reflected in $^2$H NMR spectrum of deuterated *n*-octane-$d_{18}$ at 253 - 373 K as *effective* fast "rotations" of the separate methylene and methyl groups simultaneously about two and three C-C bonds of the molecule with characteristic time $\tau_C \sim 10^{-11}$ s and activation energy $E_R \sim 10$ - 12 kJ/mol. In fact, this mode of the motion may correspond to the fast interconversion between different conformations of *n*-octane molecule while its movement along straight channel. Upon heating at 373 K for 1 hour, *n*-octane molecules, formerly located in the straight channels, become redistributed over straight and zig-zag channels. Subsequent translational motion of *n*-octane consists of two independent modes of the motion. One of them represents the movement along tortuous zig-zag channel. Another mode of the motion represents either the movement of *n*-octane inside the zeolite channels via interchange between the straight and zig-zag channels or, more probably, the movement along straight channels, disturbed by the collisions with the other molecules at channel intersection. At the loading of 3.5 molecules per u.c. a liquid-like signal appears in $^2$H NMR spectrum at 253 K. This signal corresponds to isotropically reorienting *n*-octane molecules, changing the direction of their translational motion because of collisions with the other molecules at channel intersections. According to $^1$H nuclear magnetic relaxation data and $^1$H second moment measurements single-file diffusion of *n*-octane probably takes place for highest adsorbate loading. In order to explain the values of effective quadruple constants $C_Q$ and asymmetry parameters $\eta$ determined by $^2$H NMR an attempt to simulate short term *n*-octane backbone dynamics at given adsorption sites will be performed.

#### Grants Provided by INTAS-RFBR

### I. Small Alkanes Activation on Solid Acids at Moderate Temperatures

Project Coordinator:

**Prof. J. Sommer,** Universite Louis Pasteur, Strasbourg, France.

Project Head from the Russian Side:

**Dr. A.G. Stepanov**, Boreskov Institute of Catalysis, Novosibirsk, Russia.

The activation of 2-$^{13}$C labeled propane and isobutane on acidic zeolite H-ZSM-5 in the presence of $^{13}$C labeled CO and $H_2O$ has been studied by *in situ* solid state NMR and GC analysis. Evidence was provided that at 373-473 K, i.e. at temperatures well below that usually required for cracking of the alkane itself, propane converts via C-C bond cleavage to produce isobutyric acid (IBA) with evolution of both methane and ethane. Isobutane was transformed into pivalic acid with simultaneous production of hydrogen. The low conversion (1-2 %) was rationalized by the existence of a small number of very strong acid sites (perhaps 1-2 % of total amount of the acid sites) at the origin of a superacidic type of reactivity. A formate species was observed when CO and $H_2O$ were present on H-ZSM-5, which disappeared in the presence of the alkane. At 573 K the generation of large amount of $CO_2$ indicates a much higher conversion of the alkanes in carboxylic acids which decompose however under the reaction conditions.

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 $^1H$ and $^2H$ NMR with isobutane on various $D_2O$ exchanged solid acids. The activation energy of the process was estimated from the variable temperature *in situ* $^1H$ 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.

In relation to the development of methodology of *in situ* NMR analysis of the expected from the alkanes the carbonyl group containing organic products, the interaction of isobutane with CO on H-ZSM-5 was studied. Friedel-Crafts acylation of olefin by CO to form unsaturated ketone was observed for the first time on acidic zeolite at room temperature.

It was shown that the oxidative activation of small alkanes $C_1$-$C_3$ with participation of active oxygen species formed from $N_2O$ on zeolites does not require a presence of any acid sites on the surface, the reactivity of the alkanes being determined by the C-H bond strength. Though the acidity of the surface does not influence the oxidative activation it is important for secondary conversion of the activated hydrocarbons and their active intermediates. Depending on the acidity of the surface the active intermediates can either decompose to give $CO+CO_2$ (from $CH_4$), olefins (from $C_2$-$C_3$ alkanes) or undergo the secondary reactions with the hydrocarbons present to give oligomeric residues held on the surface or relatively low molecular weight products ($C_{4-}^{+}$-aliphatic, alkylated aromatic compounds, phenol derivatives). It was found out that oxidative methylation of benzene and phenol by methane occurred at comparatively low temperatures (360-400°C) giving toluene and cresols. It was shown that it is the acidity that favors the progress of the methylation reaction in the system $C_6H_6$-$CH_4$-$N_2O$, less acidic samples give more deep oxidation products ($CO_2$, CO) and ammonia inhibits the reaction. A fraction of methane participating in the formation of the different products was determined using labelled $^{13}CH_4$. Label distribution in the hydrocarbons formed has shown that two main reaction routes lead to the alkylated substances: direct methylation and decomposition of surface oligomeric hydrocarbons. Influence of decationation degree and Si/Al ratio of zeolites on the conversion of surface oligomers has been elucidated. Based on these data a reaction sequence which describes the oxidative conversion of small alkanes on acidic zeolites in the presence of $N_2O$ was proposed.

## II. *In situ* Detection of Electrocatalytic Centers on Novel Materials During the Oxygen Reduction using the EXAFS Technique

Project Coordinator:

**Dr. N. Alonso-Vante**, Hahn-Meither-Institut, Berlin, Germany.

Project Head from the Russian Side:

**Prof. D.I. Kochubey**, Boreskov Institute of Catalysis, Novosibirsk, Russia.

General structural characteristics of the active sites in Ru-X (X = S, Se, Te) catalysts for oxygen electroreduction, which seem to be responsible for their reactivity, have been determined on the basis of earlier EXAFS data on the environment of Ru in such catalysts.

Thin films of $Co_3O_4$ and $NiCo_2O_4$ catalysts for oxygen electroreduction supported on glass graphite have been prepared by ion spraying technique at Lab. d'Electrochimie, Faculte de Chimie, Universite Louis Pasteur. The thickness of the films is 150-700 Å. Phase composition of the films has been proved by DRES and EXAFS of full external reflectance.

## III. Novel Pt Nanostructured Materials for Electrocatalysis

Project Coordinator:

**Prof. D.J. Schiffrin**, University of Liverpool, Department of Chemistry, UK.

Project Head from the Russian Side:

**Dr. E.R. Savinova**, Boreskov Institute of Catalysis, Novosibirsk, Russia.

New techniques have been developed for chemical and electrochemical synthesis of a) monodispersed monoblock (monocrystalline) Pt nanoparticles on the basal plane of highly oriented pyrographite (HOPG) with the average size of 1.5-2.5 nm; and b) Pt particles with micrograined structure (i.e. particles consisting of several grains). The electrodes prepared were studied by TEM, high resolution electron microscopy, STM and XRD. Special original techniques for the analysis of dispersed materials by STM have been developed.

It has been shown that the highest dispersion of Pt can be obtained when Pt(II) forms $\pi$-complexes with the HOPG surface. A systematic comparative study of the Pt electrochemical deposition on different supports (HOPG, GC, polycrystalline graphite and Pt) from different precursors ($[PtCl_4]^{2-}$, $[PtCl_6]^{2-}$, $Pt(NH_3)_x(H_2O)_y$ and $H_2Pt(OH)_6$) has been performed at potential varied from 0.65 to –0.65 V relative to standard hydrogen electrode. The effect of the potential and the nature of the precursor on the dispersion of the electrodes have been determined. From the bulk of the results it was concluded that the electrochemical deposition in all cases results in the formation of particles with the micrograined structure on all the supports studied.

The effect of aging of nanosized electrodes during the cycling of the potential has been discovered and studied. It has been shown to consist in the coalescence of nanoparticles, formation of particles with the micrograined structure from initially monoblock ones. The resultant electrodes demonstrated an increase of the average diameter and width of the size distribution.

The dependence of the electrocatalytic properties of nanostructured materials on the particle size and microstructure has been studied in the anodic oxidation of ethylene glycol (EG), oxalic acid (OA), adsorbed CO and electrochemisorption of water using cyclic voltammetry, stationary voltammetry and potentiostatic electrolysis. The increase of the dispersion has been found to result in the decrease of the overpotential in EG and CO oxidation on nanoparticles supported on the HOPG surface in comparison with smooth Pt electrodes. A significant difference in the specific catalytic activity of platinum electrodes with different size and microstructure of nanoparticles and their stubility to self-poisoning with strongly chemisorbed species has been observed. It has been found that the size effect manifests itself in a different way in different potential regions.

The aging of Pt/Pt electrodes has been found to result in a substantial increase of their specific activity in the oxidation of EG and OA. A novel phenomenological model allowing determine the existence of the size effect has been developed and used for quantitative analysis of the experimental data.

Methods for analysis of EG oxidation products by HPLC have been developed. The derivatization method has been used for lowering the detection limits. Glycol aldehyde has been shown to be the major product of the EG oxidation on dispersed and smooth Pt electrodes at low overpotentials (0.1 V relative to $Hg/Hg_2SO_4$) in acid solutions.

## COPERNICUS

### 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:

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

The samples of V-Ti catalysts were prepared by the method of molecular adsorption $VOCl_3$ from a gas phase and the catalysts with the various content of $K_3PO_4$ promoter were prepared by a method of impregnation. The samples were tested in laboratory Flow reactor in the o-xylene and toluene oxidation reactions.

The experimental data show that the activity and selectivity of the samples of $V/TiO_2$ prepared by the adsorption method depend on purity of $TiO_2$. The data of Raman spectroscopy (Lausanne) show uniform distribution of V over the surface of $TiO_2$ with admixture. The selectivity of catalysts, prepared by the impregnation method, increases in row $V_2O_5$, $V/TiO_2$(rutile), $V/TiO_2$(anatase), $V(+K)/TiO_2$(an). The selectivity towards the C8 products is independent on temperature and o-xylene conversion up to 90-95%. The rate of phthalic anhydride oxidation calculated from kinetic data is 0.1-1% of the rate of o-xylene oxidation. The preliminary experimental kinetic regularities of toluene oxidation over steady and unsteady state are similar to that of o-xylene oxidation reaction. The reaction proceeds according to associative oxidation-reduction mechanism.

## CRDF

### Nanometric Closed Curved Graphite-Like Structure on Diamond

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:

**Prof. S.V. Stankus**, Institute of Thermal Physics, Novosibirsk, Russia;

**Dr. A.K. Gutakovskii**, Institute of Semiconductor Physics, Novosibirsk, Russia;

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

The graphitization of diamond monocrystals with (100) and (111) faces has been performed in a high-vacuum installation and studied by LEED, XPS and ARXPS. The LEED study has shown that diamond monocrystals of both types have (1x1) surface structures. XPS and ARXPS studies of annealing of the diamond monocrystals have shown that a) oxygen is completely removed from the diamond surface after heating at 900 °C; b) the diamond graphitization starts at 1050 °C; c) the annealing at 1500 °C for 3 h results in the formation of 2-3 graphite layers of nonuniform thickness on the surface of the diamond with the (100) face; and d) additional $sp^3$ carbon assigned to atoms located at the border between the diamond and the graphite layer are formed after heating at 1050 °C. The AFM study of annealed diamond monocrystal with the (100) face has shown that the diamond surface is uniformly covered with 10-100 nm hillocks.

## GRANTS PROVIDED BY DUTCH ORGANIZATION FOR SCIENTIFIC RESEARCH (NWO*)*

### I. Anion-Modified Oxides as Catalyst Precursors: Identification of Promotion Effects, Active Sites and Mechanism of Hydration on Copper Catalysts

Project Coordinators:

**Prof. A. Bliek, Prof. E.K. Poels,** University of Amsterdam, Amsterdam, The Netherlands.

Project Head from the Russian Side:

**Prof. T.M. Yurieva**, Boreskov Institute of Catalysis, Novosibirsk, Russia.

Participants:

**Prof. H.H. Brongersma**, Technical University, Eindhoven, The Netherlands;

**Dr. V.N. Ikorskii**, Institute of Inorganic Chemistry, Novosibirsk, Russia;

**Dr. A.M. Balagurov**, United Institute of Nuclear Studies, Dubna, Russia.

1998 is the last year of the project. The following results have been obtained this year.

1. The investigation of the thermal dependence of the magnetic susceptibility of copper-zinc oxides by the Faraday method has shown that a) copper ions are incorporated into the ZnO structure as Cu (II) rather than Cu (I) as used to be considered in the literature; and b) the reaction of the solid solution with hydrogen in the middle temperature range results in the reduction of Cu (II) ions to Cu (I) and Cu (0), the ratio between the latter being determined by the reduction conditions. The reduction is 80% reversible during the first reaction with hydrogen and 100% reversible during the following ones. The reversibility can be achieved by the oxidation in an inert gas flow containing low (~ 0.05%) concentration of oxygen. These results indicate that the main pathway of the reduction of the copper-zinc oxide solid solution does not include the formation of water with the participation of protons.

2. The investigation of the composition and structure of $SiO_2$-supported catalysts has shown that supported copper-chromium samples consist of copper-chromium spinel $CuCr_2O_4$ on the $SiO_2$ surface, whereas copper and copper-zinc samples are copper and zinc-copper silicates, respectively. According to the IR data, copper silicates with $Cu/Si \leq 1$ have the chrysocolla structure. For $CuZn/SiO_2$ samples the interaction between Zn and Si is decisive from the structural point of view. Two different silicates are formed. At $Zn/Si = 2$ zinc silicate with the hemimorphite structure is formed, in which copper ions are not solvable. At $Zn/Si \leq 0.75$ zinc silicate with the zincsilite structure is formed, in which zinc ions are partly (30-40 %) substituted with copper ions.

3. The investigation of the reduction of copper-zinc hydrosilicate with hydrogen has shown that a) copper ions substitute zinc ions both in the water layer between the stacks and in the octahedral positions of the stacks; and b) copper ions located in different structural positions of zincsilicate are distinguished by the temperature and character of their reduction. Copper ions located between the stacks in the layer of water molecules (type 1 ions) are reduced in the temperature range of 230-260°C with a constant activation energy, while copper ions located in the octahedral positions of the stacks (type 2 ions) are reduced during the temperature increase from 280-300°C to 400-450°C, with the their reduction activation energy depending on the reduction degree.

4. Catalytic properties of copper-zinc silicates have been studied in the transformations of methanol. Methyl formate, CO and $H_2$ appeared to be the main reaction products. The ratio of Cu (type 1 ions) and Cu (type 2 ions) in the catalyst determine the composition of reaction products.

## II. Clusters in Zeolite Materials

Project Coordinator:

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

Project Heads from the Russian Side:

**Prof. V.B. Kazansky**, Zelinsky Institute for Organic Chemistry, Moscow, Russia;
**Prof. G.M. Zhidomirov**, Boreskov Institute of Catalysis, Novosibirsk, Russia.

The following studies have been performed in accordance with the plan for 1998:

1. ZnNaY zeolites with high degree of exchange of $Na^+$ to $Zn^{2+}$ cations have been investigated by UV-VIS spectroscopy and DRIFT spectroscopy of adsorbed molecular hydrogen and CO used as probes for the states of charge compensating cations in zeolite framework. The combined spectroscopic study showed that besides of $Zn^{2+}$ localization in cationic positions of zeolites, the formation of small zinc oxide particles takes place;

2. Ab initio study of sixth fould cluster $Si_4Al_2O_6H_{12}$ considered as a model of exchangeable cationic site for $Zn^{2+}$ in faujasites has been performed with different level of theory (HF, $MP_2$ and DFT). Calculations show quite large stabilization energy of $Zn^{2+}$ ion in this site. This results

in rather endothermic processes of the reduction of $Zn^{2+}/Z$ by dehydration and by light alkanes ($CH_4$, $C_2H_6$). The growth of $Zn^{2+}/Z$ activity may be facilitated by some destabilization of this center in real zeolite structure. At the same time, small zinc oxide clusters $(ZnO)_n$ could give rise the dissociative adsorption of alkanes. This is the reason for suggestion that dehydrogenation ability of Zn-zeolites systems could be caused by small extra lattice species, probably by some intermediate forms, such as $[Zn\text{-}O\text{-}Zn]^{2+}$, containing extra lattice oxygen.

## INTERNATIONAL SCIENCE AND TECHNOLOGY CENTER (ISTC)

### 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

Organizations from the Russian Side:

1. Boreskov Institute of Catalysis
2. Novosibirsk State Project and Survey Institute VNIPIET
3. Novosibirsk Chemical Concentrates Plant
4. Siberian Chemical Plant, Tomsk-7
5. Mining Chemical Plant, Krasnoyarsk-26
6. Electrochemical Plant, Krasnoyarsk-45
7. Angarsk Electrolysis Chemical Plant

Foreign organizations:

1. Lawrence Livermore National Laboratory, USA
2. EG&G Rocky Flats, Inc., Rocky Flats, USA
3. Universite Louis Pasteur, Laboratory LERCSI, France
4. British Nuclear Fuel Ltd., UK
5. GEC-ALSTHOM Engineering Systems Ltd., UK

An ecologically safe technology for catalytic neutralization of mixed organic wastes containing radioactive materials has been developed and demonstrated at the pilot scale.

An enormous amount of radioactive wastes has been accumulated to date. The most dangerous are the so-called mixed wastes containing organic compounds, such as oils, extracting agents and solvents polluted with U, Pu and products of their fission. The main danger of mixed wastes is caused by the combination of fire risk, explosion risk and radioactivity. There are thousands of tons of such wastes in Russia, in particular in Siberian nuclear plants in Tomsk-7, Krasnoyarsk-26, Krasnoyarsk-45 and Angarsk. Hundreds of tons of mixed wastes are formed annually at Novosibirsk Chemical Concentrates Plant during production of the fuel for nuclear power stations. Most of them are stored. Some of the wastes were earlier subjected to open combustion or placed into a tailing pit. Naturally, such methods for utilization of wastes are dangerous and result in the pollution of the environment with radionuclides.

On the basis of experience in the combustion of fuels in catalytic heat generators, an ecologically safe process for treatment of mixed organic wastes in a fluidized catalyst bed have been developed.

Effective modified copper-magnesium-chromium catalysts for combustion of wastes with high mechanical and thermal stability have been developed at Boreskov Institute of Catalysis. Pilot-scale batches of the catalysts have been produced.

Two pilot installations with the waste processing productivity 1 kg/h have been developed, designed and built. The installation at Novosibirsk Chemical Concentrates Plant is devoted for making experiments with radioactive wastes of this plant for investigation of the efficiency of the catalysts in neutralization of real radioactive materials. Experiments with oil wastes containing U-238 and U-235 radionuclides have shown high efficiency of the wastes oxidation at stable working regimes and a phenomenon of the gradient accumulation of radionuclides in the catalyst granules. With the account of the critical conditions in working with fissionable materials, this installation can become a block module of an industrial scale installation.

The other installation was specially constructed for investigation of the purification of gases after the catalytic reactor from dust, oxides of radioactive metals and acid gases. The installation includes the main block of catalytic combustion in a catalytic heat generator, a block of CO combustion and a four-stage system for gas purification with the use of a cyclone, a foam scrubber of original construction, an absorber-condenser and an aerosol filter. A nuclear-safe circular catalytic reactor has been developed.

Optimal process regimes have been studied for catalytic combustion with subsequent gas purification of the wastes formed at Novosibirsk Chemical Concentrates Plant and other nuclear plants in Tomsk-7, Krasnoyarsk-26, Krasnoyarsk-45 and Angarsk. A catalytic reactor and a honeycomb catalyst for the CO combustion in dust-laden gas exhausts and purification of exhaust gases from CO have been developed, built and tested. It has been shown that the developed complex gas purification system allows purify gases from radioactive dust, acid gases and CO to the levels determined by sanitary regulations for each component.

Based on the results of these studies, the project documentation for production of an industrial installation for neutralization of organic radioactive wastes with the productivity of 50 ton/year has been prepared. This installation was built at Novosibirsk Chemical Concentrates Plant in 1998. Starting and testing of the installation is scheduled for 1999.

## TWINNING BIC-IRC PROGRAM (COOPERATION BETWEEN BORESKOV INSTITUTE OF CATALYSIS (BIC) AND INSTITUT DE RECHERCHES SUR LA CATALYSE (IRC), LYON, FRANCE

**Project Coordinators:**

**Prof. B.S. Bal'zhinimaev,** Boreskov Institute of Catalysis, Novosibirsk, Russia.
**Prof. A. Renouprez**, Institut de Recherches sur la Catalyse, Lyon, France.

In 1998 the works on BIC-IRC Twinning Program were continued. In the frame of this program two RFBR-CNRS (on JUMELAGES Program) Grants were obtained:

1. Development and Application of Novel Instruments and Methods for Investigation of the Catalysts (Project Head from the Russian Side - **Prof. D.I. Kochubey**, from the French Side - **Prof. A. Renouprez**)
2. Novel Materials and Composites for Non-Traditional Catalysis (Project Head from the Russian Side - **Prof. V.A. Likholobov,** from the French Side - **Prof. P. Gallezot**).

Project Coordinators from Russian and French Sides and the head of Chemistry Department of the CNRS Pierre Dixneuf participated in a Workshop held in July, 1998, in St. Petersburg, Russia. The results obtained during 1994-1998, and program for next 4 years were discussed at this Workshop.

The Cooperation Program for 1999-2002 is approved by CNRS. It includes following projects:

**1. Synthesis of new catalytic materials**

1.1. Zeolite membrane for new catalytic reactors.
1.2. Catalytic membrane contactors for gas-liquid applications.
1.3. Study of mesoporous and divided oxides by advanced techniques.

**2. New catalytic reactions on novel materials**

2.1. Epoxidation of ethylene.
2.1.1. Epoxidation of ethylene on clusters prepared by laser vaporization.
2.1.2. Study of light olefin epoxidation by transient kinetic techniques.
2.1.3. Modelling of catalytic reactions.
2.2. Catalysts based on synthetic mesoporous carbon materials for hydrodechlorination reactions.
2.3. Mechanism of the NO-$CH_4$ reaction.
2.4. Dynamics of hydrocarbons entrapped in zeolite pores.

## EUROCAT OXIDE CATALYSTS

Work on the program EUROCAT OXIDE CATALYST was continued in 1998. The aim of the program is the creation of a standard European catalyst to be used for calibration of modern spectrometers and standardization of characterization technique. At a Workshop on the Program EUROCAT OXIDE CATALYSTS held in May 1998 in Lyon, France the results on investigation of two oxide catalysts for selective nitrogen oxides catalytic reduction (fresh $V_2O_5/WO_3/TiO_2$ and the same catalyst after reaction, 1000 hours) were discussed. The Organizer of the Workshop was Prof. **Jacques Vedrine**. 20 participants from the European countries took part in the Workshop, among them - Prof. V.I. Bukhtiyarov, Boreskov Institute of Catalysis, Novosibirsk, Russia, one of the Project Coordinators. Project Coordinators gave lectures concerning main physical methods of investigation. The decision to publish all the results in one of the issues of Journal "Catalysis Today" was adopted. It was marked at the Workshop an enormous use of such investigations, when different groups of researches study one and the same catalyst samples by wide variety of physical methods.

## 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 the most productive to familiarize scientists with innovations outside their own research and to disseminate the information about the results achieved to a wider audience.

**In 1998 the Boreskov Institute of Catalysis participated in 3 exhibitions abroad and 7 exhibitions in Russia:**

*2nd International Exhibition of High Technologies*, 19-25 January, Taibay, Taiwan.

*New Technologies to Protect Environment from Industrial Wastes and Emissions*, Exhibition-Presentation of Russian Technologies, June 15-20, Helsinki, Finland

At commission of Ministry of Science of Russian Federation Boreskov Institute of Catalysis was responsible for organization of presentation of technologies for environmental protection developed by leading research institutions of Russia.

*"Innovations-98"*, 3-6 November, Leipzig, Germany

"*Russian Regions-98*", 25 February - 2 March, Moscow

"*Ecology. Public Health", 23 March - 3 April, Moscow

*"XVI Mendeleev Congress*", 24-29 May, St. Petersburg

*"40th Anniversary of the Borerskov Institute of Catalysis",* 4-5 June, Novosibirsk

*"Innovations-98",* 20-23 October, Moscow

*"SIBPOLYTECH-98",* 26-30 October, Novosibirsk

*"Catalytic Processes, Catalysts and Innovations"*, in the frame of RFBR Seminar, 3 November, Tomsk.

Special expositions on definite subjects, such as “New materials”, “Technologies and catalysts for environmental protection”, “Developments in medicine”; perspective developments of the Boreskov Institute of Catalysis in oil chemistry, fine organic synthesis, production of many-tonnage output, etc. were presented at above exhibitions.

**Researchers of the Institute presented their papers and took an active part in numerous national and international conferences, symposia and schools.**

One of the directions of the scientific-organizational work carried out in the Institute is aimed on conducting conferences and seminars not only with the participation of Russian scientists and scientists from CIS, but International as well**. During 1998 the Institute became the main organizer of 5 conferences and seminars.**

### XIV INTERNATIONAL CONFERENCE ON CHEMICAL REACTORS, “CHEMREACTOR-14”
### Tomsk, Russia, June 23-26

The Conference took place in Tomsk – one of the ancient cities of Siberia, at the House of Oil. The Conference was organized by:

- Boreskov Institute of Catalysis, Novosibirsk, Russia
- State Research Center of Russia "Karpov NIPCI", Moscow, Russia
- Tomsk Polytechnic University, Tomsk, Russia
- East Oil Company, Tomsk, Russia
- Scientific Council on Catalysis and its Industrial Application of RAS and Ministry of Russian Federation on Sciences and Technologies, Moscow, Russia
- Siberian Association of Chemical Engineering, Novosibirsk, Russia.

The General sponsor of the Conference – East Oil Company, the main distributor of oil in Siberia. Ministry of Russian Federation on Sciences and Technologies and Boreskov Institute of Catalysis also provided financial assistance to the Conference.

The Conference attracted attention of 87 researchers, interested in the collaboration in the field of Chemical Reaction Engineering, among them 14 foreign participants from 7 countries - Switzerland, Italy, Belgium, Portugal, Poland, UK, USA. World leaders in the field of chemical technology - **Prof. A. Renken** (Swiss Federal Institute of Technology, Lausanne, Switzerland), **Prof. P. Forzatti** (Technological University of Milan, Italy), **Prof. G. Froment** (University of Gent, Belgium), **Prof. J. Witton** (Cranfield University, UK), **Prof. V. Parmon** (Boreskov Institute of Catalysis, Novosibirsk, Russia) took part in the Conference.

The Conference Program was divided into 4 sessions according to the following subjects:

- ♦ Physico-Chemical and Mathematical Fundamentals of Processes on Catalysts Surface
- ♦ Physico-Chemical and Mathematical Fundamentals of Processes in Chemical Reactors
- ♦ New Types of Chemical Processes and Reactors
- ♦ Chemical Reactors for Solving the Fuel and Energy Production Problems. Oil and Gas Production and Processing.

The Conference Program included 4 plenary invited lectures, 27 oral presentations and 47 posters. Plenary lectures concerning the most important trends of chemical reaction engineering were given by:

**Prof. V.N. Parmon**, Boreskov Institute of Catalysis, Novosibirsk, Russia – "Physical Methods for Handling the Problems of Chemical Technology";

**Prof. A. Renken** and R. Doepper, Swiss Federal Institute of Technology, Lausanne, Switzerland - "Unsteady State Reactor Engineering";

**Prof A.S. Noskov**, Boreskov Institute of Catalysis, Novosibirsk, Russia, and M.G. Slin'ko, State Research Center "Karpov NIPCI", Moscow, Russia – "Prospects for Developing Heterogeneous Catalytic Processes";

**Prof. V.S. Babkin**, Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia – "Porous Media and Problems of Fire-Safety and Explosion-Proofing".

The event provided a comprehensive look at the best achievements in the field of chemical engineering and enjoyable stay in Siberia.

**International Workshop on "Unsteady-State Operation and *In-Situ* Measurements of Surface Species under Transient Conditions"** took place in the frame of the Conference on June 26, 1998. The Workshop was supported by Swiss National Science Foundation. The leading scientist in this field presented plenary lectures:

**Prof. R. Doepper** and A. Renken, Swiss Federal Institute of Technology, Lausanne, Switzerland – "Dynamic Experimental Methods Applied to the Determination of Reaction Mechanism";

**Prof. G. Yablonsky**, Washington University, St. Louis, USA – "Pulse-Response-Tap-Studies for Understanding Heterogeneous Catalytic Processes;

**Prof. P. Forzatti**, Technological University of Milan, Italy – "Unsteady-State Kinetics of DeNOx-SCR Catalysis".

The Poster Session numbered 7 presentations of young scientists from Russia and Switzerland.

## THE THIRD INTERNATIONAL CONFERENCE ON UNSTEADY-STATE PROCESSES IN CATALYSIS, "USPC-3"

### St. Petersburg, Russia, 30 June - 3 July

The Conference continued the tradition established in Novosibirsk, Russia in 1990 and in St. Louis, USA in 1995, and was organized by

- Matros Technologies, St. Louis, USA
- Boreskov Institute of Catalysis, Novosibirsk, Russia
- Monsanto Enviro-Chem System, St. Louis, USA
- DuPont, Wilmington, USA

The Conference was co-sponsored by American Institute of Chemical Engineering, Canadian Society for Chemical Engineering, The Society of Chemical Engineers, Japan.

The number of Conference participants was 172, among them 118 foreign scientists from 20 countries (Belgium, Bulgaria, Canada, China, Czech Republic, Denmark, Finland, France, Germany, Greece, Israel, Italy, Japan, Poland, Portugal, Sweden, Switzerland, The Netherlands, UK, USA).

**Three plenary lectures:**

"Dynamic Approaches to Heterogeneous Catalysis" by **Prof. B. Bal'zhinimaev**, Boreskov Institute of Catalysis, Russia

"Industrial Applications of Unsteady-State Processes" by **Dr. G. Bunimovich** and V.O. Strots, Yu.Sh. Matros, Matros Technologies, USA

"Periodic Flow Reversal in Chemical (Reaction) Engineering" by **Prof. G. Eigenberger**, University of Stuttgart, Germany,

**62 oral presentations** covering the topics**:**

- Dynamic Processes on Catalyst Surface
- Dynamics of Chemical Reactors
- Forced Unsteady-State Operation
- Reactors with Flow Reversal
- TAP (Temporal Analysis of Products) Reactor Studies
- Dynamic Operation of Three Phase Reactors
- Nonlinear Phenomena in Heterogeneous Catalytic Systems
- Dynamics of Automotive Converters,

**and Poster Session,** numbering 46 poster presentations**,** formed the scientific program of the Conference.

The USPC-3 Conference proved to be an interdisciplinary, highly focused forum that brought together specialists in catalysis and chemical reaction engineering. It united well-known scientific schools in the field of chemical technology, presented by scientists from greatest Universities of the world: **Prof. A. Bell**, University of California, USA; **Prof. G. Froment**, University of Gent, Belgium; **Prof. J. Haber**, Institute of Catalysis and Surface Chemistry, Krakow, Poland; **Prof. M. Menzinger**, University of Toronto, Toronto, Canada; **Prof. D. Luss**, University of Houston, Houston, USA; **Prof. A. Renken**, Swiss Federal Institute of Technology, Lausanne, Switzerland**; Prof. P. Silveston**, University of Waterloo, Waterloo, Canada; **Prof. M. Baerns**, Institute of Applied Catalysis, Berlin, Germany, and others, and leading companies and firms, such as Monsanto Enviro-Chem Systems Inc., The Dow Chemical Company, ABB LUMMUS GLOBAL Inc., UOP, DuPont Nylon, Alternative Fuel Systems Inc., Hitachi Zosen Europe LTD, Haldor Topsøe, Ammonia Casale S.A., ICI Katalco.

The Conference objective was to discuss recent results from academic research and industrial advances that pave the way for using unsteady state processes for creation of better, more efficient and environmentally friendly chemical technologies.

The Conference helped to establish new connections between academia and industry, and between engineers and scientists from different parts of the world.

The Seminar of EC Inco-Copernicus Grant-holders and Workshop of Boreskov Institute of Catalysis, Novosibirsk, Russia and Institut de Recherches sur la Catalyse, Lyon, France took place in the frames of Conference.

Splendid architecture and rich historic and cultural heritage of St. Petersburg made attending the USPC-3 Conference especially enjoyable.

## INTERNATIONAL SYMPOSIUM ON MOLECULAR ASPECTS OF CATALYSIS BY SULFIDES, "MACS"

### St. Petersburg, Russia, October 6-8

The Symposium took place at the St. Petersburg Hotel, situated at the historical center of St. Petersburg on the bank of the Neva River, the main waterway of the city.

The "MACS" Symposium was organized by

- Boreskov Institute of Catalysis, Novosibirsk, Russia
- Haldor Topsøe A/S, Lyngby, Denmark
- Scientific Council on Catalysis and its Industrial Application of the Russian Academy of Science and the Ministry of Science and Technologies of the Russian Federation, Moscow, Russia
- St. Petersburg Department of the Mendeleev Russian Chemical Society, St. Petersburg, Russia

The Organizers expressed the warmest gratitude for the financial support of the Symposium to

- Haldor Topsøe A/S, Lyngby, Denmark - general sponsor
- Russian Foundation for Basic Research, Moscow, Russia - general sponsor
- Bourevestnik Inc., St. Petersburg, Russia
- Boreskov Institute of Catalysis, Novosibirsk, Russia
- AOOT "Plastpolimer", St. Petersburg, Russia.

The Symposium was attended by 71 scientists, including 56 foreign participants from France, Belgium, Denmark, Hungary, Japan, Germany, Korea, Italy, The Netherlands, Switzerland and USA.

The Scientific program of the Symposium comprised 8 plenary lectures, 27 oral and 10 poster presentations. Plenary lectures were presented by:

**Dr. C. Bianchini** and A. Meli, S. Moneti, F. Vizza, Instituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, ISSECC-CNR, Firenzer, Italy **-** "Mimicking the HDS Activity of Ruthenium-Based Catalysts. Hydrogenation and Hydrogenolysis Reactions of Benzo[b]thiophene and Dihydrobenzo[b]thiophene Catalyzed by Soluble Ruthenium Complexes in Different Phase-Variation Systems";

**Dr. M. Breysse,** University P. et M. Curie, Paris, France; C. Geantet, M. Lacroix, Institut de Recherches Sur la Catalyse, Lyon, France and J.-L. Zotin, Petrobas S.A., Cenpes/Dicat, Rio de Janeiro, Brazil – "Characterization of Active Sites on a Molecular Level and Reactivity of Ruthenium Sulfide Catalysts";

**Dr. S. Kasztelan,** Institut Francais du Petrole, Rueil-Malmaison, France – "Hydrotreating Reaction Mechanisms over Metal Sulfides";

**Prof. I. Mochida,** Institute of Advanced Material Study, Fukuola, Japan – "Molecular Aspects in Deep Desulfurization of Gas Oil Over Supported Sulfide Catalysts";

**Prof. A. Startsev**, Boreskov Institute of Catalysis, Novosibirsk, Russia – "Concerted Mechanisms in the Heterogeneous Catalysis by Sulfides";

**Dr. E. Stiefel,** Exxon Research and Engineering Co., Annandale, USA – "Transition Metal Sulfur Sites in Enzymes and Molecular Complexes: Internal Redox and Ligand-Based Reactions";

**Prof. J. Norskov**, L.S. Byskov, Th.H. Rod, Technical University of Denmark, and B.S. Clausen, Haldor Topsøe Research Laboratories, Lyngby, Denmark – "Reactivity of Transition Metal Sulfides - Density Functional Calculations and Models";

**Prof. R. Angelici,** M.A. Reynolds, Iowa State University, Ames, USA – "New Transition Metal Complexes with Coordinated Thiophene and Dibenzothiophene Ligands: Models for Thiophene Adsorption on HDS Catalysts".

Poster and Oral Sessions covered the following topics:

- Molecular Aspects of Deep Hydrodesulfurization, Design of Sulfide Catalysts
- Hydrodenitrogenation of Oil Fraction, Bio-Crude-Oil Upgrading, Catalysis by Nitrides and Related Model Compounds

- Quantum-Chemical Studies on the Electronic Structure of the Active Components and Molecule Adsorption on the Active Sites; Mechanisms of Hydrogenolysis and Hydrogenation Reactions on a Molecular Level
- Catalysis by Metal Sulfides; Mechanism of Hydrogen Activation
- Molecular Models of the Active Component and Mechanisms of Hydrogenolysis and Hydrogenation Reactions
- Molecular Structure of the Active Component of Sulfide HDS and HYD Catalysts; Mechanisms of Catalysis by Sulfides.

The Symposium proved to be very fruitful, as it gave a good opportunity to the representatives of three scientific schools (headed by **Dr. S. Kasztelan,** Institut Francais du Petrole, Rueil-Malmaison, France; by **Dr. H. Topsoe**, A/S Topsøe, Lyngby, Denmark, and by **Prof. A. Startsev**, Boreskov Institute of Catalysis, Novosibirsk, Russia) to discuss aspects of sulfide catalysts action on a molecular level.

### RFBR SEMINAR “CATALYTIC POCESSES, CATALYSTS AND INNOVATIONS”

### Tomsk, Russia, December 1-3

The Seminar was held in the House of Scientists, in Academy Town of Tomsk, one of the biggest industrial and scientific centers of Siberia.

The Seminar was organized by

- Boreskov Institute of Catalysis, Novosibirsk, Russia
- Russian Foundation on Fundamental Researches, Moscow, Russia
- Scientific Council on Catalysis and its Industrial Application of the Russian Academy of Science and the Ministry of Science and Technologies of the Russian Federation, Moscow, Russia
- Department of Education and Scientific-Technical Policy of Administration of Tomsk Region, Tomsk, Russia
- Institute of Oil Chemistry, Tomsk, Russia.

The sponsors of the Seminar:

- Russian Foundation on Fundamental Researches, Moscow, Russia
- “Tomsktransgas”, daughterly enterprise of RSC “Gasprom”, Tomsk, Russia
- Department of Education and Scientific-Technical Policy of Administration of Tomsk Region, Tomsk, Russia
- Boreskov Institute of Catalysis, Novosibirsk, Russia
- Resort Place “Kedrovyi”, Tomsk, Russia
- House of Scientists of Academy Town, Tomsk, Russia
- Institute of Oil Chemistry, Tomsk, Russia
- JSC “Tomskgas”, Tomsk, Russia

The aim of the Seminar was to acquaint the representatives of industrial enterprises and potential investors with the most important and perspective achievements of scientific groups of academician, educational and industrial sciences in such directions, as:

- Catalysts and Catalytic Technologies of Natural Gas and Accompanying Hydrocarbons Processing
- New Generation of Highly Effective Catalysts for Oil Processing
- Catalytic Technologies in Inorganic Substances Production
- Catalysts and Catalytic Technologies of Synthesis of Complex Chemical Products and Polymers with Desired Properties
- Catalytic Technologies of Toxic Wastes Detoxification
- Catalytic Composites and Technologies for Energetic and Nontraditional Use.

45 scientists from Moscow, St. Petersburg, Novosibirsk, Kazan, Tomsk took part in the Seminar. The Scientific Program of the Seminar included 7 plenary lectures and 25 oral presentations.

The Seminar participants discussed opportunities of catalysis and Russian chemical industry development, they enjoy staying in Tomsk for many fruitful scientific discussions, new acquaintances.

### PRESENTATION SEMINAR "ZEOFORMING – NEW INDUSTRIAL TECHNOLOGY OF GASOLINE PRODUCTION"

### Novosibirsk, Russia, December 14-18

The Seminar was organized by:

- Scientific-Engineering Center "Zeosit", Novosibirsk, Russia
- Boreskov Institute of Catalysis, Novosibirsk, Russia
- JSC "Novosibirsk Chemical Concentrates Plant (NCCP)", Novosibirsk, Russia
- Lurgi GmbH, Germany
- Refinery "Glimar", Poland.

The Program of the Presentation Seminar included:

- ♦ Lectures concerning Zeoforming fundamentals and operational experience integration with demonstration and data analysis on ecological, economical and technological indexes getting during the Zeoforming process industrial running (Lurgi GmbH, SEC “Zeosit”, Refinery “Glimar”, JSC “NCCP”). Lectures were presented by **Prof. K.G. Ione,** SEC “Zeosit”, Novosibirsk, Russia - “New Resources-Saving Technologies of Motor Fuel Production and Attendant Materials”, **Dr. V.G. Stepanov,** SEC “Zeosit”, Novosibirsk, Russia - “Scientific and Technological Fundamentals of Zeoforming Process”, **R. Schoenfeld** and E. Shneider, Lurgi GmbH Company, Germany - “Zeoforming Installations Designing and Delivering Opportunities by Lurgi GmbH Company”, **S. Ptak,** Refinery “Glimar”, Poland - “Estimation of the Operation Experience of Zeoforming Installation on Refinery “Glimar”, Poland”, **Prof. G.V. Echevskii,** SEC “Zeosit”, Novosibirsk, Russia, and I.E. Abroskin, A.B. Aleksandrov, JSC "Novosibirsk Plant of Chemical Concentrates, Novosibirsk, Russia - “Industrial Experience of Motor Fuel Catalysts Manufacture”, **S.V. Lopatkin** and K.G. Ione, V.G. Stepanov, SEC “Zeosit”, Novosibirsk, Russia - “New Technologies on Heavy Oil Fractions Processing”.

- Participation in the International Exhibition-Seminar “Energy-Resources Saving of Siberia-98”
- Excursion to JSC “Novosibirsk Chemical Concentrates Plant” where the industrial production of the catalysts for Zeoforming process was developed.

The Seminar gathered 83 participants, among them 6 foreign participants from Germany, Poland, Yugoslavia. Representatives of Oil and Gas production and Coal mining Companies, Regional Administrations interested in formation of enterprises for carbon-containing raw materials processing into high-octane gasoline and products of organic synthesis participated in the Seminar.

Participation in the seminar allowed receive the unique information on results of successful operation of the first industrial plant on high-octane gasoline "Eurosuper-95" and liquefied gas production on "Zeoforming" technology (started in April 1997 on "Glimar" Rifinery, Poland).

## 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 is the principal source of recruitment of the personnel of the Institute.

### 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.

# BRIEF HISTORY OF THE INSTITUTE

## 1958-1968

*In the mid-1950s the problem about the creation a multi-purpose scientific center in Siberia arose. The purpose of the center with highly skilled workforce, and supplied with the modern necessary equipment should be researches in various fields - physics, chemistry, mathematics, biology and the humanities. This was essential, and is still, for a number of reasons, including the solution of industrial, technical and environmental problems. The Soviet Union couldn't develop dynamically unless its national economy made an active use of Siberian Resources. Siberian scientists were called to make a valuable contribution to the development of not only the productive forces of the region, but social development and cultural enrichment as well.*

*The Siberian Branch of the USSR AS was organized in 1957 by Academician Mikhail A. Lavrentiev. All academician institutions existed before beyond Ural formed it. In a short time a set of new institutes was born. The leading scientists elaborated the theses about great scientific and social experiment - creation of Novosibirsk Scientific Center in Akademgorodok (Academy Town) in the forest 30 km from Novosibirsk - a major industrial, transport, cultural, scientific and administrative center of Siberia.*

50-s years in the history of catalysis may be considered as a crucial moment. Exactly at that time an impetuous process of birth and development of different conceptions of the theory of catalysis took place. The prospects of industry development on many years ahead were under consideration. At the suggestion of initiative group headed by G.K. Boreskov in 1958 the Central Committee of the Communist Party and the Soviet Government made a decision to establish the Institute of Catalysis at the Novosibirsk Scientific Center. It became the first in the Soviet Union and forth in the World. To that time the decision about organization of 12 other institutes was made (1957). Creation of the Institute of Catalysis constituted a very clear indication that catalysis began to play an important role in the development of chemical industry.

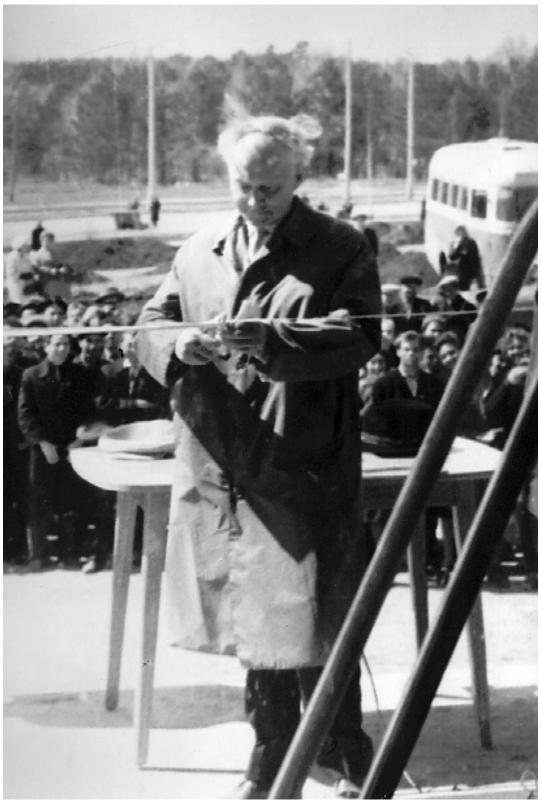
Here is the brief consideration of the history of how the Institute arose and came to reach it present position.

Georgii K. Boreskov became the Director of the Institute. His idea was to combine the fundamental research in the theory of catalysis and design of new methods for catalyst preparation with the mathematical simulation of catalytic processes accompanied by the solution of applied problems suggested by the demands of industry. The principle was to follow precisely the planned structure of the Institute which included the laboratory premises, workshops, services and two very important subdivisions - catalysts testing and preparation plant and department of mathematical modeling, a key facilities in the prompt passage from laboratory elaboration to experimental-industrial tests. Administrative subdivisions of Siberian Branch, and even a great many of leading scientists did not imagine the whole complexity of the Institute, considering it to be just an ordinary chemical institution. The lectures, reports and statements by G.K. Boreskov concerning the existing problems, methods of their solutions, importance of catalysis for industry played the great role.

The first members of the Institute were hired in **1958.** The building was started, and it demanded a lot of efforts. K.I. Matveev, who was engaged in project of building of model installations, and first deputy director L.A. Sazonov, who was engaged in project of the main building of the Institute and workshops, creation of services and scientific subdivisions came to Novosibirsk. In 1961 Deputy Director and at the same time the Chief Engineer Roman A. Buyanov arrived to Novosibirsk with the aim to control the construction of the Institute building**.**

The main Institute building with manufacturing facilities was put into operation in **1963 -** the remarkable date! A radiochemical unit and block of model installations were added to the Institute’s premises in **1964.** The radiochemical unit was arranged for the work with radiochemical isotopes and sources of ionizing radiation. The block of model installations consisted of department for catalysts preparation, department of automating installations for catalyst testing, and department for gases preparation and storing. The construction of the whole complex of the Institute’s buildings was completed in October, **1967**, when the Center of mathematical modeling came into operation.

In the summer of 1959 the administration of Siberian Branch was surprised, what for the Institute of Catalysis (the building of which was not existed at that time) asks to engage the glass-blowing apprentices. The future famous masters Ts.P. Mazur (later the Head of the **Glass-blowing shop**), V.F. Korzh, E.V. Eremeev were hired in 1960. In that same year the organization of



**Mechanical shop** started. The workshops grew, preparing the wares and constructing the experimental installations for R&D work.

It was necessary to create the management departments of the Institute, and S.Ya. Khorkov - deputy Director on administrative work, L.V. Sanina - The Head of Personnel Department, G.I. Plenkov - The Head of Supply Department were engaged.

It is a remarkable fact that already in 1962-1964 thanks to the big assistance rendered by the Soviet Government, and as a result of joint efforts of all the collaborators, it became possible to equip the Institute with the modern (according to that time) physico-chemical devices. A large set of experimental installations for physico-chemical studies of catalysts and catalytic processes (X-ray diffraction analysis, electron microscopy, IR- and mass spectroscopy, EPR and NMR technique, and others) was put into operation. In 1962 the Institute got the first analog computer MN-14, and in a year it was mastered and 25 programs were worked out to simulate reactors of different types.

Side by side with research and development plant the formation of the Institute staff took place. The number of people quickly grew (Fig.). The average age of the workforce at the Institute was under 35.

The specialists from the following institutions formed the main body of the Institute:

Laboratory of Engineering Catalysis of L.Ya. Karpov Institute of Physical Chemistry, Moscow (V.A. Dzisko, M.G. Slinko, K.I. Matveev, V.V. Popovskii, M.S. Borisova, G.M. Polyakova). Exactly in this laboratory V.A. Dzis'ko during a number of years prepared specialists for the Institute of Catalysis. Exactly from this Institute K.I. Matveev “withdrew” and sent to Novosibirsk a fair amount of glass wares;

Institute of Physical Chemistry, Moscow (N.P. Keier, I.S. Sazonova);

Moscow Mendeleev Institute of Chemical Technology, Moscow (V.S. Muzykantov, T. Khokhlova, T.M. Yurieva, V.N. Bibin, V.S. Beskov);

Moscow Institute of Fine Chemical Technology, Moscow (Yu.I. Yermakov. T.V. Andrushkevich, G.D. Kolovertnov);

Leningrad Chemical-Technological Institute, Leningrad (K.G. Ione, A.V. Khasin);

Moscow Lomonosov State University, Moscow (A.P. Karnaukhov, L.A. Sazonov, R.K. Motorkina, N.E. Buyanova, N.S. Kotsarenko).

It is necessary to say that G.K. Boreskov spared a special attention to the staff policy. The main criteria were high level of training, the ability of self-initiative work, scientific-creative work and activity.

Not waiting the finishing of main laboratory institute building construction, a part of staff members arrived to Novosibirsk and began to organize their working places primarily in the laboratory premises of the Institute of Hydrodynamics - the first building of Akademgorodok, which was completed in 1959, and even in dwelling houses, later - in the institutes of Geology and Geophysics and Chemical Kinetics and Combustion. So, in the first years the scientific body of the Institute was disconnected. Only during 1962 all collaborators and departments, temporarily worked in L.Ya. Karpov Institute of Physical Chemistry were transferred to Novosibirsk.

It was necessary to join all collaborators by common aim, correctly determine the directions of research work, and to evaluate the perspective of different physical methods of investigation in catalysis. It is needless to say that all of the members took an interested part in the life of the Institute and actively supported its undertakings.

The R&D directions of the Institute activities were formulated already in 1958:

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

The main object was the overall development of the theory of catalysis, allowing the prediction of the catalytic action and conditioning the progress in design of new catalysts and processes. The unity of theory and practice was the peculiarity of organization and carrying out the scientific-research works. Fundamental researches were primarily aimed at the development of the theory of catalysis that largely determined the progress in finding novel catalysts and processes. In turn, the choice of the proper field for the theoretical research depended on the dictates of practical application.

In **1963** the Scientific Council (Photo) recommended a structure of the Institute:

**Laboratory of Oxidation**
**Head: Georgii K. Boreskov (in 1960 - Group of Oxidizing Catalysis headed by Boris I. Popov)**

**Laboratory of Semiconductor Catalysts**
**Head: Nadezhda P. Keier**

**Laboratory of Organic Catalysts (since 1960)**
**Head: Klavdii I. Matveev**

**Laboratory of Catalysts Preparation**
**Head: Vera A. Dzis'ko**

**Laboratory of Kinetics of Catalytic Processes**
**Head: Roman A. Buyanov**

**Laboratory of Mathematical Modeling (since 1960)**
**Head: Mikhail G. Slin'ko**

**Laboratory of Radiochemistry (since 1960)**
**Head: Leonid A. Sazonov**

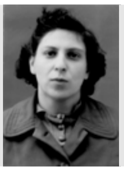
**Laboratory of Polymerization and Catalytic Condensation**
**Head: Yurii I. Yermakov**

**Laboratory of Physical Methods of Investigation (since 1961)**
**Head: Lidiya M. Kefeli**

**Laboratory of Metal Catalysts, since 1964 - Laboratory of Optical Spectroscopy and Mass-Spectroscopy**
**Head: Boris L. Kurbatov**

**Laboratory of Analytical Chemistry (since 1960)**
**Head: Raisa K. Motorkina**

**Laboratory of Adsorption (since 1961)**
**Head. Anatolii P. Karnaukhov**



**Laboratory of Catalytic Transformations of Sulfur-Containing Compounds (since 1960)**
**Head: Anna V. Mashkina**

**Laboratory of Quantum-Chemical Methods**
**Head: Viktor D. Sutula**

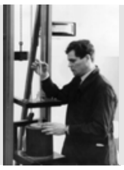
**Department of Chief Mechanic**
**Head: Vladimir V. Esin**

**Mechanical Shop**
**Head: Ivan S. Fedoseev**

**Department of Chief Power Engineering Specialist**
**Head: Aleksandr M. Buryndin**

**Designing Bureau**
**Head: Viktor S. Lakhmostov**

**Department of Experimental Devices**
**Head: Yurii A. Alabuzhev**



**Glass-Blowing Shop**
**Head: Tsezar P. Mazur**

**Administrative Department**
**Head: Fedor T. Kalinchenko, Deputy Director**

**Subdivision of Model Installations**
**Head: Yurii S. Kabanov**

**Preparatory sub-unit**

**Library of scientific literature**

The first Scientific Secretary - Vladislav V. Popovskii

The Institute of Catalysis operated with this structure for many years. It ensured the broad spectrum of the Institute's activities, and promoted the important contribution to the science.

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.

## SCIENTIFIC RESULTS

The creation in the USSR of **new chemical school,** presented by three main directions - heterogeneous catalysis, homogeneous catalysis and mathematical modeling of catalytic processes was considered to be the main achievement of the Institute over the ten years period.

**The following topics were under research for the first time:**

- *Elucidation of regularities of substances oxidation over oxide solid catalysts* (Leaders: G.K. Boreskov, R.A. Buyanov, A.A. Ivanov, V.V. Popovskii, N.P. Keier, L.A. Sazonov, I.S. Sazonova, V.A. Dzisko, V.S. Muzykantov).
- *Developing of methods of mathematical modeling of catalytic processes* **(**Leaders: M.G. Slin'ko, V.S. Beskov, Yu.I. Kuznetsov, Yu.Sh. Matros).
- *Sulfur organic compounds transformation* (Leader: A.V. Mashkina).
- *Elucidation of the regularities of hydroxides surface and pore structure formation* **(**Leaders: V.A. Dzisko, D.V. Tarasova).
- *Preparation of supported catalysts based on metal organic compounds of transition elements. Regulation of metal complexes catalytic activity* **(**Leader: Yu.I. Yermakov).

**A series of catalysts for different chemical processes was developed and transferred for pilot testing and commercialization**:

*Ferric-molybdate catalysts for methanol oxidation to formaldehyde.* At Novosibirsk Chemical Plant the experimental batch of the catalyst for industrial tests was produced in amount of 1 t (Leaders: B.I. Popov, E.P. Prokopiev, G.D. Kolovertnov, L.N. Shkuratova, N.G. Skomorokhova, D.V. Tarasova, I.Sh. Itenberg). A project of a unit with capacity 15 th t/y for Kemerovo Chemical Plant with the tubes of enlarged diameter was designed (Leaders: Yu.Sh. Matros, B.I. Popov, V.S. Lakhmostov).

*Industrial catalyst K-16 for butylene dehydrogenation* (Leaders: R.A. Buyanov, L.P. Shadrin).

*Effective catalysts based on mixed copper-magnesium chromites for low temperature carbon oxide conversion with water vapor* (Leaders: V.V. Popovskii, T.M. Yurieva).

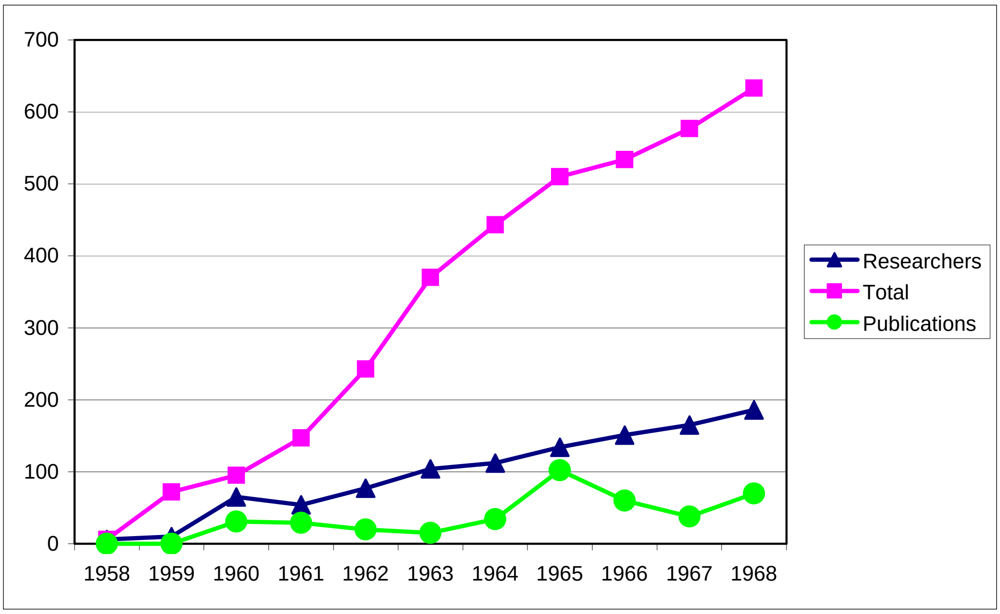
*Catalysts and method for catalytic air purification* from harmful products, evolving upon wires enameling (Leader: V.V. Popovskii).

*Water-soluble catalysts based on cobalt phthalocyanine tetrasulfur derivatives for waste waters purification* (Leader: N.N. Kundo).

**New physicochemical methods and installations for catalysts testing:**

- Application of radioactive isotopes and irradiation in catalysis (Leader: L.A. Sazonov);
- The adsorption methods for investigation of a large number of catalysts, chromatographic method for specific surface measuring, and the convenient high-productive and high-sensitive installation for catalyst surface determination (A.P. Karnaukhov, N.E. Buyanova);
- An installation for quantitative thermograph analysis (A.A. Ostankovitch, Yu.A. Alabuzhev);
- An emissive microprojector for investigation of gas chemisorption on metals (V.I. Savchenko, V.V. Gorodetskii);
- An original installation for chemisorption study by method of second ion-ion emission (P. Zhdan);

### Number of staff and publications 1958-1968



## CLOSE CONNECTION OF CATALYSIS WITH INDUSTRY

In **1962** State Committee of Council of Ministers of the USSR recognized the Institute of Catalysis as the head organization of the country in the field of heterogeneous catalysis.

In November, **1963** G.K. Boreskov became a president of the Scientific Council on “Catalysis and its Industrial Application” at the State Committee of the USSR Council of Minister, the aim of which was coordination of all R&D activities in the country. According to the decision of Scientific Council in **1964** five complex teams have been organized at the Institute on design and intensification of industrial processes: sulfur acid production, synthesis of ammonia, synthesis of high alcohols from carbon oxide and hydrogen, production of methanol-free formaldehyde. Specialists from academician and branch scientific research institutes, project-construction organizations and plants formed these teams.

The Institute of Catalysis became the coordinator of the works in the field of “Mathematical modeling and optimization of chemical-technological processes” (Leader: M.G. Slin’ko, **1965**).

The increasing amount of a number of industrial catalysts required systematic studies of them. The Institute of Catalysis became in **1967** the scientific leader of the investigations in the field of industrial catalyst development and scientific examination of their technology. The Department of Industrial Catalysts (Head: A.A. Samakhov), comprised of 5 laboratories, has been created. Basing on the analysis of the state of manufacturing and influence of technological parameters on catalysts quality, the main principles of technology improvement were suggested (A.A. Samakhov, N.M. Zaidman).

The reference book “Industrial Catalysts and Carriers”, containing information about the most important catalysts and carriers, produced in USSR, was issued and the collection of 250 samples of industrial catalysts has been amassed.

## SCIENTIFIC-ORGANIZATIONAL WORK

During 10 years the Institute was the main organizer of the following events:

**1963** - the 1st All-Union Conference on Modeling and Optimization of Catalytic Processes. It gathered 300 participants from 90 institutions. The discussion about the very term "mathematical modeling" and reality of its existence took place at the conference.

**1965** - two Conferences - 2nd All-Union Conference on Chemical Reactors and Processes Modeling and All-Union Conference on Methods of Investigation of Catalysts and Catalytic Reaction. The first was attended by 300 participants from 57 institutions, the second by 420 participants.

In March, **1966** the All-Union Educational Seminar on Catalytic Processes Modeling was held.

**1967** - IV All-Union Conference on Electron Microscopy. The subject of the Conference was an application of electron microscopy in physics, crystallography, chemistry, biology and medicine.

**1968** - International Symposium "Pore Structure and Transfer in Heterogeneous Catalysis" within the framework of IV International Congress on Catalysis (Moscow, 1968). 263 scientists and specialists from 27 countries were the participants of Symposium. The International Exhibition "Catalysts and Scientific-Engineering Literature on Catalysis, Adsorption and Adjacent Fields of Chemistry" took place in Academy Town.

## INTERNATIONAL COOPERATION

From its inception the Institute promoted international cooperation, first of all, with the scientists from socialist countries. The enlargement of the Institute connections with foreign organizations testified about its growing scientific authority.

In **1960** the program of joint work in the field of quantum-chemical calculations with the Institute of Physical Chemistry of Czech Academy of Sciences and the Institute of Mathematics, Novosibirsk has been worked out.

Delegations from the Institute participated in the II (July, **1962**, France) and III (July, **1964**, The Netherlands) International Congress on Catalysis.

M.G. Slinko (**1964)** visited Japan to become acquainted with the works in the field of catalysis at Sapporo, Tokyo, Osaka and Kyoto Universities, and central scientific laboratories of a number of companies.

In October, **1965** the delegation of Belgium Concern UCB (Union Chemique - Chemische Bedrijven) visited the Institute. In the frame of cooperation the Institute of Catalysis took part in the design and mathematical modeling of the process of nitrile to acrylic acid production over Fe-Sb catalysts in flowing-circulation system, and kinetics model of the process. It was the first large project in Siberian Branch on the cooperation with capitalist countries (S.A. Veniaminov, V.S. Beskov). During this year prominent scientists from different countries: Director of the Institut de Recherches sur la Catalyse Prof. Marcel Prettre, Lyon, France (Photo), Director of the Institute of Catalysis of Hokkaido University Prof. Jory Horiuti, Supporo,

Japan (Photo), Director of the Institute of Inorganic Catalysis of AS GDR Prof. Gunter Rienacker were the guests of the Institute. The short-term visits of sciences from Japan (4 scientists), France, USA, UK and representatives of French companies took place.

Since **1966** the scientific-engineering connections with research centers of socialist countries got the further development - in accordance with the agreement about the cooperation of USSR Academy of Sciences and Academies of Sciences of Socialist Countries the Institute began to receive foreign senior scientists and research workers for probation (in 1966 - 2 scientists from GDR, 6 form Czechoslovakia, 2 from Poland, and 1 from Hungary; in 1968 - 1 from Bulgaria, 2 from Hungary, 2 from CPP, and 1 from China.

## INTERNAL EVENTS

In **1962** R.A. Buyanov initiated the first Competition on the best scientific-research work, which then became the annual.

The Institute needed its logo. Among many other projects, the one by T.V. Andrushkevich - benzene ring with two curves - was recognized as the best and didn't undergo any changes up till now.

In **1962** the Institute branch of "All-Union Mendeleev Chemical Society" was organized. N.P. Keier became the Chairman. The first "Mendeleev Party" devoted to 130th anniversary of D.I. Mendeleev was hold in **1964**. N.E. Buyanova gave a lecture devoted to the life and activity of great Russian scientist. Holding of these annual parties became the tradition of the Institute. The participation in All-Union Competitions, organized by "All-Union Mendeleev Chemical Society", were discussed at these parties, the collaborators told about their visiting foreign countries. The parties were always natural; there was a tea-drinking, a lot of jokes, humor.

Already in the first years the library of artistic literature was organized, at the beginning by the efforts of all collaborators, and then with the help of administration.

## CREATION OF WORKSHOPS

The glass-blowing shop became one of the best in the country and the most powerful in Siberia and Far East. High-qualified personnel staffed it. Each order was unique, and all articles were of the best quality. The three-step diffusion pumps gave vacuum up to $10^{-8}$. In the Union there were two or three institutes (Institute of Catalysis among them) in the workshops of which it was possible to produce the unique devices - magnetic-circulating pumps. During 10 years about 170 glass installations were made. The shop prepared the personnel for Middle Asia, Far East and Siberia.

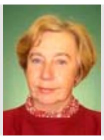
(To be continued)

# SCIENTIFIC DEPARTMENTS

# DEPARTMENT OF HETEROGENEOUS CATALYSIS

## HEAD OF THE DEPARTMENT PROF. ROMAN A. BUYANOV

**Laboratory of Oxidation 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 Oxidation on Metals**
**Head: Prof. Aleksandr V. Khasin**

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

**Group of Catalytic Transformation over Solid Surface**
**Head: Dr. Andrei V. Simakov**

The Department consists of 7 laboratories and 3 groups. Research in the department spans many topics in the field of heterogeneous catalysis.

The **Laboratory of Oxidation Catalysis over Zeolites** (headed by Prof. Gennadii I. Panov**)** proceeded with the study of catalytic nature of Fe-containing pentazyl type zeolites in the oxidation of benzene to phenol. Main attention was paid to the formation and chemical stability of active $\alpha$-sites in the presence of modifying elements exemplified by alkali metals.

Researchers from the **Laboratory of Heterogeneous Selective Oxidation** (headed by Prof. Tamara V. Andrushkevich) continued investigation on the intermediate's nature and active centers formation in binary and modified V-Ti-O systems for the processes of carbonic acids formation.

Members of the **Laboratory of Dehydrogenation** (headed by Prof. Roman A. Buyanov) were active in research under a number of problems, the most interesting results obtained are:

- four hydrogen states were revealed under treatment of nickel-carbon catalysts with hydrogen. The hydride state is responsible for hydrogenation of the acetylene and diene hydrocarbons to corresponding alkanes;
- the kinetics of alkyl radicals generation by heterogeneous catalysts was investigated for the first time;
- the phenomenon of defects formation upon magnesium oxides hydration was disclosed;
- for the first time it was shown that catalytic graphitization of Ni-Cu and Ni-Pd catalysts in certain conditions leads to the formation of carbide-like hexagonal microphase named 'active phase';
- the principal opportunity to prepare polyfunctional catalyst based on modified platinum supported over acid carriers with dehydroisomerization properties has been shown.

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

- it was shown for the first time that liquid Fe-C particles (catalytic intermediates), which catalyze amorphous carbon transfer to graphite, are formed at low temperature not only in vacuum, but also in inert gases ($N_2$, Ar) medium;
- the peculiarities of structural and thermal transformations in highly-conductive protonic composite electrolytes $(1-x)CsHSO_{4-x}SiO_2$ based on the highly-dispersed silica have been studied by differential scanning calorimeter analysis, $^{133}$Cs NMR and XRD;
- the influence of method of preparation on phase composition, dispersity and pore structure of iron oxide - zirconia system have been determined;
- the investigation of modified $V_2O_5$-$TiO_2$ system contributed much to an understanding of their reaction ability;
- macroporous microspherical alumina support has been developed.

The **Laboratory of Catalytic Conversion of Carbon Oxides** (headed by Prof. Tamara M. Yurieva) provides the investigations in elucidation of active copper state and active hydrogen species in copper containing hydrogenation catalysts. The mechanisms of methanol conversion, alcohol and hydrocarbons synthesis are also studied.

The silicates formation takes place in Cu-Zn/$SiO_2$ catalysts, copper ions occupying two crystallographic positions. The catalytic properties are determined by the copper position in silicate structure. The possibility to control the mean size of metallic cobalt particles was studied for Cobalt-containing catalysts. The effect of $Co^0$ particle size on its properties in the Fischer-Tropsch synthesis was investigated.

The main results of the **Laboratory of Catalysts for Deep Oxidation** (headed by Prof. Vladislav A. Sadykov) are:

- A method for synthesis of a new promising class of acid catalysts – complex zirconium phosphates with high surface area has been developed in cooperation with the Institute of Solid-State Chemistry. The method is based on mechanochemical activation of a mixture of solid reagents – ammonium phosphates and nitrate (chloride) salts of zirconium and lanthanum with the following hydrothermal treatment in the presence of surfactants. The genesis of such systems at all stages of synthesis has been studied by EXAFS, IR and $^{31}P$ MAS NMR. It has been shown that the type of the structure of zirconium phosphates is primarily determined by the effect of the crystalline matrix of solid ammonium salts – side products of the reaction - easily formed during the mechanical activation, where the nuclei of zirconium phosphates are distributed.
- The compositions of supported monolith catalysts for oxidative dehydrogenation of propane to olefins at short contact times have been developed. At optimal catalyst compositions and reaction conditions it is possible to increase the propylene yield significantly in comparison with the literature data and patented materials. The economic efficiency of such process with achieved activity and selectivity has been evaluated. It has been shown that it is possible to develop a process competitive with industrial processes used for preparation of olefins, especially, propylene.
- A construction of a diesel neutralizer equipped with monolith catalysts based on thin oxidized and heat-stabilized aluminum foil with supported active components of four types has been developed in cooperation with "Prikladnaya Fizika" corporation. The active components are designed for oxidation of CO and hydrocarbons, oxidation of particulates, and reduction of nitrogen oxides with the liquid fraction of smoke particles. Performance trials of this neutralizer are being performed at Fili bus-trolleybus park (Moscow). The trials have shown that this neutralizer provides removal of at least 75% of nitrogen oxides and decrease of the exhaust opacity to the level 1.5-2 times below the state standard.

The **Laboratory of Adsorbents and Supports** (headed by Prof. Boris P. Zolotovskii) developed and in 1998 inculcated at the AO "Shchelkov Company AGROKHIM" (Shchelkovo, Russia) technology to produce of alumina spherical catalyst IC-27-25 of the Claus process.

Members of the Laboratory also succeeded in improvement of microspherical alumina carrier for the catalysts which may be used in fluidized and beds, including catalyst for ethylene to dichloro ethane oxychlorination.

Catalytic activity tests of the supported Fe-containing catalysts (Fe/$SiO_2$), differing by active component precursor ($FeSO_4$, $Fe(NO_3)_3$) and conditions of its formation (temperature, reaction mixture) allowed to conclude, that reaction of hydrogen sulfide to $SO_2$ oxidation proceeds over the catalysts containing surface sulfide compounds of $FeS_2$ type. Sulfur is produced over the catalysts containing sulfate or oxide Fe-compounds.

The **Group of Oxidation on Metals** (headed by Prof. Aleksandr V. Khasin) made a progress in studying the mechanism features of Cu-containing oxide catalysts reduction by hydrogen and kinetic regularities of ethylene epoxidation on silver films.

The **Group of Catalytic Conversion of Sulfur-Containing Compounds** (headed by Prof. Anna V. Mashkina) has again been concerned with investigation of novel catalytic systems for sulfur-organic compounds synthesis. Studying of the regularities of redox reactions allowed suggest the efficient catalysts for the processes of thioanizol and methylmercaptane synthesis.

The **Group of Catalytic Transformation over Solid Surface** (headed by Dr. Andrei V. Simakov) started only in 1998. The FTIR in situ, ESR in situ and TPD studies of the surface adspecies dynamics on zeolite catalysts at reduction of NO with hydrocarbons allowed to propose the reaction pattern including the adsorption of intermediates on a surface of the catalyst. Unsteady-state kinetics study of separate steps of the reaction has elucidated the contribution of different stages to the mechanism of nitrogen formation.

# DEPARTMENT OF HOMOGENEOUS AND COORDINATION CATALYSIS

## HEAD OF THE DEPARTMENT PROF. VLADIMIR A. LIKHOLOBOV

**Laboratory of Catalysis by Metal Complexes**
**Head: Prof. Vladimir A. Likholobov**

**Group of Catalysis by Anchored Complexes**
**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 Industrial 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**

The characteristic feature of research activities at the Department of Homogeneous and Coordination Catalysis is that they are based on the idea of unity of phenomena of homogeneous and heterogeneous catalysis, on conception of active sites of a heterogeneous catalyst as a surface compound of certain composition and structure, on potentiality of designing active sites of heterogeneous catalysts using methods and approaches of coordination and organometallic chemistry. Thus, the traditional objects of investigations are both conventional homogeneous systems (metal complex solutions) and heterogeneous systems, in particular those, which are at the interface between traditional homogeneous and heterogeneous systems (the so-called heterogenized homogeneous and homogenized heterogeneous compositions).

Among the most exciting scientific results obtained at the Department in 1998 were:

Catalytic properties of Ni, Co and Fe systems for methane decomposition to synthesize filamentous carbon were studied in the **Laboratory of Catalysis by Metal Complex Compounds** (headed by Prof. Vladimir A. Likholobov). It was discovered that the smaller is the inclination of graphite-like layers to the axis of a carbon filament, the faster is encapsulation of the active metal surface in graphite.

Introduction of platinum and, in particular, rhodium and iridium into the Fe/C system was found to result in a remarkable acceleration of the process of ammonia synthesis over a wide range of temperatures (200-400°C), such a synergistic effect being the most pronounced within the low-temperature region (200-250°C).

$^{129}$Xe NMR studies of carbon materials with various surface nanotexture allowed a strong dependence of the signal position in the spectra on the nature of stacking carbon atoms at the carbon surface to be established for the first time. The minimal chemical shift is observed for the surfaces built-up predominantly by basal planes of carbon crystallites, and the highest chemical shift for the carbon with exposed edge planes.

For preparation of Pd/Sibunit catalysts using palladium polyhydroxo complexes (Pd-PHC) as catalyst precursors, the nature of the alkali metal hydroxide (LiOH, NaOH, CsOH) used for synthesis of the Pd-PHC was found to affect the catalytic properties of the target system, even though no alkali metal compound is comprised in the target catalyst. This phenomenon is accounted for by the influence of the nature of the alkali metal ion constituent of Pd-HPC on selective sorption of this precursor on alternating hydrophilic and hydrophobic fragments of the carbon surface.

Regularities of formation of aerogel Si-Ti oxide supports prepared using the sol-gel technology were studied by the **Group of Catalysis by Anchored Complexes** (headed by Dr. Aleksandr F. Danilyuk). A method for preparation of granulated silica aerogel was developed. The granulated aerogel was used for preparing $TiO_2/SiO_2$ catalysts with shell-like distribution of titanium oxide through the granules.

In the **Laboratory of Catalytic Polymerization** (headed by Prof. Vladimir A. Zakharov), NMR and EPR spectroscopic techniques were used to get new knowledge on the structure and reaction sites of polymethylaluminoxane [-Al($CH_3$)O-]$_n$ (MAO), which is the activator of metallocene catalysts, and on the process of formation of active sites during interaction between MAO and zirconocene. Unique data on the presence of Lewis acidic sites of various types in MAO were obtained using EPR technique with nitroxyl radicals as spin label.

Formation of the catalyst in the MAO/$(C_2H_5)_2Zr(CH_3)_2$ was studied by $^{13}$C NMR. The use of high molar ratios of Al/Zr=200-4000, corresponding to polymerization conditions, and TMA and MAO with $^{13}$C-labeled methyl groups were pioneered. A number of cation intermediate precursors of active sites were detected and characterized. A scheme for formation of active sites of the metallocene catalysts was suggested based on the obtained experimental data.

The influence of the composition of the supported zirconocene ($Cp_2ZrX_2$ where X=$CH_3$, Cl; Y$(Ind)_2ZrCl_2$ whereY=$C_2H_4$ or $Me_2Si$, Ind=indenyl) on the activity to polymerization of ethylene and propylene and on the molecular structure of the synthesized polymers was studied. The catalysts prepared using bridge ansa-zirconocenes Y$(Ind)_2ZrCl_2$ were found to reveal a higher activity, a higher copolymerizing ability for ethylene/$\alpha$-olefin systems and to allow for polymers with a higher molecular weight to be synthesized.

Catalysts for oxidation of substituted phenols and naphthols into corresponding 1,4-quinones at the selectivity higher than 98% were developed in the **Group of Industrial Catalysts and Processes Based on Heteropolyacids** (headed by Prof. Klavdii I. Matveev).

A new method was developed in the **Laboratory of Sulfide Catalysts** (headed by Prof. Anatolii N. Startsev) for synthesis of molybdenum complexes with S-containing ligands. The method allows for the atomic S:Mo ratio to be varied. The complex with S:Mo=4 being the most stable, it was chosen for preparing supported catalysts for hydrodesulfurization. A method for supporting this complex onto the alumina surface. Such a system is used as a precursor for preparing bimetallic sulfide catalysts to provide the activity sufficient for the industrial use without additional sulfurization.

In the **Group of Catalysts on Carbon Supports** (headed by Prof. Vladimir A. Semikolenov), the technology for hydrogenation of 1-vinyl-2-pyrrolidone and 1-ethyl-2-pirrolidone into 1-ethyl-2-aminonethylpyrrolidine was improved and a laboratory method for processing of turpentine into geraniol and nerol was developed.

The process of surface graphitization of diamond single crystals was studied in the **Group of Synthesis of Surface Compounds** (headed by Dr. Vladimir L. Kuznetsov). They established for the (100) planes that the graphitization process starts at the edges of growth steps and at surface defects. For graphitization of ultradispersed diamond particles, formation of onion-like carbon particles and carbon nanotubes was found to proceed at lower temperatures if nanosized iron species occur on the diamond surface. Intentional synthesis of silica aerogel of extremely low density and carbon condensation on its surface were achieved. It was established that the first carbon portions are deposited into fine pores, and then this carbon behaves as the site around which the carbon coat grows up.

# DEPARTMENT OF MATHEMATICAL MODELLING OF CATALYTIC PROCESSES

## HEAD OF THE DEPARTMENT PROF. VALERII A. KIRILLOV

**Laboratory of Multiphase Processes Modelling**
**Head: Prof. Valerii A. Kirillov**

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

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

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

Highly exothermic hydrogenation reactions in reactors with irrigated catalyst bed with the evaporation of the liquid-phase components in the catalyst bed are accompanied by local overheatings resulting in an unstable work of the reactors. Experimental techniques suitable for investigation of these phenomena have been developed, and the following results have been obtained in the **Laboratory of Multiphase Processes Modeling** (headed by Prof. V.A. Kirillov):

- The experimental method to study heat regimes on dry, filled and partially wetted catalyst particles under exothermic conditions of hydrocarbon hydrogenation has been developed. The method permits one to carried out experiments using dry and saturated hydrogen in the temperature region of liquid hydrocarbon boiling point.

Experimental studies were performed on a partially wetted particle of five catalyst types differing in preparation procedure, active component, porous structure, wettability and heat conductivity. The limiting values of the liquid AMS feeding, resulting in submerging of the particle blown by saturated hydrogen, have been experimentally determined. It was established that the gas-vapor flow nonequilibrium is responsible for drying and ignition of the catalyst particle. Ignition of the submerged particle is essentially affected by such catalyst properties as porous structure, heat conductivity and position of the active component. The multiplicity of steady states of the catalyst particle blown by dry hydrogen on AMS feeding has been experimentally observed.

- Mass transfer between the vapor-gas flow and catalyst particles on which AMS hydrogenation takes place in the external diffusion region in fixed catalyst bed has been experimentally studied. In course of the experiment were measured: temperature of the gas-vapor flow; temperature of catalyst particles; the composition of the vapor-gas phase at the reactor outlet. The experimental data permitted us to determine the coefficients of mass transfer. The obtained results agree well with well known correlation in the literature.
- The experimental set-up and procedures for studying the processes in the trickle catalyst bed have been developed. This procedure permits one to measure temperature along the catalyst bed, to determine concentration of the liquid and vapor phases at the reactor outlet. Experiments on varying the liquid AMS flow rate, inlet temperature, length of the catalyst bed, reagent concentration in the vapor-gas phase were carried out.

The data on the apparent reaction rate, AMS evaporation rate, and cumene condensation were obtained. The hysteresis phenomena in trickle bed have been found, and the impact of inlet temperatures, mass flow velocity, vapor mass fraction on the hysteresis area existence have been studied. The mathematical model for analysis of the experimental data with the assumption of an equilibrium between the vapor-liquid phases have been developed. A considerable concentration phase non-equilibrium was observed in the trickle catalyst bed. Because of the presence of wetted and dry catalyst particles, there is an essential inhomogeneity in the reactor cross section. Non-equilibrium (or over-saturation of the vapor-gas flow by reagents) and inhomogeneity in the reactor cross section may provide appearance of critical phenomena in the catalyst bed.

Important activities were carried out by the **Laboratory of Catalytic Processes for Desulfurization** (headed by Prof. Nikolai N. Kundo):

- The mechanism of the catalytic oxidation of $H_2S$ in the liquid and vapor phases has been studied. Factors accounting for the appearance of fluctuations in the reaction rate, temperature and yield of oxidation products have been determined. Both in the liquid and gas phases, the reaction was found to involve polysulfides as intermediate products. The presence of polysulfides in the vapor phase was proved by *in situ* chromatographic analysis. Their role in the appearance of unsteady-state phenomena in the liquid and vapor phases has been elucidated. Catalyst-adsorbent compositions have been developed for the $H_2S$ removal from the flue gases of sulfur-producing plants during additional purification of the flue gases of Claus installations by the low-temperature oxidation of $H_2S$ with oxygen.
- New catalysts for oxidation of $H_2S$ and sulfides to sulfur based on cobalt phthalocyanine have been prepared. It has been shown that it is possible to prepare highly defective matrices containing the active component CoPcX by a sol-gel method. Compounds with the $TiO_2$ matrix

have shown the highest stability and durability in the oxidation of sodium sulfide and mercaptoethanol.

- For optimization of the processes used for purification of industrial gases containing $H_2S$, $SO_2$ and accompanying impurities: COS, HCN, $As_2O_3$, the investigation of the kinetics of the $As_2O_3$ interaction with polythionate with the IR detection of the reaction products has been performed.
- The kinetics and mechanism of the catalytic reduction of nitrogen oxides with oxygenated sulfur compounds have been studied for optimization of the purification of industrial gases from $SO_2$ and $NO_x$. It has been found that the $[H^+]$ reaction order of the nitrogen formation during the decomposition of nitrite, which is the product of the adsorption of nitrogen oxides, is changed at pH = 4. This indicates a change of the mechanism of the reaction resulting in the formation of molecular nitrogen. An optimal range of pH = 3-5 where the formation of secondary NO is minimal has been chosen as a practical recommendation for performing the process of the gas purification from nitrogen and sulfur oxides.

The following most interesting results obtained in the **Laboratory of Catalytic Processes in Dynamic Phases** (headed by Prof. Gennadii G. Kuvshinov) should be noted:

- A novel method for the preparation of high-percentage metal catalysts has been developed. The method is based on the sol-gel synthesis of silica inside a porous matrix of a metal oxide with the use of polyesters of silicic acid as precursors. The application of the new catalyst for the production of filamentous carbon made it possible to increase the carbon yield per unit weight of the catalyst more than three-fold.
- A new method for the preparation of high surface area silica gel has been developed. The method is based on the sol-gel synthesis of silica gel inside the nanopores of catalytic filamentous carbon. The new material has an unusual texture consisting of nanotubes, which provides high specific surface area exceeding 1200 $m^2/g$.
- Catalytic filamentous carbon has been shown to have high catalytic activity and selectivity in selective oxidation of hydrogen sulfide to sulfur in large excess of molecular oxygen.
- The kinetics of the formation of filamentous carbon from methane and physicochemical peculiarities of this process have been systematically studied

During the past year the research activities of the **Group of Energetic Chemical Technologies** (headed by Prof. Vladimir I. Anikeev) have been concentrated on two major research fields:

- Thermodynamics of Multiphase Multicomponent Chemically Active Mixtures

A mathematical model for determination of the spinodal line and critical point of a multicomponent mixture has been suggested. Criteria describing the positions of the spinodal line and critical point have been found. A two-parameter homotopy algorithm more effective than other known algorithms has been developed. The algorithm is distinguished by the fact that physical parameters of the system, such as temperature and pressure or temperature and molar volume, are used as a continuation parameter.

The phase transformations and regions of metastable states have been studied for some reaction mixtures practically important for supercritical technologies. A mathematical model and algorithms have been developed for quantitative characterization of the formation of new phases or disappearance of existing ones in gas-liquid systems. Solution existence and uniqueness, and necessary criteria for the choice of the initial approximations for the iteration process have been studied.

- Modeling of Chemical Reactions of Oxidation of Organic Compounds in Supercritical Solvents on a Porous Catalyst Grain

With the account of the advantages of supercritical fluids, which are implemented most effectively in a porous catalyst grain, models for oxidation of benzene and ethanol in supercritical $CO_2$ and oxidation of acetic acid in supercritical water on porous catalysts have been developed. Specific features of the binary diffusion coefficients and viscosity coefficients in supercritical fluids have been studied. Algorithms and computer programs for numerical analysis of chosen processes have been developed. The effect of the chosen parameters on the selectivity, conversion and temperature regime has been studied.

# 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**

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

**Group of Biocatalysis**
**Head: Dr. Galina A. Kovalenko**

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

**Laboratory of Energy Accumulating Processes and Materials**
**Head: Dr. Yurii I. Aristov**

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

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

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

**Membrane Research Group**
**Head: Prof. Oleg M. Il’initch**

Department of Nontraditional Catalytic Technologies is very young: it was formed only in 1998 by bringing in several laboratories and research groups, existing earlier mainly in the Department of Physicochemical Methods for Catalyst Investigation, but which were engaged nevertheless, in design of principally new catalytic technologies of the very different purposes.

Among the main interesting scientific results, obtained by the new Department in 1998, it is possible to refer to following:

In the **Laboratory of Catalytic Methods of Solar Energy Conversion** (headed by Acad. Valentin N. Parmon) the first acting analog of prosthetic group of enzymes methane monooxygenase type was found: 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 were success this year in studying for the first time the phenomena of mass transport of liquids fluids inside the pore catalyst granules during drying by NMR-tomography technique.

The **Group of Stereoselective Catalysis** (headed by Dr. Oksana A. Kholdeeva) observed many common features in catalytic behavior of mesoporous silicates containing ions of some transition metals, and corresponding soluble substituted heteropolytungstates upon studying selective oxidation of organic compounds.

The **Group of Biocatalysis** (headed by Dr. Galina A. Kovalenko) revealed the peculiarities of catalytically active microorganisms immobilization on carries of different nature.

The **Group of Photocatalysis on Semiconductors** (headed by Prof. Eugenii N. Savinov) successfully continued the works on investigation of photocatalytic properties of colloid superconductors and on design of effective heterogeneous catalysts for photocatalytic air purification from traces of organic compounds.

In the **Laboratory of Energy Accumulating Processes and Materials** (headed by Dr. Yurii I. Aristov) the work on development of composite materials, so-called Selective Water Sorbents (SWS) or Chemical Heat Accumulators (CHA), was going on. The first pilot tests on a large scale of these materials were conducted both for low potential heat accumulation, and to protect very different objects from intensive heat influence.

New **Group of Aerosol Catalysis** (headed by Dr. Valerii N. Snytnikov) started in 1998 by development of conception of “planetary catalysis”, the phenomenon which took place in the moment of our planetary system arising.

The **Laboratory of Catalytic Processes in Fuel Cells** (headed by Prof. Vladimir N. Sobyanin) completed in 1998 systematic study of high temperature electrocatalytic methane oxidation to syngas on Pt electrode-catalyst in electrocatalytic reactor with solid oxygen-conducting electrolyte.

The **Group of Catalytic Synthesis of Biologically Active Compounds** (headed by Prof. Aleksandr G. Tolstikov) successfully carried out processes of enantioselective catalytic hydrogenation of several important biologically active compounds.

# 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**

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

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

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

Department of Catalytic Methods for Environmental Protection concentrates on fundamental research, catalyst and process development in 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. Z.R.Ismagilov) developed and studied processes of catalytic combustion of fuels in a fluidized bed of spherical catalyst. Mechanically strong and thermally stable alumina supports, modified aluminas and supported oxide catalysts were developed. Catalytic combustion of nitrogen containing fuels and wastes was studied, the combustion process was optimized for minimizing $NO_x$ formation.

Catalytic heaters with fiber mat and ceramic catalysts running on natural gas, liquified gas and gasoline were developed. Two-stage air heaters burning natural gas with the second catalytic stage over monolithic catalysts were designed, fabricated and tested.

Ceramic and metal foam supported catalysts combining catalytic properties of perovskyte active component and optimum geometric structure of the support were developed.

A plasma spraying technique for preparation of alumina coating on the metal foam to obtain better adhesive properties has been designed. The regularities of plasma sprayed layer formation for alumina coating on the ceramic and metal supports of different geometry depending on preparation conditions, particle size and phase composition of spraying material are revealed. These catalysts will be used in catalytic heat-exchanging reactors for combined methane combustion and methane steam reforming.

Cu, Co, and Fe exchanged zeolites for $NO_x$ abatement by SCR with ammonia and hydrocarbons were synthesized and tested.

Environmentally safe technology for catalytic destruction of mixed organic wastes containing radionuclides was developed for former nuclear weapons industry. The process was studied at pilot installations, and design documentation for the construction of a prototype industrial plant with a capacity of 50 t/year was elaborated. The plant is built at Novosibirsk Chemical Concentrates Plant LTD (Novosibirsk, Russia).

New process for catalytic destruction of toxic rocket fuel unsymmetrical dimethyl hydrazine was developed and tested in an experimental installation.

The **Laboratory of Catalytic Conversion of Solid Fuels and Wastes** (headed by Prof. Aleksandr D. Simonov) has carried out successful studies on the kinetics of supported carbon burning, development of catalytic lattices based on metal ceramics and porous metal in the form of pressed nichrome rings and investigation of the effect of aerodynamic characteristics of catalytic lattices on the solid fuels combustion.

The **Group of Monolith Honeycomb Supports and Catalysts** (headed by Prof. Rimma A. Shkrabina) was formed only in 1998. The basic research program of the laboratory includes development of granulated supports and catalysts, honeycomb catalysts and membranes with controlled properties of secondary (membrane) coating; design of monolith honeycomb materials - supports and catalysts - for the processes of CO and hydrocarbons oxidation, SCR of nitrogen oxides with hydrocarbons and ammonia, exhaust gas neutralization.

The **Group of Direct Hydrogen Sulfide Oxidation** (headed by Dr. Mikhail A. Kerzhentsev) suggested the mechanism of hydrogen sulfide direct oxidation on supported oxides ($Fe_2O_3/Al_2O_3$, $MgCr_2O_4/Al_2O_3$) based on IR-spectroscopy data of adsorbed CO.

Kinetics of heterogeneous hydrogen sulfide decomposition over massive oxides ($\gamma$-$Al_2O_3$, $\alpha$-$Fe_2O_3$, $V_2O_5$) has been studied in temperature interval 500-900 $^{o}$C. The reduction of catalysts based on transition metal oxides ($\alpha$-$Fe_2O_3$, $V_2O_5$), as well as sulfide formation under the influence of reaction medium were shown by X-ray and ESDR techniques. Hydrogen sulfide interaction with alumina at low temperatures results in formation of adsorbed $H_2S$ forms - $HS^-$ and $S^{2-}$, which at heating are transformed to elemental sulfur: c-$S_8$, c-$S_{12}$, $S_4$. The results obtained show the principal possibility of such oxide catalyst to be used for the above process.

# 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 Modeling of Adsorption and Catalytic Processes**
**Head: Dr. Natalia A. Chumakova**

**Laboratory of Dynamics of Catalytic Systems**
**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**

The Department was established in 1995. Today the Department has 60 employees. The average age is 44 years. The main research activity of the Department is in development of technology of catalytic processes with the use of heterogeneous catalysts designed in the Boreskov Institute of Catalysis.

The Department is comprised of 5 laboratories and 3 Groups.

The research interest of the **Laboratory of Zeolites and Acid Base Catalysis** (headed by Prof. Eugenii A. Paukshtis) focus on development of scientific bases of heterogeneous acid base catalysis, first of all, in the field of fine organic synthesis. The purpose of the nearest researches is studying of mechanisms of aldol condensation and olefins and alcohol’s carbonylation.

The research work in the recently formed **Group of Zeolites and Zeolite-Based Catalysts** (headed by Prof. Gennadii V. Echevskii) is aimed at synthesis of zeolites and zeolite-based catalysts for the processes of petrochemistry, petroleum refining and organic synthesis.

The **Group of Petrochemical Synthesis** (headed by Dr. Vyatcheslav N. Romannikov) designs and studies new zeolite-like materials, in particular, mesoporous mesophase materials of different chemical compositions.

The **Laboratory of Kinetic of Catalytic Processes** (headed by Dr. Sergei I. Reshetnikov) develops theoretical and experimental methods to study the effect of reaction medium on catalytic properties and studies the mechanism of reaction mixture component interaction with the catalyst surface over unsteady state of a catalyst. The information obtained is used to build mathematical model of catalytic processes and new catalyst synthesis.

A new **Group of Mathematical Modeling of Adsorption and Catalytic Processes** (headed by Dr. Natalia A. Chumakova) provides the mathematical modeling of adsorption and catalytic processes taking into account the dynamic character of catalyst and sorbent surface, develops the modern software for computational experiment and technological calculations.

The mission of the **Laboratory of Dynamics of Catalytic Systems** (headed by Dr. Andrei N. Zagoruiko) is mathematical modeling of unsteady-state processes and developing of adsorption-catalytic processes considering the dynamic character of adsorbed species transformation.

The **Laboratory of Industrial Catalytic Processes** (headed by Il’ya A. Zolotarskii) is active in development of theoretical and experimental bases for catalytic processes on honeycomb catalysts at millisecond contact times (ammonia oxidation at nitric acid production, oxidative dehydrogenation, etc.).

The main task of the **Laboratory of Unsteady-State Catalytic Methods for Gas Purification** (headed by Prof. Aleksandr S. Noskov) is development of processes for nitrogen-containing compounds transformation. These are processes of partial ammonia oxidation at low pressure over ruthenium catalysts and liquid phase heterogeneous oxidation of nitrogen-containing compounds.

# 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:

1. In situ EPR technique was applied to study iron states in FeZSM-5 zeolites. A set of tests has been suggested which allowed to "dispaly" the unobservable iron states in FeZSM-5 zeolites and to study their reaction ability;
2. 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 enterelectron interaction integrals and energies of spectroscopic states have been obtained;
3. Ab initio DFT method was used to analyze electronic structure and reaction ability of polymethylalumoxane $(\text{-Al(CH}_3\text{)O})_n$ - 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 $n=1\text{-}6$ the "double-cage" structure became more stable than cyclic one, while for $n \geq 9$ - the "triple-cage" structure;
4. 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.
5. 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.

6. 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.
7. 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.
8. 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.

The following provides a description of the main results the **Laboratory of Investigation of the Mechanisms of Catalytic Reactions** (headed by Prof. Eugenii P. Talsi) obtained in 1998.

- Intermediates of N-methylmorpholine N-oxide (NMO) interaction with Jacobsen's catalyst (R,R)-(-)-N,N'-Bis(3,5-di-tert-butyl-salicylidene)-1,2-cyclohexanediaminomanganese(III) chloride, $\mathrm{Mn^{III}}$Salen, practically attractive for enantioselective epoxidation of unfunctionalized alkenes, for the first time was studied with EPR and NMR spectroscopies. It was found that EPR spectrum of initial complex markedly changes via axial ligation of NMO and exhibits hyperfine structure from manganese nuclei. EPR spectrum of $\mathrm{Mn^{III}}$(Salen) can be clearly distinguished from those of complexes $\mathrm{Mn^{II}}$(Salen) and $\mathrm{Mn^{IV}}$(Salen) (Figure 1). This possibility is very important for monitoring of the valent state of the catalyst in the course of epoxidation.

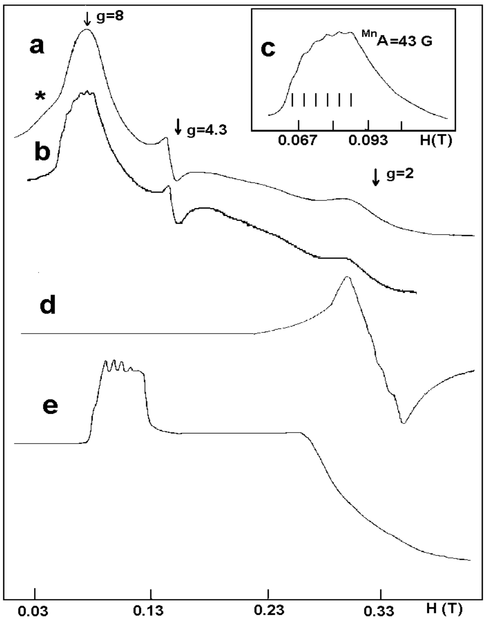


Figure 1. ESR spectra of complexes: $\mathrm{Mn^{III}}$(Salen) (a); $\mathrm{Mn^{III}}$(Salen)+NMO (b, c); $\mathrm{Mn^{II}}$(Salen) (d) и $\mathrm{Mn^{IV}}$(Salen) (e).

- 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 and the substructural characteristrcs of the carbons, micropore volume and specific surface area was revealed. The $^{129}$Xe NMR parameters are determined mainly by the contribution of the egde faces of quasi-graphitic crystallites to the total surface area of the carbons and the concentration of surface heteroatoms. The obtained results point out that the $^{129}$Xe NMR technique can serve as the useful tool for studies of both nanotexture and the chemical state of the carbon surface and, being combined with a common procedures for determination of surface area of solids may open a way to estimate the contribution of the edge faces of carbon crystallites to the total surface area of unoxidized carbons.

- The nature of Mo and W heteropolyacids (HPA) interactions with $NO_2$-$C_6H_4$-$NH_2$ base molecules in solutions was studied with NMR spectroscopy. The obtained dependencies of $^{14}$N NMR chemical shifts of this base and $^{17}$O of water upon concentration and type of acid (perchloric, trifluoromethanesulfonic and HPA) demonstrate that indicator base interacts with HPA; therefore testing of these acids with Hammet bases becomes ambiguous. New method to characterise an acidic strength of HPA solutions based on $^{17}$O and $^{14}$N NMR was developed and found to be valuable for practice using.
- $^{129}$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.
- High temperature NMR studies on $Cs_2S_2O_7$-$V_2O_5$-$H_2O$ system important for optimisation of environmental cleaning catalytic processes (weak $SO_2$-containing gases, water presence) were performed. The molecular level structure and dynamic behaviour of this system at elevated temperatures (including molten state) were elucidated with $^{133}$Cs, $^{51}$V, $^{17}$O NMR. For model $CsDSO_4$ and $CsHSO_4$ solid samples high cation mobility was found below the melting point in accordance with expected solid-solid phase transition.

The **Laboratory of the Texture Studies (**headed by Prof. Vladimir B. Fenelonov**)** is concerned with the development of methods of catalyst texture testing:

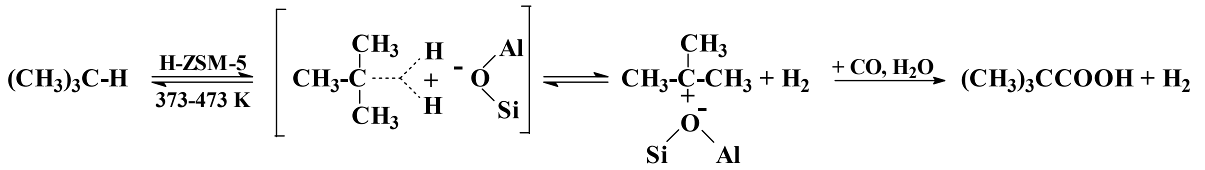
- A new technique for the determination of the partial accessible surface area of multicomponent catalysts based on small differences in the specifics of physical adsorption has been developed. The technique has been used for separate determination of the surface area of $SiO_2$ and $Al_2O_3$ in mechanical $SiO_2/Al_2O_3$ mixtures and surface area of carbon deposited on $SiO_2$ and $Al_2O_3$.
- A new technique has been developed for the investigation of the morphology and location of components supported on a porous support. The technique is based on analytical ratios between relative changes of total accessible surface area, degree of the support surface covered with a component (with the account of technique 1) and ratio between the surface area formed and screened during the introduction of an additional component. The efficiency of the application of this technique has been demonstrated during the investigation of a series of carbosils (partly carbonized silica gels).
- A new technique for correct calculation of the pore size and wall thickness in mesoporous mesophase materials, such as MSM-41, has been developed. The technique was used for the investigation of the mechanisms of formation of such mesophases.

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

- The adsorption of CO, $H_2$ and NO on a Pd tip was studied by a field emission microscopy. The isosteric heat of adsorption was measured for CO ($Q_{\theta\approx0}$ ~ 154 kJ/mol, $Q_{\theta=0.5}$ ~ 133 kJ/mol) and for hydrogen ($Q_{\theta\approx0}$ ~ 127 kJ/mol, $Q_{\theta=0.5}$ ~ 104 kJ/mol). At 300 K a work function of the tip, $\Delta\Phi$, increases up to 0.98, 0.21 and 0.46 eV for $CO_{ads}$, $H_{ads}$ and $NO_{ads}$ coverages, respectively. The low-temperature adsorption of hydrogen at 140 K and $P_{H_2} = 10^{-3}$ mbar was found to produce *nano*-particles of surface hydride of palladium PdH following a *staccato* mechanism. It was shown that a phase conversion of β-PdH into a mixture of α- and β-PdH occurs under the heating. During the phase transition, the *nano*-particles of PdH decompose with a fast surface wave propagation of hydrogen evolution. This is in agreement with the appearance of a sharp desorption peak of hydrogen from a Pd(110) single crystal surface observed at the same conditions.
- A non-linear behaviour of $NO+H_2$ reaction on an Ir(110) single crystal surface was discovered by means of mass spectrometry as sustained isothermal oscillations of a reaction rate in the temperature interval of 474-490 K, total pressure of ~ $10^{-6}$-$10^{-5}$ mbar and $H_2$ to NO ratio between 20 and 100. Oscillations in selectivity accompany the rate oscillations: a high activity state is characterized by a predominant ammonia formation, whereas the low activity state gives mainly nitrogen. It was found that the increase of temperature and/or $H_2$:NO ratio prolongs a residence time of the oscillating system in the high activity state, and conversely, reduces the residence time in the low activity state. The characteristic properties of the oscillations in the $NO+H_2$ reaction on Ir(110) were compared with those observed on Pt(100) and several Rh surfaces.
- A method was worked out for preparation of non-homogeneous Pt(100)-hex/1x1 surfaces with a specified ratio of contributions of the (hex) and (1x1) structural phases. With HREELS and TDS methods used, it was found that the hydrogen adsorption at 300 K occurs solely on patches of the 1x1 unreconstructed phase. In a similar way, the adsorption of NO and CO proceeds first on the 1x1 phase to produce $NO_{ads}$/1x1 or $CO_{ads}$/1x1 islands. Once the 1x1 phase is saturated with $NO_{ads}$ or $CO_{ads}$ molecules, the adsorption involves the hex phase causing its back reconstruction into the 1x1 phase. The hex → 1x1 transition is assumed to proceed with a growth of the $NO_{ads}$/1x1 or $CO_{ads}$/1x1 islands in size. The adsorption process on the non-homogeneous surfaces was compared with that on the regular Pt(100)- 1x1 and hex surfaces.
- The electron properties of a Pt(100)-1x1 single crystal surface were studied for a first time using a Disappearance Potential Spectroscopy (DAPS) method. Spectral characteristics of a threshold excitation for a 4d core level of Pt are in a reasonably good agreement with those calculated theoretically for a local density of vacant states near the Fermi level.
- Enthalpies of formation of stable $NH_{x,ads}$ (x = 0, 1, 2, 3) species adsorbed on Pt(100) and Pt(111) surfaces were calculated by a semi-empirical method of interacting bonds. Heats of interconversion of these species in the adsorption layers were determined.

The methodology of the **Group of NMR Spectroscopy for Catalytic Hydrocarbon Conversion** (headed by Dr. Alexander G. Stepanov) - application of the magic angle spinning and cross-polarization technique for *in situ* NMR analysis of adsorbed hydrocarbon products on catalyst surface, analysis of the NMR line shape of static solid state spectra (wide line NMR) of the adsorbed hydrocarbons in respect to the study of their dynamics on catalyst surfaces - allowed to obtain an interesting results.

- By *in situ* solid state NMR the evidence was provided that at 373-473 K, i.e. at temperatures well below that usually required for cracking of the alkane itself, isobutane was transformed into pivalic acid with simultaneous production of hydrogen, according to the scheme:



Propane converts via C-C bond cleavage to produce isobutyric acid (IBA) with evolution of both methane and ethane.

- The peculiarities of the dynamics of a linear alkane, *n*-octane, adsorbed in zeolite ZSM-5 was studied using deuterium solid state NMR ($^2$H NMR). It has been found that at low loading (1.8 molecules per unit cell), the adsorption of *n*-octane occurs exclusively into the straight channels of the zeolite. In the course of translational movement along the straight channels, some coupled rotational motions of all $CH_n$- (n=2, 3) groups of the hydrocarbon skeleton of the molecule take place. They are reflected in the $^2$H NMR spectrum of deuterated *n*-octane-$d_{18}$ as fast rotations of the separate methylene and methyl groups simultaneously around two and three C-C bonds of the molecule. Upon heating at 373 K for 1 hour, *n*-octane molecules, formerly located in the straight channels, become redistributed over straight and zig-zag channels. Subsequent translational motion of *n*-octane consists of two independent modes of motion. One of them represents the movement along tortuous zig-zag channels. The other one represents the movement along straight channels, disturbed by the collisions with the other molecules at the channel intersections.

The **Laboratory of Catalysts Activity Testing** (headed by Dr. Nikolai N. Bobrov) is concerned with the development of modern physico-chemical methods of investigation, which provide study of the reaction mechanism, structure of catalysts and adsorbed molecules under real catalytic conditions. A set of methods for high precision control of catalyst activity for single-route stationary processes, based on combination of continuously stirred tank reactor and plag flow reactor has been realized.

AO META (Novosibirsk) and BIC have started production of developed in the Laboratory unique automatic instrument SORBI which guaranties reliable control of the specific surface area of catalysts, supports, adsorbents, and any materials for a number of industries.

# OMSK DIVISION OF BORESKOV INSTITUTE OF CATALYSIS

**EXECUTIVE DIRECTOR VASILII S. ALFEEV**

**SCIENTIFIC MANAGER PROF. VALERII K. DUPLYAKIN**

## SCIENTIFIC-RESEARCH SUBDIVISIONS

**Laboratory of Deep Petroleum Refining**
**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**

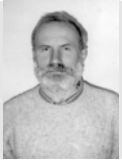
**Laboratory of Kinetics and Modelling of Petrochemical Processes**
**Head: Prof. Nikolai M. Ostrovskii**

**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 Roentgenographic 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) are active under two main subjects:

– development of the process of isobutane alkylation with butylene over solid superacid catalysts;

– catalytic process and catalyst for olefins skeletal isomerization and oligomerization (jointly with the Laboratory of Kinetics and Modeling of Petrochemical Processes and Group of Zeolite-Containing Catalysts for Petrochemistry and Petroleum Refining).

The research activity of the **Group of Carbon Materials** (headed by Dr. Georgii V. Plaksin) has been in the 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.

The research program of the **Laboratory of Catalytic Methods for Atmosphere Protection (**headed by Prof. Pavel G. Tsyrul'nikov) included 1) development and improvement of highly thermal stable aluminium-managanese catalysts for combustion of organic admixtures and carbon oxide; 2) development of active thermal stable catalysts for fuel combustion; 3) development of catalysts for low temperature synthesis of ammonia over carbon support "Sibunit".

The generalization of data on thermal activation of catalysts for deep oxidation, and on thermal dispersing observed for aluminum-manganese catalysts allowed make a conclusion, that this phenomenon spreads to a number of catalytic systems and catalytic reactions. The effects of thermal activation for reaction of deep oxidation of n-pentane over $MnO_x$-$ZrO_2$, and CuO-$ZrO_2$ systems were revealed.

Studying of the dynamics of phase transition in the $MnO_x$-$Al_2O_3$ system showed that at 900-970 $^oC$ during the first 1-3 h the defect aluminum-manganese compound is formed. The decomposition of these compound at further heating leads to the evolving and thermal dispersing of active aluminum modified manganese oxide on the surface of corundum formed under these conditions (the temperature of corundum formation from pure $\gamma$-$Al_2O_3$ is ~ 200 $^oC$ higher).

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 **Laboratory of Kinetics and Modeling of Petrochemical Processes** (headed by Prof. Nikolai M. Ostrovskii) was formed in 1991. The research directions 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.

Among the main results it is necessary to point out the following.

1. A general form of equation of catalyst deactivation kinetics was derived for linear mechanisms. The equations for some particular nonlinear cases of deactivation, as well as for deactivation by coke, have been proposed.

2. The catalytic properties of metallic ($Pt^o$) and ionic ($Pt^\sigma$) platinum were investigated and their roles in naphtha reforming reactions were elucidated. Also kinetics and mechanisms of $Pt^o$ and $Pt^\sigma$ deactivation by coke were established.

3. The influence of capillary condensation on the catalytic reaction kinetics and dynamics was studied using theoretical consideration and experiments in gradientless condition.

4. The role of active component distribution among the pores of different size in supported catalysts has been examined.

5. Dynamics of active center transformation in HDS-HDA catalyst was studied. A corresponding model has been proposed, and the unsteady-state operation of the HDS-HDA process was elaborated.

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, development of catalysts for the processes of diesel fuels hydrodeparaffinezation and development of catalysts and supports based on natural clays and their intercalates.

# SUBDIVISION OF PHYSICOCHEMICAL METHODS OF INVESTIGATION

The **Group of Adsorption** (headed by Dr. Vladimir A. Drozdov) was formed in 1991. The Group 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.

The investigation of perspective composite catalysts and adsorbents of micro-mesoporous structure based on natural clays and modified zeolites anchored in oxide matrices is necessary to note among the most interesting results (jointly with the Group of Zeolite-Containing Catalysts for Petrochemistry and Petroleum Refining). The results obtained allow prediction of textural and adsorption-catalytic properties of composites.

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 clays) is among new 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) was formed in 1986. It 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 Roentgenographic and Electron Microscopy Technique** (headed by Dr. Aleksandr I. Nizovskii) are:

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

X-ray photoelectron spectroscopy (electron spectrometer SER-1);

Electron microscopy (electron microscopes PEM-100, BS-350).

# RESEARCH ACTIVITY

# Quantum-Chemical Studies

### SURFACE INTERMEDIATES IN THE CATALYTIC REACTION OF NO+H$_2$ ON Rh STUDIED BY METHOD OF INTERACTING BONDS CALCULATIONS

**A.R. Cholach, N.N. Bulgakov**

*Catal. Lett.***,** 48 (1997) 191-198.

The semi-empirical method of interacting bonds was used to clarify the mechanism of oscillatory behavior of the catalytic system (NO+H$_2$)/Rh. Various rhodium planes and surface defect regions were characterized by the strength of the nitrogen bond to the surface, the stability of the adsorbed NH$_n$ species ($n$ = 0, 1, 2, 3), and the reactivity of NH$_n$ species towards hydrogen. Calculations admit the earlier suggested reaction mechanism, which attributes the surface wave propagation to the intermediate formation of NH$_a$ species. The activity of the rhodium surface in oscillations is expected to increase in a raw of planes: (100)<(111)<(335). The activity of Rh (335) single crystal in the *reaction rate* oscillations is probably governed by the presence (in contrast to ideal terraces) of gradient and broad range of the reaction intermediate properties.

### OXIDATIVE ADDITION OF DIHYDROGEN TO Ni(II) COMPLEXES. AB INITIO MO/MP4 CALCULATIONS OF THE ELECTRONIC STRUCTURE OF NiH$_2$Cl$_2$(PH$_3$)$_2$ COMPLEX

**I.I. Zakharov, A.N. Startsev, G.M. Zhidomirov**

*React. Kinet. Catal. Lett.*, 64 (1998) 247-254.

Electronic state d$^6$ Ni(IV) in the complex [NiH$_2$Cl$_2$(PH$_3$)$_2$] was studied by means of ab initio MO/MP4 calculations.

### ON THE INTEGRATION OF THE GREEN FUNCTION OVER THE BRILLOUIN ZONE

**V.M. Tapilin**

*Phys. Low-Dim. Struct.*, 3/4 (1998) 65-72.

An integration scheme based on residue theorem and 2-dimensional interpolation which take into account behavior of the Green function near singularities are presented. The efficiency of the scheme is demonstrated on the transformation of the Bloch Green function of a "cubium" to point representation. The latter Green function is used for the calculation of the local densities of states (LDOS) nearby a point defect.

### THE ELECTRONIC STRUCTURE OF A TUNGSTEN TIP MODEL OF A SCANNING TUNNELING MICROSCOPE

**V.M. Tapilin**

*Phys. Low-Dim. Struct.*, 7/8 (1998) 29-34.

The electronic structure of a clean W(110) surface and the surface with chemisorbed W atom are calculated. The local density of states (LDOS) at chemisorbed atom has a sharp resonance peak at the Fermi level consisting of d- and s-states and a peak of p-states 0.3 eV above this level.

### XPS AND UPS STUDY OF OXYGEN STATES ON SILVER

**A.I. Boronin, S.V. Koshcheev, G.M. Zhidomirov**

*J. Electron Spectr. & Relat. Phenom.*,
96 (1998) 43-51.

The investigation of the nature of silver-oxygen bond of different oxygen states on the silver surface has been carried out by XPS and UPS. The XPS analysis shows the E$_b$ (O1s) to range from 528.0 to 534.0 eV that is much wider than for other oxygen-metal systems. The low O1s binding energies with E$_b$(O1s)=528.0-529.0 eV can be reliably related to atomic oxygen of oxide-like structures characterised by the ionic O-Ag bonding. The higher binding energies indicate the covalent character of the Ag-O bond with no charge polarisation. UPS allowed to reveal five additional characteristics in the valence band after high-temperature oxygen treatment, when the oxygen states with E$_b$(O1s)=530.4 eV appear in spectra. They are related to quasi-molecular oxygen species. On the basis of these data, the quasi-molecular character of the oxygen states with E$_b$(O1s)>530 eV is postulated. The experiments demonstrate an abnormally high thermal stability (T$_{des}$>800 K) of these oxygen states. Some proposals to account for the obtained results are discussed.

## AN EFFECT OF THE Zn3D-STATES ON UV AND X-RAY SPECTRA IN ZnO

**E.P. Mikheeva, S.V. Koshcheev, S.Ph. Ruzankin, G.M. Zhidomirov, S.A. Leontiev, V.G. Devaytov, A.E. Cherkashin**

*J. Electron Spectr. & Relat. Phenom.*, 94 (1998) 59-71.

The present study deals with ZnO photoelectronic spectra (PES) recorded at 1253.6 eV as well within a wide photon energy range of 30-150 eV. It has been shown that the shape of O2p valence band PES depends on the incidence photon energy. On the basis of SCF Xα-scattered waves (Xα-SW) cluster approximation the O2p valence band PES have been calculated in the given photon energy range. The changes in the O2p PES shape are proved to be caused by Zn3d electrons, which participate in the covalent binding along with Zn4s electrons. The percentage of the Zn3d-states was obtained on the base of the quantum-chemical calculations and using the photon energy dependence of the integral intensity ratio $I_{O2p}/I_{Zn3d}$. Based on this result the ZnO stoichiometry and the concentration ratio profile [O]/[Zn] as a function of escape depth have been calculated.

The weight of Zn3d-states as evaluated from the photon energy dependence is 9%, theoretical prediction for this weight is 7%, which is very close to experimental value.

## COUPLING COEFFICIENTS SYMMETRY DILEMMA IN THE RESTRICTED OPEN-SHELL HARTREE-FOCK METHOD

**B.N. Plakhutin**

*J. Mathem. Chem.*, 22 (1997) 203-233.

Two opposite conclusions are known on the symmetry of the vector coupling coefficients (VCC), $a_{mn}$ and $b_{mn}$, in the restricted open-shell Hartree-Fock (ROHF) method. The first one states that the VCC are symmetric for all spectroscopic terms, i.e. $a_{mn}=a_{nm}$ and $b_{mn}=b_{nm}$. An opposing statement is that the "non-Roothaan" terms, arising from the degenerate open-shell electronic configuration $\gamma^N$, can be characterized by non-symmetric VCC matrices only: $||a_{mn}||\neq||a_{nm}||$, $||b_{mn}||\neq||b_{nm}||$. The article presents a detailed analysis of the VCC symmetry problem. A general approach to the VCC determination has been developed leading to non-symmetric VCC for $\gamma^N$ systems with dim $\gamma>3$. The main purpose of this work is to eliminate the contradiction arising in the ROHF theory when the latter is applied to highly symmetric open-shell molecules and atoms.

## INTEGRAL INVARIANTS FOR OPEN-SHELL MOLECULES OF HIGH SYMMETRY. I. INVARIANT REPRESENTATIONS FOR ELECTRON REPULSION INTEGRALS

**B.N. Plakhutin**

*Zh. Strukt. Khim.,* 39 (1998) 3-17.

A numerical procedure for the expansion of interelectron interaction integrals $\langle mm'|nn'\rangle$ on degenerate molecular orbitals of symmetry γ (γ = e, t, g, h) to integral invariants (reduced matrix elements) $H^k$ (γ, γ) has been developed. The meaning of the latter is similar to that of Slater-Condon parameters $F^k$ (l, l) for an atom with the electron configuration $l^N$ (l = p, d, ). This method is applicable for molecules of arbitrary symmetry, including "not easily reducible" groups.

## INTEGRAL INVARIANTS FOR OPEN-SHELL MOLECULES OF HIGH SYMMETRY. II. ENERGY OF SPECTROSCOPIC TERMS

**B.N. Plakhutin**

*Zh. Strukt. Khim.,* 39 (1998) 183-195.

A method for calculation of the energy of electron terms formed from a degenerate open shell $\gamma^N$ in the terms of integral invariants $H^k$ (γ, γ) is presented. The method is based on the expansion of interelectron interaction integrals $\langle mm'|nn'\rangle$ on degenerate molecular orbitals of symmetry γ in the terms of $H^k$ (γ, γ). The energies of terms for electron configurations $\gamma^N$ with dim $\gamma \leq 3$ (configurations $e^N$ and $t^N$) are tabulated.

## NUCLEAR MAGNETIC RELAXATION AND STATE OF HYDROCARBON MOLECULES IN ZSM-5 ZEOLITE PORES

**G.G. Pimenov*, O.A. Opanasyuk*, V.D. Skirda*, A.A. Shubin (Kazan State University, Kazan, Russia)**

*Structure and Dynamics of Molecular Systems*, Mariisk State University, Yoshkar-Ola-Kazan-Moscow, 2 (1998) pp. 50-53.

Perpendicular magnetic relaxation of $^1H$ nuclei was used for investigation of a ZSM-5 zeolite with Si/Al = 58. N-hexane, n-octane, n-decane and cyclohexane in the concentrations of 3.7-19.9 wt.%

were used as adsorbates. Curves of the perpendicular magnetization decay consist of a quickly dropping and slowly dropping components. This indicates that there are at least two states of the adsorbate molecules. Quickly relaxing Gauss component of the free induction decay (FIC), in turn, is very complex and seems to consist of two Gauss exponents. Judging from the second moment values of the FIC Gauss component, the quickly relaxing FIC component was attributed to molecules in micropores with frozen rotational mobility. The slowly relaxing FIC component was related to molecules in larger pores on the surface of zeolite particles.

## SPATIAL ORGANIZATION OF LINEAR POLYTRIMETHYLENEIMINE GLOBULES CONTAINING COPPER (II), NICKEL (II), AND ZINC (II) COMPLEXES IN SOLUTION

**A.I. Kokorin*, A.A. Shubin (Semenov Institute of Chemical Physics, Moscow, Russia)**

*Zh. Fiz. Khim.*, 72 (1998) 60-64.

Spatial organization of coils of linear polytrimethylenimine containing variable number of coordinated Cu (II) ions in vitrified 50% water-methanol solutions has been studied by ESR at 77 K. The simulation of the ESR spectra allowed to determine more precisely spin-gamiltonian parameters and discover three-axis anisotropy of the spectra, i.e. tetrahedral distortions of copper coordination sites in polytrimethyleneimine. Cu (II), Ni (II) and Zn (II) ions have been shown to fill the polytrimethylenimine coils with the same probability at low Cu (II) concentrations. At [Cu (II)] > 0.01 mol/l the distribution of the complexes in the coils becomes non-uniform. At all Cu (II) concentrations the local concentration of Cu complexes in polytrimethylenimine is significantly lower than in the case of linear polyethyleneimine.

## ADDUCTS OF HYDROGEN AND METHANE WITH Os(II) AND Os(IV) COMPLEXES: THEORETICAL ANALYSIS OF $(\eta^2\text{-}H_2)OsCl_2(PH_3)_2$ AND $(\eta^2\text{-}CH_4)OsCl_2(PH_3)_2$ MOLECULAR COMPLEXES BY RHF, MP2 AND DFT METHODS

**V.I. Avdeev, G.M. Zhidomirov**

*Catal. Today,* 42 (1998) 247-261.

A theoretical study of model $OsCl_2(PH_3)_2$ complex and its adducts with hydrogen and methane is reported. Geometry of two isomers of $OsCl_2(PH_3)_2$ complex and structures of possible σ complexes $(\eta^2\text{-}H_2)OsCl_2(PH_3)_2$, $(\eta^2\text{-}CH_4)OsCl_2(PH_3)_2$ have been calculated using density functional theory and MP2-method. It was shown that some isomers of weakly bonded hydrogen σ complex $OsH_2Cl_2(PH_3)_2$ can form stable methane adducts followed by reductive elimination of hydrogen. Calculations of the reaction pathways for methane oxidative addition to isomers of 14-electron intermediate $OsCl_2(PH_3)_2$ have been performed. For the isomer active in this reaction, structures of the transition state and methylhydride product were calculated. Frequencies of vibrations of stable σ complex $(\eta^2\text{-}CH_4)OsCl_2(PH_3)_2$ along with its deuterated form $(\eta^2\text{-}CD_4)OsCl_2(PH_3)_2$ have been computed in the MP2/LAN1DZ approximation.

## METHANE ACTIVATION BY Os(II) COMPLEXES: THEORETICAL STUDY OF METHANE OXIDATIVE ADDITION TO ISOMERIC $OsCl_2(PH_3)_2$ COMPLEXES BY RHF, MP2, AND DFT METHODS

**V.I. Avdeev, G.M. Zhidomirov**

*Kinet. Katal.*, 39 (1998) 513-522.

Theoretical analysis of the methane oxidative addition to a model $OsCl_2(PH_3)_2$ complex has been performed in the Hartree-Fock (RHF) approximation with the following account of the electron correlation energy by the second-order Moeller-Plesset method (MP2) and by the density functional theory (DFT). The calculations predict the existence of several stable isomers of the $OsCl_2(PH_3)_2$ complex. Quantum chemical evaluations of the methane interaction with three isomers lead to the conclusion that σ-complexes $(\eta^2\text{-}CH_4)OsCl_2(PH_3)_2$ can be formed for some isomers. Computation of the reaction pathways of the methane oxidative addition to three possible isomers has been performed. The initial isomer with the tetrahedron structure forms the most stable σ-complex with methane but is not capable of activating the C-H bond. It has been shown that only the isomer with the square pyramid structure can effectively conduct the methane oxidative addition to form a methylhydrate product with low activation energy.

# Elementary Physico-Chemical Processes on the Surface. Monte-Carlo Simulation

## ISLAND FORMATION IN CHEMISORPTION. I. CHEMISORPTION MODEL

**A.N. Salanov, V.N. Bibin, N.A. Rudina**

*React. Kinet. Catal. Lett.*, 64 (1998) 261-268.

A model of dissociative chemisorption on a surface with a square lattice was studied using the Monte-Carlo method. The model is based on two chemisorption pathways: “direct” - nucleation of adsorption islands, and “indirect” - their growth. The development of the surface distribution picture of chemisorbed particles was found to depend significantly on the contribution of these two pathways ($S_{indir}/S_{dir}$).

## ISLAND FORMATION IN CHEMISORPTION. II. CHEMISORPTION KINETICS

**A.N. Salanov, V.N. Bibin, N.A. Rudina**

*React. Kinet. Catal. Lett.*, 64 (1998) 269-274.

Influence of “direct” and “indirect” pathways of dissociative chemisorption on the form of kinetic dependencies θ(MCS) and S(θ) was studied by the Monte Carlo method. Langmuir adsorption observed at $S_{indir}/S_{dir} \leq 0.1$ gradually changes to island-mediated adsorption with an increase of the “indirect” adsorption contribution at $0.1 \leq S_{indir}/S_{dir} \leq 1.0$. At $S_{indir}/S_{dir} \geq 1.0$ the island-mediated adsorption dominates: large adsorption islands arise and gradually grow.

## ISLAND GROWTH AND PHASE SEPARATION IN CHEMICALLY REACTIVE OVERLAYERS

**V.P. Zhdanov**

*Surf. Sci.*, 392 (1997) 185-198.

The formation of islands in an adsorbed overlayer have been studied by Monte Carlo simulations employing the lattice-gas model with attractive interactions between nearest-neighbor particles in two situations. (i) The first one corresponds to the island growth when the adsorbed overlayer is quenched at t=0 from high temperature in a disordered phase to a temperature below the critical one. Using a realistic algorithm of surface diffusion and also the Metropolis dynamics for times up to 10^6 Monte Carlo steps, it has been shown that in analogy with the spin-exchange kinetic Ising model the growth law for the average island size can be represented in this case at all the coverages as $R(t) \sim X+Yt^{1/3}$. The parameter Y is found to be weakly dependent on coverage and on the details of the dynamics employed. On the other hand, the value and the coverage dependence of the parameter X are sensitive to the mechanism of diffusion. (ii) The second situation corresponds to phase separation in chemically reactive systems under the steady-state conditions. As an example, the $A+B \rightarrow AB$ reaction, occurring via the Eley-Rideal mechanism, including A adsorption on vacant sites, $A(gas) \rightarrow A(ads)$, and A consumption in collisions with gas-phase B particles, $A(ads)+B(gas) \rightarrow AB(gas)$ has been analyzed. For a realistic algorithm of surface diffusion, the average size of A islands is found to be rather low even if surface diffusion is many orders of magnitude faster compared to the adsorption/reaction processes. In contrast, the Metropolis dynamics predicts the formation of relatively large islands or even mesoscopically-ordered structures. The physics behind these findings is discussed in detail.

## MONTE CARLO SIMULATION OF PROTEIN FOLDING WITH ORIENTATION-DEPENDENT MONOMER-MONOMER INTERACTIONS

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*Proteins,* 29 (1997) 508-516.

The results of lattice Monte Carlo simulations of protein folding in the framework of a model are presented taking into account (i) the dependence of the energy of interaction of amino acid residues on their orientation and (ii) the rigidity of the polypeptide chain with respect to the formation of kinks. If the chain is flexible, the final protein structures are predicted to be compact. Increasing the energy cost of the creation of kinks is found to favor formation of flat structures mimicking an ideal antiparallel "beta" sheet. The kinetics of folding in these two limits are demonstrated to be qualitatively different. The latter indicates that the scenario of protein folding is in general not universal.

## MONTE CARLO SIMULATION OF DENATURATION OF ADSORBED PROTEINS

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

*Proteins*, 30 (1998) 168-176.

Denaturation of model protein-like molecules on the liquid-solid interface is simulated in a wide temperature range by employing the lattice Monte Carlo technique. Initially, the molecule containing 27 monomers of two types is assumed to be adsorbed in the native folded state (a 3x3x3 cube) so that one of its sides is in contact with the surface. In this case, the details of the denaturation kinetics are found to be slightly dependent on the choice of the side, but the main qualitative conclusions hold for all the sides. In particular, the kinetics obtained obey approximately the conventional first-order law at $T>T_c$ ($T_c$ is the collapse temperature for the bulk). With decreasing temperature below $T_c$ but above $T_f$ ($T_f$ is the folding temperature for the bulk), there appear deviations from the first-order kinetics. For the most interesting temperatures (below $T_f$), the denaturation kinetics are shown to be essentially different from the conventional ones. In the latter case, the process was found to occur via a few steps due to trapping to the metastable states.

## MONTE CARLO SIMULATION OF THE KINETICS OF PROTEIN ADSORPTION

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*Proteins*, 30 (1998) 177-182.

Adsorption of proteins occurs via diffusion towards the interface, actual adsorption, and subsequent irreversible conformational changes resulting in denaturation of the native protein structure. The conventional kinetic model describing these steps are based on the assumption that the denaturation transitions obey the first-order law with a single value of the denaturation rate constant $k_r$. Meanwhile, recent Monte Carlo simulations indicate that in general the denaturation process cannot be described by a single rate constant $k_r$. One should rather introduce a distribution of this rate constant (physically, different values of $k_r$ correspond to the transitions to the altered state via different metastable states). The kinetics of irreversible adsorption of proteins with and without distribution of the denaturation rate constant $k_r$ in the limits when protein diffusion in the solution is respectively rapid or slow have been calculated. In both cases, the adsorption kinetics with distribution of $k_r$ are found to be close to those with a single-valued rate constant $k_r$ provided that the average value of $k_r$ in the former case is equal to $k_r$ for the latter case. This conclusion holds even for wide distributions of $k_r$. The consequences of this finding for the fitting of global experimental kinetics on the basis of phenomenological equations are briefly discussed.

## MONTE CARLO SIMULATIONS OF THE KINETICS OF PROTEIN ADSORPTION

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

*Surf. Rev. Lett.*, 5 (1998) 615-634.

The past decade has been characterized by rapid progress in Monte Carlo simulations of protein folding in a solution. The present review summarizes the main results obtained in this field, as a background to the major topic, namely, corresponding advances in simulations of protein adsorption kinetics at solid-liquid interfaces. The latter occur via diffusion in the liquid towards the interface followed by actual adsorption, and subsequent irreversible conformational changes, resulting in more or less pronounced denaturation of the native protein structure. The conventional kinetic models describing these steps are based on the assumption that the denaturation transitions obey the first-order law with a single value of the denaturation rate constant $k_r$. The validity of this assumption has been studied in recent lattice Monte Carlo simulations of denaturation of model protein-like molecules with different types of the monomer-monomer interactions. The results obtained indicate that, due to trapping in metastable states, (i) the transition of a molecule to the denatured state is usually non-exponential in time, i.e., it does not obey the first-order law, and (ii) the denaturation transitions of an ensemble of different molecules are characterized by different time scales, i.e., the denaturation process cannot be described by a single rate constant $k_r$. One should rather introduce a distribution of values of this rate constant (physically, different values of $k_r$ reflect that the transitions to the altered state occurs via different metastable states). The phenomenological kinetics of irreversible adsorption of proteins with and without a distribution of the denaturation rate constant values have been calculated in the limits when protein diffusion in the solution is, respectively, rapid or slow. In both cases, the adsorption kinetics with a distribution of $k_r$ are found to be close to those with a single-valued rate constant $k_r$, provided that the average value of $k_r$ in the former case is equal to $k_r$ for the latter case. This conclusion holds even for wide distributions of $k_r$. The consequences of this finding for the fitting of global experimental kinetics on the basis of phenomenological equations are briefly discussed.

### FOLDING TIME OF IDEAL "BETA"-SHEETS VS. CHAIN LENGTH

**V.P. Zhdanov**

*Europhys. Lett.*, 42 (1998) 577-581.

The results of 3D lattice Monte Carlo simulations of protein folding in the framework of a model taking into account the dependence of the energy of interaction of amino acid residues on their orientation and the rigidity of the polypeptide chain are presented. For the model parameters corresponding to the formation of ideal β sheets, the folding time of chains of length n is found to scale as $t_f \sim n^x$ with x= 7.5.

### SURFACE RECONSTRUCTING, THERMAL DESORPTION, KINETIC BISTABILITY, AND CHEMICAL WAVES

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

*J. Stat. Phys.*, 90 (1998) 79-101.

Adsorbate-induced surface restructuring is treated in the framework of a statistical lattice-gas model taking into account the possibility of formation of a metastable substrate structure on the clean surface and stabilization of this structure by adsorbate-substrate interaction. With these assumptions, surface restructuring is described in terms of the theory of first-order phase transitions. The proposed model is then employed to analyze (i) the influence of adsorbate-induced changes in the surface on thermal desorption spectra and (ii) the effect of surface restructuring on the propagation of chemical waves in the $2A+B_2 \rightarrow 2AB$ reaction. The interplay between reaction-diffusion kinetics and surface restructuring is shown to result in formation of chemical waves with atomistically sharp spatial features.

### DOMAIN GROWTH AND RATE PROCESSES IN ADSORBED OVERLAYERS

**V.P. Zhdanov**

*Surf. Sci.*, 401 (1998) 412-426.

Special features of the kinetics of three different surface processes affected by or interfering with domain growth (i.e., with the continuous order-disorder phase transition) in the adsorbed overlayer have been shown employing Monte Carlo simulations. (i) The formation of the c(2x2) A domains is studied in the situation when this process is complicated by the Eley-Rideal $A+B \rightarrow AB$ reaction occurring under the steady-state conditions in the gas phase. The reaction mechanism includes A adsorption on vacant sites, A(gas) → A(ads), and A consumption in collisions with gas-phase B particles, A(ads)+B(gas) →AB(gas). Diffusion of adsorbed A particles is simulated by using the realistic and Metropolis algorithms. In both cases, the reaction terminates the domain growth. The average size, R, of domains formed under the reaction conditions is found to be approximately proportional to $1/P^2$, where $P<1$ is the parameter characterizing the ratio of the rates of reaction and diffusion. If the reaction is switched off, the domain growth is described by the standard Allen-Cahn equation, $R(t) \sim t^{1/2}$. (ii) Dissociative adsorption, $A_2(gas) \rightarrow 2A(ads)$, occurring via trapping of $A_2$ molecules into precursor states followed by the transitions to the chemisorbed state, is analyzed in the case when adsorbed A particles form domains. The $A_2$ sticking coefficient is demonstrated first to decrease with increasing R and then to become independent of R. The latter is realized in the limit when $R^2$ is much larger than the mean-square displacement of an $A_2$ molecule during its random walk over precursor states. (iii) Tracer diffusion of single B particles, occurring via jumps to nearest-neighbor vacant sites, is studied in the situation when these particles are cooperatively coadsorbed with A particles which form domains. For employed (presumably reasonable) adsorbate-adsorbate interactions, the effective diffusion coefficient of B particles is found to increase with increasing the average size of A domains, because the rate of B diffusion inside the A domains appears to be faster than near the domain boundaries.

## MONTE CARLO SIMULATION OF THE KINETICS OF RAPID REACTIONS ON NANOMETER CATALYST PARTICLES

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

*Surf. Sci.,* 405 (1998) 27-37.

The kinetics of the $2A+B_2 \to 2AB$ reaction, occurring via the standard Langmuir-Hinshelwood (LH) mechanism, have been analyzed using an original Monte Carlo algorithm, in the two limits corresponding to the infinite surface and to interacting facets (by surface diffusion) of a nanometer-sized crystallite, respectively. The latter mimics possible kinetics on real supported catalysts, and on recent nanofabricated model catalysts. The simulations were carried out with a realistic ratio between the rates of the elementary steps (the LH step is rapid compared to A and $B_2$ adsorption and slow compared to A diffusion, and B particles are immobile). The results demonstrate that the kinetics for nanometer-sized particles can be remarkably different compared to those for the infinite surface. Depending on the values of model parameters, the reaction window (along the $A+B_2$ gas mixture scale) on the nm catalyst particle may be wider or narrower than on the infinite surface and its position may be shifted. These findings have implications for interpretation of experimental data and for the design of real catalysts and also have important consequences for the continuing efforts to bridge the so-called pressure and structure "gaps" in catalysis.

## KINETICS OF RAPID HETEROGENEOUS REACTIONS ACCOMPANIED BY THE RESHAPING OF SUPPORTED CATALYST CRYSTALLITES

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

*Phys. Rev. Lett.*, 81 (1998) 2482-2485.

The steady-state kinetics of the practically important catalytic reaction $2A+B_2 \to 2AB$ occurring on a nanometer-sized crystallite in the case when its shape depends on the amount of adsorbed B particles are analyzed using the Monte Carlo technique. The simulations, carried out with a realistic ratio between the rates of the elementary steps, demonstrate that the adsorbate-induced catalyst reshaping may result in qualitatively new reaction regimes.

## KINETICS OF THE $2A+B_2 \to 2AB$ REACTION COMPLICATED BY SPATIAL CONSTRAINTS FOR ADSORPTION, FORMATION OF ISLANDS, AND STEPS

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

*Surf. Sci.*, 412 (1998) 527-543.

Monte Carlo simulations of the steady-state kinetics of the $2A+B_2 \to 2AB$ reaction, occurring via the Langmuir-Hinshelwood (LH) mechanism on perfect and stepped surfaces are presented. The calculations are carried out with a realistic ratio between the rates of the elementary steps (the LH step is rapid compared to A and $B_2$ adsorption and slow compared to A diffusion). The main novel factor introduced into the model is that $B_2$ adsorption is considered to occur on next-nearest-neighbor (nnn) sites (location of B particles in nn sites is prohibited). This constraint, mimicking $O_2$ adsorption on Pt(111), changes qualitatively the reaction regimes compared to those predicted by the conventional reaction scheme. In particular, the model does not predict complete poisoning of the surface by B even if the relative $B_2$ pressure is high and B diffusion is negligible. On the other hand, the model easily predicts formation of B islands if the nnn B-B lateral interaction is attractive. The size of islands is found to be very sensitive with respect to the details of the LH step. Simulating the reaction on a stepped surface, it has been considered that the step sites are much more reactive compared to terrace sites and that the $B_2$ sticking coefficients for steps is much higher than for terraces. In this case, the model predicts gradients in the distribution of B particles on the surface. Such nonuniform distributions are however generated only in a limited range of the model-parameter values. Dramatic changes in the distribution of B particles due to formation of B islands or B diffusion towards steps are demonstrated to result in nearly negligible changes in the apparent reaction kinetics.

## SURFACE ROUGHENING: KINETICS, ADSORBATE-INDUCED EFFECTS, AND MANIFESTATION IN CATALYTIC REACTIONS

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

*J. Chem. Phys.*, 108 (1998) 4582-4590.

Using the Monte Carlo (MC) technique, the kinetics of roughening of a clean surface at $T>T_R$ ($T_R$ is the roughening temperature), the kinetics of relaxation from a roughened to a flat surface at $T<T_R$, the effect of adsorption on surface roughening, and the influence of adsorbate-induced roughening on the kinetics of the catalytic $2A+B_2 \rightarrow 2AB$ reaction have been analyzed. (i) For a clean surface, the results were obtained by employing the standard restricted-solid-on-solid (RSOS) model with surface diffusion occurring via jumps to nearest-neighbor and next-nearest-neighbor sites. The kinetics of surface roughening at $T>T_R$ and of surface relaxation at $T<T_R$ are found to be logarithmic in time. In particular, the mean-square height difference at $T>T_R$ increases with time as $w^2 \sim \ln(t)$. (ii) Complementing the RSOS model by terms describing adsorption, the adsorbate-induced surface roughening have been demonstrated to occur with significant lowering of $T_R$, due, respectively, to indirect next-nearest-neighbor adsorbate-substrate repulsion, attractive nearest-neighbor adsorbate-substrate lateral interaction, and/or repulsive adsorbate-adsorbate lateral interaction. In all these cases, the ratio of $T_R$ near adsorbate saturation and for the clean surface, respectively, is given by an analytical expression which is a simple combination of the corresponding interactions. The coverage dependence of $T_R$ in MC simulations is nonlinear and slightly different compared to the mean-field-type prediction. (iii) The effect of adsorbate-induced roughening on a catalytic reaction can be dramatic even at weak roughening, with qualitative and quantitative changes in the kinetics. For example, the absolute conversion rate at maximum rate, and the reactant mixture corresponding to this maximum can be very different on the flat and roughened surface. The behavior of the adsorbate coverages near the points corresponding to the kinetic phase transitions can change character qualitatively.

## SURFACE DIFFUSION NEAR THE POINTS CORRESPONDING TO CONTINUOUS PHASE TRANSITIONS

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*J. Chem. Phys.,* 109 (1998) 3197-3203.

Employing the scaling arguments, it has been shown that the temperature dependence of the chemical diffusion coefficient, $D_c$, near the points corresponding to continuous phase transitions has power-law or inverse logarithmic singularities. Monte Carlo simulations, executed with the parameters corresponding to the O/W(110) system, indicate that these singularities, occurring in a very narrow temperature interval, can be reproduced only if the lattice size is large ($L>500$). Outside the critical region, the temperature dependence of $D_c$ is regular and the deviations from the ideal Arrhenius behavior are relatively weak. In particular, at appreciable coverages, the variations of the activation energy for chemical diffusion are about 10 kJ/mol.

## DIFFUSION-LIMITED REACTION KINETICS IN NANOFABRICATED POROUS MODEL CATALYSTS

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*Catal. Lett.,* 50 (1998) 131-134.

Electron beam lithography allows fabrication of ideal, representative models of supported, porous catalysts (with pore and particle dimensions and separations of 10 nm and up). This allows systematic exploration of various scientifically and technically important phenomena associated with porous, supported catalysts. In this work, general equations to describe different limiting cases for such model catalysts have been derived. Depending on the geometrical parameters and boundary conditions the reaction rate may be limited by bulk or Knudsen diffusion of reactants inside pores or by diffusion in the regions near or far from the support surface. All these regimes are treated in detail. The results will help both to guide and interpret experiments with nanofabricated catalysts.

## CATALYTIC IGNITION IN THE CO-$O_2$ REACTION ON PLATINUM: EXPERIMENT AND SIMULATIONS

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*Surf. Sci.,* 376 (1997) 297-309.

Catalytic ignition temperatures for the $CO+O_2$ reaction on a Pt wire, and the corresponding transient ignition curves, have been measured and analyzed theoretically for nonflammable reactant mixtures in Ar and He at atmospheric pressure. At very low relative CO concentrations (<0.02 %), the experimental ignition temperature rises rapidly with increasing concentration, and then more slowly at higher concentrations. These data are explained by employing a kinetic model based on the standard three-step mechanism for CO oxidation on Pt(111), combined with time-dependent mass and heat transport. The simulations reproduce both the dependence of ignition temperatures on the reactant concentrations and the transient behavior after ignition without any kinetic fitting parameters. The model predicts that ignition at intermediate CO concentrations is entirely governed by the interplay between the reaction kinetics on the CO-covered surface and the heat transport. At very low $CO/O_2$ ratios, CO concentration gradients are established in the pre-ignition regime, which facilitates ignition. After ignition, but before the mass-transport controlled steady-state is established, a kinetic phase transition occurs from a CO-covered to an oxygen-covered surface.

## SIMULATION OF OXYGEN DESORPTION FROM Pt(111)

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

*Surf. Sci.*, 415 (1998) 403-410.

The kinetics of temperature-programmed associative desorption (TPD) of oxygen atoms from Pt(111) at coverages below a quarter of the monolayer are simulated using the Monte Carlo technique. Oxygen atoms are assumed to be adsorbed on a triangular lattice of fcc sites. Nearest-neighbor (nn) O-O lateral interactions are considered to be strongly repulsive so that there are no occupied nn sites. The second- and third-nn interactions are chosen to reproduce the p(2x2) ordering of oxygen atoms. Comparison between the simulations and experimental TPD spectra for the O/Pt(111) system is supporting repulsive O-O interactions. More specifically, the TPD spectra are hard to reconcile with the assumption that the O-O lateral interactions are partly attractive and that this attraction is sufficiently strong to stabilize the p(2x2) islands at low coverages and relatively high temperatures (about 400 K). The consequence of this finding for interpretation of available experimental data on oxygen diffusion on Pt(111) is discussed in detail.

## SIMULATION OF THERMAL DESORPTION FROM NANOMETER CATALYST PARTICLES

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

*Surf. Rev. Lett.,* 5 (1998) 551-558.

General equations are derived to describe monomolecular desorption from small supported catalyst particles in the cases when (i) the desorption process occurs simultaneously from different facets and (ii) adsorbed molecules are allowed to jump from the catalyst onto the support, diffuse on the support, and then desorb (a so-called slipover effect). Numerical calculations carried out on the basis of obtained equations indicate that the TPD spectra for interconnected facets might be qualitatively different compared to those for extended single crystals. The support-mediated channel has been shown to be important if the binding energy on the support is not too low.

# Studies of the Mechanism of Catalytic Reactions NO+CO, NO+$H_2$

## FORMATION OF MIXED $(NO_{ads} + CO_{ads})/(1 \times 1)$ ISLANDS ON THE Pt (100)-(hex) SURFACE

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*Surf. Sci.,* 414 (1998) 409-422.

The coadsorption of NO and CO on the reconstructed Pt(100)-(hex) surface at 300 K was studied by means of high-resolution electron energy-loss spectroscopy (HREELS). NO+CO coadsorption layers prepared in three different ways were investigated: (1) CO adsorption after coverage of the surface with $NO_{ads}/(1\times1)$ islands; (2) NO adsorption after coverage of the surface with CO, which was mainly adsorbed on structural defects of the reconstructed (hex) phase (low coverage of $CO_{ads}$); and (3) NO adsorption after coverage of the surface with $CO_{ads}/(1\times1)$ islands (high coverage of $CO_{ads}$). In all cases the strong mutual interaction between $NO_{ads}$ and $CO_{ads}$ molecules resulted in the formation of mixed $(NO_{ads}+CO_{ads})/(1\times1)$ islands. The mixed islands of $NO_{ads}$ and $CO_{ads}$ covered unreconstructed $(1\times1)$ patches. The islands were separated from each other by either free (hex) phase or a region consisting of structural defects, which appeared during the course of a surface (hex) $\rightarrow$ $(1\times1)$ back-reconstruction. In the mixed $(NO_{ads}+CO_{ads})/(1\times1)$ islands, it was found that structural defects were occupied preferentially by molecularly adsorbed CO.

## NON-LINEAR BEHAVIOR IN THE NO-$H_2$ REACTION OVER Ir(110)

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*Surf. Sci.,* 411 (1998) L904-L905.

The present paper describes experimental findings concerning non-linear behavior in the NO-$H_2$ reaction over Ir(110). This is, very likely, the first report of catalytic rate oscillation over Ir(110). The oscillatory behavior was obtained in the $10^{-6}$ mbar NO pressure regime around 475 K in a large excess of hydrogen. The $N_2$ production rate oscillates out of phase with the rates of $NH_3$ and $H_2O$ formation. No $N_2O$ was formed under the conditions examined. The oscillatory behavior found over Ir(110) is compared with those reported earlier for Pt(100) and Rh single crystal surfaces.

## FORMATION OF LOW WORK FUNCTION PATCHES IN THE NO+$H_2$ REACTION ON A ROUGHENED Rh(110) SURFACE

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*Surf. Sci.,* 391 (1997) L1172-L1177.

Chemical wave patterns in the NO+$H_2$ reaction on Rh (110) have been investigated on a surface roughened by $Ar^+$ ion sputtering (4 keV, exposure $10^{16}$ ions/cm$^2$). The study has been conducted in the $10^{-6}$-$10^{-5}$ mbar range employing photoemission electron microscopy (PEEM) as a spatially resolving method. While the formation of rectangularly and elliptically shaped target patterns is not notably influenced by the roughness produced by sputtering, patches with reduced work functions develop on the surface upon collision of wave fronts. These patches, which are absent on a smooth Rh (100) surface, were attributed to a subsurface oxygen species whose formation is facilitated by structural defects on the surface.

# CO Oxidation over Platinum Metals and Heterophase Surfaces Studied with the Monte Carlo Simulation

### STATISTICAL LATTICE MODEL OF PHYSICOCHEMICAL PROCESSES IN CATALYTIC REACTIONS: AUTOOSCILLATION, ADSORPTION ON THE ROUGH SURFACE, AND CRYSTALLIZATION

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*Kinet. Katal.,* 39 (1998) 264-287.

Imitation models of various catalytic processes are considered: autooscillations and autowaves in CO oxidation reaction over the platinum metals occurring with formation of subsurface form of oxygen; monomolecular and dissociative adsorption on the catalyst surface with the dynamically changing morphology; and crystallization of a melt of an active component of vanadium catalysts for sulfur dioxide oxidation. All models are unified by the common statistical nature of the physicochemical processes under study.

### EFFECT OF ACOUSTIC EXCITATION ON THE CO RATE OXIDATION OVER Pt(110)

**T. Mitrelias*, S. Kelling*, R.I. Kvon, V.P. Ostanin*, D.A. King* (University of Cambridge, Cambridge, UK)**

*Surf. Sci.,* 417 (1998) 97-106.

A unique UHV compatible excitation system combined with an advanced ultra high amplitude and frequency resolution acoustic spectrometer has been designed and constructed to permit accurate studies of the fundamental mechanism by which acoustic excitation may influence heterogeneous catalytic reactions. Here, the first results are presented which demonstrate a remarkable non-thermal six-fold increase in the rate of carbon monoxide oxidation when a Pt(110) thin single crystal is excited with low frequency, low energy Surface Acoustic Waves (Raleigh waves). It is proposed that the acoustic excitation results in an enhancement of the sticking coefficient of oxygen, which in turn affects the reactivity of the platinum catalyst.

### KINETICS OF ADSORPTION ON THE NONUNIFORM SURFACE WITH REGARD TO SURFACE MIGRATION

**V.I. Savchenko†**

*Kinet. Katal.,* 39 (1998) 132-137.

The effect of process of diffusion of intermediate adsorbed particles (spillover) between different patches of heterophase surface on the reaction kinetics are considered. The possibility of synergism is demonstrated for a catalysts, the surface of which consists of patches of two types - $s_1$ and $s_2$, with the adsorption heats $q_1<q_{opt}$ and $q_2> q_{opt}$.

# Gas Phase Reactions

### MOLYBDENUM OXIDE CLUSTER IONS IN THE GAS PHASE: REACTIONS WITH SMALL ALCOHOLS

**E.F. Fialko, A.V. Kikhtenko, V.B. Goncharov**

*Organometallics*, 17 (1998) 25-31.

The gas-phase reactions of molybdenum oxide cluster ions $Mo_xO_y^+$ (x=1-3, y=1-9) with small alcohols have been investigated using Fourier transform ion cyclotron resonance mass spectrometry. Product branch ratios are reported. The reactions of $Mo_xO_y^+$ with alcohols can be envisioned as proceeding via metal insertion into C-H and C-O bonds. C-H bond insertion leads to alcohol dehydrogenation and aldehyde elimination, whereas, insertion into the C-O bonds results in alcohol dehydration and formation metal-alkyl groups Moreover, increase of the chain length and branching lead to C-C bond cleavage. The most intriguing process is the reaction of $Mo_3O_9^+$ ion with more than one $CH_3OH$ molecule yielding $Mo_3O_9(C_2H_5)^+$ and $Mo_3O_9(C_3H_7)^+$ ions. $Mo_3O_9CH_3^+$ ion was found to be the key intermediate of polymerization process. Molybdenum oxides are protonized in the presence of alcohols. Upper and bottom limits for $Mo_xO_y$ proton affinities were estimated as PA(MoO) < 180, PA($Mo_2O_4$, $Mo_2O_5$, $Mo_3O_8$) = 188 ± 8, PA($MoO_2$) = 202 ± 5, PA($MoO_3$, $Mo_2O_6$, $Mo_3O_9$) > 207 kcal/mol.

### IDENTIFICATION OF MATRIX-ISOLATED METHOXYL RADICALS BY RECORDING EPR SPECTRA UNDER PHOTOLYSIS

**I.V. Malakhova, V.A. Ermolaev**

*Mendeleev Commun.*, 3 (1998) 83-84.

For the first time gas phase radicals have been observed, using the matrix isolation method, during methanol oxidation on a $Pt/SiO_2$ catalyst. A method of identifying the radicals generated is suggested, which utilizes the differing resistance of $MeO^{\cdot}$ and $MeO_2^{\cdot}$ radicals to photolysis using the full light of a high pressure mercury lamp.

## Catalysis on Zeolites and Sulfate-Promoted Zirconia

### IN SITU ESR STUDY OF THE STATE OF Fe IONS IN FeZSM-5 ZEOLITES

**A.M. Volodin, V.I. Sobolev, G.M. Zhidomirov**

*Kinet. Katal.*, 39 (1998) 1-14.

The state and chemical properties of Fe ions in FeZSM-5 zeolites has been studied by *in situ* ESR. To reveal states of iron unobservable by ESR, it has been suggested to employ changes of their coordination and oxidation state in the reactions with suitable gaseous molecules. Zeolite hydroxylation in the water vapor has been shown to result in the formation of high-spin (S=5/2) states of $Fe^{3+}$ ions ($g_{\perp}=6.0$, $g_{||} \approx g_e$) in the octahedral coordination with strong tetragonal distortion.

### LOW-TEMPERATURE OXIDATION OF METHANE TO METHANOL ON FeZSM-5 ZEOLITE

**K.A. Dubkov, V.I. Sobolev, G.I. Panov**

*Kinet. Katal.*, 39 (1998) 79-86.

Chemical properties of a new form of surface oxygen (α-oxygen), produced upon $N_2O$ decomposition over Fe-containing zeolite ZSM-5, have been studied in stoichiometrical reaction with methane at room temperature. A possibility of single-turnover cycles of selective methane oxidation to methanol has been shown. The last can be extracted form the surface and analyzed by chromatographic method. Isotope tests excluded the opportunity of methanol production from any other sources. The concentration of α-oxygen influences the completeness of its interaction with methane. Possible connection of this phenomenon with the peculiarities of active centers localization in zeolite micropores is considered. The unique reactivity of α-oxygen allows one to consider it as a model of active oxygen of monooxygenases, capable of enzymatic methane oxidation.

### GENERATION OF ACTIVE OXYGEN SPECIES ON SOLID SURFACES. OPPORTUNITY FOR NOVEL OXIDATION TECHNOLOGIES OVER ZEOLITES

**G.I. Panov, A.K. Uriarte*, M.A. Rodkin*,**
**V.I. Sobolev (Solutia Inc., Gonzalez, USA)**

*Catal. Today*, 41 (1998) 365-385.

Generation of surface oxygen species and their role in partial oxidation reactions catalyzed by metal oxides are dicussed. Main attention is paid to a new concept related to a recent discovery of remarkable ability of Fe complexes stabilized in a ZSM matrix to generate a new form of surface oxygen (α-oxygen) from $N_2O$. At room temperature, α-oxygen exhibits a high reactivity typical for the active oxygen of monooxygenases, and mimics its unique ability to perfom selective oxidation of hydrocarbons. This open new opportunity for creating novel technologies based on biomimetic strategy. A process of direct oxidation of benzene to phenol, recently demonstrated by Solutia on a pilot plant scale, is evidence of great potential of this approach.

### THE NATURE, STRUCTURE AND COMPOSITION OF ADSORBED HYDROCARBON PRODUCTS OF AMBIENT TEMPERATURE OLIGOMERIZATION OF ETHYLENE ON ACIDIC ZEOLITE H-ZSM-5

**A.G. Stepanov, M.V. Luzgin, V.N. Romannikov,**
**V.N. Sidel'nikov, E.A. Paukshtis**

*J. Catal.,* 178 (1998) 466-477.

The nature, structure and composition of hydrocarbon products that form under oligomerization of ethylene on acidic zeolite H-ZSM-5 at room temperature (296 K) have been analyzed using a combination of *in situ* IR and $^{13}C$ NMR and *ex situ* $^{13}C$ NMR and GC-MS. It is shown that oligomers strongly retained by the zeolite framework represent a mixture of hydrocarbons, which composition ranges from $C_5$

to *ca.* $C_{14+}$ carbon atoms. Adsorbed oligomers are bound to the oxygen of the zeolite framework to form alkoxy species. Alkoxy species represent main adsorption state of the oligomers, but they are in equilibrium with olefins and carbenium ions of the same composition, the concentration of both carbenium ions and olefins seems to be beyond the sensitivity of both NMR and IR. The reactivity of the adsorbed oligomers is defined by the reactivity of equilibrated carbenium ions, which can easily interact with carbon monoxide and water to give a mixture of corresponding carboxylic acids. Oligomeric alkoxides with linear hydrocarbon fragments prevail in the mixture of the formed oligomers. The average length of the linear oligomer chain includes approximately seven carbon atoms. Prevalence of the linear hydrocarbon fragments over branched ones in adsorbed oligomers seems to be defined by both specific framework and dimensions of the channels of the zeolite H-ZSM-5.

## MESOPOROUS BASIC ZIRCONIUM SULFATE: STRUCTURE, ACIDIC PROPERTIES AND CATALYTIC BEHAVIOUR

**V.N. Romannikov, V.B. Fenelonov, E.A. Paukshtis, A.Yu. Derevyankin, V.I. Zaikovskii**

*Micropor. Mesopor. Mater.*, 21 (1998) 411-419.

Some properties of thermostable mesophase of basic zirconium sulfate with texture characteristics close to that for MCM-41 are described. After calcination at 550 $^{o}$C the mesophase exhibits specific surface area of mesopores 450-500 $m^2$/g. Peculiarities of catalytic behavior of the mesophase are related with its acidic properties.

## INTERACTION OF AROMATICS WITH BROENSTEAD SITES IN ZEOLITES: DEMARCATION LINE BETWEEN REGIONS OF STABLE EXISTENCE OF H-COMLEXES AND ION PAIRS FOR VARIOUS TYPES OF BASES

**E.A. Paukshtis, L.V. Malysheva, V.G. Stepanov**

*React. Kinet. Catal. Lett.,* 65 (1998) 145-152.

Interaction of naphthalene, α-methylnaphtalene, and hexamethylbenzene with OH groups of $SiO_2$ and H-ZSM-5 zeolites was studied by IR spectroscopy. The results are compared with data obtained for other types of organic bases. Specificity in generation of H-complexes of olefines, arenes, naphthalenes, N- and O-bases with Broenstead surface sites was elucidated. Each type of base appears to have its particular correlation of ($PA^a$-$Pa^b$) and shift of $Dn_{OH}$ band in H-complexes. It has been found that if ($PA^a$-$Pa^b$) is less than 85±5 kcal/mol, the formation of ion pairs is thermodynamically more favorable than that of H-comlexes for all types of organic compounds.

## HYDROCARBON SPECIFICITY IN THE SELECTIVE CATALYTIC REDUCTION OF $NO_X$ OVER Cu-ZSM-5 AND Co-ZSM-5 CATALYSTS

**V.A. Sadykov, S.A. Beloshapkin[1], E.A. Paukshtis, G.M. Alikina, D.I. Kochubey, S.P. Degtyarev, N.N. Bulgakov, S.A. Veniaminov, E.V. Netyaga[1], R.V. Bunina, A.N. Kharlanov[2], E.V. Lunina[2], V.V. Lunin[2], V.A. Matyshak[3], A.Ya. Rozovskii[4] ([1]Novosibirsk State University, Novosibirsk, Russia; [2]Moscow Lomonosov State University, [3]Semenov Institute of Chemical Physics and [4]Topchiev Institute of Petrochemical Synthesis, Moscow, Russia)**

*React. Kinet. Catal. Lett.*, 64 (1998) 113-120.

Transformation of surface nitrates under $CH_4$ ($CH_4$+$O_2$) was found to ensure steady-state activity of Co-ZSM-5 in the selective catalytic reduction of nitrogen oxides by methane ($CH_4$-SCR). For Cu-ZSM-5, such species are mainly converted into NO. Relaxation of the coordination sphere due to oxygen and NO adsorption, stability of C,N-containing intermediates and activation routes of hydrocarbons (methane, propane) were analyzed as factors determining catalytic properties of Cu and Co cations.

## REACTIVITY AND TRANSFORMATION ROUTES OF SURFACE NITRATES IN THE REACTION OF $NO_X$ REDUCTION BY $C_3H_8$ OVER CATION-EXCHANGED ZEOLITES

**V.A. Sadykov, E.A. Paukshtis, S.A. Beloshapkin[1], G.M. Alikina, S.A. Veniaminov, E.V. Netyaga[1], D.I. Kochubey, R.V. Bunina, E.V. Lunina[2], A.N. Kharlanov[2], V.V. Lunin[2], V.A. Matyshak[3], A.Ya. Rozovskii[4] ([1]Novosibirsk State University, Novosibirsk, Russia; [2]Moscow Lomonosov State University, [3]Semenov Institute of Chemical Physics and [4]Topchiev Institute of Petrochemical Synthesis, Moscow, Russia)**

*React. Kinet. Catal. Lett.*, 64 (1998) 113-120.

FTIR combined with $^{15}$N and $^{18}$O isotope substitution and TPD have revealed that nitrates are the most abundant ad-$NO_x$ species on over-exchanged

Cu- and Co-ZSM-5 zeolites. The transformation rates of such species under the action of a propane-oxygen mixture were found to be comparable and sufficiently high to afford steady-state catalytic activities. A scheme of the reaction mechanism including C, N-containing intermediates detected in this work is suggested.

## GAS PHASE NITRATION OF BENZENE BY NITRIC ACID ON ZSM-5 ZEOLITE

**T.G. Kuznetsova, K.G. Ione, L.V. Malysheva**

*React. Kinet. Catal. Lett.*, 63 (1998) 61-66.

Gas phase nitration of benzene on ZSM-5 zeolite has been studied at 140-170 °C. Increase in the $HNO_3/C_6H_6$ ratio of the starting mixture was shown to increase the nitrobenzene yield. Process parametrs worsened with time since reagents and products were strongly absorbed and left the zeolite surface only at 220-250 °C.

## ESR STUDY OF PARAMAGNETIC SITES IN SULFATED ZIRCONIA

**I.V. Bobricheva, I.A. Stavitsky*, V.K. Yermolaev, N.S. Kotsarenko, V.P. Shmachkova, D.I. Kochubey (Novosibirsk State University, Novosibirsk, Russia**

*Catal. Lett.*, 56 (1998) 23-27.

ESR spectroscopy was used to investigate paramagnetic sites in sulfated zirconia. Catalysts derived from ziconium oxide and zirconium hydroxide were studied. It was demonstrated that paramagnetic sites assigned to near-surface F-centers form during activation at temperature above 573 K. The catalyst derived from zirconium hydroxide shows after activation at 873 K two types of paramagnetic sites: F-centers and $Zr^{3+}$ sites. Both F-centers and $Zr^{3+}$ sites of this catalyst form complexes with reagents upon *n*-butane or hydrogen adsorption at range of 423-523 K in contrast to paramagnetic sites of the oxide-derived catalyst.

## STRUCTURE DETERMINATION OF SUPPORTED SULFATED ZIRCONIUM USING SELENIUM AS PROBE FOR EXAFS

**V.V. Kriventsov, D.I. Kochubey**

*Nuclear Instruments & Methods in Phys. Res. A*,
405 (1998) 376-377.

It is shown that a large amount of sulfated zirconium supported on silica is present in form of silicates. The substitution of sulfur anions $(SO_4)^{2-}$ on selenium anoins $(SeO_4)^{2-}$ is used for this purpose.

## SYNTHESIS OF CATALYTICALLY ACTIVE SULFATED ZIRCONIA AEROGELS

**A.F. Bedilo, K.J. Klabunde* (Kansas State University, Manhattan, Kansas)**

*J. Catal.*, 176 (1998) 448-458.

Sulfated zirconia aerogels were synthesized by a sol-gel method followed by high temperature supercritical drying. Aerogels with sulfur introduced on the gelation step had high surface areas and pore volumes. Their textural properties could be tuned by variation of the preparation conditions. Samples synthesized by this procedure and those obtained by incipient wetness impregnation of zirconia aerogels with $(NH_4)_2SO_4$ were shown to exhibit catalytic activity in the low temperature isomerization of n-butane comparable to conventional precipitated zirconia. Maximum catalytic activity of impregnated aerogels was observed at lower nominal sulfur loading. They were shown to retain more surface sulfates after calcination compared to samples prepared by two other methods. The most active samples had close to monolayer surface coverage with sulfates with the decomposition peak at 820-830°C. Overmonolayer surface sulfates hindered the isomerization activity whereas bulk sulfates had little effect on it.

## EFFECT OF LIGHT ON REACTIONS OVER SULFATED ZIRCONIA

**A.F. Bedilo, V.I. Kim, A.M. Volodin**

*J. Catal.,* 176 (1998) 294-304.

The effect of illumination with visual and near-UV light on the isomerization and cracking of n-pentane and formation of radical cations from benzene and its derivatives over sulfated zirconia has been studied. Sulfated zirconia proved to have very strong acceptor sites capable of ionizing benzene and methylbenzenes to corresponding radical cations. The ionization of aromatic molecules could be initiated with visual light. The presence of oxygen in the gas phase appeared to strengthen the acceptor sites and shift the photoreaction red edge to longer wavelengths. Electron donor-acceptor complexes are shown to be key intermediates in the ionization of aromatic molecules on sulfated zirconia. A qualitative correlation between the presence of the strongest acceptor sites and the isomerization activity was observed. Illumination with visual light significantly increased the pentane cracking selectivity with little effect on the isomerization activity. Pentane cracking is proposed to proceed via dimerization initiated by the charge transfer with the formation of unstable radical cations.

# Partial Oxidation Processes

## STUDIES ON THE CONDITIONS OF SYNTHESIS OF PICOLINIC ACID BY HETEROGENEOUS CATALYTIC OXIDATION OF 2-PICOLINE

**E.M. Al'kaeva, T.V. Andrushkevich,**
**G.A. Zenkovets, D.E. Babushkin**

*Catal. Lett.,* 54 (1998) 149-152.

Heterogeneous oxidation of 2-picoline over binary P-Ti, Sb-Ti, P-Sb, and V-Ti oxide catalysts was studied over the temperature range of 200-300 $^{o}$C. The vanadium-titanium catalysts based on titanium dioxide (anatase) were found to be the most selective to picolinic acid. With binary catalysts containing 20-50% of vanadium pentoxide, the selectivity for picolinic acid was 22-19% at the 36-74% conversion of 2-picoline. A distinguishing feature of these catalysts is regular surface stacking of $V_2O_5$ and $TiO_2$ crystallites.

## STUDY OF THE $P_2O_5$-$MoO_3$ SYSTEM IN ACROLEIN OXIDATION

**V.M. Bondareva, T.V. Andrushkevich,**
**L.M. Plyasova, R.I. Maksimovskaya,**
**N.N. Chumachenko**

*React. Kinet. Catal. Lett.*, 63 (1998) 201-206.

Catalytic properties of the binary phosphorus-molybdenum system with Mo/P=3-24,5 in acrolein oxidation have been studied. The selectivity to acrylic acid and carbon oxides practically does not depend on the chemical composition of the system, and the maximum activity is observed for Mo/P=12. The catalytic properties of the system are determined by an X-ray amorphous phase, apparently molybdenyl phosphate.

## SYNTHESIS OF NICOTINIC ACID

**T.V. Andrushkevich**

*Indust. Catal. News*, 1 (1998) 4-7.

An innovative method for synthesis of nicotinic acid developed recently is a one-stage, gas phase, catalytic oxidation of β-picoline with the oxygen coming from air. The reaction proceeds with the vanadium-titanium oxide catalyst in the temperature range of 250 $^{o}$C to 280 $^{o}$C.

The method has been checked in the pilot installation with the reactor tube of 2800 mm length and 30 mm diameter. Reaction mixture consisted of 0,7% β-picoline, 20% water-steam, 79,3% air. Nicotinic acid was deposited under 160-110 $^{o}$C in the crystallizer placed after reactor. The yield of nicotinic acid achieved 80%.

The catalyst is stable under the reaction medium: no change in activity, selectivity or mechanical strength of the granules was observed during 350 hours of operation.

## CATALYTIC OXIDATION OF 1,1-DIMETHYLHYDRAZINE WITH AIR OXYGEN IN THE DILUTED AQUEOUS SOLUTIONS

**G.L. Elizarova, L.G. Matvienko, O.P. Pestunova,**
**D.E. Babushkin, V.N. Parmon**

*Kinet. Katal.*, 39 (1998) 49-55.

The new catalytic reaction of 1,1-dimethylhydrazine oxidation in the aqua solutions is found. The catalysts are supported on the common oxides Cu-, Fe-, Co-, Mn-hydroxides. The most active are Cu-containing samples. The effect of pH, temperature and ratio of catalyst weighed portion to the solution volume is studied. The main reaction products are identified (hydrazones, formazane). It is shown that the reaction has the different mechanisms in the neutral and basic media.

# Studies on Silver Catalysts for Ethylene Epoxidation

## THE BASIS OF THE STAGE REDOX MECHANISMS OF THE CATALYTIC REACTIONS OF ETHYLENE OXIDATION ON SILVER AND AMMONIA SYNTHESIS ON IRON

**A.V. Khasin**

*"Catalysis and Catalysts: Fundamental Studies",* Ed. Prof. R.A. Buyanov, Boreskov Institute of Catalysis, SB RAS, (1998) pp. 11-12.

On the basis of adsorption and isotope exchange studies the conclusion was made that the catalytic reactions of ethylene oxidation on silver and ammonia synthesis on iron occur by a stepwise redox mechanisms and involve dissociative adsorption of $O_2$ or $N_2$ respectively as stage of catalytic process.

## REACTION OF ETHYLENE WITH OXYGEN ADSORBED ON A SILVER FILM. DEPENDENCE OF THE SELECTIVITY TO ETHYLENE OXIDE ON THE ETHYLENE PRESSURE

**A.V. Khasin**

*React. Kinet. Catal. Lett.,* 64 (1998) 289-294.

Kinetics of the reaction of ethylene with oxygen adsorbed on a silver film was studied at 333 K, initial surface coverage with oxygen close to 0.8 and initial ethylene pressures of 1.1 and 4.4 Pa. The selectivity of ethylene oxide formation was found to increase with increasing ethylene pressure.

## MICROWAVE EFFECT ON REACTION RATE IN ETHYLENE EPOXIDATION OVER SILVER CATALYSTS

**A.Yu. Klimov, B.S. Bal'zhinimaev, L.L. Makarshin, V.I. Zaikovskii, V.N. Parmon**

*Kinet. Katal*., 39 (1998) 554-559.

An effect of microwave radiation on $Ag/\alpha\text{-}Al_2O_3$ catalyst for ethylene epoxidation with silver particles 100-10000 Å and predominantly size 2000 Å has been studied. The microwave supply to the catalyst prereduced in $H_2$ resulted in the reaction rate increase both towards ethylene epoxidation and deep oxidation. This effect disappears as the system approaches the steady state. At the same time microwave radiation has no effect over the catalyst preoxidized in oxygen. The quantitative estimation of results indicates, that the catalyst in not heated under the action of microwave radiation. It has been suggested that the reason of phenomena observed may be the modification of electron properties of the catalysts under microwave radiation action.

## CATALYTIC AND STRUCTURAL PROPERTIES OF ULTRADISPERSED SILVER POWDER, PREPARED BY ELECROEXPLOSION TECHNIQUE: COMPARISON WITH CONVENTIONAL SILVER CATALYSTS

**B.S. Bal'zhinimaev, V.I. Zaikovskii, L.G. Pinaeva, A.V. Romanenko, G.V. Ivanov* (Institute of Petroleum Chemistry, Tomsk, Russia)**

*Kinet. Katal.,* 39 (1998) 775-781.

The catalytic and structural properties of ultradispersed powder (UDP) of silver prepared by electroexplosion technique, and supported Ag/C catalysts were studied. These samples demonstrate essentially lower activity, but extremely high selectivity in comparison with conventional silver powder (CP), and supported $Ag/\alpha\text{-}Al_2O_3$ sample with close silver particle size. In the case of UDP, nearly a 100 % selectivity to ethylene oxide was obtained. The correlation between high value of selectivity and appearance on the silver surface specific particles (with a size not exceeding 100 Å) with the structure, similar to $Ag_2O$ was revealed. Formation of such particles proceeds in the course of reaction or after treatment of the catalysts in $O_2$ at 230-260 $^{o}$C and results in the annealing of packing defects. It has been shown, that these particles can hardly be identified as $Ag_2O$ ionic crystals and are located only at the points where the extended defects are exposed (i.e., on the twinning interfaces). The possible mechanism of oxide-type structures formation is proposed. The release of excessive energy accumulated at the stage of silver UDP preparation is likely a driving force of the process.

The difference in catalytic properties of UDP and CP is explained considering the idea of mechanism of reactions of ethylene epoxidation and deep oxidation.

### CATALYTIC AND STRUCTURAL PROPERTIES OF ULTRADISPERSED SILVER POWDER PREPARED BY WIRE EXPLOSION TECHNIQUE

**B.S. Bal'zhinimaev, V.I. Zaikovskii, L.G. Pinaeva, A.V. Romanenko, G.V. Ivanov* (Institute of Petroleum Chemistry, Tomsk, Russia)**

*Mendeleev Commun.*, 3 (1998) 100-101.

In this work the structure of silver ultradispersed powders (UDP) exploded in an argon atmosphere have been studied to explain its extremely high selectivity in ethylene epoxidation. For comparison, similar studies were carried out with ordinary catalysts (Ag powder, Ag/C) prepared by equilibrium procedures. Under nearly steady state conditions, the activity of the samples follows the order: ordinary powder >> Ag/C > UDP. The selectivity changes in the opposite order, i.e. the ultradispersed powder shows the highest selectivity in epoxidation (90%), while the ordinary silver powder has the lowest selectivity (40%).

The correlation between high value of selectivity and appearance on the silver surface specific particles (with a size not exceeding 100 Å) with the structure, similar to $Ag_2O$ was revealed. Formation of such particles proceeds in the course of reaction or after treatment of the catalysts in $O_2$ at 230-260 $^{o}$C and results in the annealing of packing defects. It has been shown that these particles can hardly be identified as $Ag_2O$ ionic crystals and are located only at the points where the extended defects are exposed (i.e., on the twinning interfaces). The possible mechanism of oxide-type structure formation is proposed. The release of excessive energy accumulated at the stage of silver UDP preparation is likely a driving force of the process.

The difference in catalytic properties of UDP and CP is explained considering the idea of mechanism of reactions of ethylene epoxidation and deep oxidation.

## Development and Application of Physicochemical Methods for Catalysts Investigation

### CONDUCTIVITY, NMR MEASUREMENTS, AND PHASE DIAGRAM OF THE $K_2S_2O_7$-$V_2O_5$ SYSTEM

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*J. Phys. Chem. B,* 102 (1998) 24-28.

The phase diagram of the catalytically important $K_2S_2O_7$-$K_2S_2O_7$-$V_2O_5$ system has been investigated by means of conductometric and NMR spectroscopic methods up to 500 $^{o}$C. From the marked change of the specific conductivity by change of phase, found for 14 different compositions of the $K_2S_2O_7$-$V_2O_5$ binary system, the phase transition temperatures have been obtained. In the $K_2S_2O_7$-$V_2O_5$-rich region, where glass formation is pronounced, $^{39}$K NMR spectra of six different compositions showed a marked change of the line width at the liquidus temperatures. The phase diagram based on the combined results exhibits three maxima corresponding to the formation of compounds with the stoichiometry 3 $K_2S_2O_7 \cdot V_2O_5$, 2 $K_2S_2O_7 \cdot V_2O_5$, and 1 $K_2S_2O_7 \cdot V_2O_5$ and melting temperatures of 352, 398, and 425 $^{o}$C, respectively. Three eutectics were found at the compositions $X_{V_2O_5} = 0.17$, 0.27, and 0.39 with melting temperatures of 314, 348, and 366 $^{o}$C, respectively. The measured conductivities in the liquid region of 14 different compositions have been fitted to polynomials of the form $\mathrm{K} = A(x) + B(x)\ (t\text{-}450) + C(x)\ (t\text{-}450)^2 + D(x)(t\text{-}450)^3$. The phase diagram may prove to be useful for the design of new $SO_2$ oxidation catalysts.

### $^1$H MAS NMR STUDIES OF THE H/D EXCHANGE OF DEUTERATED PROPANE ADSORBED ON ZEOLITE H-ZSM-5

**A.G. Stepanov, H. Ernst*, D. Freude* (Abteilung Grenzflächenphysik, Universität Leipzig, Leipzig, Germany)**

*Catal. Lett.*, 54 (1998) 1-4.

The hydrogen exchange in the propane-$d_8$ loaded zeolite H-ZSM-5 was monitored by *in situ* $^1$H MAS NMR spectroscopy within the temperature range 457-543 K. Measurements of the H/D exchange between the acidic hydroxyl groups of the zeolite and the adsorbed deuterated propane molecules show that both methyl and methylene groups of alkane are involved in the exchange. The comparison of the experimentally obtained apparent activation energies for the exchange in methyl groups (108±7 kJ $mol^{-1}$) and methylene groups (117±7 kJ $mol^{-1}$) with theoretical values for methane and ethane supports the assumption that the H/D exchange for methyl and methylene groups takes place via a pentavalent transition state.

### EFFECT OF MAGNETIC FIELD ON THE FORMATION AND AGING OF Fe(III) HYDROXIDES

**M.A. Fedotov, E.A. Taraban, V.I. Zaikovskii,**
**S.V. Ignashin, R.A. Buyanov**

*Zh. Neorgan. Khim.,* 43 (1998) 451-457.

$^{2}$H, $^{14}$N, $^{17}$O, $^{25}$Mg and $^{27}$Al NMR, magnetic susceptibility measurements, and electron microscopy were used to study the influence of magnetic fields on polynuclear hydroxo complexes formation in hydrolytic polycondensation of aqua $Fe^{3+}$ ions and crystallisation of Fe(III) hydroxide upon ageing. Both a homogeneous magnetic field of 7 T and a nonhomogeneous magnetic field ($B$=0.8 T, grad$B$= 7 T/m) have no influence on the properties of solutions at different stages of polycondensation of $Fe^{3+}$ even up to the precipitation of Fe(III) hydroxide. The homogeneous magnetic field (7 T) significantly influences the ageing of amorphous Fe(III) hydroxide and makes it possible to modify the morphology of the resulting crystals.

### PROBING THE SURFACE ACIDITY OF MODIFIED ALUMINA WITH $^{1}$H AND $^{15}$N HIGH-RESOLUTION SOLID STATE NMR SPECTROSCOPY

**S.V. Filimonova, V.M. Mastikhin**

*React. Kintet. Catal. Lett.,* 65 (1998) 131-138.

$^{1}$H MAS NMR and $^{15}$N NMR studies of the adsorbed $N_2$ and $N_2O$ molecules were applied to characterize Bronsted and Lewis acid sites (BAS and LAS) of unmodified $\gamma$-$Al_2O_3$ and $\gamma$-$Al_2O_3$ modified with NaOH. Changes in the concentrations of surface hydroxyls for NaOH/$\gamma$-$Al_2O_3$ with the increase in the number of more "basic" OH groups have been revealed by $^{1}$H MAS NMR. Two different types of LAS in $\gamma$-alumina have been found with the $^{15}$N NMR studies. The strongest sites are poisoned even at a small NaOH concentrations (ca. 0.05 wt.%). Not only the number but also the strength of electron-accepting sites are supposed to decrease after modification of $\gamma$-alumina with NaOH.

### MULTINUCLEAR NMR SPECTROSCOPIC CHARACTERIZATION OF Co(III) SPECIES: KEY INTERMEDIATES OF COBALT CATALYZED AUTOXIDATION

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*J. Molec. Catal. A: Chemical,* 130 (1998) 131-137.

Using $^{1}$H, $^{13}$C and $^{59}$Co NMR spectroscopies, it was shown that, the so-called "Co(III) acetate" - reactive intermediate of cobalt catalyzed autoxidation, is the mixture of the oxo-centered trinuclear cations $[Co_3O(OAc)_6(AcOH)_3]^+$ (**I**) and $[Co_3O(OAc)_5(OH)(AcOH)_3]^+$ (**II**) in 1:3-1:2 ratio. Cations **I** and **II** are the major species in the freshly prepared solutions of Co(III) acetate in $CH_2Cl_2$ and AcOH. Immediately after dissolving in MeOH, **I** converts into cation $[Co_3O(OAc)_5(OMe)(MeOH)_3]^+$ and **II** into cation $[Co_3O(OAc)_5(OH)(MeOH)_3]^+$. Reactivity of **I** and **II** towards *p*-xylene was determined. The addition of *p*-xylene to the sample containing **I** and **II** under anaerobic conditions in $CH_2Cl_2$ (1:3 *p*-xylene/$CH_2Cl_2$ by volume, 293 K) gave rise to gradual decrease of their concentration. The half-life was 2 h for cation **II** and 1.3 h for cation **I**.

### $^{31}$P NMR STUDIES OF THE $H_3PW_{12}O_{40}$ HETEROPOLYACID HYDROLYSIS

**R.I. Maksimovskaya**

*Zh. Neorgan. Khim.,* 43 (1998) 1960-1972.

The titration of the heteropolyacid (HPA) $H_3PW_{12}O_{40}$ ($PW_{12}$) aqueous solutions with bases of M=$Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, and $Ca^{2+}$ have been carried out at the concentration [HPA]=0.002-0.1 mol/l in the range pH=1.5-9 using $^{31}$P NMR monitoring. It has been found that the first stage of the alkaline hydrolysis of $PW_{12}$ is not completely reversible and that its final product is the heteropolyanion (HPAn) $PW_{11}O_{39}^{7-}$ ($PW_{11}$) complex with corresponding M, i.e. $PW_{11}M$ (**I**), whose formation is accomplished by pHs equal to about 2.5 for Ca, 3.3 for Mg, 4.2 for Li, 4.5 for Na, and 5.0 for K. The conversion of $PW_{12}$ to **I** and inversely at pH=1.5-4.5 are proceeding through three intermediate species discovered in the diluted HPA solutions (≤0.01 mol/l), which arise practically together. Those are $PW_{11}H_x$ (x>1) (**II**) and two $PW_{11}$ complexes with W assumed to have composition

$PW_{11}WO_2$ (**III**) and $(PW_{11})_2WO_2$ (**IV**). Between **I** and **II**, expecting M=Ca, there is a fast chemical exchange averaging their $^{31}P$ and $^{17}O$ NMR spectra. At [HPA]=0.1 mol/l the percentage of **II-IV** decreases sharply due to their condensation into the bigger anions including $P_2W_{20}O_{70}^{10-}$ and $P_2W_{21}O_{71}^{6-}$. On the second stage (pH>7) at [HPA]=0.01 mol/l HPAns **I** decompose into $H_nPO_4^{n-3}$ and $WO_4^{2-}$ either (with Li, Na) directly or (with K, Mg) through the intermediate mainly monomeric HPAns having W/P<11. The phosphorus distribution diagrams for the pH range 1÷9 derived from the $^{31}P$ NMR spectra and a more detailed scheme of the $PW_{12}$ alkaline hydrolysis are given.

$PW_{12}$ anion is highly resistant to the acidic hydrolysis and it remains unprotonated in rather concentrated mineral acid solutions.

## IN SITU NMR IMAGING STUDIES OF THE DRYING KINETICS OF POROUS CATALYST SUPPORT PELLETS

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*J. Phys. Chem. B,* 102 (1998) 3090-3098.

The proton NMR imaging (microscopy) technique is employed to study the process of drying of alumina and titania porous catalyst support pellets impregnated with various liquids. Despite the short-spin relaxation times usually exhibited by liquids that permeate porous solids, the possibility to monitor their evaporation in real time by detecting one-dimensional liquid concentration profiles along the diameter of a cylindrical sample is demonstrated. In the qualitative discussion of the results, it is shown that the experiment is sensitive to the fine details of the drying process, such as the efficiency of liquid transport and peculiar profile shape transformations in the course of drying. A simple experiment is proposed that yields an empirical relation between the detected profile intensity and the actual liquid content, which allows one to correct the detected profiles for the inevitable $T_2$-weighting effects.

## $^{125}$Te NMR IN $TeO_2$ SINGLE CRYSTAL: Te-Te CHEMICAL BONDING AND TUNNELING OF $5s^2$ ELECTRONS

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*Chem. Phys. Lett.,* 282 (1998) 245-249.

The Te-O and Te-Te bonds in $TeO_2$ have been studied from $^{125}$Te NMR single crystal data. The $^{125}$Te NMR chemical shift tensor has principal components $\delta_{11}$=727.5, $\delta_{22}$=1586.2 and $\delta_{33}$=2065.8 ppm. The $^{125}$Te magnetic shielding tensor is represented as a sum if constituents characterizing the of-ionic parts of the separated Te-Te and Te-O interactions. It is shown that the Te-Te exchange interaction is associated with a strong polarization of the $Te^{4+}$ ion under the intramolecular electric field and with tunneling of $5s^2$ electrons along the Te-Te bonds.

## PHASE COMPOSITION OF MANGANESE-ALUMINA CATALYSTS FOR THE REACTIONS OF DEEP OXIDATION

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*React. Kinet. Catal. Lett.*, 64 (1998) 113-118.

Using X-ray powder diffraction, transmission electron microscopy and differentiate dissolution peculiarities of the phase transformation of biphase manganese-alumina catalysts upon their thermal treatment were studied. Effect of the interaction between manganese and aluminum oxides in $MnO_x/\gamma\text{-}Al_2O_3$ catalyst calcined at 900-950 °C is found. Sample preparation procedure affects strongly the character of interaction between two oxides. Compounds formed on the base of $\delta\text{-}Al_2O_3$ are cored solid solutions, that appears to lead to their partial desintegration followed by the appearance of $\alpha\text{-}Al_2O_3$. In turn, solid solution of Al ions in $Mn_3O_4$ is in the state of metastable equilibrium due to the specific micrograined structure characterized by a developed coherent boundaries in the vicinities of those Al ions seems to be localized.

## FEATURES OF THE FORMATION OF REAL STRUCTURE OF $(La_{1-x},Sr)CoO_{3-y}$ PEROVSKITES AT THE RANGE OF MORPHOTROPOUS PHASE TRANSITION

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*Zh. Strukt. Khim.*, 39 (1998) 92-97.

Using X-ray powder diffraction with synchrotron radiation technique and transmission electron microscopy it has been shown that at the exchange of Sr for La in the $(La_{1-x},Sr)CoO_{3-y}$ system the transformation of the microstructure appeared as increase of the microstrains followed by the formation of grain boundaries, and the decrease of the degree of the hexagonal disordering of the perovskite cell took place. Micrograin structure of the perovskite particles in the range of morphotropous phase transition $(0.3<x>0.4)$ caused by the metastable state of this system seems to be a reason for the high catalytic activity of these samples.

## OXYGEN STATES DURING THERMAL DECOMPOSITION OF $Ag_2O$: XPS AND UPS STUDY

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*React. Kinet. Catal. Lett.*, 63 (1998) 291-296.

Using photoemission XPS and UPS methods the oxygen states in the silver metal lattice during the thermal decomposition of $Ag_2O$ have been studied. It has been shown that one half of the lattice oxygen inside subsurface layers of $Ag_2O$ is transformed to subsurface oxygen in metallic silver characterized by a quasimolecular structure. Thermal annealing up to 1000 K did not result in the removal of the residual subsurface oxygen.

## STRUCTURAL PROPERTIES OF Pd CATALYSTS SUPPORTED ON $Al_2O_3$-$La_2O_3$ PREPARED BY SOL-GEL METHOD

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*Appl. Catal. B: Environmental*, 17 (1998) 221-231.

The structure of palladium catalysts (0.3 wt.% Pd), supported on sol-gel alumina-lanthana mixed oxides, was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). The investigation of the structure of lanthana-promoted Pd catalysts, prepared by different methods, is of great importance for the improvement of palladium-only three-way catalysts. The data obtained show the presence of crystalline phase, different from alumina, lanthana or alumina-lanthana reported compounds, in $Al_2O_3$-$La_2O_3$ and $Pd/Al_2O_3$-$La_2O_3$. Attempts to assign this crystalline phase to a known one were unsuccessful. According to XPS data, in lanthanum-containing samples, the state of lanthanum is different from that in $La_2O_3$. After calcination in air at 1273 K for 3 h this phase vanishes and large crystals of $LaAlO_3$, metastable for studied composition, appear. The sol-gel preparation method, in comparison with traditional preparation methods, leads to stabilization of $LaAlO_3$ phase under the considered conditions and the increase of the stability of $\gamma$-$Al_2O_3$ phase at high temperature. The improvement of the catalytic activity at medium temperature and the increase of the selectivity to $NH_3$ at high temperatures for lanthanum-promoted Pd catalysts are ascribed to a lanthanum-containing phase. The increase in $NH_3$ production decreases its practical value for an NO reduction catalyst.

## SYNTHESIS OF HIGHER ALCOHOLS ON Cu-CONTAINING CATALYSTS: INVESTIGATION OF THE CATALYST UNDER THE REACTION CONDITIONS

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*Kinet. Katal.*, 39 (1998) 767-774.

The phase composition of a copper-cobalt catalyst in the course of the reduction by hydrogen and under the reaction medium is studied by high-temperature in situ X-ray diffraction analysis, ex situ transmission microscopy, and thermography. In the hydrogen medium at 230 °C, a model $CuCoO_2$ catalyst is completely transformed into the copper-cobalt melt, which partially decomposes on heating to 280 °C in $CO+H_2$ mixture to give cobalt carbide and $Cu^o$. Heating up to 370 °C causes the decomposition of cobalt carbide and the Cu-Co melt yielding cobalt and copper metallic phases. This is accompanied by the carbon formation from cobalt carbide. The correlation between phase composition of the catalyst in the reaction medium and selectivity in reaction of CO hydrogenation has been revealed. The role of carbide in the formation of active sites in the synthesis of higher alcohols is discussed.

### STRUCTURE AND PHASE COMPOSITION STUDY OF EUROPT-1 CATALYST BY DIFFERENTIAL ANOMALOUS SCATTERING

**A.N. Shmakov, E.M. Moroz, A.L. Chuvilin**

*Nuclear Instrum. & Methods in Phys. Res. A*,
405 (1998) 470-472.

Using Differential Anomalous X-ray Scattering (DAXS) method the structure and phase composition of Pt-containing particles of standard catalyst EuroPt-1 has been investigated. It has been demonstrated that EuroPt-1 catalyst consists of metal platinum and platinum oxide PtO. About 60 % Pt is oxidized in fresh sample. No metal-support interaction has been detected.

### STRUCTURE INVESTIGATION OF DEFECT MgO - HIGH TEMPERATURE PROCESS CATALYST

**L.M. Plyasova, N.A. Vasilieva, S.V. Cherepanova, A.N. Shmakov, A.L. Chuvilin**

*Nuclear Instrum. & Methods in Phys. Res. A*,
405 (1998) 473-475.

Structure refiniment of defect MgO containing acetate and carbonate groups has been performed. The experiment was carried out on high resolution powder diffractometer in Siberian Synchrotron Radiation Center, Novosibirsk. The results demonstrated possibility of admixtures to insert into the structure of MgO by two different ways. The reliability of both models has been estimated. These models provided the decrease of R-factor down to 2.0-2.2 % in contrast to the ideal MgO structure (R-factor=9.5 %).

### X-RAY PERFORMANCE OF MULTILAYER GRATINGS: RECENT ADVANCES AT SSRC

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*Nuclear Instrum. & Methods in Phys. Res. A*,
405 (1998) 310-318.

The main results at the fabrication, theoretical and experimental studies of X-ray multilayer gratings are presented. The multilayer grating reflectivity measurements in both hard and soft X-rays were performed. The features observed in these experimental data are identified and interpreted by means of numerical simulation method of eigenvectors. The effects of diffuse X-ray scattering from Ni/C multilayer and Ni/C multilayer grating have been investigated. Novel aspects of polychromatic optics based on the application of the multilayer grating in hard X-rays are discussed.

### THE EFFECT OF OXYGEN DEFICIENCY ON THE ELECTRONIC AND LOCAL STRUCTURES OF $BaPb_{1-x}Bi_xO_{3-\delta}$-$Ba_{0.6}K_{0.4}BiO_{3-\delta}$: AN X-RAY ABSORPTION STUDY

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*Nuclear Instruments & Methods in Phys. Res. A*,
405 (1998) 370-375.

The X-ray absorption spectroscopy (XAS) measurements at the $BiL_3$ and $PbL_3$ edges were made for Bi-based perovskite oxides: $BaPb_{1-x}Bi_xO_{3-\delta}$ (x=0, $\delta\leq0.2$; x=0.25, $\delta\leq0.15$; x=1, $\delta\leq0.4$) and $Ba_{0.6}K_{0.4}BiO_{3-\delta}$ ($\delta\leq0.2$). The oxygen reduction leads to larger changes in the $BiL_3$ edge of $BaPb_{1-x}Bi_xO_{3-\delta}$ (x=0.25, 1.0) and $Ba_{0.6}K_{0.4}BiO_{3-\delta}$ than in the $PbL_3$ edge of $BaPb_{1-x}Bi_xO_{3-\delta}$ (x=0, 0.25). The extended X-ray adsorption-fine structure (EXAFS) measurements indicate that the local structure around the Bi sites is more sensitive to the variation in oxygen stoichiometry than the local structure around the Pb sites. The single Pb-O bond length exhibits a certain dependence in $BaPb_{1-x}Bi_xO_{3-\delta}$ (x=0, 0.25) on the oxygen reduction. On the contrary, the separation between two different Bi-O bond lengths increases with $\delta$ in $BaPb_{1-x}Bi_xO_{3-\delta}$ (x=0.25, 1). The Bi-O distances could be distinguished in a semiconducting $Ba_{0.6}K_{0.4}BiO_{2.8}$. The local structure of oxygen deficient compounds was found to be essentially different from the crystalline structure refined from diffraction data.

The Bi valence states are discussed. The XAS data are in agreement with a $2Bi^{+4}\rightarrow Bi^{+3} + Bi^{+3}\underline{L}^2$ charge disproportionation model in BaPbBiO and BaKBiO, where $\underline{L}^2$ denotes the spread of two holes on 2p orbitals of six oxygen atoms surrounding the Bi ion.

## MULTILAYER GRATING AS A SR MONOCHROMATOR FOR MOESSBAUER SPECTROSCOPY

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**Novosibirsk, Russia)**

*Nuclear Instrum. & Methods in Phys. Res. A*,
405 (1998) 337-340.

The nuclear resonant diffraction of synchrotron radiation (SR) from a multilayer grating (MG) is theoretically investigated. The nuclear scattering of SR to one of the first orders of the MG allows one to suppress greatly the nonresonant SR scattering. The advantages of the MG as a SR monochromator for Moessbauer spectroscopy are studied. A new type of nuclear MG with the spatial lateral modulation of magnetic field is proposed. The possibility of a complete separation of Moessbauer photons from SR by this grating is shown.

## SYNCHROTRON RADIATION AND FREE ELECTRON LASER ACTIVITIES AT SSRC

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*Nuclear Instruments & Methods in Phys. Res. A*,
405 (1998) 179-190.

The Siberian SR Centre has implemented a wide program of SR and FEL research in cooperation with various research centres and institutions in Russia and abroad. The report illustrates this program, including joint experiments with the use of SR and FEL sources available at the Budker Institute of Nuclear Physics (INP), the implementation of new joint projects in Novosibirsk and at other centres, as well as the delivery of equipment designed and fabricated at the Budker INP or in collaboration with the Russian industry. Some technical information about the SR storage rings, wigglers, undulators and free electron lasers which are being constructed, used or developed at Budker INP is given as well.

## AN EXAFS STUDY OF THE AMORPHOUS CUPRUM HYDROXIDE

**V.V. Kriventsov, G.L. Elizarova, D.I. Kochubey**

*Nuclear Instruments & Methods in Phys. Res. A*,
405 (1998) 341-343.

It was shown that for the bulk cuprum hydroxide the amorphization is determined only by an excess of water without which the $Cu(OH)_2$ presents in the crystal form only. In the case of the supported cupric hydroxide, the amorphization is achieved by stabilization of the hydroxide particles on high dispersed silica surface under low concentration of the cupric ions, so that the sizes of the supported complexes are small. The data obtained suggests that the cuprum from dilute solution ($4\times10^{-3}$ M) under low values of pH is adsorbed on the surface $SiO_2$ as a polymer-like structure similar to that of $Cu(OH)_2$ rather than as isolated ions. This inference is confirmed by previously obtained results on adsorption of $Cu^{2+}$ on $TiO_2$.

## EXAFS STUDY OF ULTRADISPERSE NOBLE METAL NANOPARTICLES STRUCTURE PHASE CONVERSION

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*Nuclear Instruments & Methods in Phys. Res. A*,
405 (1998) 351-354.

The structure and its difference from bulk metals was studied for nanoparticles of Pt and Pd by EXAFS-spectroscopy. These particles were obtained by different methods and forms different precursors. The measurements have been conducted to investigate the process of phase transition under thermal relaxation and reagents adsorption. It was shown for Pt clusters that the initial structure has form of the polymeric chains, which changes on heating to usual bulk metal one.

## THE APPLICATION OF THE ATOM LABEL METHOD TO STUDYING SURFACE STRUCTURE OF THE CARBON DEPOSITED NICKEL PARTICLES BY USING EXAFS

**V.V. Kriventsov, B.N. Novgorodov, D.I. Kochubey**

*Nuclear Instruments & Methods in Phys. Res. A*,
405 (1998) 382-383.

The work is an effort to use the atom label method for studying surface structure of the carbon deposited nickel particles by EXAFS. All the data show that $H_2Se$ may be used as label atom.

### EXAFS DETERMINATION OF THE STRUCTURE OF SILVER STEARATE, $[Ag(O_2C(CH_2)_{16}CH_3]_2$, AND THE EFFECT OF TEMPERATURE ON THE SILVER COORDINATION SPHERE

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*Nuclear Instruments & Methods in Phys. Res. A*, 405 (1998) 428-434.

The structure of silver stearate, $[Ag(O_2C(CH_2)_{16}CH_3]_2$, has been refined using Ag K-EXAFS spectroscopy and known unit cell parameters. The silver carboxylate complex is similar to known short chain silver carboxylate derivatives and is a dimer formed from an eight-membered ring comprised of two silver atoms bridged by two carboxylates from the stearate molecules. The Ag···Ag distance is 2.90 (0.03) Å, similar to the bond distance in metallic silver. The dimers are further bonded to each other by long 2.60, Ag-O bonds. Moderate increases in temperature does not affect the structure, however, upon exposure to higher temperatures a new structure results which exhibits a Ag···Ag distance of 4.2 Å

### CHARGE DENSITY WAVES IN 1T-$TaS_2$: AN EXAFS STUDY

**D.I. Kochubey, T.K. Kim, V.P. Babenko, Sh.K. Shaikhutdinov**

*Physica B*, 252 (1998) 15-20.

Two polytypes (2H- and 1T-) of $TaS_2$ have been investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy. The EXAFS data were in good agreement with trigonal-prizmatic coordination of Ta in 2H-$TaS_2$. For 1T-$TaS_2$, a lattice distortion of Ta local surrounding was observed attributed to charge density waves (CDW). In order to fit the EXAFS data, a new model of the CDW cluster has been suggested which includes both the Ta and S atoms' displacements.

### DESTRUCTION OF THE CHARGE DENSITY WAVE STRUCTURE IN 1T-$TaS_2$ UNDER PYRIDINE INTERCALATION

**T.K. Kim, V.P. Babenko, B.N. Novgorodov, D.I. Kochubey, Sh.K. Shaikhutdinov**

*Nuclear Instruments & Methods in Phys. Res. A*, 405 (1998) 348-350.

XANES data for 1T- and 2H-$TaS_2$ were obtained for $L_{III}$ and $L_{II}$Ta edges. The changes of the electron density were determined after pyridine intercalation.

### LOCALIZATION OF COPPER ATOMS IN THE STRUCTURE OF THE ZnO CATALYST FOR METHANOL SYNTHESIS

**D.O. Klenov, G.N. Kryukova, L.M. Plyasova**

*J. Mater. Chem.*, 8 (1998) 1665-1669.

The microstructure of a copper-zinc oxide catalyst has been studied using HREM. Two alternatives for the arrangement of copper atoms in the ZnO crystallite were suggested and discussed. The high concentration of copper atoms in the sample (up to 10 at.%) against the known solubility of copper ions in ZnO (not more than 2 at. %) as well as the high density of dislocations seen in the micrographs, may be accounted for by the occurrence of octahedral copper atomic clusters of 0.25 nm radius built up into the host oxide lattice. These clusters lie at the dislocation wall along (001) plane of ZnO. Copper atoms were also shown to be involved in isolated square planar CuO clusters not more than 0.5-1 nm in size.

### THE EFFECT OF SURFACE ION-INDUCED DEFECTS ON CO ADSORPTION ON POLYCRYSTALLINE Ni

**S.N. Trukhan, V.P. Ivanov**

*React. Kinet. Catal. Lett.*, 65 (1998) 353-362.

CO adsorption on polycrystalline nickel was investigated by dynamic secondary ion mass-spectroscopy at $10^{-5}$-$10^{-3}$ Pa and 300-500 K. An increase of secondary ion currents $NiCO^+/Ni^+$ ratio was found in the range from 300 to 350 K, while at T>350 K it decreases sharply. These data were explained by a kinetic model, in which adsorption and desorption of tightly bound CO goes through weakly bound CO formed due to ion-induced defects.

### A PARTIAL SURFACE AREA MEASUREMENT METHOD FOR MULTICOMPONENT CATALYSTS AND ADSORBENTS

**M.S. Mel'gunov, V.B. Fenelonov**

*React. Kinet. Catal. Lett.*, 64 (1998) 153-160.

A new universal method for partial area measurements (PSAM) of multicomponent catalysts and adsorbents is proposed. The method is based on the dependence of specific adsorption on the surface area composition. It was realized in fast gas-chromatographic regime. The effectiveness of this method was shown for $SiO_2$-carbon mechanical mixtures with *n*-butane used as an adsorbate.

### STUDY OF CATALYTIC FIBROUS CARBON MICROPOROSITY BY A NEW GAS-CHROMATOGRAPHIC PROBE METHOD

**V.B. Fenelonov, M.S. Mel'gunov, N.A. Baronskaya**

*React. Kinet. Catal. Lett.*, 63 (1998) 305-312.

A new gas-chromatographic probe method (GCPM) is proposed to study the microporous structure of solids. This method was applied to analyze the catalytic fibrous carbon (CFC) microtexture by the adsorption of halogenated benzene derivatives used as molecular probes. The micropore size distribution in the range of 0.34-0.40 nm was measured.

### INVESTIGATION OF REFERENCE CATALYSTS IN THE BORESKOV INSTITUTE OF CATALYSIS: TEXTURE OF REFERENCE PLATINUM CATALYSTS

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*Appl. Catal. A: General*, 172 (1998) 7-13.

Texture investigations of a series of InCatPt reference catalysts prepared on a large scale are presented, including some basic characteristics: specific surface area, pore volume, average pore size. All the samples have clearly demonstrated a mesoporous structure. The preparation procedure did not modify appreciably the surface area or the pore volume, but substantially changed the pore size distribution. Such reference platinum catalysts can be used for test and calibration purposes and for co-ordination of new investigations. In addition, a short summary of the standardization of the surface area determination by the BET-nitrogen adsorption method is presented. A set of Russian state standard samples for calibration of instruments for specific surface area measurements of various dispersed and porous materials is described.

### NEW TYPE OF NANOPARTICLES, NANOMICELLES FORMED IN WATER-SATURATED ORGANIC SOLUTIONS OF $HFeCl_4$ AND $HClO_4$: COMPOSITION, STRUCTURE AND PROPERTIES

**E.S. Stoyanov**

*J. Chem. Soc., Faraday Trans.*,
94 (1998) 2803-2812.

It has been shown, by IR spectroscopy, that two types of nanomicelles are formed in water-saturated tributylphosphate (TBP) containing $HFeCl_4$ or HClO. Nanomicelles of type A contain one HAn molecule, whereas nanomicelles of type B contain up to 3-4 HAn molecules. Unlike classic micelles, nanomicelles A and B have a stable, almost stoichiometric, composition. The core of type A contains 26 or 30 $H_2O$ molecules and one $H_5O_2^+$ cation. Two protons of $H_5O_2^+$ are bonded to two TBP molecules from the solvate shell around the core. The first and second hydrate shells are formed around the other two protons from six water molecules inequivalent to the other water molecules of the core. The $FeCl_4^-$ anion is located in the solvate shell from a bimolecular layer of TBP molecules, whereas $ClO_4^-$ contacts with the core. The composition and structure of type B with different numbers of incorporated HAn molecules has been determined. The polarizing effect of the $ClO_4^-$ anion on the $H_5O_2^+$ cation has been found to be sufficiently strong to be detectable in the IR spectra only in nanomicelles B containing $HClO_4$ molecules. In this case the effect of the anion is experienced even by 2 TBP and 2 $H_2O$ molecules from the first coordination sphere of $H_5O_2^+$. Possible explanations for the ease of formation of mixed (HCl + $HFeCl_4$) nanomicelles are discussed.

### IR SPECTROSCOPIC STUDY OF INTERACTION BETWEEN $H_2S$ AND $O_2$ ON THE SURFACE OF $V_2O_5/\gamma$-$Al_2O_3$ CATALYSTS

**N.M. Dobrynkin, A.A. Davydov, M.V. Batygina, A.A. Budneva**

*Zh. Fiz. Khim.*, 72 (1998) 1027-1030.

The interaction of $H_2S$ with $O_2$ on the surface of $V_2O_5/\gamma$-$Al_2O_3$ catalysts has been studied by IR spectroscopy. The character of the $H_2S$ adsorption has been shown to depend significantly on the $V_2O_5$ content in the catalyst. Two types of the $H_2S$ adsorption (physical and dissociative) were observed on the catalyst with low $V_2O_5$ content (3.5 mass. %). Together with $V_2O_5$, $Al_2O_3$ played a significant role in the $H_2S$ chemisorption in this case. At the $V_2O_5$ content of 14 mass.% only one type of dissociative $H_2S$ adsorption was observed. In this case there was practically no sulfating during the $O_2$ interaction with sulfided catalyst surface.

## COMPOSITION, STRUCTURE AND IR SPECTRA PECULIARITIES OF PROTON HYDRATOSOLVATES $H^+(H_2O)_NL_P$ FORMED IN TRIBUTYLPHOSPHATE SOLUTIONS OF STRONG ACID $HFeCl_4$

**E.S. Stoyanov**

*J. Chem. Soc., Faraday Trans.*, 93 (1997) 4165-4175.

Stepwise formation of several $H^{+}\cdot NH_2O\cdot pTBP$ proton hydrates in tributylphosphate (TBP) solutions of $HFeCl_4$ has been studied under a slight, disturbing action of unsolvated $FeCl_4^-$ anions. As the basic properties of TBP and $H_2O$ molecules are comparable, consecutive proton hydration in the liquid phase takes place under conditions where proton hydrates interact with surrounding TBP molecules with the same strenght as with water molecules. Symmetric and asymmetric trisolvates of hydroxonium ion $[H_3O^{+}\cdot 3TBP]$, dihydratosolvate $[H_5O_2^{+}\cdot 4TBP]$, dimer $\{[H_5O_2^{+}\cdot \mu H_2O\cdot 2TBP]\cdot 2TBP\}_2$ and associates $\{[H_5O_2^{+}\cdot 2H_2O\cdot 2TBP]\cdot 2TBP\cdot nH_2O\}_p$, where $n$=0 - 2.5 (N=4 - 6.5), have been found to form. The associates containing $H_5O_2^+$ as a structural unit have characteristic IR bands. A profile of continuous background absorption (cba) free from other absorption bands has been obtained for the first time. This absorption appeared to be extended, its intensity rising almost proportionally to the frequency decrease in the 3000-1000 $cm^{-1}$ interval and attaining a maximum at *ca.* 1000-220 $cm^{-1}$. Cba is obsertved in IR spectra of those cations whose $H_5O_2^+$ ions are bond with water molecules and are associated.

## THE HEMATITE ($\alpha$-$Fe_2O_3$) (0001) SURFACE: EVIDENCE FOR DOMAINS OF DISTINCT CHEMISTRY

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**M. Ritter*, M. Petersen*, F. Wagner*,**
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*Phys. Rev. Lett.*, 81 (1998) 1038-1041.

Using spin-density functional theory various possible structures of the hematite (0001) surface were investigated. Depending on the ambient oxygen partial pressure, two geometries are found to be particularly stable under thermal equilibrium: one being terminated by iron and the other by oxygen. Both exhibit huge surface relaxations (-57 % for the Fe- and -79 % for the O-termination) with important consequences for the surface electronic and magnetic properties. With scanning tunneling microscopy two different surface terminations coexisting on single crystalline $\alpha$-$Fe_2O_3$ (0001) films, which were prepared in high oxygen pressures, were observed.

## FORMATION AND DECOMPOSITION OF PALLADIUM HYDRIDE PARTICLES. IMAGIN PICTURES ON THE NANOMETRE SCALE

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**V.V. Gorodetskii, V.N. Parmon (Leiden University, Leiden, The Netherlands)**

*Platinum Metals Rev.*, 42 (1998) 141-144.

Nanoscale changes in surface structure that accompany the low temperature exposure of palladium to hydrogen are reported. Field Emission Microscopy, a method for rapid in situ imaging of surface processes, has been used to examine palladium tips of radius ~ 200 nm, produced by a novel technique. Images are presented of the initial stages of the uptake of hydrogen. Subsurface hydrides were initially formed when palladium tips were exposed to hydrogen gas at low temperatures, starting at highly open surfaces present on the tip. Extruding PdH particles were also formed on top of the palladium tip and their growth was observed to proceed in a 'staccato'-like manner. Palladium crystallites remained on the surface after most of the hydrogen had been removed from the palladium sample by heating in vacuum. On heating the crystallites remained quite stable up to a temperature of ~ 700 K, but then melted back into the tip.

### HIGH RADIATION CHEMICAL YIELD OF SEPARATED ELECTRON-HOLE PAIRS IN RADIOLYSIS OF DISPERSED MAGNESIUM OXIDES IN THE PRESENCE OF $N_2O$ OR $H_2$

**A.Yu. Gladkii, Yu.I. Aristov**

*Khim. Vysokikh Energii*, 32 (1998) 179-184.

It has been shown by ESR that yields of stabilized paramagnetic $F^+$ and $V^-$ sites in the radiolysis of highly dispersed magnesium oxide depend significantly on the specific surface area of the samples (70-450 $m^2/g$) and presence of acceptors (molecular hydrogen or nitrous oxide), and can reach abnormally high values up to 10 particles/100 eV. For explanation of such yields, possible mechanisms of selective ionization of crystalline lattice defects with low ionization potentials are discussed.

## Chain-Radical Heterogeneous-Homogeneous Reactions

### THE CATALYTIC PYROLYSIS OF DICHLOROETHANE: CALCULATION OF THE CATALYSIS SPHERE

**N.A. Vasilieva, R.A. Buyanov**

*Kinet. Katal.,* 39 (1998) 631-634.

Method for calculation of the catalysis sphere, i.e., the sphere with concentration of chlorine atoms generated by the surface higher than that for thermal pyrolysis in equal conditions, has been suggested. An increase of concentration of chlorine atoms able to participate in chain process is the contribution of heterogeneous catalyst to non-branched chain-radical pyrolysis of dichloroethane. The size of the sphere was shown to determine optimal grain size of catalyst used and spatial arrangement of the catalyst in the volume of the reactor.

### CATALYTIC GENERATION OF RADICALS DURING PYROLYSIS OF n-UNDECANE

**N.A. Vasilieva, R.A. Buyanov**

*Chemistry for Sustainable Development***,**
6 (1998) 311-320.

The generation of ethyl radicals during pyrolysis of n-undecane on quartz and magnesia has been studied by freezing the radicals in an ESR spectrometer cavity. Methodic features making it possible to avoid uncontrolled effect of satellite pyrolysis stages and reactions are described. The activation energy of the generation of radicals on quartz is shown to equal 322 kJ/mol and correspond to the rupture of the C-C bond in the hydrocarbon molecule during the thermal pyrolysis. On magnesia the phenomenon of the surface "ignition" is observed at 903 K. Below this temperature ordinary thermal pyrolysis takes place, while at higher temperatures radicals are generated with the activation energy of 62.8 kJ/mol. The catalyst is shown to generate additional radicals at these values of the activation energy in comparison with the thermal pyrolysis under similar conditions. The role of the reaction medium in the "ignition" of the catalyst surface is discussed.

# Studies on Electrocatalytic Processes

### ELECTROCATALYTIC CONVERSION OF METHANE TO SYNGAS OVER Ni ELECTRODE IN A SOLID OXIDE ELECTROLYTE CELL

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**V.A. Sobyanin (Institute of High Temperature Electrochemistry, Ekaterinburg, Russia)**

*Appl. Catal. A: General*, 165 (1997) 301-308.

Electrocatalytic conversion of methane in a cell with a solid oxygen conducting electrolyte:

$CH_4$, Ni | $0.9ZrO_2$+$0.1Y_2O_3$ | Pt+$PtO_2$, air

was studied at the temperature range 750-850 $^oC$. The Ni electrode was found to be an active electrode-catalyst for partial oxidation of $CH_4$ to syn-gas with the concentration ratio $[H_2]:[CO_2]\cong2$. The $CH_4$ conversion and CO selectivity attained 85-95 % and 90-95 %, respectively, at 800-850 $^oC$. Under these conditions the Ni electrode-catalyst was stable to coking and had a negative value of electrode potential with respect to an air counter electrode. The direct partial oxidation mechanism was shown to be the most probable for the electrocatalytic conversion of $CH_4$ to syn-gas.

### SYNGAS PRODUCTION FROM METHANE IN AN ELECTROCHEMICAL MEMBRANE REACTOR

**V.A. Sobyanin, V.D. Belyaev, V.V. Gal'vita**

*Catal. Today,* 42 (1998) 337-340.

Electrocatalytic conversion of methane over Ag-, Pt-, Ni- and Pt+$CeO_2$-based electrode-catalysts in a cell with a solid oxygen conducting electrolyte:

$CH_4$, el.-cat. | $0.9ZrO_2$+$0.1Y_2O_3$ | Pt+$PtO_2$, air

was studied at 660-850 $^oC$ and the ratio of methane and electrochemically pumped oxygen flows of 0.8-2.0. Unlike Ag and Pt+$CeO_2$, the Ni and Pt electrodes were found to be active electrode-catalysts for partial oxidation of methane to syngas with the concentration ratio of $[H_2]/[CO]\approx2$.

### EFFECT OF ANODIC CURRENT ON CARBON DIOXIDE REFORMING OF METHANE ON Pt ELECTRODE IN A CELL WITH SOLID OXIDE ELECTROLYTE

**V.D. Belyaev, V.V. Gal'vita, V.A. Sobyanin**

*React. Kinet. Catal. Lett.,* 63 (1998) 341-348.

The carbon dioxide reforming of methane in a cell with a solid oxygen-conducting electrolyte:

$CH_4$ + $CO_2$, Pt | $0.9ZrO_2$+$0.1Y_2O_3$ | Pt+$PtO_2$, air

has been studied. The results evidence that the anodic polarization of the Pt electrode does not influence its catalytic activity in the $CO_2$-$CH_4$ reaction. In other words, a Non-Faradaic Modification of the Catalytic Activity is not observed in this system. Electrochemically supplied oxygen is consumed completely to oxidize methane as well as hydrogen and carbon monoxide produced by the $CO_2$-$CH_4$ reaction. As a result, the $CH_4$ conversion slightly increases, while the $CO_2$ conversion and yields of $H_2$ and CO decrease as compared to their open-circuit values.

### MODELING OF PRESSURE-DRIVEN MEMBRANE SEPARATION OF ELECTROLYTES. HIGH TEMPERATURE APPROXIMATION

**A.G. Maryasov, G.L. Semin**

*J. Membrane Sci.*, 142 (1998) 205-212.

A model of pressure-driven process of electrolyte separation is presented allowing to explain qualitatively the effect of negative rejection, that is the increase in transmembrane concentration of some components as compared with those for pre-membrane region. This effect was used earlier in the homogeneous catalyst regeneration. (Jointly with the Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia)

### STUDY OF AlN COATINGS FOR MICROSTRIP GAS CHAMBERS

**A. Buzulutskov*, A. Bondar*, L. Mironenko*,**
**V. Nagaslaev*, L. Shekhtman*, A. Tatarinov*,**
**S. Koshcheev, A. Belyanin*, A. Blaut-Blachev*,**
**L. Bouilov*, B. Spitsyn* (Budker Institute of Nuclear Physics, Novosibirsk, Russia)**

*NIM*, 409 (1998) 33-36.

A new semiconducting coating material for microstrip gas chambers (MSGCs) has been studied: AlN. The conductivity of AlN films at room temperature varies from $10^{-10}$ to $10^{-12}$ $\Omega^{-1}cm^{-1}$ depending on the preparation conditions; it increases with temperature with activation energy of 0.8-0.9 eV. The electron-induced secondary electron emission yield from AlN has been measured: it is about 5 at the maximum. The influence of the substrate nature and that of the film's and MSGC's preparation conditions on the structure and composition of AlN films were investigated using scanning electron microscopy and X-ray photoelectron spectroscopy

### PARTIAL OXIDATION OF ETHANE IN A THREE-PHASE ELECTRO-FENTON SYSTEM

**E.R. Savinova, A.O. Kuzmin, A. Parmaliana*, V.N. Parmon (Institute of Energy Transformation and Accumulation, Messina, Italy)**

*Stud. Surf. Sci. & Catal., Natural Gas Conversion V*, 119 (1998) 429-434.

Partial oxidation of ethane to acetaldehyde and ethanol in a three-phase electrocatalytic system under mild conditions (1 bar, 360 K) is demonstrated. Factors controlling the rate and selectivity of the process have been evaluated and the radical-chain oxidation mechanism has been proposed.

## Fractal Geometry to Give New Models of Porous Media for Catalysts Investigation

### ACETONE ADSORPTION ON HYDROXYLATED SILICA GEL: CORRELATION OF SORPTION ISOTHERMS AND IR SPECTRA

**A.G. Okunev, E.A. Paukshtis, Yu.I. Aristov**

*React. Kinet. Catal. Lett.*, 65 (1998) 161-167.

Results of adsorption and IR studies on the interaction of acetone with fully and partially hydroxylated surfaces of a KSS-3 silica gel are presented. Two plateaus on adsorption isotherms and two CO bands in IR adsorption spectra are in close connection, which clearly indicates two adsorption complexes of acetone with different surface OH groups of silica. The weaker adsorption form (CO stretching vibration at 1705 $cm^{-1}$) corresponds to the formation of an adsorption complex between an acetone molecule and a terminal OH-group (OH-stretching vibration at 3740 $cm^{-1}$). An abnormally high fractal dimension of silica gel surface has been obtained and discussed.

### EVALUATION OF THE FRACTAL DIMENSIONALITY OF DISPERSED SYSTEMS BY AN EQUATION DESCRIBING ADSORPTION IN MICROPORES

**G.Yu. Cherkashinin, V.A. Drozdov**

*Zh. Fiz. Khim.*, 72 (1998) 88-92.

Equation describing the adsorption of vapor in micropores with inhomogeneous pore size distribution has been used to derive a simple relation between the filling of the pore volume and the adsorption potential: $W(A) \propto A^{D-3}$, where D is the fractal dimension. Comparative analysis of this relation with equation used for evaluation of the fractal dimension from SAXS data has shown their functional similarity. The relation was used for processing of experimental nitrogen adsorption isotherms (T = 77 K) on a series of carbon sorbents. Obtained values of the fractal dimensions of the micropore space in the carbon materials studied are in the range of 2.61-2.72.

## Catalysis by Metal Complexes

### SILICA-SUPPORTED ZIRCONOCENE CATALYSTS: PREPARATION, CHARACTERIZATION, AND ACTIVITY IN ETHYLENE POLYMERIZATION

**B.L. Moroz, N.V. Semikolenova, A.V. Nosov, V.A. Zakharov, S. Nagy*, N.J. O'Reilly** (*Occidental Chemical Corporation, Technology Center, Grand Island, USA; **Lyondell Petrochemical Corporation, Lyondell Technology Center, Alvin, USA)**

*J. Molec. Catal. A: Chemical,* 130 (1998) 121-129.

Supported catalysts for ethylene polymerization have been prepared by interaction of $Cp_2ZrX_2$ (Cp = $h^5$-$C_5H_5$, X = Cl or $CH_3$) with silica chemically modified with $(CH_3)_3SiCl$ (TMCS) or trialkylaluminium compounds $AlR_3$ (R= $C_2H_5$ (TEA) and ${}^iC_4H_9$ (TIBA)). The interactions between the modificators and the silica surface have been examined by $^1H$ solid-state MAS NMR spectroscopy, DRIFTS and chemical analysis. The $Cp_2Zr(CH_3)_2/SiO_2$-TMCS catalyst showed a fairly high activity in ethylene polymerization (30-300 kg PE $(mol\ Zr{\cdot}h{\cdot}bar)^{-1}$ ) even in the absence of any cocatalysts specially added. The addition of the cocatalyst (MAO or TIBA) led to further increase in the activity of the supported catalysts. Polyethylene obtained with the $Cp_2Zr(CH_3)_2/SiO_2$-TMCS catalyst without any cocatalyst consisted of uniform polymer particles of a spherical shape replicated that of the silica particles, whereas the shapeless aggregates of finely dispersed polymer particles similar to those usually obtained with homogeneous systems were produced with the same supported catalyst in the presence of the MAO cocatalyst.

## THE IRS-DR STUDY OF UNTERACTION OF THE SUPPORTED CATALYST BASED ON THE ORGANIC NICKEL CHELATE WITH CARBON MONOXIDE AND ETHYLENE

**V.N. Panchenko, V.A. Zakharov, E.A. Paukshtis**

*J. Molec. Catal. A: Chemical,* 135 (1998) 115-120.

The interaction of the supported catalyst based on the organic nickel chelate compound (I) with carbon monoxide and deuterated ethylene has been studied using IRS-DS. The surface nickel compound (SNC) interacts with carbon monoxide in the same manner as the initial nickel complex (I). The reaction of SNC or nickel complex (I) with CO yields nickel acyl complex (V) (a product of the CO insertion into the Ni-Ph bond), ester (VIII) and various nickel carbonyls (VI).

According to the IRS data, the interaction between SNC and deuterated ethylene gives a polymer. The subsequent carbon monoxide introduction results in the same products as in the case of the CO reaction with SNC. The interaction between ethylene and SNC pretreated with carbon monooxide does not lead to polymerization.

## ACID- AND BASE-INDUCED REVERSIBLE TRANSFORMATIONS OF PLATINUM CARBONYL CLUSTERS IN WATER-ACETONE SOLUTIONS AND ON ALUMINA SURFACE

**N.B. Shitova, L.Ya. Alt, I.G. Perelevskaya**

*Zh. Neorgan. Khim.,* 43 (1998) 800-804.

Mutual transformations of platinum carbonyl clusters of different nuclearity and the same stoichiometric composition $[Pt_3(CO)_6]_n^{2-}$ (n = 2, 3, 5, ~10) in water-acetone solutions under the effect of acids and bases have been studied. It has been shown by IR and NMR spectroscopy that the change of the nucleation number of the clusters accompanying their redox transformations is a reversible reaction:

$$[Pt_3(CO)_6]^{2-}_{\sim10} \underset{HCl}{\overset{H_2O}{\rightleftarrows}} [Pt_3(CO)_6]^{2-}_{5} \underset{HCl}{\overset{NaOH}{\rightleftarrows}} [Pt_3(CO)_6]^{2-}_{2\sim3}$$

Meanwhile, both decrease and increase of the cluster nuclearity is accelerated by an increase of the water concentration. This indicates that $OH^-$ and $H^+$ ions, whose concentration grows with the $[H_2O]$ increase due to higher dissociation of NaOH and HCl in the water-acetone solution, participate in the redox transformations. As in solutions of strong acids, $Pt_6$ cluster has been shown to transform into $Pt_{15}$ in the presence of alumina, which has high surface acidity. The preservation of the cluster with the low nucleation number on the support surface was possible only in the presence of a competitive adsorption agent blocking strong acid sites of $\gamma$-$Al_2O_3$ surface.

## REACTIVITY OF TRANSITION-METAL-MODIFIED, KEGGIN-TYPE HETEROLOPYCOMPLEXES IN THE HOMOGENEOUS OXIDATION OF CYCLOHEXANE AND ADAMANTANE

**M.R. Cramarossa*, L. Fortri*, M.A. Fedotov, L.G. Detusheva, V.A. Likholobov, L.I. Kuznetsova, G.L. Semin, F. Cavani**, F. Trifiro** (*University of Modena, Modena, Italy; **University of Bologna, Bologna, Italy)**

*J. Molec. Catal. A: Chemical,* 127 (1998) 85-94.

The oxidation of cyclohexane and adamantane catalyzed by Keggin-type transition-metal-containing heteropolycomplexes (TMC-HPCs) is reported. The reactions were carried out at 20 °C in $CCl_4$ or in $CH_2Cl_2$ as reaction solvent in the presence of *t*-butylhydroperoxide (*t*-BuOOH) as oxidizing agent. A radical chain mechanism of oxidation by *t*-BuOOH in the presence of molecular oxygen is proposed for all complexes tested, involving a R-H hydrogen atom abstraction by an intermediate active form of the TMC-HPC. Under the examined conditions molecular oxygen was necessary to initiate the reaction. The preparation of Co(II), Fe(III) and Cr(III)-HPC samples and their composition under reaction conditions are also discussed, based on $^{31}$P-NMR and UV-VIS adsorption spectra.

## Stereoselective Catalysis

### OXIDATION OF METHYL PHENYL SULFIDE WITH HYDROGEN PEROXIDE CATALYZED BY Ti(IV)-SUBSTITUTED HETEROPOLYTUNGSTATE

**O.A. Kholdeeva, R.I. Maksimovskaya,**
**G.M. Maksimov, K.I. Zamaraev**

*React. Kinet. Catal. Lett.*, 63 (1998) 95-102.

Alkylammonium salts of Ti(IV)-substituted heteropolytungstate, $PW_{11}TiO_{40}^{5-}$, catalyze oxidation of methyl phenyl sulfide with hydrogen peroxide at ambient conditions. The yield of the corresponding sulfoxide and sulfone is practically quantitative. $^{31}P$ NMR study reveals the formation of two peroxotitanium heteropoly complexes, which differ dramatically in their activity towards the organic sulfide.

## Selective Water Sorbents and Heat Accumulating Materials

### THE PROPERTIES OF THE "LiBr-H$_2$O" SYSTEM IN SILICA GEL PORES: SORPTION EQUILIBRIUM

**L.G. Gordeeva, D. Restuccia*, D. Cacciola*,**
**Yu.I. Aristov (Institute of Energy Transformation and Accumulation, Messina, Italy)**

*Zh. Fiz. Khim.*, 72 (1998) 1236-1240.

The sorption equilibrium of the pair water-lithium bromide dispersed in the mesopores of the KSKG silica gel was studied by TGA in the temperature range of 40-135 °C at the water pressure $p_{H_2O}$= 7.5-81.0 mbar. The sorption has been shown to be monovariant at low relative water pressures and result in the formation of dispersed crystalline monohydrate $LiBr\cdot H_2O$ with the sorption ability higher than that of the bulk one. Further water sorption results in the formation of a water solution of the salt in the pores with the properties close to those of the bulk solution. The isosteric water desorption heat measured in the dispersed system was equal to 77.0±1.5 kJ/mol at N=1 and 44.5±2.0 kJ/mol at N>1 (N, mole $H_2O$/mole LiBr). The apparent activation energy of water desorption (27.4±1.5 kJ/mol) appeared to be significantly lower than its desorption heat. Therefore, it was suggested that the water diffusion in the silica gel pores and/or in the dispersed solution is the rate-determining stage of the desorption process. The main features of the water sorption appeared to be similar in composite systems LiBr – mesoporous silica gel and $CaCl_2$ – mesoporous silica gel. This means that the features of the water sorption in a system impregnated salt – mesoporous host-matrix are mostly determined by the character of the system rather than the chemical nature of the salt. Obtained data can be useful for understanding of phenomena taking place during the transformation of a substance into the dispersed state and for analysis of possible applications of the material under study in adsorption thermal pumps, systems for air conditioning and drying, etc.

### SELECTIVE WATER SORBENTS FOR MULTIPLE APPLICATIONS. 5. LiBr CONFINED IN MESOPORES OF SILICA GEL: SORPTION PROPERTIES

**L.G. Gordeeva, G. Restuccia*, G. Cacciola***
**(Institute of Energy Transformation and Accumulation, Messina, Italy), Yu.I. Aristov**

*React. Kinet. Catal. Lett.,* 63 (1998) 81-88.

The paper presents sorption properties of a selective water sorbent based on mesoporous KSKG silica gel as a host matrix and lithium bromide as a hygroscope salt. Sorption isobars, isochores and isotherms measured at T=40-120 °C and partial vapor pressure of 7.5-81.0 mbar indicated two types of water sorption: 1) formation of a solid crystalline LiBr monohydrate at low amounts of sorbed water, and 2) vapor absorption by the salt solution at higher sorptions. Sorption properties of the LiBr monohydrate are found to change significantly due to salt impregnation into the mesoporous silica gel, whereas the solution confinement to the mesopores did not change its water sorption properties as compared to the bulk solution. Desorption curves follow a first order kinetics in the temperature range of 60-130 °C at different vapor pressures.

### SELECTIVE WATER SORBENTS FOR MULTIPLE APPLICATIONS. 6. FRESHWATER PRODUCTION FROM THE ATMOSPHERE

**L.G. Gordeeva, M.M. Tokarev, V.N. Parmon, Yu.I. Aristov**

*React. Kinet. Catal. Lett.*, 65 (1998) 153-159.

An application of new selective water sorbents for freshwater production from the atmosphere is considered. A general scheme of water production is presented and its efficiency in different climatic areas is discussed. The results of lab-scale tests have demonstrated the feasibility of this method with the output of 3-5 kg of water per 10 kg of the dry sorbent per day.

### SELECTIVE WATER SORBENTS FOR MULTIPLE APPLICATIONS. 7. HEAT CONDUCTIVITY OF $CaCl_2$ - $SiO_2$ COMPOSITES

**Yu.I. Aristov, G. Restuccia*, G. Cacciola*, M.M. Tokarev (Institute of Energy Transformation and Accumulation, Messina, Italy)**

*React. Kinet. Catal. Lett.*, 65 (1998) 277-284.

The experimental data on the low temperature heat conductivity of a consolidated bed made of the $CaCl_2$-$SiO_2$ composite material measured by the “hot wire method” are presented. The conductivity appears to increase strongly with a raise of the sorbed water amount and reaches 0.53 W/m K at a high water content when the bed is completely saturated with the salt solution. $\lambda$ values obtained appear to be much higher than those for zeolite 4A, which is a competitor solid adsorbent proposed for sorption cooling and heating machines. Finally, the influence of the thermal conductivity on the specific power of sorption heat pump based on the “$CaCl_2$/ $SiO_2$-water” pair is briefly discussed.

### $^1$H NMR IN NANOCRYSTALS $CaCl_2 \cdot XH_2O$ AND ADSORPTION ISOBARS OF WATER IN SYSTEM $CaCl_2$ - SILICAGEL

**M.M. Tokarev, S.G. Kozlova, S.P. Gabuda, Yu.I. Aristov**

*Zh. Strukt. Khim.*, 39 (1998) 261-266.

Mobility of $H_2O$ molecules in nanocrystals and other phases $CaCl_2 \cdot xH_2O$ (X=0÷12), formed in silicagel nanopores upon water vapor sorption have been studied by $^1$H NMR. Sorption properties of $CaCl_2$, confined in pores of micro- and mesoporous silcagels have been measured.

## Nature, Mechanism and Physicochemical Essence of the Low-Waste, Environmentally Friendly Methods of Catalyst Preparation

### PROPERTIES OF LANTHANUM AND BARIUM HEXAALUMINATES, PREPARED BY SOLID-STATE REACTION AND BY 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 and Mechanochemistry, Novosibirsk, Russia)**

*Neorg. Mater.*, 34 (1998) 996-1002.

Catalytic activity, specific surface and radiospectroscopic characteristics of substituted barium hexaaluminates, prepared by mechanochemical activation, are determined. Data of X-ray phase analysis of synthesized pure barium and lanthanum hexaaluminates are represented.

### EFFECT OF MECHANICAL ACTIVATION ON PHASE TRANSFORMATION IN TRANSITION ALUMINAS

**O.V. Andryushkova*, O.A. Kirichenko*, V.A. Ushakov, V.A. Poluboyarov* (Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia)**

*Solid State Ionics*, 101-103 (1997) 647-653.

The influence of mechanical activation (MA) on $\gamma$- and $\chi$-$Al_2O_3$ is studied by means of X-ray phase analysis. The change of specific surface of aluminum oxide after MA is estimated. It is shown that the mechanical treatment leads to the change of the sequence of solid-phase transitions in aluminum oxide and a decrease of $\alpha$-$Al_2O_3$ formation temperature.

## MECHANOCHEMICAL SYNTHESIS OF DICALCIUM FERRITE WITH THE PEROVSKITE STRUCTURE

**N.V. Kosova*, E.T. Devyatkin*, E.G. Avvakumov*, I.I. Gainutdinov*, A.Yu. Rogachev*, Yu.T. Pavlyukhin*, L.A. Isupova, V.A. Sadykov (Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia)**

*Neorg. Mater.,* 34 (1998) 478-484.

Mechanochemical synthesis of dicalcium ferrite with the perovskite structure from waterless and hydrated Ca and Fe oxides has been studied by X-ray, DTA, IR and N  spectroscopy methods. It was shown, that in the first case $Ca_2Fe_2O_5$ synthesis proceeds with high rate in one stage directly in the activator. In the second case there is no interaction of components, however preliminary mechanochemical activation of mixture essentially decrease the temperature interval of $Ca(OH)_2$ dehydration and subsequent formation of $Ca_2Fe_2O_5$ (up to 600 $^oC$). The product formed upon heating is well crystallized and is characterized by high specific surface 13 $m^2/g$, enough for catalytic processes to be effective.

## USE OF MECHANOCHEMICAL METHODS IN PREPARATION OF SUPPORTED CATALYSTS

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

*Kinet. Katal*., 39 (1998) 465-471.

Mechanochemical activation of supports results in the increase of their sorption capacity, decrease of the reduction temperature of supported nickel chloride and growth of the catalytic activity of supported nickel in the ethylene hydrogenation. The increase of the sorption capacity is caused by the formation of ‘juvenile’ surface and appearance of the ends of defects of the crystalline structure on it. The reduction temperature of supported nickel is decreased either due to the participation of conductivity electrons of mechanically activated supports in certain reaction stages or due to the strengthening of the electron-donor properties of $O_2^-$ anions after the mechanochemical activation of oxides. The growth of the catalytic activity can be explained both by the increased dispersity of supported metal and by the effect of the defects of the support. A number of properties of catalytic systems are caused entirely by the effect of defects.

## NEW CATALYSTS FOR SELECTIVE HYDROGENATION

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*Chemistry for Sustainable Development*, 5 (1997) 585-589.

The hydrides of magnesium intermetallides (HIM) with the metals of iron subgroup ($Mg_2MH_x$, where M=Fe, Co, Ni, x~4-6) were studied in reactions of diene and acetylene hydrocarbons hydrogenation. Highly efficient catalysts of diene and acetylene hydrocarbons reduction to olefines with selectivity close to 100% are revealed. Mechanism of diene and acetylene hydrocarbons hydrogenation over hydrides of magnesium intermetallides has been considered. Methods to prepare catalysts based on HIM with the use of mechanochemical activation and pseudoboehmite and metallic magnesium and aluminum as a binder were developed.

## MECHANOCHEMICAL ACTIVATION IN THE TECHNOLOGY OF HIGH-TEMPERATURE OXIDE CATALYSTS

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*Chemistry for Sustainable Development*, 6 (1998) 207-210.

The mechanochemical activation of various solid-phase precursors is shown to result in the decrease of the annealing temperature during the synthesis of perovskites and make it possible to prepare highly dispersed powders. Factors determining the relative easiness of the interaction between activated compounds (oxides, hydroxides or carbonates) are discussed. The thermodynamics of the corresponding reactions and acid-base properties of the initial compounds are the most important among them. The reactivity of the synthesized perovskites in the dissolution and catalytic oxidation of CO and $CH_4$ has been determined. It has been shown to be a complex function of the calcination temperature due to the differences in the defect structure, dispersity and morphology of the particles.

## EFFECT OF MECHANICAL ACTIVATION ON BULK AND SURFACE DEFECT STRUCTURE AND REACTIVITY OF SOME TRANSITION METAL OXIDES

**V.A. Sadykov, L.A. Isupova, N.N. Bulgakov**

*Chemistry for Sustainable Development***,**
6 (1998) 215-222.

Factors determining the structural sensitivity of the CO oxidation catalyzed by some dispersed transition metal oxides and mixed oxides of transition and rare-earth metals with the perovskite structure are discussed. The surface structure of defects, which is often dependent on the bulk structure, is shown to be the most important factor. The mechanical activation makes it possible to create uniquely high density of the surface and bulk point defects and study their effect on the density of extended defects, cooperative lattice deformations and reactivity (catalytic activity) of simple and complex oxides. With the exception of spinel oxides with a broad region of instoichiometry, in all systems studied point defects do not affect the steady-state catalytic properties, which are determined by the extended defects. Nevertheless, they play a decisive role in the relaxation of the structure of defects and reactivity of oxides during their annealing or under the action of the reaction medium.

## REGULARITIES OF THERMOCHEMICAL ACTIVATION OF BAYERITE AND PROPERTIES OF THE RESULTING PRODUCTS

**E.A. Taraban, B.P. Zolotovskii, R.A. Buyanov, G.S. Litvak**

*Chemistry for Sustainable Development***,**
5 (1997) 541-545.

It has been elucidated that thermochemical activation (TCA) of bayerite leads to the formation of chemically active product. The process of this product hydration has been studied in different conditions, and resulting phases were identified. The properties of hydrargillite and bayerite TCA products were compared.

## ABOUT MECHANISM OF METHANOL SYNTHESIS

**T.M. Yurieva, O.V. Makarova, L.M. Plyasova, T.A. Krieger**

*Stud. Surf. Sci. & Catal., Natural Gas Conversion IV,*
107 (1997) 35-40.

The reduction of a.m. ZnO-based solid solution, which is proved to be the active component of methanol synthesis catalyst, in $H_2$ results in the allocation of 50% Cu as metal particles over ZnO surface and the dissolution of a corresponding amount of hydrogen in the bulk of ZnO. Upon $CO_2$ adsorption the formation of methanol and oxygen-containing sites $Cu^{+1}$-O-$Cu^{+1}$ proceeds. There are two main directions of oxygen-containing sites transformation: (1) interaction with hydrogen to produce water and copper atoms; (2) interaction with CO with methanol formation. Probably the total methanol formation rate is mainly contributed by the rate of CO hydrogenation, though CO hydrogenation is not possible but in the presence of $CO_2$.

## COPPER/COBALT CATALYST FOR HIGHER ALCOHOLS SYNTHESIS FROM SYNGAS

**G.G. Volkova, T.A. Krieger, L.M. Plyasova, V.I. Zaikovskii, T.M. Yurieva**

*Stud. Surf. Sci. & Catal., Natural Gas Conversion IV,*
107 (1997) 67-72.

It was shown that $CuCoO_2$ was the most active and selective precursor of Cu-Co-Al-Zn mixed oxide catalysts for higher alcohols synthesis. $CuCoO_2$ transformed to low-temperature alloy Cu-Co and cobalt carbide under stream of $CO+H_2$. Temperature range of higher alcohols formation was coincident with temperature of existing $Co_2C$ in this catalyst - 310-390 °C. Hydrocarbons were the main products out of this temperatures where catalyst consists of only metal phases: Cu-Co alloy (<300 °C) or individual Cu and Co metals (>390 °C). It was suggested that cobalt carbide was the active state responsible for nondissociative adsorption and oxygenates synthesis.

## MECHANISM OF FORMATION OF POROUS $Al_2O_3$/Al COMPOSITES IN HYDROTHERMAL CONDITIONS

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*React. Kinet. Catal. Lett.*, 64 (1998) 301-308.

Main features of the formation of porous composites by hydrothermal treatment of powdered aluminum were studied by scanning electron microscopy, TEM, XPD, IR spectroscopy of lattice modes, and thermal analysis. Hydrothermal oxidation of aluminum was shown to proceed *via* generation and subsequent oriented growth of well-crystallized boehmite platelets, whose subsequent dehydration yields γ-alumina. Relation between the degree of the metal oxidation and specific surface area/crushing strength of the composites was analyzed.

### THE STUDY OF FORMATON OF SUPPORTS AND CATALYSTS BASED UPON $Al_2O_3$/Al CERMETS

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**A.N. Salanov, G.N. Kustova, G.S. Litvak,**
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**A.S. Ivanova, A.Ya. Rozovskii*, G.I. Lin*,**
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*Stud. Surf. Sci. & Catal.*, *Preparation of Catalysts VII,* 118 (1998) 797-806.

The regularities of formation of porous metalloceramic supports and catalysts of A/$Al_2O_3$/Al type via hydrothermal oxidation of powdered aluminium in mixture with various dispersed additives (A) have been investigated. The interrelation between the parameters of composites synthesis (temperature and time of processing, type of the aluminium powder and nature of additives) and their properties including phase composition, texture, mechanical and catalytic properties (CO and butane oxidation, methane steam reforming, Fischer-Tropsch synthesis) was analysed.

### NEW TYPE OF CATALYTIC MATERIAL BASED UPON ALUMINA EPITAXIALLY GROWN ONTO THIN ALUMINUM FOIL

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**A.N. Salanov, S.V. Tsybulya, G.M. Alikina,**
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**Novosibirsk, Russia)**

*Mater. Res. Soc. Symp. Series*, 497 (1998) 71-78.

Formation of planar layered $Al_2O_3$/Al composites via aluminium foil anodic-spark oxidation was studied by using SEM and XRD. A lateral growth of the primary non-porous alumina islands was shown to proceed up to covering all the surface, and mainly this layer determines high thermal stability of composite. A washcoating by alumina suspension substantially increases pore volume and water absorption capacity. The catalysts based upon platinum group metals and transition metal oxides demonstrate high activity in the reactions of CO and hydrocarbons oxidation and selective reduction of nitrogen oxides by hydrocarbons.

### ADVANCED METAL/CERAMIC CATALYSTS FOR HYDROGEN GENERATION BY STEAM REFORMING OF HYDROCARBONS

**S.F. Tikhov, V.A. Sadykov, A.N. Salanov,**
**Yu.V. Potapova, S.V. Tsybulya, G.S. Litvak,**
**S.N. Pavlova**

*Mater. Res. Soc. Symp. Series*, 497 (1998) 121-128.

The main features of porous metal/ceramic catalysts of hydrocarbons steam reforming upon their formation via hydrothermal treatment of the powdered aluminum and lanthanum nickelates mixture in the confined space are elucidated. For catalysts obtained via this route, their polymodal pore structure was found to approach the optimum one. The phase composition of the acive component precursor was shown to have a great impact on the specific catalytic activity of catalysts.

### PHYSICOCHEMICAL PROPERTIES OF $M_nO_m$-$ZrO_2$ (M=Ca, Ba, Sm, Yb) COMPOSITIONS

**A.S. Ivanova, E.M. Moroz, G.S. Litvak**

*React. Kinet. Catal. Lett.*, 65 (1998) 169-175.

The influence of the nature of $M_nO_m$ and treatment temperature of zirconia-based systems $M_nO_m$-$ZrO_2$ (M=Ca, Ba, Sm, Yb) of approximately equimolar composition on their phase composition and dispersity has been studied. The samples are shown to contain solid solutions based on cubic $ZrO_2$. Besides, $CaZrO_3$ perovskite is present in the CaO-$ZrO_2$ system, and a solid solution based on $Sm_2O_3$ is present in the $Sm_2O_3$-$ZrO_2$ system. The particle sizes in the corresponding solid solution vary from 25 to 150 A, while in the perovskite phase they are in the 300-500 Å range, with the treatment temperature increasing from 623 to 1273 K.

### EFFECT OF HEAT-TREATMENT CONDITIONS ON THE SPECIFIC SURFACE AREA OF CALCIUM OXIDE

**A.S. Ivanova, B.L. Moroz, G.S. Litvak, L.G. Okkel'**

*Neorgan. Mater.*, 34 (1998) 432-435.

The effect of $Ca(OH)_2$ calcination conditions on the specific surface area and pore structure of the resultant CaO was studied. Materials with a large specific surface area and pore volume were obtained by vacuum calcination. Exposure to air was found to give rise to hydration and carbonation of CaO, accompanied by a decrease in specific surface and total pore volume.

## INFLUENCE OF THE CONDITIONS OF THERMAL TREATMENT ON THE FORMATION OF THE POROUS STRUCTURE OF VANADIUM-TITANIUM OXIDE CATALYSTS

**G.A. Zenkovets, V.Yu. Gavrilov, G.N. Kryukova, S.V. Tsybulya**

*Kinet. Katal.,* 39 (1998) 122-127.

Influence of the conditions of thermal treatment on the formation of porous structure of vanadium-titanium oxide catalysts at wide variation of composition was studied. It has been shown, that $V_2O_5$ additives stabilize the $TiO_2$ surface value and promote maintaining of its thin porous structure upon thermal treatment in consequence of vanadium oxide crystals introducing into the structure of aggregates, consisting of dispersed anatase particles. Transformation of binary samples texture proceeds mainly by mechanism of surface diffusion.

## COMPOSITION, PHYSICOCHEMICAL PROPERTIES, AND CATALYTIC PERFORMANCE OF THE PRODUCTS OF THERMAL TREATMENT OF $Al_2(SO_4)_3 \cdot 18H_2O$

**N.S. Kotsarenko, V.P. Shmachkova, V.M. Mastikhin**

*Kinet. Katal.,* 39 (1998) 575-582.

Influence of $Al_2(SO_4)_3 \cdot 18\ H_2O$ thermal treatment on properties of the products formed has been studied by a complex of physico-chemical methods. Catalytic activity of the products of thermal treatment has been studied in model reactions of butene-1 to butene-2 isomerization and isobutyl alcohol dehydration. By NMR $^{27}Al$ MAS it has been shown, that changes take place in coordination sphere of aluminum upon the calcination - water molecules are substituted by hydroxyl and sulfate groups. The processes of hydrolysis and condensation of AlOH- and SOH-groups, leading to substitution of all ligands by sulfate, are completed at temperatures up to 250 °C. Specific surface and catalytic activity of aluminum sulfate in reactions studied are defined by thermal treatment conditions. Waterless crystal $Al_2(SO_4)_3$, heated at 400-500 °C, is characterized by the most high activity.

## STUDY OF COMPOSITION OF LIQUID AND SOLID PRODUCTS OF THERMAL AND THERMAL CATALYTIC DECOMPOSITION OF POLYETHYLENE, POLYVINYL ALCOHOL AND POLYSTYRENE

**N.I. Maksimova, O.P. Krivoruchko, V.N. Sidel'nikov**

*Zh. Prikl. Khim***.,** 8 (1998) 1315-1321.

The comparison of the products of thermal catalytic decomposition of polymers: polyethylene, polyvinyl alcohol and polystyrene with the products of their thermal decomposition has been made at temperatures 300-600 °C in flowing nitrogen using chromato-mass spectroscopy and X-ray methods.

## PHYSICOCHEMICAL BASES FOR THE PREPARATION OF SPINEL SUPPORTED BIMETALLIC PLATINUM CATALYSTS FOR DEHYDROGENATION OF LOWER PARAFFINS

**N.A. Pakhomov, R.A. Buyanov, B.P. Zolotovskii**

*Stud. Surf. Sci. & Catal., Preparation of Catalysts VII,* 118 (1998) 185-194.

The demand in lower olefins for the production of high-octane ecologically benign gasoline additives such as MTBE and alkylates has considerably grown, stimulating the interest to the dehydrogenation of lower paraffins. The latest tendency in the improvement of the lower paraffin dehydrogenation technology is the use of bimetallic systems based on supported platinum instead of traditional environmentally harmful $Cr_2O_3$-$Al_2O_3$ catalysts. The use of high thermally stable zinc- and magnesium-aluminum spinels to support such catalysts opened an absolutely new possibility to perform the dehydrogenation in water vapor, thus significantly increasing the yield of desired products.

The present situation in this field is somewhat paradoxical: practically all possible methods for preparation of such catalysts are already patented, while no satisfactory preparation theories have been developed. In the present communication an attempt is made to fill the gap in this field. Physicochemical bases for the preparation of new generation catalysts for dehydrogenation of $C_3$-$C_5$ paraffins presented in this paper are based on the results of investigations performed lately in our laboratory. For the development of the scientific bases for the preparation of such catalysts, it was necessary to find a complex solution of two interconnected problems: i) development of the method for the synthesis of the spinel support with desired composition and textural characteristics, and ii) development of theoretical and experimental approaches for the synthesis of bimetallic active component with desired composition, structure and dispersity.

## FISCHER-TROPSCH SYNTHESIS OVER COBALT-CONTAINING UNSUPPORTED CATALYSTS IN SLURRY REACTOR. EFFECT OF THE METALLIC CO PARTICLE SIZE ON THE CATALYST SELECTIVITY

**A.A. Khassin, T.M. Yurieva, V.N. Parmon**

*React. Kinet. Catal. Lett.,* 64 (1998) 55-62.

Catalytic properties of a variety of Co-MgO and Co-ZnO unsupported catalysts were investigated in Fischer-Tropsch synthesis in a tetradecane-filled slurry reactor at atmospheric pressure and a $CO/H_2$ ratio 1:2. An effect of size of dispersed metallic cobalt on the selectivity of catalyst in the FT synthesis (the $\alpha$ value of the Anderson-Schulz-Flory distribution) has been found: the smaller the particle, the higher the $\alpha$ value. A possibility to control the $\alpha$ value in the range of 0.6-0.8 for both saturated and unsaturated hydrocarbons has been shown. An explanation of the above data can be based on an assumption that hydrogen atoms dissolved in octahedral interstitial positions of the metallic cobalt particle lattice are responsible for hydrogenation of the FT hydrocarbon intermediates into the hydrocarbons.

## EFFECT OF METALLIC COBALT PARTICLES SIZE ON OCCURRENCE OF CO DISPROPORTIONATION. ROLE OF FLUIDIZED METALLIC COBALT-CARBON SOLUTION IN CARBON NANOTUBE FORMATION

**A.A. Khassin, T.M. Yurieva, V.I. Zaikovskii, V.N. Parmon**

*React. Kinet. Catal. Lett.,* 64 (1998) 63-71.

The behavior of Co-MgO catalysts in the reaction of CO disproportionation was studied in the temperature range up to 800 $^oC$. Two temperature regions that differ by the morphology of graphite produced (“egg-shells” or nanotubes) were detected. The experimental data obtained were analyzed in terms of the phase equilibrium “amorphous carbon” - “carbon solution in metallic Co” and “graphite” - “carbon solution in metallic Co”. Under certain assumptions, the $Co^o$ particles are considered to dissolve amorphous carbon under the reaction conditions and transform to oversaturated fluidized carbon-cobalt solution, these fluidized particles being responsible for the formation of carbon nanotubes.

## FORMATION OF PORE STRUCTURE IN GROUP 4 BINARY OXIDES CRYSTALLIZING WITH DIFFICULTY

**V.Yu. Gavrilov**

*React. Kinet. Catal. Lett.*, 63 (1998) 185-192.

An analysis of texture formation in binary oxides of group 4 crystallizing with difficulty, prepared by mixing and coprecipitation has been conducted. The effect of mixing conditions, pH in particular, on the mutual disposition of elements has been shown. Coprecipitation of chemically non-interacting components results in the preservation of particle dispersity of individual oxides and the decrease of their packing density.

## FORMATION OF TIN DIOXIDE PORE STRUCTURE

**V.Yu. Gavrilov, G.A. Zenkovets**

*React. Kinet. Catal. Lett.,* 64 (1998) 79-87.

Formation of tin dioxide pore structure has been studied under various hydrogel precipitation conditions. Desired volumes of micro- and mesopores can be obtained when the pH and precipitation temperature are controlled. A relationship between the initial salt hydrolysis rate and the oxide phase nucleation rate appears to be of key importance. Peculiarities of thermal treatment of tin dioxide xerogel are shown.

## FORMATION OF THE POROUS STRUCTURE OF TITANIUM DIOXIDE PREPARED BY SOL-GEL METHOD

**V.Yu. Gavrilov, G.A. Zenkovets, G.N. Kryukova**

*Stud. Surf. Sci. & Catal.*, *Preparation of Catalysts VII*, 118 (1998) 609-616.

Effect of the precipitate conditions and ageing of titanium dioxide hydrogel on the formation of xerogel porous structure was investigated. Results obtained demonstrated that hydrogel precipitation with ammonia solution in a sol-gel method of hydrogel $TiO_2$ synthesis, independently from pH, provides limiting dispersion of the primary oxide particles

(5 nm). Porosity and the character of the porous volume distribution are determined by ions adsorption at the stage of hydrogel synthesis. Xerogels, received close to IEP, have the big porosity (0.78-0.79) and heterogeneous porous structure. A deviation of pH from IEP results in the formation of similarly fine-porous xerogel. Hydrogel precipitated by NaOH solution leads to the formation of xerogels with a greater porosity (0.84-0.85) and smaller surface value. During ageing of $TiO_2$ hydrogel, firstly, the appearance of anatase results to disordering the skeleton of amorphous titania, decreasing the porosity and rasing the xerogel strength. Long ageing is accompanied by aggregation of crystalline particles, resulting already to decrease of mechanical strength.

## SCIENTIFIC BASES FOR PREPARATION OF OXIDE SUPPORTS AND CATALYSTS VIA SOL-GEL METHODS

**O.P. Krivoruchko**

*Stud. Surf. Sci. & Catal., Preparation of Catalysts VII*, 118 (1998) 593-600.

The sol-gel processes occuring on the formation of individual and binary, poorly soluble hydroxides, materials-precursors of supports and catalysts, which contain Al(III), Fe(III) and Cu(II) are considered.

A very important phenomenon of “inheritance” of the structure of key polynuclear hydroxocomplexes (PHC) by hydroxides have been established, which determines a genetic relation of the nearest order between gels of amorphous hydroxides and the structure of the corresponding PHC.

## THE EFFECT OF THE STRUCTURE OF Cu-Ti OXIDE SYSTEMS OBTAINED BY SOL-GEL SYNTHESIS ON THE NATURE OF CATALYTIC CENTERS AND CATALYTIC ACTIVITY IN LOW-TEMPERATURE CO OXIDATION

**E.A. Trusova*, M.V. Tsodikov*, E.V. Slivinskii*, G.G. Hernandez*, O.V. Bukhtenko*, T.N. Zhdanova*, D.I. Kochubey, J.A. Navio** (*A.V. Topchiev Institute of Petrochemical Synthesis, Moscow, Russia; ** University of Seville, Seville, Spain)**

Mendeleev Commun., 3 (1998) 102-104.

It has been shown by X-ray diffraction analysis, EXAFS and XPS methods and in experiments on the low-temperature oxidation of CO that two types of catalytic oxidation centers are formed during sol-gel synthesis of single-phase Cu-Ti oxide systems (0.5-5.0 mass. % Cu) based on anatase: the first type involves $Cu^+$ ions in the [111] crystal planes, while the second type involves $Cu^{2+}$ ions, which isomorphically substitute titanium ions in the [100] planes of $TiO_2$.

## COPPER ION-MODIFIED TITANIUM OXIDE CATALYSTS FOR CO OXIDATION IN LEAN MIXTURES

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*Neftekhimiya,* 38 (1998) 185-193.

A series of Cu-Ti oxide catalysts based on $TiO_2$ was obtained by alkoxysynthesis method from $Ti(O_nBu)_4$ and $Cu(C_{17}H_{35}COO)_2$. These catalysts showed high catalytic activity in low-temperature CO oxidation in lean mixtures.

## SYNTHESIS, STRUCTURE AND CATALYTIC ACTIVITY OF CuO/TiO$_2$ MIXED OXIDES OBTAINED BY ALKOXO-METHODS IN CO OXIDATION

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*Stud. Surf. Sci. & Catal., Preparation of Catalysts VII*, 118 (1998) 679-689.

Structural, electronic and catalytic properties of Cu-O/$TiO_2$ mixed oxide catalysts tested for CO oxidation, which were obtained by a modified alkoxysynthesis method from $Ti(O_nBu)_4$ and $Cu(C_{17}H_{35}COO)_2$, have been studied by X-ray diffraction, EXAFS, XPS, magnetic susceptibility techniques and kinetic measurements. Partial chelation of $Ti(O_nBu)_4$ by acetylacetone was shown to stabilize sols and to ensure anatase-based single phase $Cu_xTi_{1-0.5x}O_2$ ($x \leq 0.06$). For $x \geq 0.06$, the formation of cupric oxide and titania gives evidence of phase separation. At temperatures $T<150$ °C, an overall CO conversion over the $Cu_xTi_{1-0.5x}O_2$ depends on the parameter x and on mean crystal size <d>: by increasing x and decreasing <d>, there is a marked increase in activity. It is suggested that terminal (non-bridged) oxygen of the bond $Cu=O_s$, surface anion vacancy $V_s$, related to the reduced $Cu^{+1}$ state and surface labile species $O_s$ participate in CO oxidation. At temperatures T>150-200 $^oC$, the participation of lattice oxygen in the reaction mechanism is postulated.

### STABILITY AND ACTIVITY OF Pd NANOPARTICLES ON SILICA AND ULTRADISPERSED DIAMOND

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*React. Kinet. Catal. Lett.,* 64 (1998) 169-175.

In contrast to $Pd/SiO_2$, Pd/diamond is extremely dispersed in the $H_2$ atmosphere up to 400 $^oC$. Turnover number of Pd/diamond in benzene hydrogenation remains almost constant in a wide range of Pd particle size (15-100 Å) and is 5 times lower than that of $Pd/SiO_2$.

### ELECTROCHEMICAL BEHAVIOR OF QUASI-GRAPHITIC CARBONS AT FORMATION OF SUPPORTED NOBLE METAL CATALYSTS

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G.N. Kryukova, A.L. Chuvilin, S.V. Bogdanov,
E.M. Moroz, V.A. Likholobov**

*Stud. Surf. Sci. & Catal., Preparation of Catalysts VII,* 118 ( 1998) 15-30.

Regularities for adsorption of $HAuCl_4$ and $H_2PtCl_6$ on carbon supports as a stage of preparation of supported metal catalysts have been studied. The results obtained have been interpreted in terms of the electrochemical theory of adsorption of electrolytes. Relationship between the nature of adsorption of these precursors and the metal state in the target catalysts has been revealed.

### PREPARATION OF Ru/CARBON-CATALYSTS FOR AMMONIA SYNTHESIS

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N.B. Shitova, I.A. Polukhina, G.G. Savelieva,
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*Stud. Surf. Sci. & Catal., Preparation of Catalysts VII,* 118 (1998) 213-218.

The problems of creation ruthenium-carbon catalysts for ammonia synthesis from initial compounds of ruthenium and alkali metals, accessible and convenient for use, are surveyed in order to prepare the new generation ammonia catalysts for the industrial application. Graphite-like active carbon “Sibunit” was used as a support for preparation of the catalysts. Potassium and cesium as promoters were introduced through hydroxides. Ruthenium (II) and (III) complexes with N-containing polydentate organic ligands are used for direct regulation of a dispersity of ruthenium-potassium and ruthenium-cesium systems. The important role at preparation of the active catalysts is stipulated by a nature of inner sphere ligand and even outer sphere of a counter-ion in the ruthenium complexes. It has been found that samples synthesized from Cl-free Ru precursors possess a considerably high activity in the ammonia synthesis at temperatures 573-673 K, pressure 5-50 bar, $N_2$-$H_2$=1:3, than that prepared from Cl-containing compounds. It is assumed that the most active are catalytic centres, containing ruthenium in low degrees of oxidation.

### ANIONIC RUTHENIUM CLUSTER $K_2[Ru_4(CO)_{13}]$ AS PRECURSOR OF CATALYTICALLY ACTIVE RUTHENIUM PARTICLES AND POTASSIUM PROMOTER. NEW EFFICIENT AMMONIA SYNTHESIS CATALYSTS BASED ON SUPPORTED $K_2[Ru_4(CO)_{13}]$

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*J. Molec. Catal. A: Chemical*, 123 (1998) 263-265.

New efficient potassium-promoted catalysts for ammonia synthesis are reported. For preparation of the catalysts, anionic ruthenium cluster $K_2[Ru_4(CO)_{13}]$ was used as a precursor of both catalytically active metal particles and potassium promoter while magnesium oxide and new original graphite-like active carbon CFC-1 were employed as supports. The catalysts found are capable of catalyzing the ammonia synthesis starting from 250 $^oC$ (1 atm) and exceed markedly in their activity at 300-400 $^oC$ and atmospheric pressure the industrial ammonia synthesis catalyst (SA-1). Especially effective is the $K_2[Ru_4(CO)_{13}]$ catalyst on MgO.

The replacement of MgO by $\gamma$-$Al_2O_3$ and $SiO_2$ results in a sharp decrease in activity of the catalyst in ammonia synthesis. This indicates the importance of the basic properties of a support for the achievement of high ammonia synthesis rates.

### SUPERCRITICAL EXTRACTION AS A METHOD FOR MODIFYING THE STRUCTURE OF SUPPORTS AND CATALYSTS

**A.F. Danilyuk, T.A. Gorodetskaya, G.B. Barannik, V.F. Lyakhova**

*React. Kinet. Catal. Lett.,* 63 (1998) 193-199.

Supercritical solvent extraction has been used for drying of wet gels in the production of $SiO_2$ monoliths, with methanol and liquid $CO_2$ used as solvents. The influence of various process parameters and nature of the solvent on the structural and mechanical properties of the monoliths obtained has been studied.

### PREPARATION AND STUDY OF MONOLITH CATALYSTS WITH A SECONDARY THERMOSTABLE FACING FOR THE PURIFICATION OF EXHAUST GASES FROM ORGANIC COMPOUNDS

**Z.R. Ismagilov, R.A. Shkrabina, D.A. Arendarskii, N.V. Shikina**

*Kinet. Katal.,* 39 (1998) 653-656.

The conditions of the preparation and properties of the catalysts with a thermostable secondary facing, containing Pt and Pd as active components and the Ce, La, and Zr cations as modifying additives, are studied. The method used for the preparation of the catalysts and their properties suggest that they can also be applied to the purification of exhaust gases.

### METHOD FOR THE PREPARATION OF SUPPORTED MONOLITH CATALYSTS FOR THE SELECTIVE REDUCTION OF NITROGEN OXIDES BY AMMONIA

**L.T. Tsykoza, Z.R. Ismagilov, R.A. Shkrabina, V.A. Sazonov, N.V. Shikina**

*Kinet. Katal.,* 39 (1998) 661-664.

The methods for the preparation of supported monolith catalysts containing an active component (V-Ti-O, Cu-Ti-O, CuZSM-5, or CoZSM-5) in the secondary cover on the surface of monolith ceramic and oxide supports with the honeycomb structure and their activity in the reactions of selective reduction of $NO_x$ by ammonia are discussed. Under certain conditions of active component formation, the activity of the samples studied over a wide temperature range are comparable to that of bulky monolith catalysts obtained by extrusion.

### PREPARATION AND STUDY OF A NEW MONOLITHIC CATALYSTS FOR PURIFICATION OF FLUE GASES FROM CARBON MONOXIDE AND ORGANIC COMPOUNDS

**Z.R. Ismagilov, R.A. Shkrabina, M.A. Kerzhentsev, V.A. Ushakov, N.V. Shikina, D.A. Arendarskii, I.A. Ovsyannikova, N.A. Rudina, Yu.V. Ostrovskii*, G.M. Zabortsev* (Novosibirsk Research Institute "All-Russia Scientific and Design Institute of Energetic Technology", Novosibirsk, Russia)**

*Kinet. Katal.,* 39 (1998) 665-669.

A new platinum catalyst supported on a honeycomb aluminosilicate monolith is developed for purifying flue gases from CO and organic vapours. The catalyst has no secondary support that simplifies its preparation. A choice of the optimal conditions for drying and calcination is justified. The effect of preparation conditions on the distribution of the active component over the catalyst channels and the state of platinum are studied by electron spectroscopy, X-ray microanalysis, and IR spectroscopy of adsorbed CO. The activity of the catalyst in oxidation of CO, butane, and methanol is studied. The catalyst was tested in an industrial-scale process of thermal catalytic after-burning of CO in flue gases of an incinerator of liquid organic radioactive waste. It is found that the CO conversion at a space velocity of 6000 $h^{-1}$ and 230-255 $^oC$ is higher than 98%.

### EFFECT OF NICKEL OXIDE DISPERSITY ON CARBON CAPACITY OF NICKEL CATALYSTS OF LOW-TEMPERATURE METHANE CRACKING

**M.A. Ermakova, D.Yu. Ermakov, G.G. Kuvshinov, L.M. Plyasova**

*Kinet. Katal.,* 39 (1998) 791-794.

The effect of nickel oxide dispersity on the carbon formation capacity of high-percentage nickel catalysts for methane cracking was studied using 96% Ni-4% $SiO_2$ as a model system. A new procedure for catalyst preparation was proposed. The procedure provides the nickel oxide pores by the impregnation of the latter with an alcohol solution of hydrolyzed tetraethoxysilane. The necessary dispersity of NiO was achieved by its preliminary calcination at a certain temperature over a 300-900 $^oC$ range. Using the catalysts with different specific surface areas (from 200 to 0.7 $m^2/g$, which correspond to the average sizes of NiO particle from 3 to >100 nm), it was shown that their carbon capacity correlates with the specific surface area of nickel oxide and, hence, with the average size of NiO particles. The carbon capacity has a maximum (300 g C/g Ni) in the region of 50 $m^2/g$ (d av NiO ~ 19 nm). The results obtained point to the possibility of the formation of catalytic systems with the optimum size distribution of active particles.

## THERMAL ACTIVATION OF A POST-COMBUSTION MANGANESE-ALUMINA CATALYST STUDIED BY IR, UV SPECTROSCOPY, AND EXAFS

**D.I. Kochubey, V.V. Kriventsov, G.N. Kustova, G.V. Odegova, P.G. Tsyrul'nikov, E.N. Kudrya**

*Kinet. Katal.,* 39 (1998) 294-301.

The dependence of the phase composition, including X-ray amorphous phases, for manganese oxide catalysts supported on $\alpha$- and $\gamma$-alumina on the calcination temperature has been determined. Highly defective phases with the structures not completely matching those of the corresponding bulk oxides were formed in all cases. The formation of such phases were shown to result from the dissolution of $Al^{3+}$ in the manganese oxides, nonstoichiometric composition of the oxides and stabilizing effect of their interaction with the support. The $\gamma$-$Al_2O_3$ transformation into $\alpha$-$Al_2O_3$ in the presence of supported manganese oxides was proved to take place at lower temperatures than in unsupported systems. Highly defective $\beta$-$Mn_3O_4$ and $\beta$-$Mn_2O_3$ phases modified with $Al^{3+}$ ions, which are formed during the thermal activation, were supposed to be structures active in deep oxidation.

## SILVER CLUSTERS AND NANOPARTICLES: PREPARATION IN WATER-IN-OIL MICROEMULSIONS AND SOME PHYSICAL PROPERTIES

**L.A. Pavlyukhina*, T.O. Zaikova*, G.V. Odegova, S.A. Savintseva**, V.V. Boldyrev* (*Institute of Solid State Chemistry and Mechanochemistry, **Institute of Inorganic Chemistry, Novosibirsk, Russia)**

*Neorgan. Mater.,* 34 (1998) 159-164.

Silver clusters and nanoscale colloid particles have been synthesized by the reduction of $AgNO_3$ with sodium hypophosphate in microdrops of the aqueous phase of water-in-oil microemulsions in the presence of ethoxylated alkylphenol. Ag/surfactant/$Al_2O_3$ samples containing 0.04-0.13 wt.% Ag prepared by the deposition of the microemulsions on the support were studied by diffuse reflectance electron spectroscopy (DRES), SAXS and XRD. Silver particles in Ag/surfactant/$Al_2O_3$ were shown to have the average size about 70 Å. The absorption band in DRES spectra at 385 nm indicates the formation of nanoparticles consisting of isolated clusters.

## STRUCTURAL EVOLUTION OF Co-Mg OXIDE CATALYST IN HYDROGEN AND CARBON MONOXIDE ATMOSPHERES. EFFECT OF THE COBALT PARTICLE SIZE ON THE STRUCTURE OF CARBON FORMED IN THE REACTION OF CO DISPROPORTIONATION

**A.A. Khassin, T.M. Yurieva, V.I. Zaikovskii, L.M. Plyasova, V.N. Parmon**

*Kinet. Katal.,* 39 (1998) 431-441.

The behavior of solid solutions of Co and Mg oxides in hydrogen and carbon monoxide during heating from room temperature to 750 and 500 °C, respectively, has been studied by TGA, XRD and electron microscopy. The dependence of the crystal structure, microtexture and morphology of the samples on their initial composition, preparation method and type of the following treatment has been analyzed. It has been found that $Co^{2+}$ existing in the solid solution is reduced in hydrogen to the metal form with the formation of $\beta$-Co phase at 360-600 °C. The dispersion of cobalt metal prepared from $Co_{1-x}Mg_xO$ solid solutions is significantly higher than in the case of CoO reduction. The treatment of reduced samples with carbon monoxide at $T > 280$ °C results in the CO disproportionation with the formation of two types of graphite-like carbon: 100 Å "hoods" over Co particles with the diameter above 250 Å and nanotubes with the outer diameter 100-200 Å and inner diameter 30-50 Å, which are related to parent Co particles with the diameter 100-200 Å. High structural defectiveness of large Co particles treated with CO (in the form of regular extended defects) has been observed. Meanwhile, there was almost no defects in the structure of particles with the size about 100 Å after such treatment.

### EFFECT OF THE MECHANOCHEMICAL ACTIVATION ON THE REACTIVITY OF CARBON DURING OXIDATION WITH OXYGEN

**V.S. Babenko, V.V. Molchanov, T.A. Konovalova**

*Kinet. Katal.*, 39 (1998) 62-67.

The effect of mechanical activation of carbon materials of different origin in centrifugal ball mills on their reactivity to the oxidation with oxygen at 573-973 K has been studied. Mechanochemical activation has been shown to result in the decrease of the apparent activation energy and growth of the carbon oxidation rate. A linear dependence of the oxidation rate on the concentration of strong electron-acceptor sites has been observed. These sites are supposed to be oxidation sites formed by carbon atoms with unsaturated bonds located in planes perpendicular to basal planes of the graphite lattice.

### EFFECT OF SILICA PORE STRUCTURE ON THE CONDUCTION PROPERTIES OF COMPOSITE PROTON ELECTROLYTE $CsHSO_4$-$SiO_2$

**V.G. Ponomareva*, G.V. Lavrova*, L.G. Simonova**
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*Neorgan. Mater.,* 34 (1998) 1347-1352 .

Transport properties of highly-conductive protonic composite electrolytes (1-x)$CsHSO_{4\text{-}x}SiO_2$ (where x=0-0.8) have been studied. The used silica were different in their specific surface area (100-580 $m^2/g$) and pore size ($V_{por}=1cm^3/g$, $r_{por}$=14-1000 Å).

It was shown that the low-temperature conductivity depends on composition, and goes through maximum at x=0.5-0.7, where its value 2-2.5 orders of magnitude higher than that of the pure $CsHSO_4$. The conductivity was shown to depend on silica pore size. The optimum pore size was in the range 35-100 Å, where the most composite conductivity increase takes place. This dependence is determined both by dimensional effect, which determine the changes of thermodynamic properties of ionic salt in small pores, and by character of conductive phase localization in pore space of solid matrix.

### PROPERTIES OF CESIUM HYDROGEN SULFATE DISPERSED IN SMALL PORES OF AN INERT CARRIER

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**(Institute of Solid Chemistry and Mechanochemistry, Novosibirsk, Russia)**

*Neorgan. Mater.,* 34 (1998) 1499-1502.

Peculiarities of structural and thermal transformations in highly-conductive protonic composite electrolytes (1-x)$CsHSO_{4\text{-}x}SiO_2$ (where x=0-0.8) based on the highly-dispersed silica with different pore structure ($r_{por}$=14-170 Å) have been studied by differential scanning calorimeter analysis and XRD. It has been established that localization of $CsHSO_4$ in small pores of heterogeneous component leads to a decrease both of temperature and enthalpy of melting and phase transition, amorphization of cesium hydrosulfate. Structural and thermodynamic composite properties depend on silica pore size. The most decrease of enthalpy of melting and phase transition for cesium hydrosulfate is exhibited by composites based on silica with pore size 35-70 Å, for which partial or complete $CsHSO_4$ amorphization is observed in dependence of composition. Change of ionic salt properties of composites based on silica with pore size 170 Å occurs probably due to $CsHSO_4$ crushing. The observed changes of thermodynamic and structural properties of $CsHSO_4$ causes a significant increase of composite conductivity at corresponding compositions and pore radii.

## Carbon and Carbon Containing Materials. Synthesis and Processes with Their Participation

### ELECTRON MICROSCOPY STUDY OF THE CELLULAR CARBON SUPPORT STRUCTURE

**V.I. Zaikovskii, G.V. Plaksin, V.A. Semikolenov**

*Kinet. Katal.*, 39 (1998) 600-606.

The structure of a new high-porous carbon support formed on reactor walls during pyrolysis of a propane-butane mixture has been studied. It has been found that the skeleton of the support is formed from flat carbon layers in the form of ribbons. These ribbons have an ordered graphite-like structure at the microscale and consist of fragments of (002) hexagon networks located in (002) layers and oriented with their basal planes to each other and with their ends to the surface of the ribbons. Specific features of the structure of the cellular carbon support in comparison with supports prepared by pyrolysis of hydrocarbons are shown.

## POROUS CARBON MATERIALS PREPARED FROM $C_1$-$C_3$ HYDROCARBONS

**V.B. Fenelonov, V.A. Likholobov,**
**A.Yu. Derevyankin, M.S. Mel'gunov**

*Catal. Today*, 42 (1998) 341-345.

The inexhaustibility of various solid porous carbons produced from $C_1$-$C_3$ hydrocarbons, which may be used as catalyst supports, adsorbents and so on is reported.

## THE CARBON STATES AND KINETICS OF CARBON DEPOSITION FROM ETHYLENE AT PT(110) SURFACE

**R.I. Kvon, E.A. Ivanov, A.I. Boronin**

*React. Kinet. Catal. Lett.*, 65 (1998) 381-388.

The nature of high temperature carbon states at Pt(110) has been studied by X-ray photoelectron spectroscopy. Diamond-like carbon (DLC) was reported at the first time. The kinetics and temperature-programmed reactions of DLC were numerically simulated.

## KINETICS OF CARBON FORMATION FROM $CH_4$-$H_2$ MIXTURES OVER A NICKEL CONTAINING CATALYST

**G.G. Kuvshinov, Yu.I. Mogil'nykh,**
**D.G. Kuvshinov**

*Catal. Today*, 42 (1998) 357-360.

The experimental data, corroborating the effect of $CH_4$-$H_2$ mixture compositions and temperature on the formation of catalytic filamentary carbon (CFC) in methane decomposition over a highly loaded Ni-containing catalyst, are presented. A model of the catalyst deactivation is proposed: carbon blocks the surface of a CFC growth center (GC). Using this model, the equation has been derived for calculating the deposition rate of CFC and its maximum quantities which may form during the time of complete catalyst deactivation.

## REALIZATION OF THE PROCESS OF GRANULATED CATALYTIC FILAMENTOUS CARBON PRODUCING ON THE PILOT SCALE

**G.G. Kuvshinov, S.G. Zavarukhin,**
**Yu.I. Mogil'nykh, D.G. Kuvshinov**

*Khim. Prom.,* 5 (1998) 300-306.

The results of tests of two different pilot reactors with vibrofluidized catalyst bed and output up to 3 kg of carbon per one cycle are presented. The tests were conducted with the use of pure methane, natural gas and model mixtures over catalysts of two types - nickel containing and nickel-copper containing. It was obtained that on going on from microreactor with catalyst load 0.1 g to the pilot reactor with the load 30 g the specific carbon yield decreases twice and makes up ca. 80. The peculiarity of reactors operation consists in necessity of inert material loading simultaneously with the catalyst. The value of dust carrying away was measured. It was shown, that the technology of carbon producing can be simplified by the refuse from special operations of catalysts reduction and passivation.

## A NEW CELLULAR CARBON SUPPORT FOR CATALYSTS: PREPARATION AND STUDY OF STRUCTURE

**G.V. Plaksin, V.A. Semikolenov, V.I. Zaikovskii,**
**E.M. Moroz, V.Yu. Gavrilov**

*React. Kinet. Catal. Lett.*, 63 (1998) 157-163.

Cellular carbon has been prepared by pyrolysis of a propane-butane mixture in a flow reactor at 700-1250 K. Its structural characteristics were studied by scanning electron microscopy, high resolution transmission electron microscopy, X-ray diffraction and adsorption methods. It was shown that cell-type carbon possesses a unique structure in contrast to carbon composite "Sibunit" and filamentous carbons and it may be a promising support for catalyst preparation.

## NEW METAL-CARBON CATALYSTS: I. PREPARATION PROCEDURE AND APPLICATION AREA

**V.V. Molchanov, V.V. Chesnokov, R.A. Buyanov,**
**N.A. Zaitseva**

*Kinet. Katal.,* 39 (1998) 407-415.

New catalytic systems, composed of metal and filamentous carbon which principally differ from all known catalyst both for their structure and method of preparation have been discovered. Metal-carbon catalysts are formed upon carbon decomposition on metals of iron subgroup or on their alloys with other metals, and comprise metal particles, attached to the faces of carbon filaments. Varying conditions of hydrocarbon decomposition, it is possible to obtain metal-carbon systems with properties allowing their use as catalysts for different reactions (full and partial hydrogenation of unsaturated hydrocarbons and unsaturated fatty acids, vapor and carbonic methane conversion, CO methanation, Fischer-Tropsch Synthesis, reducing chloro-benzene dechlorination, n-butane dehydrogenation, CO oxidation). The catalysts obtained may conduct both deep and partial hydrogenation of dienes and acetylenes in dependence of carbon to metal ratio. Selectivity to olefins is near 100 % at high carbon to metal ratio.

## NEW METAL-CARBON CATALYSTS: II. THE ORIGIN OF SELECTIVITY OF NICKEL CATALYSTS IN HYDROGENATION REACTIONS

**V.V. Molchanov, V.V. Chesnokov, R.A. Buyanov,**
**N.A. Zaitseva, V.I. Zaikovskii, L.M. Plyasova,**
**V.I. Bukhtiyarov, I.P. Prosvirin, B.N. Novgorodov**

*Kinet. Katal.,* 39 (1998) 416-421.

It has been shown, that selectivity of nickel catalysts in reaction of butadiene hydrogenation depends both on nature of crystallographic surfaces accessible for reaction mixture, and electronic metal state, conditioned by morphology of its particles. Selective hydrogenation to butylene proceeds on (100) nickel surface, while full hydrogenation occurs on (111) and (100) surfaces. The qualitative estimation of catalytic properties of the nickel surfaces in reactions of hydrogenation under normal pressure has been made for the first time.

## STUDY OF FILAMENTOUS CARBON GROWTH ON NICKEL-CONTAINING CATALYSTS

**V.V. Chesnokov, R.A. Buyanov, V.I. Zaikovskii**

*Chemistry for Sustainable Development*,
5 (1997) 619-624.

Regularities of filamentous carbon formation from methane over the $Ni/Al_2O_3$, $Ni\text{-}Cu/Al_2O_3$ and Ni-Cu/MgO catalysts in temperature range of 550-700 $^oC$ were studied by means of electron microscopy and XRD. Four period in filamentous carbon formation have been determined: induction period, period of acceleration, stationary period and period of deactivation. The reasons and processes, which cause the transformation of catalytic particles and morphology of filamentous carbon at each period are established.

## PECULIARITIES OF FILAMENTOUS CARBON FORMATION IN METHANE DECOMPOSITION ON Ni-CONTAINING CATALYSTS

**G.G. Kuvshinov, Yu.I. Mogil'nykh,**
**D.G. Kuvshinov, V.I. Zaikovskii, L.B. Avdeeva**

*Carbon,* 36 (1998) 87-97.

Experimental data on the effect of $CH_4$+$H_2$ mixture composition and temperature on catalytic filamentous carbon (CFC) formation in methane decomposition on Ni-containing catalyst are presented. Microscopy studies have shown that at the lowest methane concentration (2.5 %) the amount of CFC produced per unit of catalyst mass is limited by the surface effects imposed by the carbon growth centers (GC) rather than by volume ones. The shape of GC where carbon filaments forms depends on the reaction medium composition and temperature. By varying the $H_2$ concentrartion in the reaction medium, one can change the texture of the CFC produced.

## FORMATION OF POROUS FILAMENTOUS CARBON PARTICLES AND PROPERTIES OF NEW MATERIALS

**G.G. Kuvshinov, Yu.I. Mogil'nykh,**
**D.G. Kuvshinov, D.Yu. Ermakov, M.A. Ermakova,**
**A.N. Salanov, N.A. Rudina**

*Amer. Chem. Soc., Division Fuel Chem.,*
43 (1998) 946-951.

The growth of catalytic filamentary carbon granules formed on methane decomposition over Ni catalysts have 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 was proposed.

## DIRECT OXIDATION OF HYDROGEN SULFIDE TO SULFUR OVER FILAMENTARY CARBON

**G.G. Kuvshinov, Yu.I. Mogil'nykh, M.Yu. Lebedev**

*Amer. Chem. Soc., Division Fuel Chem.,* 43 (1998) 846-851.

The possibility of using the catalytic filamentary carbon as a catalyst in the direct oxidation of hydrogen sulfide to sulfur is investigated. The dependencies of the hydrogen sulfide conversion and selectivity of the direct oxidation hydrogen sulfide to sulfur from the process conditions for the different types of the catalytic filamentary carbon are analyzed. The parameters were as follows: temperature - 160-220 $^oC$, $H_2S$ concentration in the initial gas - 0.5-2 %, oxygen concentration - 5-15 %, and water vapor content - 0-60 %. The competitiveness of filamentary carbon with respect to activated carbons and the water vapour concentration in the initial gas is shown.

## PRODUCTION OF FILAMENTOUS CARBON AND HYDROGEN BY SOLARTHERMAL CATALYTIC CRACKING OF METHANE

**A. Steinfeld*, V.A. Kirillov, G.G. Kuvshinov, Yu.I. Mogil'nykh, A. Reller** (*Paul Scherrer Institute, Villigen-PSI, Switzerland; **University of Hamburg, Hamburg, Germany)**

*Chem. Eng. Sci.,* 52 (1997) 3399-3603.

The technical feasibility of the solar decomposition of methane has been demonstrated using a small scale fluidized-bed solar reactor. The direct irradiation of the catalyst provided effective heat transfer to the reaction site. Potential applications of such process are the clean conversion of natural and oil tail gases into valuable chemical commodities.

## HIGH-TEMPERATURE CARBON STATES AT Pt(110) SURFACE AND THEIR REACTIVITY TOWARDS $H_2$ AND $O_2$

**R.I. Kvon, A.I. Boronin**

*Catal. Today*, 42 (1998) 353–355.

Ethylene decomposition on Pt(110) surface at 650-850 K was found to result in the formation of “chemisorbed” carbon. At T>850 K the other carbon state of $sp^3$ hybridization was revealed by XPS and AES. As this carbon state is rather inert towards both oxygen and hydrogen, it has been concluded it has diamond-like nature.

## STM OBSERVATION OF THE Ni(100) SURFACE WITH SEGREGATED CARBON

**Sh.K. Shaikhutdinov**

*Surf. Sci.*, 395 (1998) L215-L219.

With scanning tunneling microscopy (STM), carbon atoms segregated onto the Ni(100) surface were imaged as protrusions at bias voltages of 0.5 V, in contrast to the depressions previously observed for C atoms at lower voltages ~ 0.02V. At coverage of about 0.15 ML, the carbon atoms form slightly distorted p(2×2) domains on the Ni(100)-(1×1) surface. In addition, a tip apex reconstruction is suggested to explain the corrugation inversion observed on Ni(100). Our data indicate that the electronic states of both the tip and the sample should be accounted for an explanation of the highly resolved STM images of the metal surfaces.

## A NEW PHENOMENON INVOLVING THE FORMATION OF LIQUID MOBILE METAL-CARBON PARTICLES IN THE LOW-TEMPERATURE CATALYTIC GRAPHITIZATION OF AMORPHOUS CARBON BY METALLIC Fe, Co AND Ni

**O.P. Krivoruchko, V.I. Zaikovskii**

*Mendeleev Commun.*, 3 (1998) 97-100.

The reaction of Fe, Co and Ni with amorphous carbon and its catalytic graphitization at relatively low temperatures (600-700 $^oC$) *in vacuo* is accompanied by the formation of liquid mobile metal-carbon particles; the mechanism by which these particles are formed and maintained in the liquid state is suggested.

## FORMATION OF LIQUID PHASE IN THE CARBON-METAL SYSTEM AT UNUSUALLY LOW TEMPERATURES

**O.P. Krivoruchko, V.I. Zaikovskii**

*Kinet. Katal.,* 39 (1998) 607-617.

A phenomenon of the formation of liquid mobile metal-carbon particles at relatively low temperature (600-700 $^oC$) *in vacuo* has been studied in the reaction of Fe, Co, Ni particles with amorphous carbon and its catalytic graphitization. The mechanism of such particles formation and maintaining in the liquid state is suggested, characterized by the presence of transition and quasistationary regimes. Liquid particles (catalytic intermediates) are shown to form abnormally saturated solution of carbon in metal (to 50 at.% at 700 $^oC$).

### CATALYTIC ACTIVATION OF C-H BONDS OF ALKANES, ETHENE AND AROMATIC HYDROCARBONS BY ADDUCTS OF ACTIVE CARBONS WITH METALLIC POTASSIUM

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***Universitat Leipzig, Leipzig, Germany)**

*J. Molec. Catal. A: Chemical*, 132 (1998) 277-280.

It has been shown that the adducts of active carbons with metallic potassium are able to activate C-H bonds of alkanes, ethene and aromatic hydrocarbons and introduce these compounds into the hydrogen-deuterium exchange reaction at room temperature. This paper describes the reactions of the redistribution of hydrogen isotopes in $CD_3H$, $C_6H_5CD_3$ and $C_6D_5CH_3$ catalyzed by the potassium-carbon adducts as well as the similar isotope exchange reactions in the systems $C_2H_4$-$C_2D_4$, $C_6H_6$-$C_6D_6$, n-$C_6H_{14}$-n-$C_6D_{14}$ and $CD_4$-n-$C_5H_{12}$. A study of the isotope exchange between $C_6H_6$ and $C_6D_6$ has shown that the efficiency of the process is strongly dependent on the potassium content in the catalyst passing through a maximum at the K:C molar ratio of 1:7.45.

### RAMAN INVESTIGATION OF ONION-LIKE CARBON

**E.D. Obraztsova*, S.M. Pimenov*, V.I. Konov*,
M. Fujii**, S. Hayashi**, V.L. Kuznetsov,
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*Molec. Mater.,* 10 (1998) 249-254.

Combined investigation (Raman scattering, HRTEM and X-ray diffraction techniques) performed for 5-nm-size ultradispersed diamond powder and the products of its annealing in vacuum has revealed the highest percentage of the spherical carbon onions in the powder annealed at T=1800 K.

### 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, Kobe, Japan)**

*Carbon,* 36 (1998) 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 pure graphite) is interpreted as an influence of shell curvature. The summary contribution of the shells constituting the 5-nm diametr 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 graphitic network in shells.

### CLOSED CURVED GRAPHITE-LIKE STRUCTURES FORMATION ON MICRON-SIZE DIAMOND

**V.L. Kuznetsov, A.L. Chuvilin, Yu.V. Butenko,
S.V. Stankus*, R.A. Khairulin*, A.K. Gutakovskii**
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**Institute of Semiconductor Physics, Novosibirsk, Russia)**

*Chem. Phys. Lett.*, 289 (1998) 353-360.

The annealing of diamond particles ($d \approx 1000$ nm) at 1800-2000 K leads to the formation of nanometric closed curved graphitic structures (CCGS) with tubular or conical forms as well as to defective extended graphitic structures. The intermediate structures that occur during the diamond transformation to curved graphitic structures have been observed. At the interface between diamond and evolving graphite the formation of two curved graphite sheets from three diamond planes (111) were detected. The CCGS formation is probably a self-assembling process. CCGS are proposed to enhance electron emission from diamond surfaces.

# Catalysts for Synthesis Sulfur-Organic Compounds

## HYDROGENATION OF 3-THIOLENE-1,1-DIOXIDE IN ALCOHOL-ALKALI SOLUTIONS OVER PALLADIUM CATALYSTS

**A.V. Mashkina**

*Kinet. Katal.*, 39 (1998) 204-209.

The hydrogenation of 3-thiolene-1,1-dioxide to thiolane-1,1-dioxide has been studied in alcohol-alkaline solutions over $\gamma$-$Al_2O_3$-supported palladium metal. The hydrogenation rate has been found to decrease in the presence of alkalis in comparison with the rate observed in the neutral solution. This is related both to the strengthening of the hydrogen-palladium bond and the formation of 3-alkoxythiolane-1,1-dioxide. The hydrogenation of the latter to thiolane-1,1-dioxide takes place only at higher temperatures and longer contact times. This results in the evolution of hydrogen sulfide and formation of palladium sulfide, which has lower catalytic activity.

## RESISTANCE OF HYDROGENATION METAL CATALYSTS TO SULFUR

**N.T. Kulishkin, A.V. Mashkina**

"*Catalysis and Catalysts. Fundamental Studies*". Ed. Prof. R.A. Buyanov, Boreskov Institute of Catalysis, Novosibirsk 1998, pp. 127-129.

The effect of compounds containing sulfur in different oxidation states on the resistance of group VIII metals to sulfur has been studied for hydrogenation of 3-thiolene-1,1-dioxide, which contains S (VI), whereas products of its hydrogenation contain S (IV) and S (II). S (VI) in 3-thiolene-1,1-dioxide does not react with the metal providing its relatively high stability in hydrogenation. However, at increased temperatures side reactions take place yielding sulfur dioxide, hydrogen sulfide, mercaptane, sulfide, which are contact poisons. Catalysts with varying metal dispersity have been shown to have the same specific stability.

## PARTIAL OXIDATION OF ORGANIC SULFIDES WITH MOLECULAR OXYGEN

**A.V. Mashkina, L.B. Avdeeva, P.S. Makoveev**

*"Catalysis and Catalysts. Fundamental Studies"*. Ed. Prof. R.A. Buyanov, Boreskov Institute of Catalysis, Novosibirsk 1998, pp. 129-131.

The possibility of oxidation of organic sulfides to sulfoxides and sulfones with molecular oxygen in the presence of oxides and complexes of transition metals has been observed. The oxidation rate is determined by the donor properties of the sulfur atom in the sulfide and acceptor properties of the cation. The gas-phase oxidation of sulfides on metal oxides goes via slow reaction of sulfide chemisorbed on the catalyst with the surface oxygen and fast reoxidation of reduced catalyst. Radical cations are formed during the liquid-phase oxidation of sulfides by transition metal complexes. In the oxidative environment they are transformed into peroxide radicals oxidizing another sulfide molecule. Reduced cations are then oxidized by oxygen.

## PRINCIPLES FOR CHOICE OF CATALYSTS FOR ORGANIC REACTIONS OF SULFUR COMPOUNDS

**A.V. Mashkina**

*"Catalysis and Catalysts. Fundamental Studies"*. Ed. Prof. R.A. Buyanov, Boreskov Institute of Catalysis, Novosibirsk 1998, pp. 123-125.

A theoretical approach to the selection of catalysts for reactions with participation of sulfur compounds has been developed. Catalysis is assumed to be a chemical phenomenon, in which activity is primarily determined by localized interaction of reagents with an individual atom or ion of a catalyst. The composition of the complex, the character of the electron density redistribution in it, the degree of the electron transfer from the sulfur atom to the catalyst determine to a great extent the direction of a catalytic reaction. The interaction of organic sulfides and hydrogen sulfide with a catalyst most often results in the formation of a complex with the charge transfer from the sulfur atom to the catalyst. This results in the activation of the sulfur atom making it capable of reacting with nucleophilic agents. Sulfoxides and thiophenes can be coordinated not only via their sulfur atom but also via C, H and O atoms. The latter forms are the only possible ones for saturated sulfones. Unsaturated sulfones and thiophenes can be coordinated to metals, their complexes and sulfides with the participation of the C=C bond. The above approach proved to be useful for realization of a number of possible but earlier unknown catalytic reactions with participation of sulfur compounds and understanding of the mechanisms of known reactions.

### HETEROCYCLIZATION OF SULFUR COMPOUNDS

**T.S. Sukhareva, A.V. Mashkina**

"Catalysis and Catalysts. Fundamental Studies". Ed. Prof. R.A. Buyanov,. Boreskov Institute of Catalysis, Novosibirsk 1998, pp. 131-132.

Mercaptanes, disulfides, aliphatic and cyclic sulfides and their oxides as well as hydrogen sulfide mixtures with hydrocarbons undergo heterocyclization to form thiophenes on sulfide catalysts. The lower is the energy of the sulfur bond with the surface, the higher is the activity of the catalyst. The thiophene formation process goes via slow interaction of surface sulfur atoms with dehydrogenated fragments formed during adsorption of sulfur compounds and fast resulfiding of the surface with sulfur.

## Membranes in Catalysis

### NANOSIZE PALLADIUM LOADED CATALYTIC MEMBRANE: PREPARATION AND CIS-TRANS SELECTIVITY IN HYDROGENATION OF SUNFLOWER OIL

**O.M. Il'initch, P.A. Simonov, F.P. Cuperus* (Agrotechnological Research Institute, Wageningen, The Netherlands)**

*Stud. Surf. Sci. & Catal., Preparation of Catalysts VII,* 118 (1998) 55-61.

Palladium catalyzed hydrogenation of sunflower oil was investigated in conventional and membrane catalysis modes. The technique of preparation of catalytic membranes containing nanosize Pd particles supported over macroporous polymeric membrane was developed. In the catalytic membrane reactor operating in the regime of forced flow of the reaction mixture through the membrane pores, the yield of trans-isomeric triglycerides was suppressed compared to the conventional slurry reactor with carbon-supported Pd catalyst.

### TRANSPORT OF $C_1$-$C_3$ HYDROCARBONS IN POLY(PHENYLENE OXIDES) MEMBRANES

**A.A. Lapkin, O.P. Roschupkina, O.M. Il'initch**

*J. Membrane Sci.,* 141 (1998) 223-229.

Transport of $CH_4$, $C_2H_4$ and $C_2H_6$ in poly(phenylene oxides) membranes at low pressures has been studied. The relation between the free volume and permeability of the polymers was analyzed in terms of the 'dual-sorption' model. The accessible free volume of the polymers was estimated assuming the density of a sorbed fluid is equal to the density of the corresponding liquid. Transient separation of the three-component mixture $CH_4/C_2H_4/C_2H_6$ was studied.

### GAS PERMEATION PROPERTIES OF PHENYLENE OXIDE POLYMERS

**A. Alentiev*, E. Drioli**, M. Gokzhaev*,**
**G. Golemme**, O. Il'initch, A. Lapkin,**
**V. Volkov*, Yu. Yampolskii* (*Institute of Petrochemical Synthesis, Moscow, Russia; **University of Calabria, Italy)**

*J. Membrane. Sci.,* 138 (1998) 99-107.

Gas permeability (*P*i) and diffusion (*D*i) coefficients in respect to several gases ($H_2$, $O_2$, $N_2$, CO, $CO_2$, $CH_4$) have been measured for poly(2,6-dimethylphenylene oxide) (PMPO), poly(2,6-diphenylphenylene oxide) (PPPO), and phenylene oxide copolymers containing methyl, phenyl, and allyl radicals as side groups. X-ray diffraction study shows that both homopolymers are semicrystalline materials, whereas all the copolymers are completely amorphous. The results show that a replacement of methyl by phenyl groups in PMPO/PPPO pair is accompanied by a decrease in the *P* values. A transition from semicrystalline PMPO to amorphous copolymers results in a decrease in permeability and solubility coefficients and not in a growth of these parameters as can be expected on the basis of the behavior of other semicrystalline polymers (e.g. polyolefins). It is supposed that the crystallites of PMPO, and possibly of PPPO are packed loosely and, hence, take part in sorption and gas transport. This assumption is in agreement with numerous X-ray data as well as the results of positron annihilation study of these polymers.

# Catalytic Reactions for Producing of Farmaceuticals and Biologically Active Compounds

## SYNTHESIS OF WATER SOLUTIONS OF SOUR SALTS OF VANADOMOLYBDOPHOSPHORIC HETEROPOLYACIDS

**V.F. Odyakov, E.G. Zhizhina,**
**R.I. Maksimovskaya, K.I. Matveev**

*Zh. Neorgan. Khim.*, 43 (1998) 1451-1455.

New method to synthesise water solutions of sour salts of Mo-V-phosphoric heteropolyacids of composition $Me_aH_{3+n-za}PMo_{12-n}V_nO_{40}$ (a - number of metal cations $Me^{z+}$; a=0,5÷0,6) through the intermediate reception of decavanadates $Me_bH_{6-zb}V_{10}O_{28}$ is offered. The last one may be received by dissolving $V_2O_5$ in mixture with $Me^{z+}$ carbonate (or oxide) in water in the presence of $H_2O_2$; its quantity is the greater, the lower is the basicity of carbonate or oxide. Examples of synthesis of Na, Li, K, Mg, Mn, Co and Zn salts of $H_7PMo_8V_4O_{40}$ (HPA-4) are presented. There are a broadening and a shift of lines in a weak field in NMR $^{51}V$ and $^{31}P$ spectra of $Co^{2+}$ and Mn $^{2+}$ salts of HPA-4. These phenomena are due to paramagnetism of these cations and possibly are caused by their interaction with internal coordination sphere of HPA-4 molecule.

## SYNTHESIS OF TETRACOORDINATED RHODIUM (I) COMPLEXES WITH CHIRAL SHIFF BASES PREPAPED FROM DEHYDROABIETIC ACID

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**O.V. Tolstikova, T.B. Khlebnikova,**
**G.A. Tolstikov*, V.I. Mamatyuk*, G.E. Salnikov***
**(Institute of Organic Chemistry, Novosibirsk, Russia)**

*Mendeleev Commun.*, 2 (1998) 60-62.

New optically active Shiff bases have been prepared from dehydroabietic acid and have been used as ligands to synthesize tetracoordinated rhodium (I) complexes. Reduction of acetophenone to phenetyl alcohol by means of a hydrogen transfer reaction was used as an example for the preliminary estimation of the catalytic activity and enantioselectivity of the new complexes.

## MASS SPECTRA OF NEGATIVE IONS OF SOME CARBAMIDES

**V.S. Shmakov*, I.I. Furlei*, A.G. Tolstikov,**
**E.V. Vyrypaev* (Institute of Organic Chemistry, Ufa Science Center RAS, Ufa, Russia)**

*Bashkirskii Khim. Zh.,* 5 (1998) 136-138.

Mass spectra of negative ions of N-isopropylcarbamide, N-decyl-N'- isopropylcarbamide and N,N'-didecylcarbamide are discussed. In the mass spectra of these compounds there are negative peaks $(M-H)^-$, $OCN^-$, $CN^-$, $H_2NCONH^-$. Meanwhile, in N-decyl-N'- isopropylcarbamide the fragmentation character of molecular negative ion is different. Pseudomolecular ions $(M-NH_3)^-$ and $(M-H_2O)^-$ are observed, their formation being related to hydrogen rearrangements. In the spectrum of didecylcarbamide pseudomolecular ions $(M-16)^-$ with m/z = 226 and $(M-31)^-$ with m/z = 211 corresponding to the loss of a part of the alkyl radical have been detected. The intramolecular coordination of the carbon atom of the decyl radical to nitrogen with the formation of a stable six-member ring seems to be a feasible explanation for the existence of such set of peaks in the mass spectrum.

## MASS SPECTRA OF NEGATIVE IONS OF NITROGEN-CONTAINING PROPYLSULFIDES

**V.S. Shmakov*, I.I. Furlei*, A.G. Tolstikov,**
**E.V. Vyrypaev* (Institute of Organic Chemistry, Ufa Science Center RAS, Ufa, Russia)**

*Bashkirskii Khim. Zh.*, 5 (1998) 139-141.

Mass spectra of negative ions of aliphatic amines, amides, carbamides and nitryls containing a propylsulfide fragment have been recorded in the resonance electron capture regime. The analysis of the spectra has shown that the formation of negative ions $(M-H)^-$, $(M-CH_3)^-$, $C_3H_7S^-$ and $NC^-$ is typical for all nitrogen-containing propylsulfides. The energy of $(M-H)^-$ resonances for amides, carbamides and nitryls in the energy region below 3 eV has been noticed to vary similar to changes in the position of vacant molecular orbitals (MO). It has been found that the dissociation of molecular negative ions in the presence of an electron-donor $NH_2$ in propylsulfides is determined by the position of vacant $\sigma_{sc}$ MO.

### HYDROGENATION OF 1-ETHYL-2-NITROMETHYLENEPYRROLIDINE TO 1-ETHYL-2-AMINOMETHYLPYRROLIDINE OVER Pd/C

**I.L. Simakova, A.V. Golovin, V.A. Semikolenov**

*Kinet. Katal.,* 39 (1998) 193-197.

Routes of 1-ethyl-2-nitromethylenepyrrolidine (ENMP) conversion upon liquid-phase hydrogenation over Pd/C, and composition of products formed are studied. The influence of used solvent and acidity of the medium on the selectivity and rate of 1-Ethyl-2-aminomethylpyrrolidine (EAMP) formation have been studied. It has been shown that side conversion of ENMP is catalyzed by EAMP, producing the basic medium. The side product 1-ethylpyrrolidine-2 is formed as a result of ENMP hydrolysis, proceeding by mechanism of specific acid-base catalysis. Methods to incerease selectivity of reaction of ENMP hydrogenation are suggested.

### THE ROLE OF $CO_2$ IN SELECTIVE HYDROGENATION OF 1-ETHYL-2-NITROMETHYLENEPYRROLIDINE TO 1-ETHYL-2-AMINOMETHYLPYRROLIDINE OVER Pd/C

**I.L. Simakova, A.V. Golovin, V.A. Semikolenov**

*Kinet. Katal.,* 39 (1998) 198-203.

The kinetic regularities of 1-ethyl-2-nitromethylenepyrrolidine (ENMP) over Pd/C in $CO_2$ presence are studied. It has been shown that selectivity to 1-ethyl-2-aminomethylpyrrolidine (EAMP) increases with increase of $CO_2$ and $H_2$ partial pressures, and amount of catalyst. IR-spectroscopy, $^{13}$C NMR and pH-metrical methods were used to study EAMP interaction with $CO_2$. It was found that reversible interaction of EAMP with $CO_2$ produces the carbamic acid thus creating nearly neutral pH of the medium. The scheme presenting the role of $CO_2$ in the process of selective ENMP to EAMP hydrogenation is suggested.

## Catalysis and Biotechnology

### METHANE HYDROXYLATION AND PROPYLENE EPOXIDATION BY RESTING CELLS OF METHYLOCOCCUS CAPSULATUS IMV 3021

**G.A. Kovalenko, V.M. Lenskaya**

*Prikl. Biokhimiya & Mikrobiologiya*,
34 (1998) 354-358.

Study on kinetics of direct biooxidation of methane into methanol and propylene into epoxypropane was carried out in suspensions of resting cells of methanotroph *Methylococcus capsulatus IMV 3021.* To improve accumulation of valuable oxy-products optimal conditions were selected, i.e. temperature, buffer, pH, concentrations of exogenic co-factors for MMO and inhibitors of further methanol oxidation. Apparent kinetic constants $\text{К}_M\text{CH}_4$ и $\text{К}_M\text{O}_2$ for microbial methane oxidation were determined.

### IMMOBILIZATION OF METHANOTROPHIC BACTERIA *METHYLOCOCCUS CAPSULATUS* ON INORGANIC SUPPORTS

**G.A. Kovalenko, V.M. Lenskaya, G.B. Barannik, N.A. Kulikovskaya**

*Prikl. Biokhimiya & Mikrobiologiya*,
34 (1998) 632-637.

Inorganic supports as granules or honeycomb monoliths based on modified or nonmodified $Al_2O_3$, $TiO_2$, $Fe_2O_3$, silica-alumina were studied for immobilization of resting cells of *Methylococcus capsulatus IMV 3021* to develop heterogeneous biocatalyst with methane monooxygenase activity. Immobilization of bacteria were carried out via adsorption or cells “immuring” by silica-gel inside the supports. “Immured” bacteria were found to retain 50% activity of suspended cells. These heterogeneous biocatlysts operated continuously for 22 h in the reaction of propylene epoxidation. The biocatalytic activity and stability of “immured” cells were in several times more than ones for cells immobilized by adsorption.

### METHODS TO OBTAIN BIOSPECIFIC HEMOSORBENTS

**G.A. Kovalenko**

*Khim.-Farm. Zh.,* 32 (1998) 36-40.

Immunosorbents were produced by immobilization of staphylococcus protein A and antiencephalitis gamma-globulin on the surface of the carbonized hemosorbents SKN and SUMS types. It was shown that the immunosorbent based on protein A extracted selectively IgG-immunoglobulins from the protein solutions of serum albumin in capacity of 1 mg of IgG per 1 mg of immobilized protein A. Hemosorbent SUMS-1 adsorbed antiencephalitis gamma-globulin in the amount of 0.17 mg per 1 $cm^3$. This immunosorbent is promising for hemosorption at a disease of tick-borne encephalitis. Immobilization of neutral protease Protosubtilin G10X on hemosorbent SUMS-1 permited to obtain hemosorbent-biocatalyst with a proteolytic activity of 100 UA per mg of protein, which can increase the hemosorbent hemocompatibility and favor extracting the aterogenic complexes of cholesterin.

### IMMOBILIZED PROTEOLYTIC ENZYMES FOR EXTERNAL APPLICATIONS IN MEDICINE

**G.A. Kovalenko**

*Khim.-Farm. Zh.,* 32 **(**1998) 41-44.

Research and development of the enzyme-containing materials based on immobilized proteases such as trypsin, fibrinolysin and neutral microbial protease Protosubtilin G10X for external use in medicine were performed. Inorganic matrixes ($SiO_2$-gel, carbon-mineral sorbents) and polymer membranes were studied as supports for enzymes immobilization. Investigation of proteolytic activity and stability of materials obtained were carried out. These materials was supposed to apply as external remedy in purulent and burn surgery.

### CARBON-MINERAL CARRIES USED FOR ADSORPTION IMMOBILIZATION OF NON-GROWING CELLS

**G.A. Kovalenko, E.V. Kuznetsova, V.M. Lenskaya**

*Biotekhnologiya,* 1 (1998) 47-56.

A comparative investigation on the adsorption immobilization of non-growing bacteria cells (methanotrophs, rhodococci, *Bacillus* and *E.coli*) on inorganic carries has been carried out. The carries used included alumina, silicagel, as well as carbon-mineral carries with the different surface carbon contents (from 0,3 to 20wt.%), and carbon materials. The adsorption characteristics of the carries with respect to the listed microorganisms was the subject of a careful study. It was shown that the biocatalytic activity of the immobilized methanotrophs (methane monooxygenase (MMO) activity, stability) were the function of the way the immobilization had been performed. The optimum method to obtain an active heterogeneous biocatalyst based on non-growing immobilized cells *Methylosinus trichosporium* was the cultivation of the previously adsorbed cells in a fresh nutrient medium. This made it possible to save 50% of the MMO activity of the cell suspension and prolong the operation stability of the preparation up to 12-16 hours.

## New Results in Studying Photocatalytic and Related Processes

### SURFACE COMPOSITION OF ATMOSPHERIC AEROSOLS

**V.P. Ivanov, D.I. Kochubey, K.P. Kutzenogii*, N.S. Bufetov* (Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia)**

*React. Kinet. Catal. Lett.,* 64 (1998) 97-102.

The composition of adsorbed gases and surface layers of atmospheric aerosols were studied by SIMS. From obtained results and a set of the possible photocatalytic reactions it can be predicted that aluminosilicates, $TiO_2$ and $CaTiO_3$ type perovskites could be active components of photocatalytic reactions. Possible catalytic reactions of these aerosols were analyzed.

### PHOTOADSORPTION AND PHOTOCATALYTIC OXIDATION ON THE METAL OXIDES - COMPONENTS OF TROPOSPHERIC SOLID AEROSOLS UNDER THE EARTH'S ATMOSPHERE CONDITIONS

**V.S. Zakharenko**

*Catal. Today*, 39 (1997) 243-249.

An overview on quantitative characteristics (quantum yield, action spectrum, maximum amount of photoadsorbed molecules) of photoadsorption and photocatalytic processes on some metal oxides, which are main components of the tropospheric solid aerosols, is presented. For the example of MgO, it is shown that the quantitative characteristics of photoadsorption of freons obtained for the air-exposed MgO samples are significantly different from that obtained for the samples experiencing a rigid pretreatment.

It is supposed that a sensitization of insulator oxides to the solar radiation spectrum in the troposphere may be due to the formation of an adlayer on their surface under conditions of the Earth's atmosphere.

## QUANTITATIVE STUDIES ON THE HETEROGENEOUS GAS-PHASE PHOTOOXIDATION OF CO AND SIMPLE VOCS BY AIR OVER $TiO_2$

**A.V. Vorontsov, E.N. Savinov, G.B. Barannik, V.N. Troitsky, V.N. Parmon**

*Catal. Today*, 39 (1997) 207-218.

The paper presents a collection of the recent results concerning the photocatalytic oxidation of gaseous organics and CO over $TiO_2$ in different kinds of reactors with the accent on providing quantitative information about the photoprocesses studied to enable comparison with results of other authors. A static reactor, an annular flow reactor and a flow-circulating reactor were used. Oxidation of acetone, ethanol and diethyl ether in the static reactor ultimately leads to $CO_2$, with acetaldehyde, acetaldehyde and ethyl acetate being the intermediate products in the oxidation of ethanol and diethyl ether, respectively. Acetone is completely oxidized to $CO_2$ during a single pass through the annular flow reactor if the residence time is greater than 1 min. Temperature dependence of the acetone photooxidation rate in the flow-circulating reactor has a maximum at 80 $^{o}$C. Four specimens of $TiO_2$ prepared by principally different methods were tested in oxidation of acetone and CO in the flow-circulating reactor. It has been found that photoplatinization retards the acetone oxidation and prohibits considerably the CO oxidation. These results indicate that the process of heterogeneous photocatalytic oxidation can be substantially improved by optimization of both the catalyst and the conditions of the photocatalytic process.

## SPECIFIC FEATURES OF LUMINESCENCE OF Q-CdS COLLOIDS WITH DIFFERENT SIZES

**D.V. Bavykin*, E.N. Savinov, V.N. Parmon (Novosibirsk State University, Novosibirsk, Russia)**

*Izv. Akad. Nauk,* 4 (1998) 651-658.

Specific features of luminescence of Q-CdS colloidal solutions with particles of different sizes and regularities of its quenching by different quenchers were studied. The luminescence spectra of Q-CdS consists of several bands, which are shifted to the longer-wave region as the size of the particles increases. The dependence of the integral quantum yield of luminescence on the particle size has a sharp maximum at the particle diameter of ~23 Å. The Stern-Volmer type equation including the adsorption isotherm of the quencher molecules on the surface of the Q-CdS colloidal particles was used to describe the regularities of luminescence quenching of Q-CdS colloidal solutions. The effect of the CdS particle size on the efficiency of luminescence quenching was observed. The regularities of luminiscence quenching depend on both the rate constant of electron transfer to the quencher molecules and the ability of the quencher molecules to adsorb on the surface of the CdS colloidal particle.

## THE INFLUENCE OF THE NON-IRRADIATED SURFACE AREA ON THE KINETICS OF HETEROGENEOUS PHOTOCATALYTIC REACTION IN A STATIC REACTOR

**A.V. Vorontsov, E.N. Savinov**

*Chem. Engin. J.*, 70 (1998) 231-235.

Mathematical modelling on the basis of Langmuir-Hinshelwood equation of a photocatalytic reaction in a static reactor taking into account in mass balance adsorption on irradiated parts of catalyst, dark parts of catalyst and support reveals that increase in surface area of dark catalyst results in prolonged kinetic curves. Neglect of adsorption on irradiated and dark catalyst in mass balance can cause error in kinetic parameters calculated from concentration-time curves. The growth in dark catalyst surface area facilitates removal of contaminants from gas or liquid phase to below threshold permitted concentration (TPC) if TPC corresponds to surface coverage of illuminated catalyst with contaminant higher than 0.37.

## APPLICATION OF HETEROPOLYANIONS AS THE REVERSIBLE ELECTRON CARRIERS FOR PHOTOCATALYTIC HYDROGEN EVOLUTION IN THE SYSTEMS OF LIPID VESICLES

**O.V. Vassiltsova, V.N. Parmon**

*Dokl. Akad. Nauk,* 360 (1998) 61-65.

Heteropolyanions $SiW_{12}O_{40}^{4-}$ have been studied as the reversible electron carriers for the very first time in the systems of lipid vesicles. The optimal conditions of functioning of heteropolyanions $SiW_{12}O_{40}^{4-}$ were determined, as well as their localization in the lipid membrane. A system for photocatalytic hydrogen evolution on the base of CdS nanoparticles, donors of electrons, and particles of $Pd^0$, attached to the surface of the lipid vesicles, have been made.

### NMR-SPECTROSCOPY AS A METHOD OF THE DETERMINATION OF THE PARAMAGNETIC ELECTRON CARRIERS LOCALIZATION IN THE LIPID BILAYER: STUDY OF LOCALIZATION CETYLVIOLOGEN CATION-RADICAL IN THE SYSPENSION OF LIPID VESICLES

**O.V. Vassiltsova, D.E. Babushkin, V.N. Parmon**

*Dokl. Akad. Nauk,* 361 (1998) 489-494.

Direct and selective influence of paramagnetic lipophilic electron carriers on the $^1$H NMR spectra of the molecules constitutive bilayer lipid membranes has been found for the first time. It was established that the paramagnetic cation-radical of cetylviologen influence mostly the signal of $^1$H NMR spectra of -N+(CH$_3$)$_3$, localized on the surface of the vesicle membrane. A remarkable change in the width of this signal corresponds to localization of the radical paramagnetic center (i.e. its aromatic groups) on the surface of the vesicle membrane and to a fast lateral diffusion of the lipid molecules around the radical.

## Catalysts for Oil Refinery. Synthesis, Physicochemical and Catalytic Properties

### SULFIDE CATALYSTS FOR HYDROGENATION OF AROMATIC HYDROCARBONS. I. BENZENE HYDROGENATION AND THIOPHENE HYDROGENOLYSIS

**A.N. Startsev, V.N. Rodin, G.I. Aleshina, D.G. Aksenov**

*Kinet. Katal.,* 39 (1998) 238-245..

The main kinetic regularities of benzene hydrogenation in the presence of tiophene and hydrogenolysis of tiophene in the presence of benzene are studied. The strong inhibition of tiophene hydrogenolysis by benzene was found. Analysis of main regularities of reactions on sulfide catalysts, obtained by different methods, and on different supports allows make a conclusion, that both reactions proceed on the same active centers by concurrent sorption of reactive molecules. Active centers of benzene hydrogenation are formed after hydrogen sulfide removal from active centers of tiophene hydrogenolysis.

### SULFIDE CATALYSTS FOR HYDROGENATION OF AROMATIC HYDROCARBONS II. BENZENE HYDROGENATION IN A NON-STEADY-STATE REGIME

**A.N. Startsev, G.I. Aleshina, D.G. Aksenov, V.N. Rodin**

*Kinet. Katal.,* 39 (1998) 391-395.

The main kinetic regularities of benzene hydrogenation over sulfided Ni, Mo- and Ni, W-catalysts in the absence of sulfur compounds in raw material are studied. It was shown, that activity of catalysts significantly increases in the reaction medium up to the level of activity of given catalysts preliminary treated by hydrogen at optimal temperature. Activity of Ni,W-catalysts slowly increases during a long time (up to 30 h), and then decreases, while activity of Ni, Mo-catalysts increases much quicker (1-3 h), and then decreases. The change of catalyst activity is reversible, and allows perform the benezene hydrogenation in non-steady-state regime.

### SULFIDE CATALYSTS FOR HYDROGENATION OF AROMATIC HYDROCARBONS. III. MECHANISM OF BENZENE HYDROGENATION

**A.N. Startsev, I.I. Zakharov, G.I. Aleshina, D.G. Aksenov, V.N. Rodin**

*Kinet. Katal.,* 39 (1998) 549-553.

The simple and effective method to determine the quantity of hydrogen sulfide, removed from the surface of sulfide catalysts in the process of their activation by reaction mixture H$_2$+benzene is suggested. It was shown, that Ni-W catalyst active in benzene hydrogenation is obtained after sulfur removal from the surface in amount of S:Ni=1. In the case of Ni-Mo catalysts this amount is 0.6-1.0. The possible structures of active centers of catalysts for hydrogenolysis and hydrogenation, their mutual transformation are considered. Tiophene and benzene molecules are adsorbed in both cases on Ni atoms entering into the composition of active component - sulfide bimetal species (SBMS). It is suggested, that chemosorption properties of nickel in SBMS are conditioned by its unusual $d^{6-}$electronic configuration, which is “kept up” by adsorbed molecules. Formation of electronic nickel structure by oxidative addition of hydrogen upon catalyst activation by sulfidation was hypothesized. The concerted mechanism of benzene hydrogenation over SBMS of any chemical composition is proposed.

# Studies on DeNOx Processes and New Catalysts for Detoxication of Industrial Gases

## PROPANE AND OXYGEN ACTION ON $NO_X$ ADSPECIES ON LOW EXCHANGED Cu-ZSM-5

**E.V. Rebrov, A.V. Simakov, N.N. Sazonova,**
**V.A. Rogov, G.B. Barannik**

*Catal. Lett.,* 51 (1998) 27-40.

A surface intermediate with a C/N ratio close to 3 has been shown by TPD to form at co-adsorption of NO and propane as well as NO, propane and $O_2$ on low-exchanged Cu-ZSM-5. The adsorption of NO, propane and oxygen has been studied to evaluate their effect on the formation of this complex. Its formation is accompanied by a decrease in the concentration of surface nitrite-nitrate. The kinetics of nitrite-nitrate adspecies formation as a function of the reagents concentration and temperature has been investigated. Some NO adspecies have been found to decompose yielding $N_2O$.

## KINETICS OF THE SELECTIVE CATALYTIC REDUCTION OF NO BY PROPANE OVER MONOLITH Cu-ZSM-5 CATALYST

**E.V. Rebrov, A.V. Simakov, N.N. Sazonova,**
**O.V. Komova, N.A. Kulikovskaya T.A. Nikoro,**
**G.B. Barannik**

*Kinet. Katal.*, 39 (1998) 716-721.

The reaction of selective catalytic reduction of NO by propane on Cu-ZSM-5 and honeycomb monoliths prepared from the parent Cu-ZSM-5 zeolite has been studied in the kinetic and diffusion regions. The effect of pore structure on the NO reduction is different for catalysts with various pore size distribution. The significance of interphase and intraparticle diffusion limitations is discussed. A simulation model for the selective reduction of NO with propane in reactor containing honeycomb catalyst and operating at temperatures between 400 and 500 $^{o}$C has been developed. The model predicts well the $NO_x$ reduction rate as a function of process variables (temperature, gas velocity, concentration) and geometry of the catalyst (pitch diameter, length of catalyst). The intrinsic chemical rate constant, coefficient of an effective intraporous diffusivity of NO, and NO gas-solid mass transfer coefficient have been estimated.

## TPD-STUDY OF $NH_3$ ADSORPTION/ DESORPTION PROCESS ON THE SURFACE OF V/Ti, V/Al BASED CATALYSTS FOR SELECTIVE CATALYTIC REDUCTION OF $NO_X$ BY AMMONIA. I. TPD TEST OF $\gamma$-$Al_2O_3$, $TiO_2$ (ANATASE FORM) AND ALUMINIA-SUPPORTED VANADIA CATALYSTS

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**L.N. Bobrova**

*React. Kinet. Catal. Lett.*, 65 (1998) 363-370.

The effect of temperature on the adsorption/desorption of ammonia from the air mixture on the surface of $\gamma$-$Al_2O_3$, $TiO_2$ (anatase) and alumina-supported vanadia catalyst samples has been investigated using temperature-programmed desorption (TPD). When the vanadia loading was increased, the fraction of the acid cites providing the $NH_3$ adsorption in the high-temperature state decreased. At the same time, the fraction of the medium temperature state significantly increased.

## TPD-STUDY OF $NH_3$ ADSORPTION/ DESORPTION PROCESS ON THE SURFACE OF V/Ti, V/Al BASED CATALYSTS FOR SELECTIVE CATALYTIC REDUCTION OF $NO_X$ BY AMMONIA. II. TPD TEST OF COMMERCIAL V/W/Ti, V/Al, Pd/V/Al CATALYSTS

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*React. Kinet. Catal. Lett.,* 65 (1998) 371-380.

The effect of temperatue on the adsorption/desorption of ammonia from the air mixture on the surface of commercial binary V/Al and ternary Pd/V/Al, V(0.65 wt.%)/W(6.73 wt.%)/Ti and V(1.8 wt.%)/W(7.3 wt.%)/Ti de-$NO_x$ catalysts has been investigated by temperature-programmed desorption (TPD) method. The ability of the commercial catalyst to adsorb ammonia in the most stable surface species was shown to correlate well with their suppression of the $NH_3$ oxidation.

# Catalysts and Catalytic Technologies for Combustion

## NOVEL MICRODESIGN OF OXIDATION CATALYSTS. I. GLASS CRYSTAL MICROSPHERES AS NEW CATALYSTS FOR THE OXIDATIVE CONVERSION OF METHANE

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*Catal. Today*, 42 (1998) 267-272.

New catalysts designed as glass crystal microspheres were obtained as a result of coal and lignite combustion, hydrodynamic classification of fly ash followed by magnetic separation. The physicochemical and catalytic properties of three different systems of new catalysts were studied by SEM, XRD and Mossbauer spectroscopy. The active component of the new systems was shown to include α-$Fe_2O_3$ and a solid solution formed from magnetite and Mg(Mn)-ferrite. High-temperature eutectics (1473-1673 K) on the base of calcium aluminosilicates are represented as a matrix material. The growth of the $Fe^{2+}$ concentration in the spinel phase results in increase of selectivity of $C_2$-product formation in oxidative coupling of methane at 1123 K and in decrease of catalytic activity of deep oxidation at 793 K.

## NOVEL MICRODESIGN OF OXIDATION CATALYSTS. II. THE INFLUENCE OF FLUORINATION ON THE CATALYTIC PROPERTIES OF GLASS CRYSTAL MICROSPHERES

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*Catal. Today*, 42 (1998) 273-277.

New catalysts designed as a glass crystal microspheres were studied by XPS, SEM, XRD and Mossbauer spectroscopy. The data obtained indicated that after treatment of catalysts with HF the fluorination of lattice took place leading to stabilization of $Fe_3O_4$ phase. The catalytic activity of initial catalysts already treated with HF in the reactions of deep oxidation and oxidative coupling of methane was determined. The yield of $C_2$-products at 1123 K was 16% for oxyfluoride systems using the gas mixture $CH_4$:$O_2$=85:15 vol %.

## ACID AND CATALYTIC PROPERTIES OF $M_nO_m$-$ZrO_2$ (M=Ca, Ba, Sm, Yb) COMPOSITIONS

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*React. Kinet. Catal. Lett.*, 64 (1998) 337-342

Influence of the nature of $M_nO_m$ in zirconia-based systems $M_nO_m$ $ZrO_2$ (M=Ca, Ba, Sm, Yb) of approximately equimolar composition on their acid and catalytic properties in oxidative conversion of methane (OCM) have been studied. The surface of $M_nO_m$-$ZrO_2$ systems has been found to contain practically no Bronsted acid sites. Lewis acid sites are represented by three types of L-sites, their total concentration per $m^2$ decreasing in the series (Zr, Ca)$O_2$>(Zr, Sm)$O_2$>(Zr, Yb)$O_2$. Activity of the catalysts in the OCM reaction is proportional to the specific surface area. Their selectivity to $\Sigma C_2$ hydrocarbons increases in the series (Zr, Ca)$O_2$<(Zr, Sm)$O_2$<(Zr, Yb)$O_2$.

## 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 Conversion V*, 119 (1998) 677-683.

The paper discusses new honeycomb catalysts for natural gas oxidation to syngas, a recently developed processes of moderate-temperature (450-650 °C) catalytic pyrolysis of natural gas and/or light hydrocarbons into hydrogen and valuable 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.

### PREPARATION AND STUDY OF THERMALLY AND MECHANICALLY STABLE CERAMIC FIBER BASED CATALYSTS FOR GAS COMBUSTION

**Z.R. Ismagilov, R.A. Shkrabina, N.V. Shikina, T.V. Chistyachenko, V.A. Ushakov, N.A. Rudina**

*Stud. Surf. Sci. & Catal., Natural Gas Conversion V*, 119 (1998) 83-86.

The effective stable fiber based catalyst with a good permeability is prepared and studied. It is shown that proposed preparation method provides stable activity of catalyst with low concentration of active components after long operation in hydrocarbon combustion.

### BEHAVIOR OF SOME DEEP OXIDATION CATALYSTS UNDER EXTREME CONDITIONS. I. COMPARISON OF RESISTANCE TO THERMAL SHOCK AND $SO_2$ POISONING

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*Appl. Catal. A: General,* 167 (1998) 31-37.

The activity of catalysts before and after heat treatment up to 950 $^{o}$C was measured in model reactions of methane and butane deep oxidation. The poisoning stability was investigated by examine the catalysts in deep oxidation of methane (1 vol.% in air) in the presence of $SO_2$ (0.05 vol.%). The alumina-manganese oxide catalyst was found to be the most resistant to overheating. It lowered the activity in deep methane oxidation ~2.5 times only after calcination at 950 $^{o}$C for 800 h. The more poison stable samples were found to be alumina-palladium and perovskite (on the base of $LaMnO_3$) catalysts. The activity of more thermostable alumina-manganese oxide catalyst is lowered up to zero activity in deep oxidation of methane at 500 $^{o}$C. But at reaction temperature 700 $^{o}$C the catalyst is sufficiently stable to poisoning.

### SELECTIVE LOW TEMPERATURE METHANE CONVERSION TO ALKENES $C_2$-$C_4$ IN THE PRESENCE OF HYDROGEN-ACCUMULATING SYSTEM

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*Dokl. Akad. Nauk.,* 361 (1988) 791-794.

Development of energy-saving technologies of methane conversion to valuable organic products is an urgent problem. The principally new decision is selective low temperature methane conversion to alkenes $C_2$-$C_4$ in the presence of hydrogen-accumulating system able to activation of C-H bond with subsequent hydrogen removal from reaction zone with stable hydrides formation.

The results obtained open new possibilities of methane direct conversion to valuable alkenes.

### METHANE PROCESSING UNDER MICROWAVE RADIATION: RECENT FINDINGS AND PROBLEMS

**Yu.Yu. Tanashev, V.I. Fedoseev, Yu.I. Aristov, V.V. Pushkarev, L.B. Avdeeva, V.I. Zaikovskii, V.N. Parmon**

*Catal. Today*, 42 (1998) 333-336.

Microwave-driven transformations of methane and methane-containing mixtures in the presence of microwave-absorbing objects have been investigated. Application of pulse microwave (MW) power is shown to be a promising way for the production of hydrogen, syngas, acetylene and filament carbon. The influence of catalyst nature, MW-power and contact time on the reaction rate is analyzed. Two pathways for the studied reactions are found - a direct MW-heating of the whole catalyst (or its active centers) and a gas discharge near the rough catalyst surface.

## Liquid Phase Catalytic Technologies

### INVESTIGATION OF $H_2S$ OXIDATION BY OXYGEN ON OXIDE CATALYSTS IN SULFUR CONDENSATION CONDITIONS

**O.N. Kovalenko, N.N. Kundo, V.M. Novopashina, V.M. Khanaev**

*React. Kinet. Catal. Lett.*, 64 (1998)129-137.

$H_2S$ oxidation with oxygen has been studied on three industrial oxide catalysts (Fe-Cr-Zn, Cu-Cr-Al, V-Ti-Al). Thermodynamically possible changes in the composition of the catalysts have been evaluated. Regularities determining deep or partial oxidation of $H_2S$ have been found. Deep oxidation is connected to the presence of active oxygen on the catalyst surface; its removal results in a decrease of activity and increase of the sulfur selectivity. Oscillations caused by periodic adsorption-desorption of sulfur on the catalyst surface have been observed on the most active V-Ti-Al catalysts in oxygen excess.

### LIQUID-PHASE HYDRODECHLORINATION OF POLYCHLOROAROMATIC COMPOUNDS IN THE PRESENCE OF Pd-PROMOTED NICKEL CATALYSTS

**V.A. Yakovlev, V.I. Simagina, V.A. Likholobov**

*React. Kinet. Catal. Lett.*, 65 (1998) 177-183.

Liquid phase hydrodechlorination of chlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene, polychlorinated biphenyls in the ethanol-containing solution, on $Me^o/C$ (where $Me^o$ - Pd, Ni or bimetallic Ni-Pd; C - carbon material "Sibunit") with $H_2$ have been studied at 20-70 °C and $P_{H2}$ = 1-50 atm. Pd and Pd-promoted Ni catalysts exhibit the highest activity. Kinetic studies show hydrodechlorination of these compounds to be consecutive reaction, which under the conditions described may produce less chlorinated compounds.

### ECOLOGICAL PROBLEMS OF THERMAL POWER INDUSTRY

**Z.P. Pai**

*Chemistry for Sustainable Development,*
6 (1998) 367-374.

Comparative evaluation of various technologies for energy production has been performed. The current state in the field of purification of the flue gases of thermal electric power stations from the most large-scale atmosphere pollutants – sulfur and nitrogen oxides is analyzed. The main tendencies are indicated, and the main methods for desulfurization and denitrofication of flue gases and their technical and economical characteristics are reported. The main attention is paid to necessary first-order and advanced measures affecting the solution of ecological problems with the account of the specific features of Russian thermal power industry.

## Mathematical Simulation of Processes and Reactors. Chemical Engineering

### INCREASE IN THE SELECTIVITY OF PARTIAL HYDROCARBON OXIDATION BY USING A TWO-REACTOR SYSTEM

**E.A. Ivanov, A.A. Ivanov, S.I. Reshetnikov**

*Teor. Osn. Khim. Tekhn.,* 32 (1998) 530-535.

A simple kinetic model for the partial oxidation of hydrocarbons containing two types of active sites has been used for mathematical modeling of a two-reactor system with the catalyst circulation. Factors affecting the selectivity to the desired products have been studied. In the frames the kinetic model used, it was possible to increase the selectivity of the reactions by 15-20 % in comparison with a one-reactor system by regulating the ratio of concentrations of deep and partial oxidation sites.

### CATALYTIC OXIDATION OF $C_3$-$C_4$ HYDROCARBONS ON A POROUS PERMEABLE PLATE WITH COUNTERCURRENT AND COCURRENT FEED OF REACTANTS

**V.A. Kirillov, S.I. Fadeev*, N.A. Kuzin,**
**A.V. Kulikov (Sobolev Institute of Mathematics, Novosibirsk, Russia)**

*Teoret. Osn. Khim. Ttekhn.,* 32 (1998) 164-174.

A mathematical model has been suggested for description of the catalytic oxidation of $C_3$-$C_4$ hydrocarbons on a porous permeable plate. The model takes into account the convection and diffusion transfer along the plate thickness and the non-isothermal process regime. An algorithm has been developed for calculation of the equations of the model by the method of solution extension by a parameter. Heat exchange coefficients between the catalytically active surface and the environment have been determined, and a significant contribution of the radiation constituent into the overall heat exchange has been shown. Numerical study of the effect of the parameters of the mathematical model on the distribution of temperatures and concentrations of the components along the plate thickness in the oxidation of propane and butane has been conducted for counterflow and joint feed of the reagents.

### MATHEMATICAL MODEL FOR THE HYDROGENATION OF NITROAROMATIC COMPOUNDS IN A FIXED BED CATALYTIC REACTOR WITH A COCURRENT UPWARD FLOW OF GAS AND LIQUID

**V.A. Kirillov, V.I. Drobyshevich**

*Teoret. Osn. Khim. Tekhn.,* 32 (1998) 72-81.

A mathematical model has been suggested for description of processes taking place in a reactor with a fixed catalyst bed with up flow of a gas or liquid during 2,4,6-trinitrotoluene hydrogenation. The model takes into account phase transformations related to the hydrogen dissolution and evaporation of the components of the liquid phase. An algorithm for calculation of the evaporation rates has been developed, coefficients of the mathematical model have been determined more precisely, and a significant effect of the rates of the chemical reaction and evaporation of the components of the liquid phase on interface exchange coefficients has been observed.

### DETERMINATION OF THE ACTIVATION ENERGIES OF ETHYLENE POLYMERIZATION ON TITANIUM-MAGNESIUM CATALYSTS: EXPERIMENT AND MATHEMATICAL MODELING

**V.B. Skomorokhov, V.A. Zakharov, V.A. Kirillov**

*Kinet. Katal.,* 39 (1998) 757-762.

The experimental data are presented on effect of temperature on the catalyst activity and kinetics of ethylene polymerization over supported titanium-magnesium catalysts with different particle size and different concentrations of electron-donor additive. The kinetic scheme of active site formation and monomer diffusion in a growing polymer particle developed earlier and modified in this work was used to estimate the rate constants and activation energies of the polymerization and the formation of active sites and unreactive by-products.

### CATALYTIC REACTIONS ACCOMPANIED BY CAPILLARY CONDENSATION. III. INFLUENCE ON REACTION KINETICS AND DYNAMICS

**N.M. Bukhavtsova, N.M. Ostrovskii**

*React. Kinet. Catal. Lett.,* 65 (1998) 321-330.

The influence of capillary condensation of reagents on the catalytic reaction kinetics and dynamics was studied. The hydrogenation of *p*-xylene over $Pt/SiO_2$ was used as a model reaction. Two types of $SiO_2$ were used (KCK-1 with large pores and KCM-5 with small pores). It was shown that capillary condensation could modify the kinetics and the transition regimes. The proposed mathematical model demonstrates good agreement with experimental results for both steady-state and dynamic regimes, including reaction rate - temperature hysteresis.

### ON THE PARTICLE METHOD FOR THE VLASOV KINETIC EQUATION

**V.A. Vshivkov, V.N. Snytnikov**

*Zh. Vychisl. Matem. & Matem. Fiz.,*
38 (1998) 1877-1883.

Self-heating in an ensemble of large particles of model plasma has been shown to be related to a special error in the approximation of force affecting each particle. This error known as self-force does not decline with the decrease of the space step in NGP, PIC and other algorithms of the particle method. A new VSP class of grid cores for particles free from this drawback has been suggested. Numerical simulation of unsteady 3D plasma dynamics has proved high efficiency of the algorithm with the new core, which is no worse than the PIC algorithm in the expenses of computational resources.

## Catalysis for Energy Conversion

### CATALYTIC THERMOCHEMICAL REACTOR/ RECEIVER FOR SOLAR REFORMING OF NATURAL GAS. DESIGN AND PERFORMING

**V.I. Anikeev, A.S. Bobrin, J. Ortner*, S. Schmidt*, K.-H. Funken*, N.A. Kuzin**

*Solar Energy*, 63 (1998) 97-104.

Advantages of thermochemical conversion of concentrated solar energy using catalytic processes are discussed. Design of solar volumetric thermochemical reactor/receiver (TCRR) with catalytic absorber, method for synthesis of catalytically activated ceramics, preparation of catalytic absorber have been described. The prototype of TCRR was tested in the high flux solar furnace at the DLR research center, Cologne by using the dioxide reforming of methane. The tests were performed to check the main concept of the TCRR design and catalytic absorber, to study the influence of solar flux distribution, the reagent flows and their ratio on the productivity or conversion, determine the reagent's conversion depending on the focal point disposition with respect to the absorber, to study the efficiency of the thermochemical conversion. The chemical and total efficiencies of the

$CO_2$-methane conversion were calculated by using the experimentally measured concentrations of the reaction products. The highest overall efficiency achieved in these experiments was 30% with the Ni-Cr catalytic absorber.

## CALCULATION OF PHASE DIAGRAMS BY HOMOTOPIC METHOD

**A. Yermakova, V.I. Anikeev**

*Zh. Fiz. Khim.,* 72 (1998) 2158-2163.

A new approach and algorithm for calculation of phase diagrams based on the homotopy method has been suggested. The function known as "criterion of tangent plane" has been used as the homotopy equation, and the pressure in the system has been used as the homotopy parameter. Examples of phase diagrams and their comparison with the experimental data are presented.

## BINARY INTERACTION COEFFICIENT FOR THE REDLICH-KWONG-SOAVE EQUATION OF STATE

**V.I. Anikeev, A. Yermakova**

*Theor. Found. for Basic Research,* 32 (1998) 508-514.

Binary interaction coefficients in Redlich-Kwong-Soave (RKS) equation of state have been calculated with the use of experimental data on the liquid-gas equilibrium in binary mixtures. The dependence of these coefficients on temperature and pressure is presented. The possibility of a substantial improvement of the RKS model precision, especially at high pressures and temperatures, and near critical points, has been shown on examples of the calculation of phase equilibria.

## THERMODYNAMIC ANALYSIS OF PHASE STATES OF THE PRODUCTS OF FISCHER-TROPSCH SYNTHESIS

**A. Yermakova, V.I. Anikeev, A.V. Gudkov**

*Zh. Prikl. Khim.,* 71 (1998) 1776-1782.

Heterogeneous three-phase equilibrium vapor gas – hydrocarbon phase – aqueous phase has been studied for multicomponent systems typical for Fischer-Tropsch synthesis in a slurry reactor in the presence of a cobalt-containing catalyst. The number, type and phase concentrations of stable coexisting equilibrium phases depending on T and P have been determined. The analysis of the deviation of the mixture properties from the ideal state has been conducted. Equations for calculation of the main thermodynamic characteristics used in the reactor modeling (energy, enthalpy and entropy of phase transformations) and their calculated values are presented.

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