INSTITUTE OF CATALYSIS AND SURFACE CHEMISTRY

POLISH ACADEMY OF SCIENCES

ANNUAL RESEARCH REPORT

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CONTENTS

INSTITUTE OF CATALYSIS AND SURFACE CHEMISTRY
Polish Academy of Sciences

From theory to experiment and application

Institute of Catalysis and Surface Chemistry (ICSC) of the Polish Academy of Sciences in Cracow is the only scientific institution in Poland and one of eight in the world devoted entirely to research in catalysis and chemistry of interfaces. The Institute pursues interdisciplinary studies of the phenomena occurring at gas/solid, gas/liquid and liquid/solid interfaces, with emphasis on their significance in catalysis, materials engineering, adsorption, coating technologies, flotation and detergency. ICSC integrates fundamental theoretical and experimental studies, and combines them with applied research so that the results obtained can be used directly to improve technological processes.

The number of employees is about 100, of which a half are research staff. Over 20 PhD students are also involved in the research. ICSC is equipped with state-of-the-art research instrumentation, which serves not only Institute's employees but is also available to the whole scientific community.

Theory

An important aspect of the research carried out at ICSC is to provide the theoretical background for experimental studies. The methodologies employed involve quantum chemistry and solid state physics modelling methods, as well as molecular mechanics and Monte-Carlo simulation techniques. The field of expertise ranges from elucidating catalytic reaction mechanisms and modelling the structures of transition metal oxides, composite nanomaterials and enzyme active centres, to describing surfactant adsorption at liquid/gas and liquid/liquid interfaces, and simulating polymer particle adsorption on solid homogenous surfaces.

Experiment

The research activities of the Institute are very broad and versatile. The size of objects investigated ranges from 1 millimetre to less than 1 nanometre. The highest atomic resolution is available with the help of the Ultra High Vacuum Scanning Tunnelling Microscope. The time-scale of processes under study varies from centuries, as in the case of historical monument deterioration, to microseconds. The fastest recording equipment available is the High Speed Camera Speedcam, which can record pictures with more than 1000 Hz frequency.

The bulk of research is focused on the practical implementation of scientific results and encompasses design, synthesis, testing and practical verification of new, advanced materials and processes. In the area of heterogeneous catalysis, lots of effort is put into developing new, “intelligent” materials, with well-defined structure-property relations, tunable to the requirements of a particular catalytic reaction. The materials under investigation include new types of oxidic structures and novel micro- and mesoporous inorganic solids. New magnetic materials and interactions between metallic nanoparticles deposited on single crystalline oxide surfaces are also investigated. The field of application encompasses selective oxidation, oxidative dehydrogenations, isomerization of hydrocarbons, end-of-pipe environmental catalysis, and green chemistry reactions. The work also involves the description of kinetic and mechanistic aspects of the studied processes. Research into homogeneous and enzymatic catalysis concentrates on bioactive and biomimicking systems. In the field of surface chemistry of dispersed systems, investigations are focused on understanding the mechanism of formation and stability of foams, nano- and colloid particle interactions and biocompatible materials, as well as on description of adsorption phenomena.

Application

Research carried out at ICSC is planned in such a way that the investigation outcomes can be turned into applications. In 1995, a spin-off company Katalizator Ltd. was created in order to promote the industrial implementation of catalytic materials designed at ICSC. This company, in which ICSC holds a control share packet, produces and sells catalysts synthesized according to ICSC-patented procedures to industrial partners in Europe and overseas.

Education

ICSC PAS is a parent institution for the International Postgraduate School, organised in cooperation with the Faculty of Engineering and Chemical Technology of the Krakow University of Technology, and the Faculty of Chemistry of the Rzeszów University of Technology. The School is attended by over 50 PhD students.

National cooperation

ICSC has a long-standing tradition of animating and coordinating research in the field of catalysis and surface science in Poland. For more than thirty years, the Institute has been organising the annual National Catalytic Colloquium, an extremely popular conference at which Polish scientists report their recent findings. As of 2004 the event is sponsored by EC. The Institute is the coordinator of the National Catalytic Network "Nanomaterials as Catalyst for New, Environmentally Friendly Processes" and National Network "Surfactant and Dispersed Systems in Theory and Practice – SURUZ", a member of the National Scientific Network „New Materials – Nanomaterials for Technical and Medical Applications", a and a member of the Polish Supramolecular Chemistry Network. In order to facilitate interdisciplinary research, a Joint Laboratory of Biotechnology and Enzymatic Catalysis (in cooperation with the Institute of Plant Physiology PAS) and a Joint Nanotechnology Laboratory (in cooperation with the AGH-University of Science and Technology and the Krakow University of Technology) have recently been created. The Institute is also a co-founder of National Laboratory for Surface Studies.

International cooperation

ICSC PAN is widely involved in international cooperation. The activities include over 40 bilateral international collaboration schemes and participation in numerous EU scientific programmes. The bilateral collaboration with the Ukrainian Academy of Sciences led, in 1993, to the establishment of a Ukrainian-Polish Laboratory of Catalysis. In 2002 ICSC was granted the status of an EC Centre of Excellence. It is known as CATCOLL – the Cracow Research Centre of Molecular Catalysis and Soft Matter Chemistry. CATCOLL activities contribute to the integration of the European scientific community through organising lectures by internationally renowned scientists, arranging study visits for researchers from different countries, and offering to young PhD students a unique opportunity to visit the leading European research laboratories. The Institute is involved in 16 projects sponsored by EC. In six of them ICSC PAS is the coordinating institution.

Cultural Heritage and Environmental Protection

One of the focal points in the research carried out at CSIC PAS is the preservation of the natural environment and historical sites. Our culture heritage research group has animated a programme on the preservation of historic wooden churches, a unique heritage on the world scale. Its work is concentrated on the structure and properties of historic building and decorative materials, the deterioration mechanisms, as well as on the conservation and protection measures. Basic research is linked to practical conservation work. Recently, an important archeological site at Wiślica, featuring a magnificently decorated gypsum floor dating back to 12th century, has been reopened to visitors thank to the research and preservation programme coordinated by the Institute’s experts on cultural heritage.

Moreover, the Institute has notable achievements in developing technologies for protecting the environment. One of them - SWINGTHERM - is a novel catalytic, low-energy-consumption process based on the Regenerative Catalytic Oxidation, targeted at the purification of waste gases from organic pollutants. It has already found its application in industry in Poland, Europe, Canada and Japan.

Popularisation

It is our firm belief that making scientific research easily understandable to ordinary people is of immense importance for gaining public support in this area of human activities. Therefore, every year, ICSC PAS organizes Open Door Days, during which visitors may listen to popular lectures, participate in spectacular laboratory presentations and attend poster sessions depicting Institute’s research. The Open Door Days are aimed especially at young people from junior and senior high schools. They are very popular among students interested in science – every year ICSC receives ca. 1000 visitors.

SCIENTIFIC TEAMS OF THE INSTITUTE

Research Groups

Adsorption

Professor Władysław Rudziński, Ph.D., D.Sc.
Tomasz Pańczyk, Ph.D., Wojciech Piasecki, Ph.D., Piotr Zarzycki, Ph.D.

Catalysis I

Professor Jerzy Haber, Ph.D., D.Sc., D.h.c.
Paweł Nowak, Ph.D., Eng., Janina Rodakiewicz-Nowak, Ph.D., Jan Połtowicz, Ph.D., Katarzyna Pamin, Ph.D., Eng, Edyta Tabor, M.Sc., Ph.D. student, Robert Karcz, M.Sc., Eng., Ph.D. student

Catalysis II - Oxide Catalysts - Oxidation Reactions

Professor Barbara Grzybowska-Świerkosz, Ph.D., D.Sc.
Marian Gąsior, Ph.D., Eng., Katarzyna Samson, M.Sc., Eng., Anna Klisińska, Ph.D., Eng., Małgorzata Ruszel, M.Sc., Ph.D. student, Irena Gressel, technician

Colloids I

Professor Zbigniew Adamczyk, Ph.D, D.Sc., Eng
Barbara Jachimska, Ph.D., Eng., Lilianna Szyk-Warszyńska,Ph.D., Eng., Paweł Weroński, Ph.D., Maria Zembala, Ph.D., Anna Bratek, M.Sc., Ph.D. student , Katarzyna Jaszczółt, M.Sc., Eng., Ph.D. student , Aneta Michna, M.Sc., Ph.D. student, Elżbieta Porębska, technician

Colloids II - Colloid and Surfactant Systems

Associate Professor Piotr Warszyński, Ph.D., D.Sc.
Grażyna Para, M.Sc., Marzena Noworyta, Eng., Ewelina Jarek, M.Sc, Ph.D. student, Tomasz Jasiński, M.Sc, Ph.D. student, Marta Kolasińska, M.Sc, Ph.D. student, Jerzy Superata, M.Sc., Ph.D. student, Anna Trybała, M.Sc, Ph.D. student

Cultural Heritage Research

Associate Professor Roman Kozłowski, Ph.D., D.Sc.
Grzegorz Adamski, Ph.D., Łukasz Bratasz, Ph.D., Sławomir Jakieła, M.Sc., Ph.D. student, Łukasz Lasyk, M.Sc. Ph.D. student

Dispersed Systems

Professor Kazimierz Małysa, Ph.D., D.Sc.
Marta Barańska, Eng., Wanda Barzyk, Ph.D., Jan Zawała, M.Sc., Eng., Marta Krasowska, M.Sc., Ph.D. student, Marcel Krzan, Ph.D.

Environmental Control

Tadeusz Machej, Ph.D.
Janusz Janas, M.Sc., Robert Janik, M.Sc., Halina Piekarska-Sadowska, Ph.D., Małgorzata Nattich, M.Sc., Eng., Ph.D. student

Heterogenous Reaction Kinetics

Ryszard Grabowski, Ph.D.
Antonina Kozłowska, Ph.D., Zofia Czuła, technician

Layered Minerals, Mesoporous Oxides, Nanostructures

Professor Ewa Serwicka-Bahranowska, Ph.D., D.Sc.
Małgorzata Zimowska, Ph.D., Roman Dula, Ph.D., Alicja Michalik, Ph.D., Daria Napruszewska, Eng., Wojciech Włodarczyk, M.Sc., Eng., Aleksandra Pacuła, M.Sc., Eng., Ph.D. student

Polyoxometalates

Professor Adam Bielański, Ph.D., D.Sc., D.h.c.
Anna Lubańska, Ph.D., Anna Micek-Ilnicka, Ph.D.

Quantum Chemistry I

Professor Małgorzata Witko, Ph.D., D.Sc.
Renata Tokarz-Sobieraj, Ph.D., Robert Gryboś, Ph.D., Dorota Rutkowska-Żbik, Ph.D., Maciej Szaleniec, M.Sc., Ph.D. student, Paweł Hejduk, M.Sc., Ph.D. student

Quantum Chemistry II

Professor Ewa Brocławik, Ph.D, D.Sc.
Tomasz Borowski, Ph.D., Artur Góra, Ph.D., Paweł Rejmak, M.Sc., Ph.D. student

Surfaces, Thin films, Nanostructures

Professor Józef Korecki, Ph.D., D.Sc., Eng.
Nika Spiridis, Ph.D., Eng., Tomasz Ślęzak, Ph.D., Eng., Kinga Freindl, M.Sc., Eng., Jacek Gurgul, Ph.D., Eng., Robert P. Socha, Ph.D.

Zeolite Chemistry I

Associate Professor Bogdan Sulikowski, Ph.D., D.Sc., Eng.
Anna Kubacka, Ph.D., Rafał Rachwalik, Ph.D., Ewa Włoch, Ph.D., Łukasz Mokrzycki, M.Sc., Ph.D. student, Urszula Filek, M.Sc., Eng., Ph.D. student

Zeolite Chemistry II

Associate Professor Mirosław Derewiński, Ph.D., D.Sc., Eng.
Joanna Kryściak-Czerwenka, Ph.D., Anita Burkat, M.Sc., Ph.D. student, Veronika Kobyzeva, M.Sc., Ph.D. student, Adam Węgrzynowicz, M.Sc., Ph.D. student

Laboratories

AFM Laboratory

Andrzej Kowal, Ph.D.
Katarzyna Kusak, Ph.D.

ESCA Laboratory

Jerzy Stoch, Ph.D.
Maciej Mikołajczyk, M.Sc., Jerz Podobiński, M.Sc.

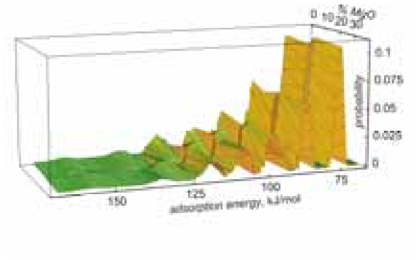
XRD and Thermoanalysis Laboratory

Wiesław Łasocha, Ph.D., D.Sc.
Maciej Grzywa, M.Sc.

Microcalorimetry Laboratory

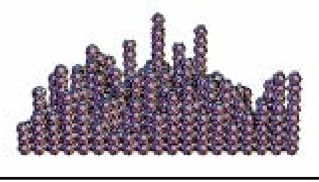
Erwin Lalik, Ph.D.

ADSORPTION

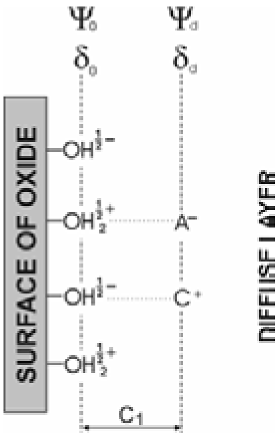


- application of the Statistical Rate Theory (SRT) for description of the adsorption kinetics
  - ➢ adsorption on model surfaces and fundamental studies of the SRT approach
  - ➢ dissociatve adsorption on catalytically important surfaces
  - ➢ generalization of the SRT approach for the case of the energetically heterogeneous surfaces

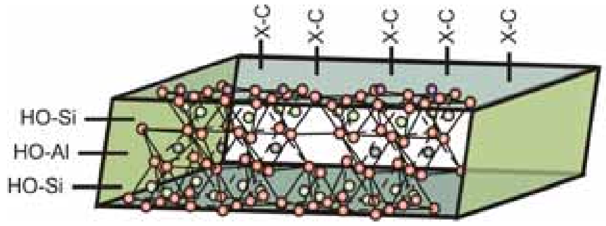
- theoretical analysis of the temperature-programmed desorption spectra
  - ➢ determination of the adsorption energy distribution functions on the active phase of nickel catalyst
  - ➢ determination of the distribution of acid centers on the catalysts support



- studies of the transport processes in geometrically irregular/fractal structures
  - ➢ determination of the collision frequency factor on fractal surfaces



- application of the 1-pK Basic Stern Model of metal oxide/electrolyte interface to analyze ion adsorption from solution.
- theoretical interpretation of proton adsorption enthalpies.
- application of the Statistical Rate Theory (SRT) to investigate ion adsorption kinetics.

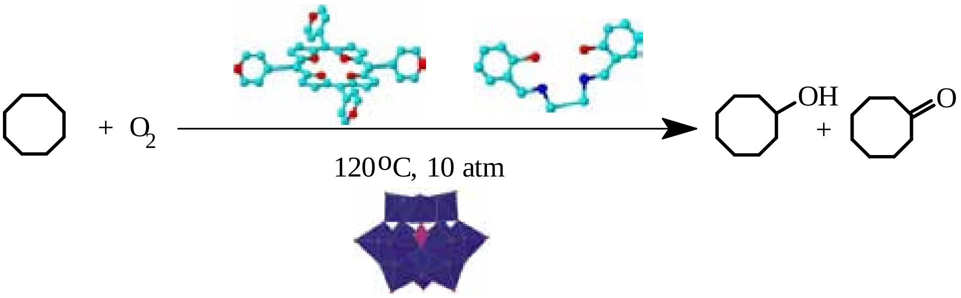


- modeling of the differential capacity of the electrical double layer formed at the metal oxide/electrolyte interface
- theoretical-simulation studies of acid-base properties of the clays
- quantum verification of the surface site charging mechanisms, formulation of the correct microscopic model and the computer simulation of the ions adsorption for such a model
- simulation-theoretical studies of the relaxation of double electrical layer
- topographical and topological aspects of the double electrical layer formed at the metal oxide/electrolyte interface

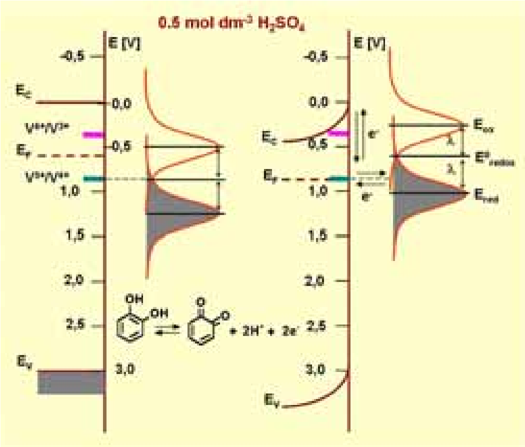
CATALYSIS I

The unit "Catalysis I" addresses in its research the fundamental questions of the oxidation chemistry. It comprises 5 research groups:

- Oxidation of hydrocarbons in the liquid and gas phase
- Electrocatalytic oxidation of hydrocarbons and oxidation of sulphides
- Oxidation of hydrocarbons by enzymes
- Total oxidation of VOC in flue gases to prevent environmental pollution
- Influence of noble gases on heterogeneous catalytic oxidation



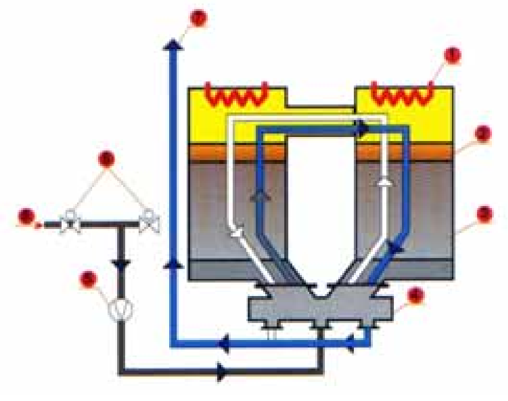
The mechanism operating in oxidation of cyclic alkanes in the liquid phase on metalloporphyrin has been elucidated, resulting in strong dependence of the rate on the type of axial ligand and the redox potential of the metalloporphyrin. The latter may be modified by electron donating substituents, which accelerate the chain initiation and electron accepting substituents, which accelerate chain propagation.



In gas and liquid phase oxidation at oxide surfaces the transfer of electrons from the adsorbed redox pair can take place only if its redox potential is situated above the Fermi level of the solid and above the bottom of the conductivity band and the extraction of the electrons from the solid – when this potential is located below the Fermi level and the top of the valence band.

Vanadium ions deposited at the surface of rutile generate local energy levels and mediate the electrocatalytic oxidation of many organic molecules.

In enzymatic oxidation the effect of physical and chemical parameters on stability and catalytic activity of polyphenol oxidases (laccases and tyrosinases) in water-in-oil microemulsions was investigated. It was found that yellow laccase is able to oxidize with very high yield polycyclic aromatic hydrocarbons.



Regenerative catalytic oxidation system for volatile organic compounds (VOCs) was developed, which permits the destruction of pollutants from flow gases autothermally.

CATALYSIS II - Oxide Catalysts - Oxidation Reactions

Subjects:

1. Oxidative dehydrogenation of lower alkanes (ethane, propane, i-butane) on supported transition metal oxides, TMO (V_2O_5, MoO_3, Cr_2O_3)

- effect of additives (alkalis, P, transition metals [Ni, Cr, Nb, Mo])
- active centres and mechanism in porous systems *(running and future research)*

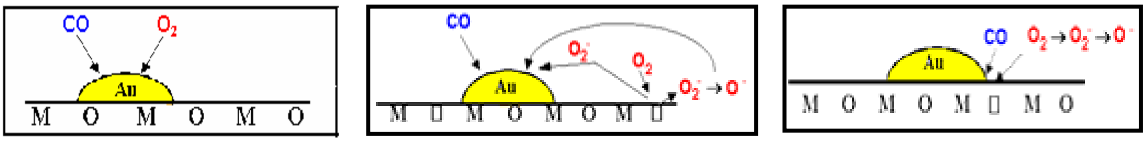
Main conclusions:

Effect of additives on catalytic performance depends on the nature of both active TMO and the support, as well as on the type of alkane, e.g.:

- ∗ selectivity to olefins (> C_2) is controlled by acido-basic properties for vanadia-based catalysts of high acidity (VO_x/SiO_2, [VSi]) and by properties of the catalysts oxygen for less acidic catalysts (VO_x/MgO, [VMg]), selectivity to C_2H_4 independent of acido-basicity,
- ∗ opposite effect of alkalis (K) on selectivity to olefins: positive for VTi, ViSi, CrTi, CrSi, negative; VMg, CrAl, CrMg: different state [desorption energy] of K on two types of catalysts
- ∗ KVSi promising catalysts for ODH of propane and CrAl, CrTi –for ODH of isobutane

2. Au-nanoparticles on oxide supports as catalysts for oxidation of CO (including preferential oxidation in hydrogen mixture, PROX) and of hydrocarbons

- **role of oxide support in the reactions (oxides of main group elements) [e.g. SiO_2, MgO], oxides of transition metals [e.g. TiO_2, FeO_x, MoO_3, V_2O_5], search for new supports**
- **Au in Ti (Ce) in porous systems (SBA-15) *(running and future research)***



Three mechanisms possible for CO oxidation on Au/oxide support catalysts

Main conclusions:

- ∗ activity in CO oxidation and selectivity in oxidation of C_3 hydrocarbons related to reducibility of the oxide supports
- ∗ chromium spinels $M^{II}Cr_2O_4$ (M^{II} = Co, Mn, Zn, Fe), MCr promising supports for Au nanoparticles in CO oxidation; Au/CoCr, Au/ZnCr: total conversion of CO at r.t., “selectivity” in PROX ~90%

COLLOIDS I

General

Understanding the dynamics of colloid and disperse systems is crucial for a quantitative prediction of such phenomena as aggregation, coagulation, flocculation, coalescence, membrane fouling, phase separation, foam formation and stability, rheology etc. being of fundamental importance for the electronic, pharmaceutical and cosmetic industries. Equally important role play interactions of colloid particles, bubbles, and bioparticles (proteins, viruses, bacteria) with interfaces leading to adsorption, deposition, and adhesion. A quantitative description of these processes has implications not only for polymer and colloid science, biophysics, and medicine but also for many modern technologies involving separation procedures, e.g. water and waste-water filtration, membrane filtration, food emulsion formulation, flotation, protein and cell separation, immobilization of enzymes in membranes, biosensors, immunological assays, etc.

On the other hand, by observing dynamic phenomena occurring in colloid system one can gain important clues on mechanisms and kinetics of processes appearing in molecular scale that cannot be studied by direct experimental methods. Especially attractive seems the possibility of exploiting colloids as reference systems for elucidating protein adsorption kinetics and to calibrate indirect methods of determining their concentration on surfaces (film thickness). Colloid particles of larger size also can be used for detecting adsorbed macromolecules and other surface features of nanometer size range.

Main Research Topics

- Convective diffusion of interacting colloid particles.
- Electrostatic double-layer interactions during particle adsorption
- Elecrokinetic phenomena and particle motion in electric fields
- Colloid (emulsion) dynamics and stability
- Electroviscous phenomena and suspension rheology
- Self assembling monolayers of colloids
- Mechanisms and kinetics of irreversible adsorption at solid/liquid interfaces
- Polyelectrolyte and protein adsorption
- Biocompatible coatings

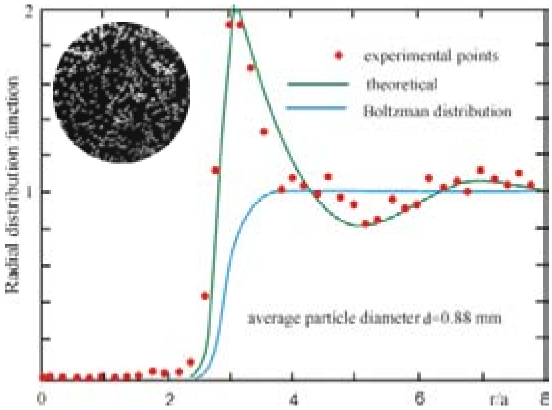


Fig.1. Distribution of latex particles on mica surface determined by direct microscope observations.

Main Achievements of the group

Generalization of Levich's convective diffusion theory,

Generalization of the Random Sequential Adsorption (RSA) model to polydisperse and nonspherical particles.

New theory of adsorption on heterogeneous surfaces.

Elaborating of a theory of electrokinetic phenomena for particle-covered surfaces.

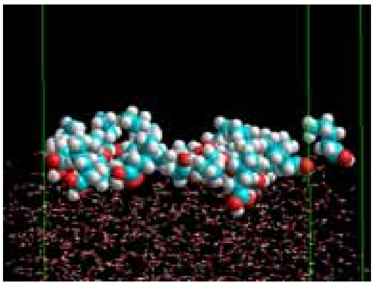
Discovery and experimental confirmation of the "inverse salt" effect.

First measurement of the 2D pair correlation function of adsorbed particles (see Fig. 1).

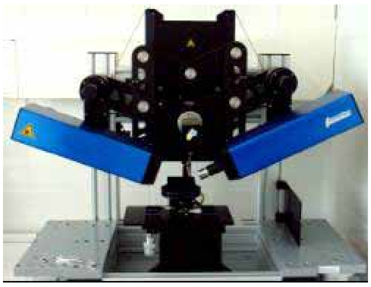
Experimental measurements of multilayer formation of polyelectrolytes.

Developing new experimental method of surface cluster formation of tergetd architecture.

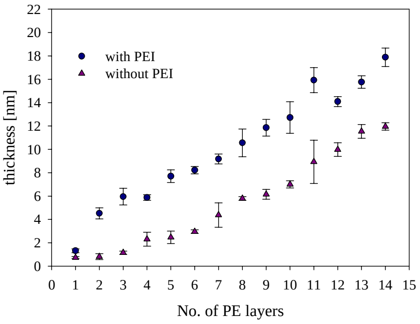
COLLOIDS II – Colloid and Surfactant Systems



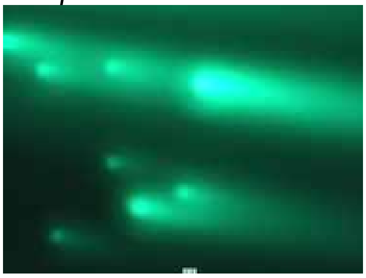
Simulation of adsorption of pentanoic acid at air/water interface



Imaging ellipsometer for thin layer thickness and topography measurements

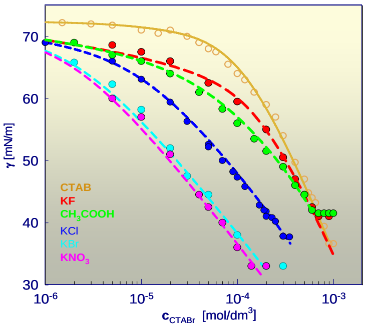


Thickness of PAH/PSS multilayer film with and without anchoring layer



Release of fluorescent dye from microcapsules attached to a surface

Profile of the pendant drop for surface tension measurements by drop shape analysis



Effect of type of anion on adsorption of cationic surfactant CTAB

RESEARCH TOPICS:

- *Thermodynamics and molecular mechanism of adsorption and self-organization of amphiphatic species at liquid/gas, liquid/liquid, liquid/solid interfaces;*
- *Experimental studies and molecular mechanics modeling of adsorption processes;*
- *Adsorption of polyelectrolytes, colloids, bio-colloid particles and microcapsules at solid/liquid interfaces in various flow regimes. Formation of nanostructured coatings;*
- *Structure and permeability of polyelectrolyte multilayers;*
- *Theoretical description of the structure of nonlinear double layer around single colloidal particle and for particle systems (including particle/interface case);*
- *Elektrokinetic phenomena with application to colloid and bio- colloid particles. Theory of electrophoretic mobility of complex systems. The electrokinetic phenomena for particles at interfaces and their role in adsorption;*
- *Colloidal hydrodynamics with application to adsorption, foam stability, etc.*

EXPERIMENTAL TECHNIQUES:

monochromatic imaging ellipsometry; fluorescent microscopy; surface tension/surface potential; drop shape analysis (surface&interfacial tension, contact angle);

MAIN ACHIEVEMENTS:

- *Description of electric double layer interactions for the charged spherical particles at charged interface and description of the fluid flow in the impinging jet and slot impinging jet cells;*
- *Theory of the transport of colloidal particles to the non-homogeneous interfaces and theory of the electrokinetic forces acting on the charged particle moving at the interface;*
- *Quantitative description of electro-hydrodynamic scattering effect;*
- *Theoretical model of the effect of deposited particles on the streaming potential of solid surfaces;*
- *Improved models of adsorption of nonionic and ionic surfactant and their mixtures at liquid/air interface;*
- *Explanation of pH dependent surface activity of alkanoic acids and explanation of the role of counterions in ionic surfactants adsorption;*
- *Determination of the role of PEI anchoring layer on the properties of polyelectrolyte multilayer films.*

CULTURAL HERITAGE RESEARCH

The research group has been active since 1986. The research is focused on structure and properties of historic building and decorative materials, mechanisms of their deterioration, and measures to conserve and protect them. Special emphasis is laid on phenomena occurring at the material surfaces such as interaction with moisture contained in the air, direct tracing of physical change in historic materials using non-destructive methods, chemical corrosion, formation and crystallisation of soluble salts. The basic research is linked to extensive case studies and practical conservation work.

The main research topics comprise:

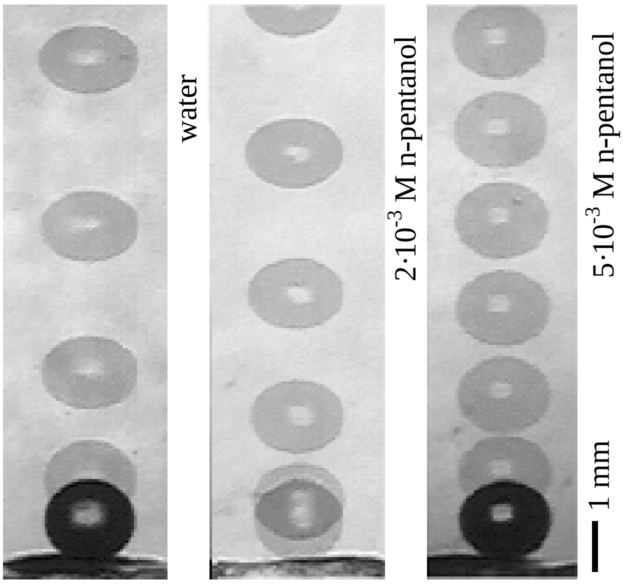
- Monitoring of microclimatic parameters in historic buildings and sites
- Elucidating the pore structure of historic materials using mercury porosimetry and sorption of gases including water vapour
- Water and water vapour transport in historic materials
- Measurements of dimensional response and acoustic emission of historic materials to changes in air parameters in the microenvironment of the historic objects and buildings
- Laser vibrometry to monitor defects in the surface decorative layers specially on polychrome wood
- Computer modelling of environmentally induced mechanical damage
- Development and implementation of strategies for protection and conservation of sites and buildings
- Re-development of manufacturing of historic materials for purposes of conservation and reconstruction

The major research accomplishments during the last three years have been:

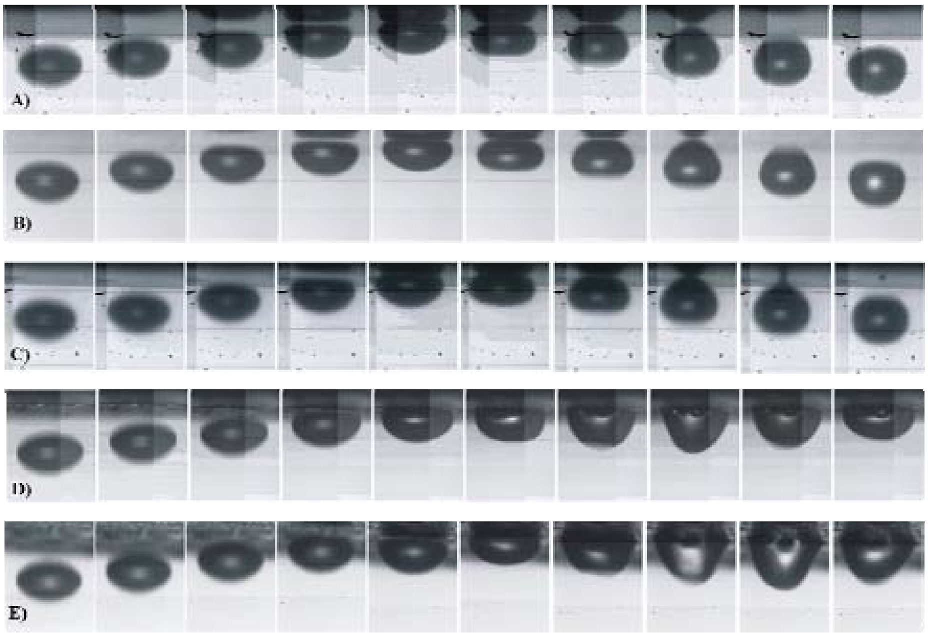
- Implementing effective systems of monitoring historic sites and objects in the field, by using a range of physical and optical sensors, and providing a remote control and data recovery via the GMS transmission system. The monitoring systems have been used to assess the effects of various heating systems on polychrome wood in churches in Italy and Poland, or to devise a protective strategy for early-Christian wall paintings in St. Paulus Cave in Ephesus, Turkey.
- Monitoring of acoustic emission to trace directly the evolution of fracturing intensity in materials at a micro-level, before a macro-failure is discernible. The usefulness of the technique was confirmed in monitoring of authentic works of art in the field, which opens perspective of practical sensors indicating risk to objects in museums or during transportation.
- Numerical modelling of moisture transport, resulting gradients of moisture contents and mechanical stresses in a cylindrical object imitating a wooden sculpture, subjected to microclimatic fluctuations reflecting real-world situations. The modelling allow determination of the thresholds in the magnitude and rate of the air parameter fluctuations, the wooden objects may endure without deformation or damage.
- Re-establishing the production and use in conservation of Roman cements, the key materials for decorating the exterior of buildings during the nineteenth and early twentieth centuries.

DISPERSED SYSTEMS

Research interest is focused on mechanism of formation and stability of dispersed systems, especially foams and flotation aggregates: bubble-grains. It has been showed that magnitude of forces, stabilizing foams formed under dynamic conditions, is determined by an actual often non-equilibrium adsorption coverage at liquid interfaces. Special interest is focused on the state of adsorption layer at gas/liquid interface under dynamic conditions and influence of the motion induced non-equilibrium adsorption coverage on stability of the thin liquid films formed (foam and wetting films). Influence of surfactant adsorption on local and terminal velocities of the bubbles, bubble bouncing and shape pulsations during collisions with various interfaces, dynamics and time-scale of the three phase contact formation (gas-liquid-solid), effect of surfactant, hydrophilic/ hydrophobic properties and roughness of solid surfaces on mechanism and time scale of the three phase contact formation have been studied. Equilibrium adsorption properties are measured and parameters characterizing the surfactant surface activity are evaluated by fitting the appropriate adsorption isotherms. Surface potential variations at air/liquid interface are determined, as well. The studies have an interdisciplinary character and have been carried out in co-operation with research teams from the Max-Planck-Institute for Colloid and Surface Chemistry in Golm/Potsdam, Institute of Physical Chemistry Bulgarian Academy of Sciences in Sofia, Universite Henri Poincare, Nancy and Université de Metz, France.



Images of the bubble departing from the capillary in water and n-pentanol solutions. Frequency of the stroboscopic lamp flashes – 100 Hz



Sequences of photos (time interval = 0.845 ms) illustrating phenomena occurring during the first collision of the bubble with Teflon plates having different surface roughness (distilled water). The roughness increases from the sequence A) to E).

HETEROGENEOUS REACTION KINETICS

The research activities include the studies of kinetic of catalytic reactions, chemisorptions of the reactants on oxides as well as synthesis of mixed oxide catalysts.

Methods

- Kinetic steady state measurements with flow reactor, gravimetric analysis using microbalance
- TPD, TPR methods
- Computer simulations for modeling and reaction kinetics

Research topics

A. Catalysts of methanol synthesis

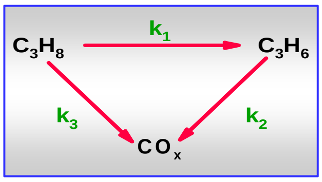
Catalyst: $Cu/ZnO/ZrO_2$

- Catalytic activity of M ($3{\cdot}ZnO{\cdot}ZrO_2$) system (M=Cu,Ag, Au) in the hydrogenation of CO_2 to methanol
- Effect of metal oxide additives on the activity and stability of $Cu/ZnO/ZrO_2$ catalysts in the synthesis of methanol from CO_2 and H_2
- Reduction kinetics of CuO in $CuO\text{-}ZnO\text{-}ZrO_2$ catalyst
- Kinetics of methanol decomposition on Cu-ZnO-ZrO2 catalysts

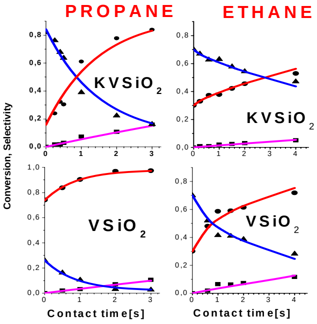
B. Kinetics of oxidative dehydrogenation of light alkanes on vanadia supported catalysts

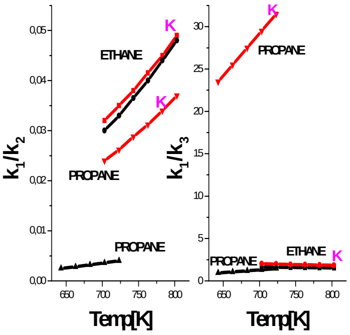
Catalytic network

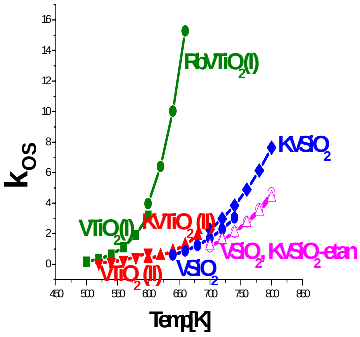
$$C_3H_{8(g)} + O_{(S)} \longrightarrow C_3H_{6(g)} + H_2O_{(g)} + V \qquad k_1$$
$$C_3H_{6(g)} + 3(1+x)\,O_{(S)} \longrightarrow 3CO_{x(g)} + 3H_2O_{(g)} + 3(1+x)\,V \qquad k_2$$
$$C_3H_{8(g)} + (4+3x)\,O_{(S)} \longrightarrow 3CO_{x(g)} + 4H_2O_{(g)} + (4+3x)V \qquad k_3$$
$$O_2 + 2V \longrightarrow 2O_{(S)} \qquad k_{OS}$$



- Examination of different types of the kinetic models (power, Langmuir-Hinshelwood, Mars-Van Krevelen, Eley-Rideal-Steady State Adsorption Model).
- Development and improvement of calculation methods (analytical for simple models, numerical for complex models)
- Use of the obtained results for the analysis of the mechanism of ODH of alkanes







LAYERED MINERALS, MESOPOROUS OXIDES, NANOSTRUCTURES

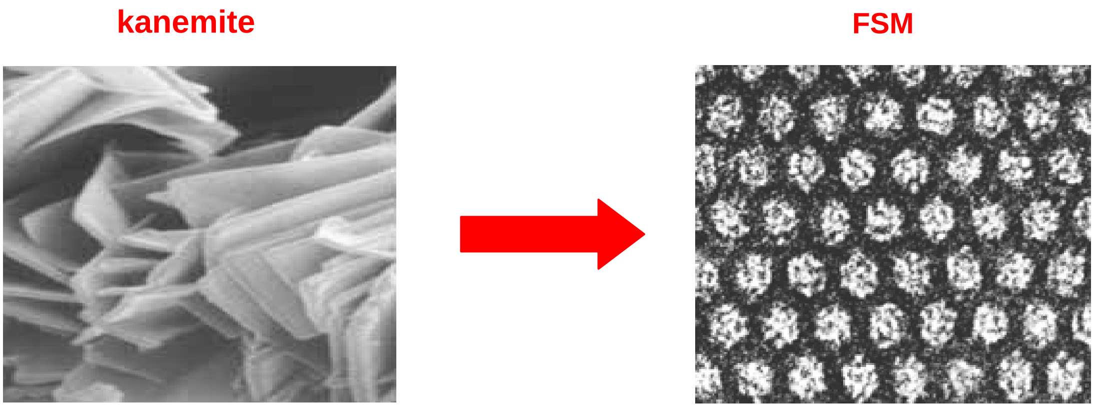
Research interests of our group include:

- application of natural and synthetic layered minerals in design and synthesis of solids with controlled catalytic and textural properties
- design and synthesis of hybrid materials based on nanoporous structures

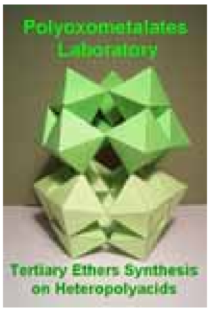
Layered minerals of interest include cationic and anionic clays, hydroxy double salts and oxides of manganese. Modification of cationic clays involves acid treatment, pillaring, doping with transition metal ions and formation of organo-clay composites. Anionic clays are synthesized using a variety of structure-forming elements and a number of compensating anions including isopoly- and heteropolyanions. Pillared clays and mesoporous oxides are used for synthesis of hybrid systems with redox functional components such as organometallic or transition metal species. The targeted catalytic reactions include abatement of nitrogen oxides, oxidative dehydrogenation of lower alkanes, combustion of volatile organic compounds, and green chemistry processes involving liquid phase oxidation of alkanes, olefins and aromatics.

Main research topics:

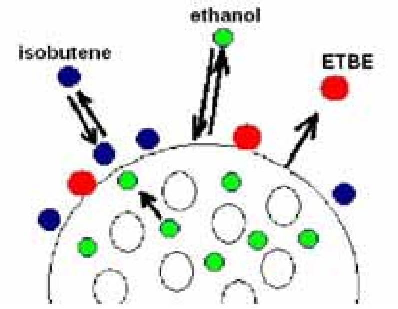
- Pillared clays as catalysts and catalyst supports
- Pillared clays with controlled textural properties
- Layered double hydroxides as hosts for isopoly- and heteropolyanions.
- Layered double hydroxides and hydroxy double salts as precursors of catalytically active mixed oxide phases.
- Layered manganese oxides as precursors of mixed oxide catalysts
- Mesoporous oxides as supports for transition metal ions and organometallic compounds.



POLYOXOMETALATES



The present interest of our team is connected with the physico-chemical and catalytic properties of heteropolyacids in acid-base type reactions. Synthesis of tertiary ethers (methyl-tert-butyl MTBE and ethyl-tert-butyl ETBE ethers) has been chosen as the reaction in which one reagent, methyl or ethyl alcohol is absorbed by the bulk of heteropolyacid crystallites and the other one, isobutene, remains only at the surface where it gets protonated. Basing on catalytic kinetic measurements supplemented by parallel sorption experiments, FTIR spectra of sorbed molecules, acidity characterisation by ammonia sorption calorimetry, a model could be proposed of the catalytic system according to which reaction occurs between protonated isobutene molecules and alcohol molecules supplied from the bulk of heteropolyacid crystallites as it is shown by the scheme.



The model assumes that there is in the bulk achieved equilibrium between non protonated alcohol molecules, protonated alcohol clusters and “free” protons, which are forming weak hydrogen bonds between heteropolyacid anions.

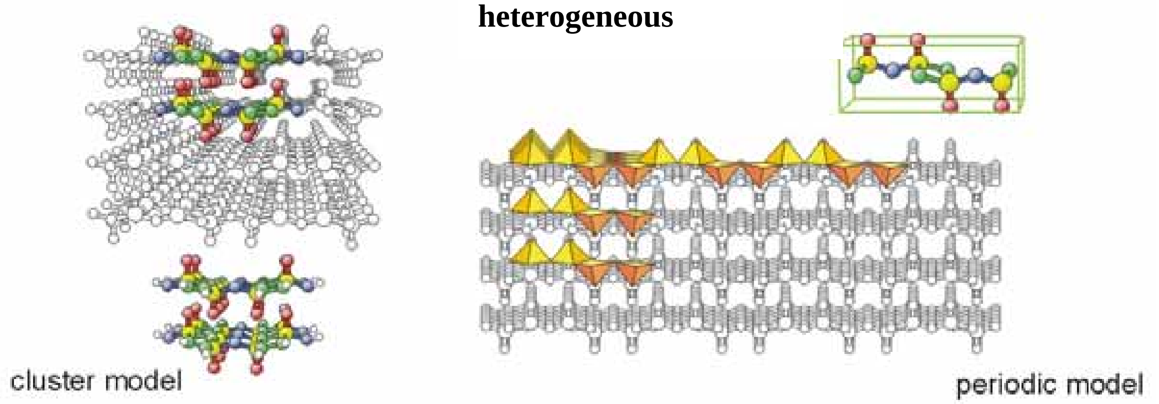
A system of kinetic equations has been proposed for the first time in the literature which, in accordance with the experimental results, shows that, depending on the pressure range, the reaction order with respect to alcohol can be either positive or negative while it is always positive with respect to isobutene.

In 2005 we plan to extend this model primarily worked out using Keggin type of dodecaheteropolyacids as $H_4SiW_{12}O_{40}$ on the until now less investigated type of heteropolyacid, Wells-Dawson octadecaheteropolyacid, $H_6P_2W_{18}O_{62}$ and to investigate the effect of water in the feed as well as in the form of crystallisation water modifying so called secondary structure of crystalline heteropolyacid. It is planned also, as the new line of research, the study of catalytic properties of some acid salts of heteropolyacid.

QUANTUM CHEMISTRY I

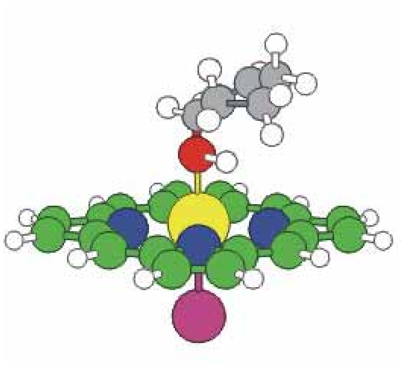
Modelling of Catalysts and Catalytic Reactions

heterogeneous

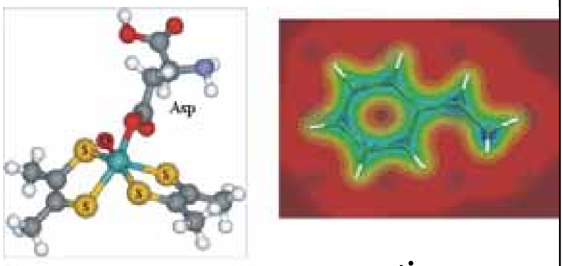


- description by first-principles methods of the V-O, Mo-O based catalysts to identify electronic and structural factors determining catalytic activity and selectivity;
- formulation of general structure-reactivity relationship for prediction of site reactivity /selectivity trends;
- studies on mechanism of catalytic reactions.

- quantum-chemical modelling of transition metal complexes, in particular tetrapyrrols;
- structure-reactivity relationship studies;
- interactions of small, inorganic molecules with complexes;
- elucidation of reaction pathways and mechanisms of homogeneous catalytic reactions.



homogeneous



enzymatic

- investigation of ethylbenzene dehydrogenase (EBDH) substrates spectrum and analysis of reaction products;
- QSAR analysis - correlation of electronic, steric and topologic features of EBDH substrates with kinetic observation of enzyme activities – quantitative model describing variation in reaction kinetics;
- modelling of monomolybdenum cofactor – EBDH active center.

QUANTUM CHEMISTRY II

Research field:

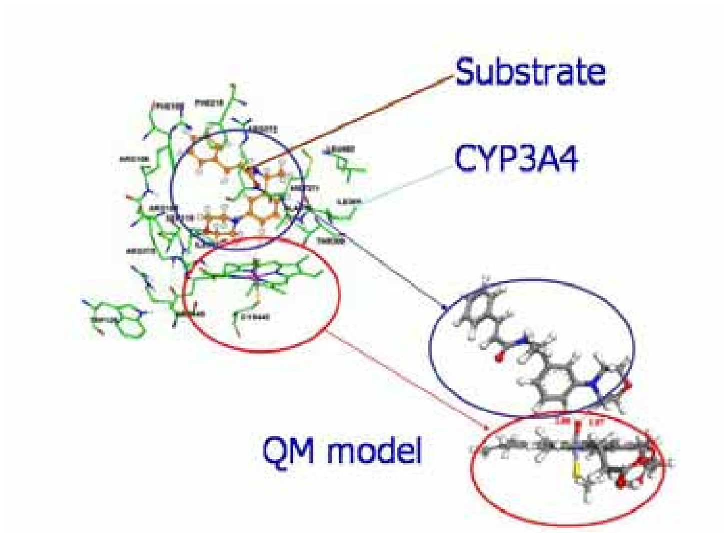
Quantum chemistry as a tool for studying catalytic systems

- advanced quantum methodologies (DFT, TDDFT, CASPT2) in revealing intricate electronic properties of active sites and their interaction complexes;
- adsorption and spectral properties in connection to experiment;
- catalytic reaction mechanisms

Selected topics:

- Properties of active centers in enzymes: structure, spectral properties and catalytic reaction mechanisms: iron centers in heme and non-heme enzymes
- Transition metal sites in zeolites: structure, adsorption and activation properties Copper and cobalt exchanged cations in MFI zeolite Properties of sorbed molecules - IR frequencies and EPR spectra
- Transition metal oxides

Main achievements:



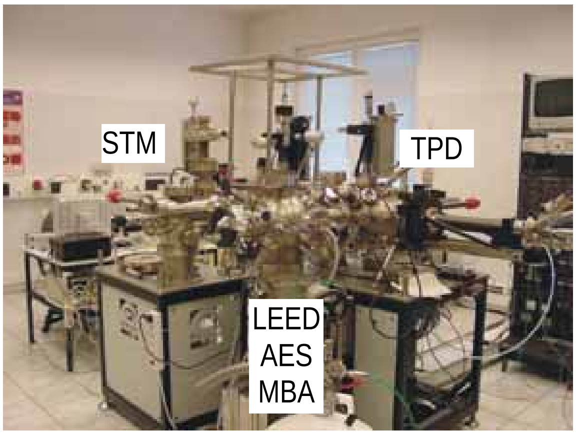
- Description of iron active site (Cpd I) in CYP 3A4 enzyme: successful design of the model for metal centre; theoretical assignment of structural and electronic factors governing enzymatic reaction mechanism; description of redox processes involved in the catalytic cycle; establishing the mechanism of catalytic reaction of CYP 3A4: oxidation of arene ring in a drug molecule by proton-shuttle mechanism.

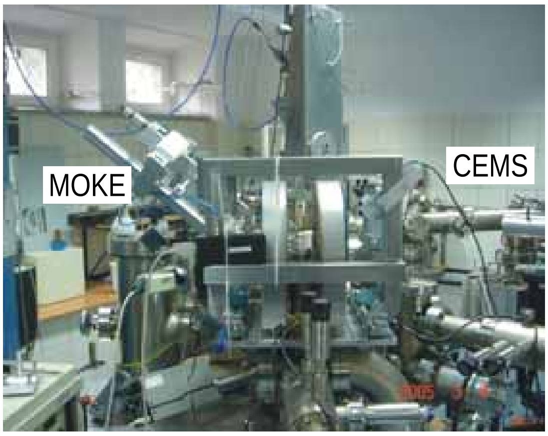
• Description of the structure and enzymatic activity of Clavaminate Synthase: theoretical study on the enzymatic reaction mechanism; reproducing UV-vis spectra for native form of the enzyme, and with bound co-substrate (α-KG) or substrate in the presence of α-KG. Methodology: Time Dependent Density Functional Theory with the innovative approach to the subsystem formulation within density functional theory.

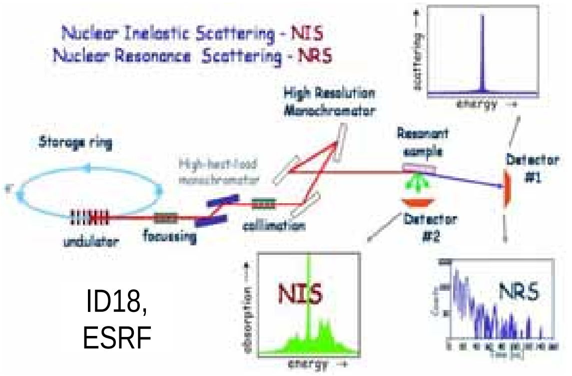
• Description of copper and cobalt active sites in ZSM-5 zeolite: successful design of models for selected positions in the zeolite framework; clarifying the activation ability of Cu^+ in ZSM-5 and its coordination changes upon CO adsorption; interpretation of IR spectra of sorbed molecules; investigation of the properties of the Cu(I) centres in faujsite (FAU) and explanation of the experimental spectra of adsorbed CO molecules. Methodology: the Combined Quantum Mechanic – Interatomic Potential Functions (QMPot) method.

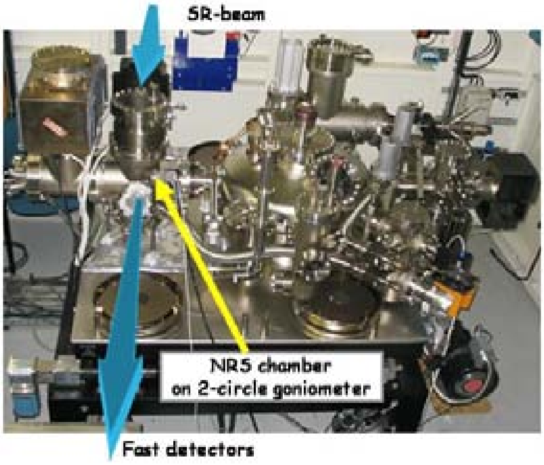
SURFACES, THIN FILMS, NANOSTRUCTURES

Methods:



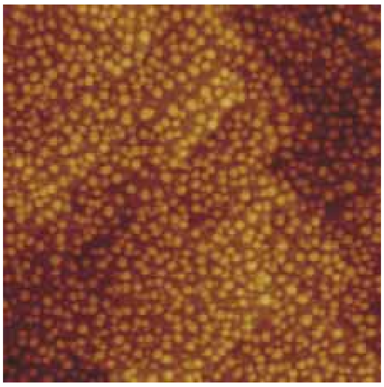






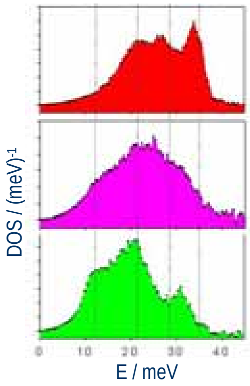
Research topics:

0.08 ML Au/Fe_3O_4(001)



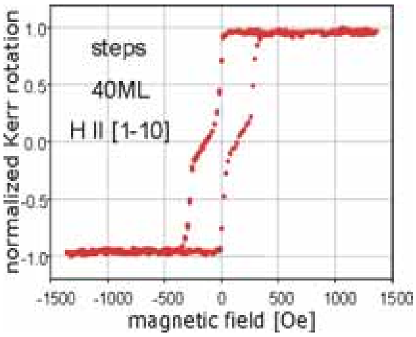
Epitaxial
Metal/Oxide
Nanostructures

Phonon DOS for Fe/W(110)



Dynamics
in
Nanostructures

In situ Magnetization Loop
for Fe/W(540)



Growth and Magnetism of
Metal and Oxide Films and
Multilayers

ZEOLITE CHEMISTRY I

The molecular systems studied are diverse, and range from zeolites and mixed oxide catalysts to mesoporous molecular sieves. Our main interest is focused on synthetic molecular sieves, particularly crystalline aluminosilicates (zeolites), MCM and SBA type solids and related materials. We synthesize, modify and characterise zeolitic solids by IR, Raman, NMR and other techniques. The reactions we study comprise, *inter alia*, isomerization and transalkylation of hydrocarbons, de-NO_x in the presence of methane and surplus of oxygen, selective oxidation of various molecules, and oxidative dehydrogenation of low molecular weight alkanes.

MAIN RESEARCH TOPICS

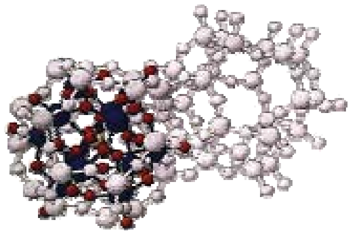
- Synthesis and properties of molecular sieves containing Al and other heteroatoms.
- Modification of zeolites with ions, metals and oxides. Solid-state ion exchange in zeolites.
- Dealumination and realumination of zeolites.
- Heterogenization and encapsulation of heteropoly acids in zeolites and mesoporous sieves.
- Synthesis and properties of mixed oxide catalysts.
- Catalysis by zeolites, mesoporous materials and related solids (de-NO_x, transformations of hydrocarbons), and by mixed oxides (oxidative dehydrogenation of alkanes).

METHODS

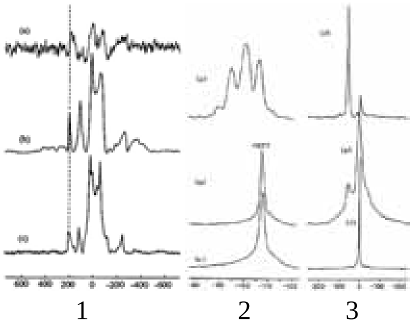
- Hydrothermal synthesis of zeolites, MCM and SBA type materials, and mixed oxide catalysts.
- X-ray diffraction, adsorption, FT IR and Raman.
- NMR studies in cooperation with Institute of Nuclear Physics (Kraków) and University of Stuttgart.
- Catalytic tests in continuous flow, pulse and batch type microreactors.

MAIN ACHIEVEMENTS

- Dealumination and realumination of faujasite, ZSM-5, Silicalite-I, mordenite and other zeolites.
- Catalytic properties of realuminated faujasite.
- Synthesis of MFI type zeolites isomorphously substituted with B and Al in the framework.
- Synthesis and characterisation of Ga-ferrierite.
- Selective transformation of methanol into hexamethylbenzene.
- NMR and catalytic studies of Ga_20_3 and Ga-containing zeolites.
- Solid-state ion exchange in zeolites under anhydrous conditions.
- Measuring the fractal dimension of dealuminated and realuminated faujasites.
- Encapsulation of 12-tungstophosphoric acid in zeolite Y.
- Synthesis, characterisation and catalysis by heteropoly acid/faujasite & heteropoly acid/SBA-15 hybrid materials.
- Synthesis, characterisation and properties of VO_x/Ga_2O_3 and VO_x/In_2O_3 systems.
- Synthesis of highly active and selective ferrierite catalysts for the de-NO_x process in the presence of methane and surplus of oxygen.
- *In situ* and *ex situ* studies of vanadium-containing mixed oxide catalysts.
- Synthesis, characterisation and properties of ferrierite and its dealuminated forms. Transformations of toluene, xylenes and trimethylbenzenes on ferrierite-based catalysts.



Keggin unit encapsulated in zeolite Y



1 2 3

^{71}Ga MAS NMR spectra of:
1. Ga-Zeolite, 2. β-Ga_2O_3, 3. α-Ga_2O_3

ZEOLITE CHEMISTRY II

Research activity of the Group is focused on synthesis and application in different fields (sorption, separation, catalysis) of porous nanomaterials including molecular sieves as well as silica and alumina based mesoporous structures. Isomorphous substitution in the zeolite framework is widely used in our group as the method to design and control the activity of molecular sieves.

In addition, studies on the synthesis of membranes from different zeolites on porous alumina supports (Fig. 1) and preparation of multimodal systems characterized by the presence in their structure of micro-, meso- and macropores are carried out.

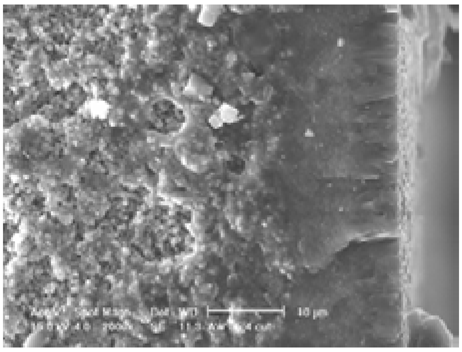


Fig. 1. Cross-section of MFI zeolite membrane supported on Al_2O_3.

Previously, we have used the isomorphous substitution of framework Si atoms for other metals (B, Fe, Ga) for tailoring acidity as well as texture of MFI, BEA and TON type zeolites (Fig.2). The influence of acid site density, acid strength and crystal size on the skeletal isomerisation of 1-butene using Al-, Ga- and Fe –ZSM-22 zeolites (TON family) with different Si/T ratios has been determined. We proved that the Fe-ZSM-22 material of the mild strength of acid sites shows the highest isobutene selectivity (90% selectivity at 40% conversion). However, the application in catalytic processes of iron containing zeolites might be limited by lower - in comparison to Al analogues – thermal/hydrothermal stability. Moreover, removal of Fe from the lattice to extraframework position could change not only the density of acid centers of Bronsted type (Si-OH-Fe) but also modify of acid strength of the remaining sites. Therefore, it was interesting to study the dependence of Fe content in parent zeolite (Si/Fe ratio) on the extent of iron removal and the role of the latter in the changes of acidity/activity.

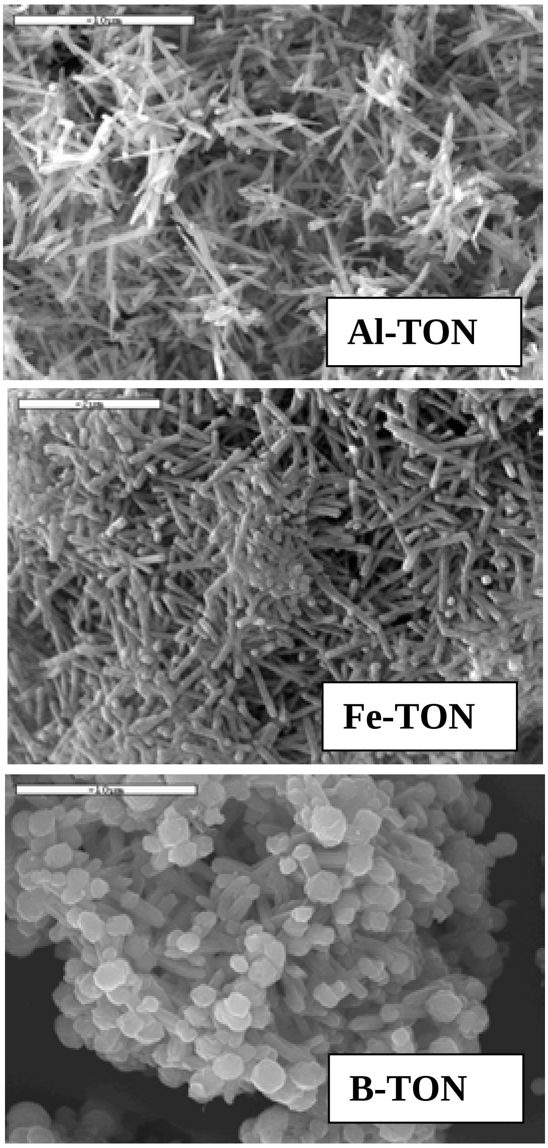


Fig. 2. SEM images of Fe- Al- and B-TON zeolites synthesized from a gel: $(K_2O)_{4.5}(D)_{195}(T_2O_3)_1(SiO_2)_{108}(H_2O)_{3750}$ where T = B, Al, Fe, D=diethanolamine

RESEARCH SUBJECTS AND PROJECTS IN 2005

Page

Statutory Research

Innovative Catalyst for Hydrocarbon Transformations

Physicochemistry of Metallic and Oxide Monolayers and Clusters

Nanoporous Structures as the Basis of New Catalytic Materials

Catalysis in Environment Protection

Mechanisms of Biocatalytic Processes

Dynamics of Dispersed and Biocolloidal Systems

Self-organizing Structures and Nanoparticles Monolayers

Protection of Cultural Heritage

Research Projects of the Ministry of Education and Science

Ph.D. Research Projects of the Ministry of Education and Science

Scientific Network of the Ministry of Education and Science

EU 5th Framework Programme Projects

EU 6th Framework Programme Projects

Other EU Projects

EU Structural Funds

STATUTORY RESEARCH

Innovative Catalysts for Hydrocarbon Transformations

Oxidative Dehydrogenation of Ethane and Propane on Chromium Oxide Systems with Additives; Comparison with Oxidative Dehydrogenation of Isobutane

(Barbara Grzybowska-Świerkosz, Katarzyna Samson, Irena Gressel)

The work is a part of studies on ODH of lower alkanes on oxide catalysts.

The studies in 2005 aimed at comparison of ODH reactions of ethane, propane and isobutane on supported chromia catalysts without and with potassium, and determination of the effect of potassium additive on catalytic activity in each reaction and selectivity to corresponding olefin.

Our previous results have shown that chromium oxide on oxide supports like Al_2O_3 (CrAl) and TiO_2 (CrTi) is active and selective in ODH of isobutane. Moreover, for these two systems: CrAl and CrTi the opposite effect of potassium on the selectivity to isobutene have been found: for CrTiK the increase of about 20% and for CrAlK the decrease of about 10% were observed.

In 2005 the studies were extended to ODH of ethane and propane on these catalysts.

The characterization of catalysts with XRD, Raman, XPS showed that the catalysts contain polymeric $Cr^{+6}O_x$ species with small amounts of Cr_2O_3.

The results obtained show:

1. The ODH reactions of lower alkanes on supported chromia catalysts depend on the nature of hydrocarbon:
    a) for isobutane predominant reaction is oxidative dehydrogenation to isobutene, for ethane and propane the main reaction is total oxidation to carbon oxides
    b) the isobutane reaction follows a parallel-conscutive scheme: carbon oxides being formed by the oxidation of the intermediate product isobutene; for ODH of ethane and propane carbon oxides are formed by parallel route
    c) the sequence of activity for undoped samples (expressed as temperature of 6% conversion of alkane, T_6; values in brackets) is:

    $$C_4H_{10}\ (250^oC)\ >\ C_3H_8\ (280^oC)\ >\ C_2H_6\ (300^oC)$$

    which indicates that C – H breaking is a rate determing step.
2. The influence of potassium on catalytic activity and selectivity to corresponding olefin is different and depends on the nature of alkane and on the type of support:
    a) for CrAl system potassium decreases selectivity to corresponding olefin for all alkanes and increases it (to C_4H_8 and C_2H_4) or has no effect (to C_3H_6) for CrTi system
    b) for both CrAl and CrTi systems – potassium decreases activity in ODH of C_2H_6 and has no effect in ODH of C_4H_{10} and C_3H_8.

Some of catalytic data are presented in Table

Catalyst	**ODH iC_4H_{10}**			**ODH C_3H_8**			**ODH C_2H_6**		
1 mnl Cr_2O_3/ S_{SA} [m^2/g]	T_r [^{o}C]	kon. [%]	sel.$iC_{4=}$ [%]	T_r [%]	kon. [%]	sel.$C_{3=}$ [%]	Tr [^{o}C]	kon. [%]	sel. $C_{2=}$ [%]
CrTi / 22	320	10.4	26	320	11	12	320	10.8	3.0
CrTiK	320	11	47	320	9.4	11	350	11	14.4
CrAl / 111	280	6	60	320	30	10	300	8.9	6.8
CrAlK	280	6.2	50	320	30	6	300	8.9	6.1

Effect of Alkali Metal Additives to VO_x/SiO_2 and VO_x/MgO Catalysts on Catalytic Properties in ODH of Propane and in Decomposition of Isopropanol (Test of Acido-basic Properties)

(Barbara Grzybowska-Świerkosz, Anna Klisińska, Irena Gressel)

In the present work, the effect of alkali (Li, Na, K, Rb) and alkaline earth (Ca, Mg) metals [A] on catalytic performance in ODH of propane have been studied for vanadia deposited on supports of different nature: a) acidic SiO_2 (on which V_2O_5 was the main V-containing phase, exhibiting high acidity), [VSi catalysts], and b) basic oxide such as MgO, (on which a thin layer of $Mg_3V_2O_8$ of low acidity and high basicity was found) [symbol VMg].

The scope of work included:

a) preparation of catalysts (1 mnl V_2O_5, A/V=0,1, impregnation, calcination 450°C),
b) characterization (XRD, XPS, isopropanol decomposition – a test for acido-basic properties),
c) catalytic tests (fixed bed reactor, 400-520°C),
d) studies of the desorption of K (in collaboration with dr A. Kotarba, Jagiellonian University).

The main conclusions of the work are:

1. The additives introduced to VSi catalysts:
   a) increase selectivity to propene (max. S_{10}= 70%, max. Y= ~15%),
   b) decrease considerably acidity and increase the basicity,
   c) decrease areal specific activity [the decrease being related to the increasing ionic radius and electronegativity],
   d) decrease considerably acidity and increase the basicity: no clear correlation is, however, observed between the selectivity and the acido-basic properties, or electronegativity of the additive ions within the series.
2. Addition of the above additives to vanadia-magnesia catalysts (VMgA) leads to:
   a) a decrease in the selectivity to propene in oxidative dehydrogenation of propane, (except for Ca additive which increases the selectivity),
   b) decrease in the specific activity of the catalysts,
   c) decrease in the acidity.

   No clear correlation is observed between the selectivity and acido-basic properties nor electronegativity or atomic radius of alkalis.

3. **Marked differences are observed between the VMgA and VSiA catalysts**.
   They consist in:
   a) opposite effect of the alkali additives on the selectivity to propene: positive for VSiA and negative for VMgA series,
   b) predominance of CO_2 over CO for VMgA catalysts and CO over CO_2 for VSiA series,
   c) parallel-consecutive mechanism of the reaction for VSiA catalysts and small extent of consecutive reactions for VMgA,
   d) higher energy of desorption of K from VMg as compared to VSi (which is equivalent to higher electron work function from the latter system, and may in turn suggest higher population of non-selective electrophilic oxygen species).

The results have been summarized in publications submitted to Polish Journal of Chemistry.

Synthesis of New Type of Heteropolyacids

(Adam Bielański, Anna Lubańska, Anna Micek-Ilnicka)

As the new subject of investigation the study of Wells-Dawson salts as the acid-base type catalysts has been undertaken. Until now the investigations in this direction were carried mainly in the case of Keggin type heteropolyacids. It is expected that such study will result in finding catalysts practically insoluble in water and organic solvents which could be used not only in gas but also in liquid phase from which they would be easily separated.

As the subjects of the present study the cesium hydrogen salts $Cs_xH_{6-x}P_2W_{18}O_{62}$ and partially reduced $Ag_6P_2W_{18}O_{62}$ were chosen. In the case of Keggin cesium salts $Cs_xH_{3-x}PW_{12}O_{40}$ described in literature a distinct maximum of catalytic activity was observed at the composition of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ which was due both to the activation of protons and the development of a large specific surface of the order of 140 $m^{2}\cdot g^{-1}$. The aim of our research was to verify whether similar effect can be obtained also in the analogous cesium hydrogen salts of Wells-Dawson heteropolyacids.

A series of $Cs_xH_{6-x}P_2W_{18}O_{62}$ (x=0, 2, 4, 5, 5.5 and 6) was obtained by partial neutralization of $H_6P_2W_{18}O_{62}$ water solution with cesium carbonate and evaporation of the solution together with the precipitate. As the catalytic test reaction synthesis of ethyl-*tert*-butyl ether (ETBE) in gas phase at 40°C was used. It has been shown that catalytic activity related to the mass of the catalyst decreased with the amount of not neutralized acid. However, the activity related to the mass of not neutralized acid reached a distinct maximum at x=5 which indicates distinct activation of protons contained in the catalyst.

In comparison with Keggin type cesium hydrogen salts, obtained by us at the analogous conditions as the Wells-Dawson cesium hydrogen salts exhibited small specific surface area of the order of 1 $m^{2}\cdot g^{-1}$, which has been attributed to the fast recrystallisation of the precipitate appearing at first as a milky suspension. The attempts to obtain high surface area product by changing the precipitation conditions and substituting water by ethanol or methanol as the solvent resulted only in obtaining specific surface area of about 1.6 $m^{2}\cdot g^{-1}$.

The pristine silver salt $Ag_6P_2W_{18}O_{62}$ obtained by precipitation from water solution was catalytically not active in ETBE synthesis. However, a high activity comparable to the activity of crystalline heteropolyacid was obtained after reducing it with methanol vapour at 250°C. Most probably reduction process is due to reaction:

$$4\,Ag_6P_2W_{18}O_{62} + (6-x)\,CH_3OH \rightarrow 4\,Ag_xH_{6-x}P_2W_{18}O_{62} + 4(6-x)\,Ag^0 + (6-x)\,CO$$

in which silver is partially reduced and simultaneously certain number of catalytically active protons are generated. This result indicates the possibility of obtaining an interesting catalyst.

Influence of Structure of Heteropolyacid Supported on Silica or Al_2O_3 on Selectivity and Yield of Propylene Hydration

(Jerzy Haber, Katarzyna Pamin)

Heteropolyacids are known to exhibit high catalytic activity and selectivity for hydration of alkenes. However, the catalytic activity should vary depending on the kind of heteropolyacid and the type of the support. This difference in catalytic activity is mostly associated with the difference in protons activity or acid strengths of different heteropolyacids. The type of the support also influences the catalytic activity significantly.

The purpose of the present study was to determine the catalytic activity of the following heteropolyacids: tungstophosphoric, phosphomolybdic, tungstosilicic and silicomolybdic deposited on oxide supports (SiO_2, γ-Al_2O_3) in the propylene hydration. Hydration is an important chemical process to produce oxygen-containing organic compounds. The hydration of olefins is catalyzed by protons which form corresponding carbocations reacting with water. The hydration of olefins is an equilibrium reaction carried out in vapour-phase at high temperatures ranging from 200 to 300^{o}C and under the pressure of 25-70 atm. Propylene hydration leads to the formation of isopropanol and acetone. The reaction mixture may also contain traces of diisopropyl ether. Heteropolyacids were deposited on flame silica formed into 3.5 mm grains and on aluminium oxide having grains 2.5 mm large. The heteropolyacids were tested in the hydration of propylene, which was carried out in batch reactor, with the reagents molar ratio $C_3H_6 : H_2O = 1.3 : 1$, at the temperature of 240^{o}C and under the pressure of 33 atm. for 2 hours.

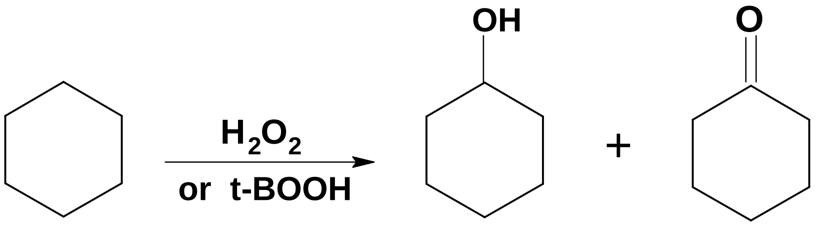
All the tested catalysts are active in the hydration of propylene. Tungstophosphoric acid supported on silica is the most acive catalyst, because it demonstrates the strongest acidic properties among tested heteropolyacids. In the series of heteropolyacids supported on silica the catalytic activity decreases in the order HPW > HSiW > HPMo > HSiMo, which is consistent with the decrease in acid strength. In the series of heteropolyacids supported on alumina HPMo and HSiMo are the most active catalysts. The deposition of HPW on Al_2O_3 results in the double decrease of its catalytic activity in comparison with the same heteropolyacid supported on silica. The deposition of HPW on different supports results in decrease of its acid strength, which is larger in the case of Al_2O_3 than SiO_2. However, the catalytic activity of HSiMo and HPMo after deposition on Al_2O_3 increases in comparison with the activity of these heteropolyacids supported on silica.

Catalytic Activity of Cobalt, Manganese and Iron Phthalocyanines with Different Substituents in Macrocyclic Ring for Hydroxylation of Hydrocarbons with Different Oxygen Donors

(Jerzy Haber, Jan Połtowicz)

Synthetic metalloporphyrins have been widely used as model compounds mimicking the ability of natural monooxygenase like cytochrome P-450 and as catalysts for oxidation of hydrocarbons. Metalloporphyrins are rather expensive and difficult to prepare. Metallophthalocyanines belong to a class of synthetic macrocyclic compounds closely related to metalloporphyrins. We have used phthalocyanine complexes as inexpensive and facile to prepare substitutes of metalloporphyrins.

The aim of the present work is to determine the catalytic activity of iron, cobalt and manganese phthalocyanines of the first and second generation: simple metallophthalocyanine MnPc, FePc, CoPc, NiPc, CuPc without substituents, halogenated complex FeCl$_{16}$Pc and nitrated compounds Fẹ$(NO_2)_4$Pc, Cọ$(NO_2)_4$Pc i Fẹ$(NO_2)_4$Pc. These complexes were used as catalysts in the liquid phase oxidation of cycloalkanes: cyclohexane and cyclooctane with hydrogen peroxide and t-butylhydroperoxide as oxygen donors. The oxidation process was performed in acetonitile and all metallophthalocyanines were active in investigatied reaction. The main products of the cycloalkanes oxidation were cycloketone and cycloalcohol.



Among metallophthalocyanine compounds used in these reactions the most active catalyst, for the both oxygen donors, was halogenated iron complex FeCl$_{16}$Pc with sixteen chloro electron-withdrawing substituents in the phthalocyanine ring. Nitrated complexes were more active than unsusbstitued metallophthalocyanine. In all cases, cycloketone to cycloalcohol ratio was close to one, which is quite different the results obtained for the metalloporphyrin catalysts.

According to the literature data the substitution of metalloporphyrins with electron-withdrawing substituents in the porphyrin rings increases their catalytic activity. The same effect was observed in the case of metallophthalocyanine complexes. Our results demonstrate that metallocomplexes susbstitued with electron-withdrawing groups are more reactive than unsubstitued catalysts. The activity of metallophthalocyanine catalysts appeared to be dependent on the character of the metal center and on the structure of the phthalocyanine ligands.

Studies of the Hydrogen Adsorption and Dissociation on the Surfaces of Catalysts for Hydrocarbons Conversion

(W*ładysław Rudziński*, *Tomasz Pańczyk*)

Within the framework of the project realization we have carried out studies of hydrogen adsorption and dissociation on the nickel surface, which is the active phase of the catalysts for steam reforming of hydrocarbons. The studies were focused on the Monte Carlo simulations of various models of the dissociative hydrogen adsorption on the Ni(100) single crystal face, and next the simulation results were compared to the experimental results. In this way we determined the most probable scheme of that process. It can be outlined as follows: dissociation occurs when the center of mass of the hydrogen molecule is located just above the nickel atom (top position, TP), then hydrogen atoms adsorb on the two neighboring, diagonally oriented hollow sites (HL), or on the two bridge sites (BR) oriented in line with the orientation of the hydrogen molecule. Another condition is that dissociation can occur only when there are no already adsorbed hydrogen atoms in the closest neighborhood. After adsorption and dissociation the hydrogen atoms can migrate on the surface without any constraints due to the permitted local configurations. The probability of diffusion has been determined as equal to 0.04 (4% diffusion steps per 96% desorption steps), that means the diffusion of hydrogen atoms on Ni(100) surface is not completely free. Using this scheme of hydrogen dissociation we have determined the chemical potential of hydrogen adsorbed on Ni(100), and next we applied this potential to compute the kinetic curves of hydrogen adsorption using Statistical Rate Theory, SRT. We obtained very good agreement between theoretical kinetics and experimental ones. These results have been published in the *Journal of Physical Chemistry B.* (Pańczyk T., Szabelski P., Rudziński W., *J. Phys. Chem. B,* 109 (2005) 10986).

The results obtained in the above article allowed us to propose a method of quantitative analysis of hydrogen thermodesorption spectra from nickel catalysts, based on the SRT. Application of that method to the series of nickel catalysts with modified support composition (addition of MgO) led to the identification of the number and energetic properties of the active centers of these catalysts; also we determined the influence of magnesia amount on the distributions of adsorption energy of the studied catalysts. The results of these studies were published in the *Langmuir* journal. (Pańczyk T, Gac W., Pańczyk M., Dominko A., Borowiecki T., Rudziński W., *Langmuir* 21 (2005) 7311

Physicochemistry of Metallic and Oxide Monolayers and Clusters

Quantum Chemical Studies of the Re-Oxidized Transition Metal Oxides Surfaces

(Małgorzata Witko, Renata Tokarz-Sobieraj, Robert Gryboś)

Surface vacancies created by incorporation of lattice oxygen into reacting molecule (Mars-van-Krevelen mechanism) may be filled in a subsequent step either through the adsorption of gaseous oxygen or through the diffusion of oxygen from the bulk.

Theoretical modeling of the re-oxidation process was carried out by means of ab initio DFT method using cluster model. The thermodynamic aspect of adsorption of O_2 molecule from the gaseous phase at three structurally different surface vacancies was studied for (010) MoO_3 and (010)V_2O_5 surfaces that are pointed out as the most active. In addition, differences in reactivity between „surface" and „adsorbed" oxygen sites were discussed.

Results of the calculations show that molecular oxygen becomes adsorbed (exothermic process) at any surface vacancy, in both parallel and perpendicular orientations with respect to the surface, where parallel adsorption is energetically preferred. The ordering of adsorption energies follows the energy order required to form the vacancy i.e. the most difficult vacancy to create - the first to be filled. So the first to be re-oxidized are: O(2)-type vacancy in case of V_2O_5 and O(1)-type for MoO_3.

Upon stabilization at the surface, molecular oxygen undergoes activation; one observes elongation of O-O bond (from 1.24Å in isolated molecule to ~1.5Å after adsorption) and its weakening (bond order changes from 1.87 in O_2 to ~1 after adsorption). Thus, adsorbed molecular oxygen can replace the surface oxygen occupying a specific lattice site, which means that the oxide surface is able to incorporate larger amount of oxygen atoms than follows from its steochiometry. The total charge of the O_2 molecule at the oxygen vacancy is very close to that of the lattice oxygen atom occupying the corresponding site at the undefected surface, which means that charge at a specific surface center is mostly determined by its crystallographic environment.

The activated oxygen molecule can undergo dissociation. The positive value of binding energy suggests that this process is spontaneous for O_2 adsorption at O(2) and O(3) vacancies in MoO_3 and at O(3) vacancy in V_2O_5. Small, negative values (close to -2 eV) describing the removal of an oxygen atom from the O_2 adsorbed at others places indicate the presence of active oxygen that can be easily released.

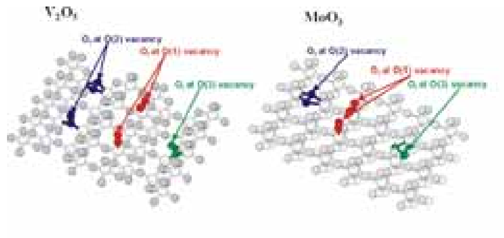


Fig. 1 O_2 molecule at different type of oxygen vacancy at V_2O_5 and MoO_3 surfaces.

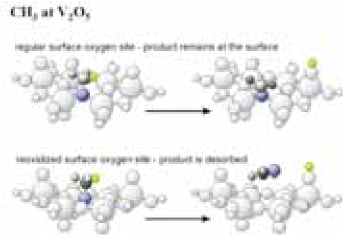


Fig. 2 Interaction of CH_3 radical with (010)V_2O_5 surface.

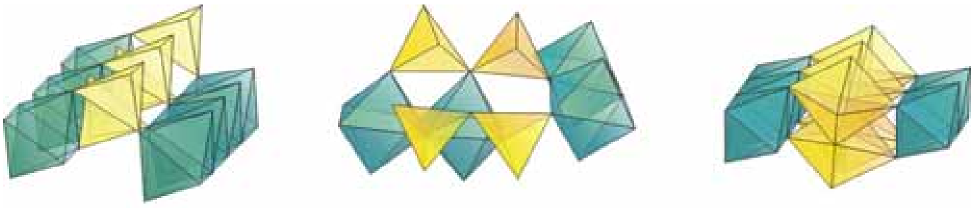
The catalytic activity of various O species was compared taking as an example the interaction of CH_3 radical with O(2) surface oxygen and oxygen resulting from the adsorption of O_2 molecule at O(2)-type vacancy at the (010)V_2O_5 surface. At the undefected (010)V_2O_5 surface activation of CH_3 leads to the formation of O-CH_2 and O-H species strongly bound to the surface. On the contrary, interaction of CH_3 radical with the re-oxidized surface leads to the formation of surface O-H species and CH_2O (with oxygen atom from the adsorbed O_2 molecule), which spontaneously desorbs from the surface.

Influence of Metal Coordination on Catalytic Properties of V-Mg-O Systems

(Renata Tokarz-Sobieraj, Małgorzata Witko)

Mixed vanadium-magnesium oxides are known to be very efficient catalysts for the oxidative dehydrogenation (ODH) of light alkanes. The selectivity for this process depends strongly on the phase of magnesium vanadate (a method of preparation, a presence of modifiers) and on type of reactant (alkane) molecule. The Mg-V-O based catalysts can contain three different magnesium vanadate phases, which differ in the V:Mg ratio and the presence of different vanadium surface species i.e. isolated VO_4 tetrahedra in $Mg_3V_2O_8$, corner-sharing VO_4 tetrahedra forming V_2O_7 groups in α-$Mg_2V_2O_7$, or chain of VO_6 octahedra in β-MgV_2O_6.

The electronic properties of the magnesium vanadate systems were examined by means of DFT (Density Functional Theory) approach (StoBe code) using the cluster model (see Fig.1). The chemical/catalytic properties of active centers were studied as a function of the coordination number and of the type of neighboring atoms. In addition, the comparison of the mixed Mg-V-O systems with the binary V-O oxide (V_2O_5) was done to allow studies of the influence of the additional atom (Mg) on chemical properties of active sites.



$Mg_3V_2O_8$ $Mg_2V_2O_7$ MgV_2O_6

Fig.1 Clusters model, which described the V-Mg-O systems.

All studied Mg-V-O systems are described by a mixed ionic and covalent nature with covalency changes in order $Mg_3V_2O_8 < Mg_2V_2O_7 < MgV_2O_6$. Characteristic of electron density states in the region of valence energy implies the same order of increase of metallic character of the system. As the result $Mg_3V_2O_8$ and $Mg_2V_2O_7$ compounds display insulator nature whereas MgV_2O_6 exhibits a metallic character.

The strong ionic character of Mg-O bond increases the covalent character of V-O bond (mainly in case of bonds with bridging oxygen atoms). Nucleophilicity of surface O sites scales with their coordination numbers. The presence of Mg ions increases nucleophilicity of oxygen center that can be seen in case of oxygen coordinated to one vanadium ion (its charge increases from 0.33 in binary V-O oxide to 0.45 in mixed V-Mg-O systems). The charge on oxygen ions depends strongly on the local geometry of neighboring vanadium. The same type of triply bounded oxygen atoms (coordinated to two Mg ions and one V ion) has the largest charge when V is in tetrahedral environment (-0.94 in $Mg_3V_2O_8$), whereas the smallest one in case of V being in octahedral geometry (-0.82 in MgV_2O_6). Population on V depends also on the coordination type: the smallest positive charge is in case of isolated VO_4 unit ($Mg_3V_2O_8$), the largest for VO_6 unit (MgV_2O_6). As compared to binary V-O system (V characterized as +1.59 ion), the positive charge on V ions is smaller (+1.25) in magnesium orthovanadate, $Mg_3V_2O_8$, larger (+1.63) in magnesium metavanadate, β-MgV_2O_6, whereas comparable (+1.58) in magnesium pyrovanadate, α-$Mg_2V_2O_7$.

Kinetics of Oxidative Dehydrogenation of Propane at Steady State Conditions on VO_x/CeO_2 i KVO_x/CeO_2 Catalysts

(*Ryszard Grabowski, Irena Gressel)*

Vanadium-containing oxide catalysts have interesting properties in various selective oxidation reactions including oxidative dehydrogenation (ODH) of lower alkanes, a reaction of considerable interest as a source of cheap olefins. Among these systems, ceria-supported vanadia catalyst, is an active and selective in ODH of propane and cerium oxide is known as oxygen ion conductor and has been used for iso-butane ODH over CrCeO catalyst; propane over CeNiO catalyst and ethane ODH with admixture of CO_2 over CaO-modified ceria systems.

The experimental data were obtained for the 1mnlVCeO and 1mnlVKCeO catalysts in the integral reactor for conversions (X_p) $0 < X_p < 0.3$. The obtained results were used for the calculations of the particular rate constants in a broad range of the independent variables (concentrations of propane, temperature of the reaction and contact time). The ER-SSAM (Eley –Rideal-Steady-State Adsorption Model) and MK (Mars van Krevelen) models have been applied to the description of the ODH. Table below gives calculated values of the pre-exponential factors and the activation energies for various reaction steps of the ODH of propane, obtained by fitting of the models to the experimental data for the both catalysts.

Model	Catalyst	Rate constants								Fit error [%]
		k_1		**k_2**		**k_3**		**k_{OS}**		
		k_1^o	**E_1**	k_2^o	**E_2**	k_3^o	**E_3**	k_{OS}^o	**E_{OS}**	
ER-SSAM	**VCeO**	3740	(66)*	23300	(59)	1770	(63)	3187000	(81)	**5.9**
	KVCeO	246	(57)	38	(27)	600	(64)	722000	(84)	**7.3**
		k_{red}						**k_{ox}**		
MK	**VCeO**	30000	(75)	72300	(60)	-		3530000	(75)	**11.4**
	KVCeO	9590	(77)	3920	(51)	-		3460000	(82)	**9.3**

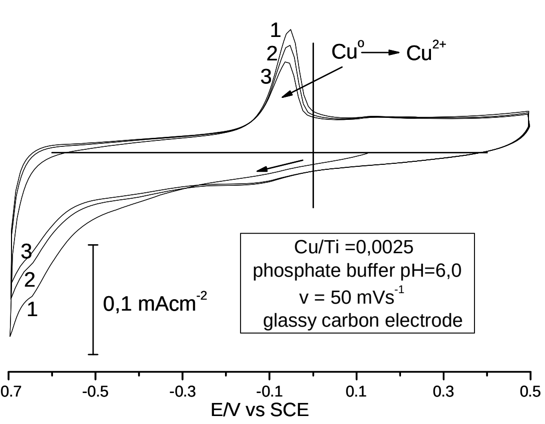
* - activation energy – kJ/mol

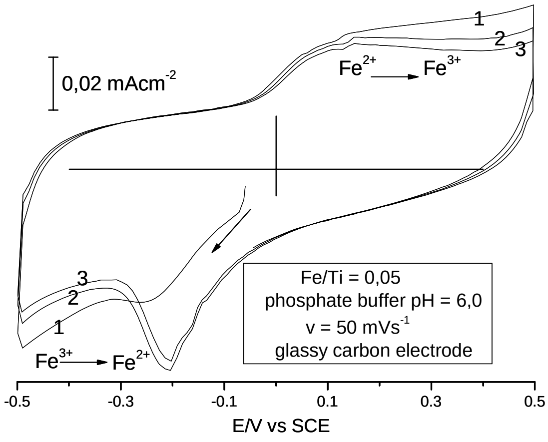
As it comes out from the modeling of the ODH reaction of propane ER-SSAM model described this reaction more adequately than MK model; both for the non doped (VCeO) and for the potassium doped (KVCeO) catalyst and gives more information about the individual steps of the ODH reaction of propane what allows investigating of the influence of potassium additive both on the steps connected with the reduction, as well as, the reoxidation of the catalyst. The calculations showed that potassium additive practically does not change the oxygen surface coverages. Addition of potassium leads to a decrease of the subsequent oxidation of propene, which is the main source of CO_x in the ODH of propane, mainly by a decrease of the pre-exponential factor of rate constant k_2, and the resulting increase in the selectivity to propene. Rate constant of the parallel formation of CO_x (k_3) for the catalyst doped with potassium is decreased, in comparison with the non-doped catalyst, which comes out from decrease of the pre-exponential factor. The decrease the pre-exponentials factors of the rate constants for the all stages of the ODH reaction of propane indicates on the blocking of the active centers by potassium and leads to the decrease of the catalytic activity of the potassium doped catalyst in comparison with the non-doped catalyst.

Redox Transformations of Transition Metals Embedded in the Structure of the TiO_2 and SiO_2 Obtained by the Sol-gel Method

(Jerzy Haber, Paweł Nowak)[1]

The object of the work was the optimization of the composition and procedure of the preparation of TiO_2 and SiO_2 gels by the sol-gel technique, to be used (among the others) as a matrix for the immobilization of enzymes in the construction of enzymatic electrodes for the determination of phenolic compounds. Composition and properties of the gels were modified by doping with the transition metal ions, which may play a role of a redox mediator. Other characteristics, like electrical conductivity of the gel or long-term stability, might be modified too. Investigations in the direction of using such gels for the preparation of catalysts and to the modification of the surface of electrodes are planned in the future. More attention was paid to titania gels, as the silica gels are widely described in the literature. Titaniu dioxide gels doped by ions of several metals (V, Mo, Ni, Cu, Ag, Sn, Co, Fe, Mn) were prepared in such a way that the solution of a precursor (tetraisopropyl orthotitanate) in isopropyl alcohol (containing a proper catalyst) was drop wise added to the solution containing metal ions, giving rise in a very stable sol. Sol was then mixed with the buffer (to initiate gelation) and poured on the surface of either Pt of glassy carbon electrode. Gel was then thickened by controlled evaporation of water and subjected to electrochemical investigations. The preparation of the silica gels was described earlier. The behavior of the metal present in the gel depends on the mode of binding the metal ions in the gel. Significant currents of the redox transformations of the metal in question were observed only in the case when the metal ions were present mainly in the pores of the gel, not being the members of the gel network (the case of copper, for example – look the figure below). However such metals shows the tendency to escape from the gel to the solution in the form of ions, which may be concluded from the disappearance of the redox transformation signal in consecutive scans (1, 2, 3 in the figure). Similar behavior to copper shows silver. Metals, that are included in the gel network give either no signal (V, Mo) or generate only very weak signal (Fe – look the figure). It may be seen, that despite 20 times higher proportion of doping metal to titanium in the case of iron in comparison to copper, the signal in the case of iron is much weaker. The obvious reason is that the electrochemical reaction occurs mainly on the surface of the electrode and the electrical signal does not propagate through the structure of the gel. In the gel layer the electrochemical reaction proceeds to a very limited extent and only in the close vicinity of the electrode surface.





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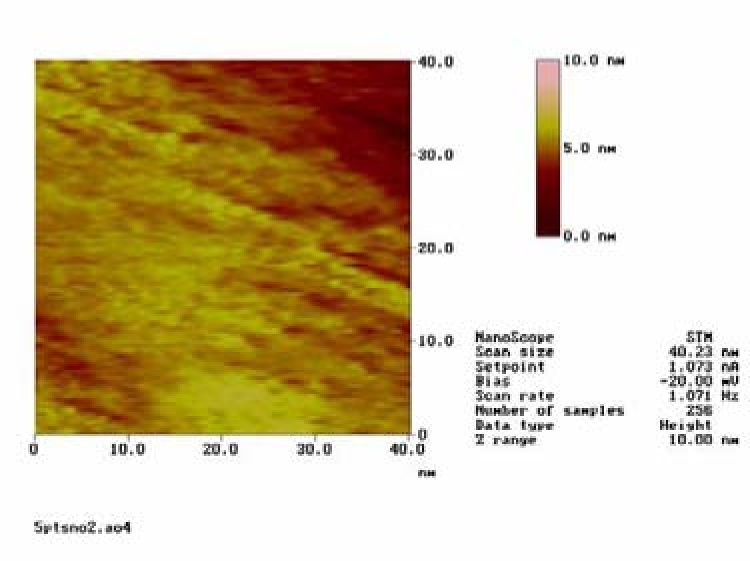
[1] Undergraduate students of the Chemistry Faculty of the Jagiellonian University, Michał Dziurka and Daria Czernek participated also in the reported work.

Investigation of Topography of Metals and Oxides in Nanometer Scale

(Andrzej Kowal, Katarzyna Kusak)

Development of an efficient, environmentally-friendly fuel cell requires preparation of new materials. We studied platinum, Pt-Ru, and Pt-Rh electrodes and then identical electrodes coated by SnO_2 clusters as anodes for the Direct Ethanol Fuel Cell (DEFC). The amount and distribution of SnO_2 clusters on Pt and Pt-Ru electrodes was observed by means of a scanning tunneling microscope (STM) and an atomic force microscope (AFM).

It was found that Sn deposited on Pt(111) in the amount of 1 monolayer (atomic Sn:Pt ratio equal 1:1) and then oxidized to SnO_2 clusters which were distributed on the edges of Pt(111) [see below] form the most efficient catalyst for ethanol oxidation in 0.1 M $HClO_4$ solution.



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NanoScope                     STM
Scan size                   40.23 nm
Setpoint                    1.073 nA
Bias                       -20.00 mV
Scan rate                   1.071 Hz
Number of samples             256
Data type                  Height
Z range                     10.00 nm
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The sizes of SnO_2 clusters deposited on Pt, Pt-Ru and Pt-Rh electrodes were in the range 1.5 to 3.5 nm.

Currents, registered at a potential equal to 0.15 V vs. Ag/AgCl(3M Cl^-) for oxidation of ethanol in 0.1 M $HClO_4$ solution, were equal: 110, 150, 180, 170, 45, 40 microamper/cm^2 for the Pt electrode covered by 0, ½, 1, 2, 5, 10 of SnO_2 monolayer (ML) respectively. It can be concluded that Sn significantly improves the process of electrochemical oxidation of ethanol in 0.1 M $HClO_4$ solution only when deposited in a small (1 ML) amount and as SnO_2 clusters on the Pt edges.

The activity of the Pt(111)/1ML SnO_2 electrode was compared to the Pt(111) electrode covered by 0.3 ML of Ru and 1ML SnO_2. It was found that ruthenium does not significantly improve the process of electrochemical oxidation of ethanol in 0.1 M $HClO_4$ solution.

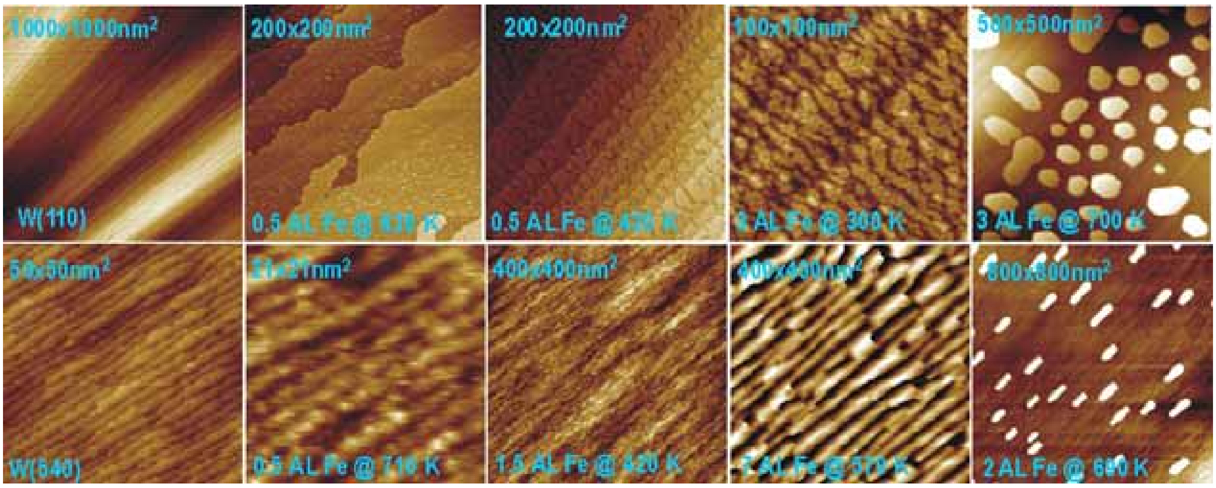
SnO_2 clusters ranging in size from 1.5-3.5 nm and with a (Sn:Pt) ratio ranging from ½ to 10 were also deposited on the Pt(111) electrode covered by 0.3 ML of Rh**.** Investigations of activity of Pt-Rh electrodes in the process of electrochemical oxidation of ethanol are in progress.

Growth and Diffusion of Fe on Vicinal W(110) Surfaces

(Józef Korecki, Nika Spiridis, Tomasz Ślęzak, Kinga Freindl)

Ultrathin epitaxial Fe films grown on (110) oriented tungsten surfaces display interesting structural and magnetic properties. Despite large almost 10% lattice mismatch, a layer-by-layer growth of Fe films can be engineered. It is believed that the first layer grows pseudomorphically, although there are no systematic quantitative diffraction investigations and STM does not give atomic resolution in this system. Thicker films relax through a complex pattern of misfit dislocations. Important role for the growth plays topography of the tungsten substrate, especially monoatomic steps which limit the lateral mass transport. The terrace growth, determined by the miscut, has a strong impact on the stabilization of the iron psudomorphism.

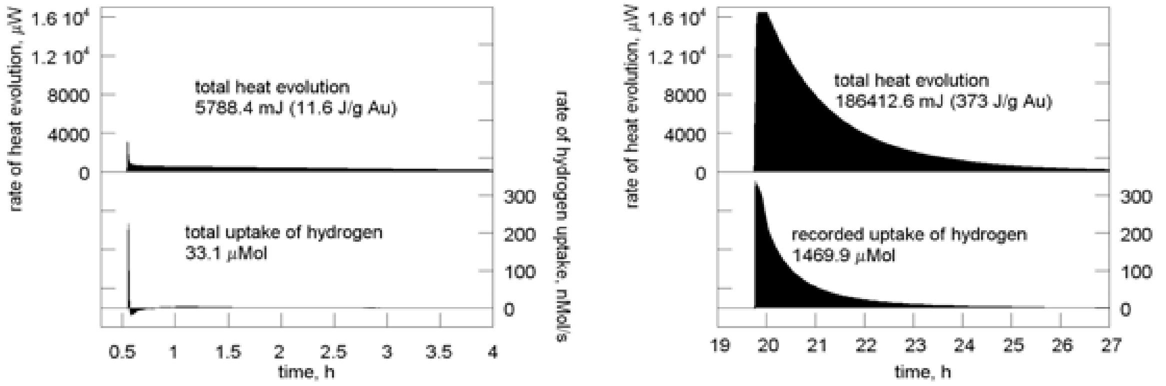
We have studied structural properties of Fe (mono)-layers on a nominally flat W(110) crystal and on a crystal with a 6.3^o miscut relative to the (110) surface, which corresponds to a nominal (540) orientation. Figure below shows selected STM pictures of the tungsten substrates and Fe films (coverage is given in atomic layers) at typical growth stages at given deposition temperature. We have found that the nominally flat surface shows ripples with amplitude approaching 5 nm over 1 μm areas. It is due to a descending/ascending terrace structure with the average width of 25 nm, separated by monoatomic steps along [110] direction. Probably, the undulation releases stresses that arising from thermal treatment. For the vicinal (540) surface, regular step structure with 2 nm periodicity stabilizes the surface and corrugation amplitude is in this case by an order of magnitude lower (0.5 nm). The STM pictures illustrate Fe growth differences for both surfaces. The most striking feature is a periodic structure along the steps for the Fe monolayer on W(540) that reassembles misfit dislocations for thicker films on flat substrates, and a strong anisotropy in the Fe island growth. The last is due to diffusion limitation along the step normal. To study details of diffusion and lattice dynamics in the Fe films, along with standard surface methods (LEED, STM), methods using synchrotron radiation were applied: Nuclear Resonance Scattering (NRS) and Nuclear Inelastic Scattering (NIS). We have found that the best fit to the NRS experimental data is achieved with an ad-atom diffusion model. Phonon density of states extracted from NIS spectra indicate that the Fe monolayer on W(110) is anisotropically strained with strong distortion along [1 -1 0].



Interaction of Noble Gases with the Surface of Transition Metals and Their Hydrides

(Jerzy Haber, Erwin Lalik)

The thermal effect of adsorption of hydrogen on metallic gold is a function of presence of neutral gases on the surface of the sorbent. In presence of nitrogen, the sorption of hydrogen on the surface of metallic gold is a fast process, but it proceeds mainly as a physisorption without dissociation of the H_2 molecules. The accompanying thermal effect is not large, and the uptake of hydrogen is proportional to the sample's surface area. The sorption is largely irreversible, and it takes several hours of purging in stream of pure nitrogen for the desorption of hydrogen from the sample to be completed. It was found that an exposure of such sample to noble gases like helium or argon results in unexpectedly large exothermic thermal effect accompanying a successive hydrogen sorptions, which can be measured in the gas flow-through microcalorimeter, and at the same time the uptake of hydrogen is also largely increased. This effect is the subject matter of the presented report.



a) **b)**

Figure 1. Sorption of hydrogen on the gold powder before (a) and after (b) the exposure of sorbent to noble gas (He), monitored with the gas flow-through microcalorimeter.

Figure 1 represents a comparison of the hydrogen sorption on the fresh sample of gold powder (Fig. 1a) with the sorption on the sample treated with helium (Fig. 1b) at the temperature 110°C and under the atmospheric pressure. The heat evolution is recorded by rising of the calorimetric (upper) curve, while the down stream detector (lower curve) shows the uptake of hydrogen. Eventually the heat evolution ceases, both curves returning to their baseline levels. The sorption of hydrogen on the fresh sample of the metallic gold powder (Fig. 1a) yields relatively weak thermal effect of 11.6 J/g Au, with the corresponding hydrogen uptake of 33.1 μmol. However, a dramatically larger thermal effect can be observed upon sorption of hydrogen on the same sample after its exposure to three pulses of helium (45 μmol He each; Fig. 1b). In this case, an exotherm as large as 373 J/g Au accompanies a much more substantial uptake of 1469.9 μmol of molecular hydrogen. Similar effects of the noble gas exposures enhancing the heat evolution during hydrogen sorption was also observed after the sample had been exposed to pulses of Ar or Kr instead of He, as well as when the gold nanoparticles supported on oxides (TiO_2, SiO_2) were used as sorbents instead of the gold powder. We have previously observed such unexpectedly large thermal effects accompanying interactions of atomic hydrogen with adsorbed forms of noble gases upon their sorption in metallic palladium powder under similar conditions, using our gas flow-through microcalormter. A detailed mechanism of the observed phenomenon remains a subject of continued investigation. The absorptive properties of both the powdered and the supported Au have been included in an international patent application, as well as in a prepared publication.

Nanoporous Structures as the Basis of New Catalytic Materials

Micro- and Mesoporous Catalytic Systems Based on Isomorphously Substituted Molecular Sieves

(Mirosław Derewiński, Joanna Kryściak-Czerwenka)

Isomorphous substitution is a commonly accepted method of tailoring acid properties of zeolites. It is particularly important if zeolites are applied as catalysts in reactions requiring acid centres of comparatively low strength, for example in a skeletal izomerization of n-olefins. Iron is among elements often used for that purpose as strength of acid sites generated by the framework Fe atoms is usually lower than that of the aluminium anologues.

In this contribution results on stability of the framework Fe atoms obtained for two members of the TON family (ZSM-22 and KZ-2) with different iron contents are presented, and show how formation of the extraframework iron species can modify the parent acidity of the Fe-TON zeolites. Mőssbauer spectroscopy has revealed that iron atoms are partially extracted from the framework both during the high temperature template elimination and during the activation of the NH_4 form prior to the reaction. The extent of the Fe removal depends on the iron content and is higher for samples with low Si/Fe ratios. Unexpectedly, strength of the Bronsted sites - determined with a TPD of ammonia and monitored with a FTIR spectroscopy – was found to be high also for iron rich samples (Fig.1).

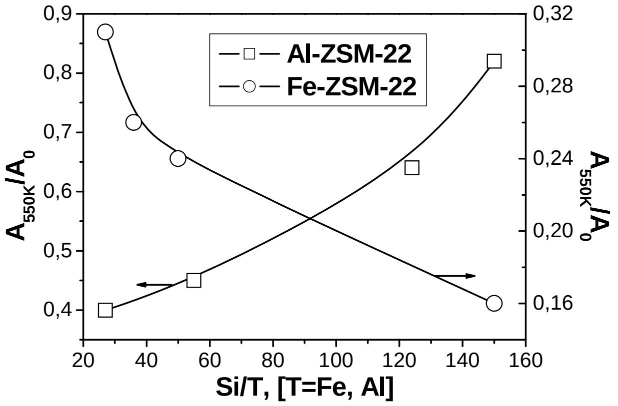


Fig. 1. Dependence of an average relative strength of Brőnsted sites on Si/Fe and Si/Al ratios.

We postulate that an interaction between the extraframework iron species of a cationic character and the neighbouring bridging Si-OH-Fe groups enhances acidity of the existing Brőnsted sites. In case of thermally stable, Fe-poor preparations - where no or very few extraframework Fe species were detected - strength of the bridging OH groups remains unchanged.

Transformations of Alkylaromatic Hydrocarbons on Zeolite Catalysts

(Bogdan Sulikowski, Rafał Rachwalik, Ewa Włoch)

In 2005, we have continued studies on zeolite and mesoporous materials modification Synthetic ferrierite was a basic material used for modification and preparation of catalysts. Its structure is unusual among crystalline aluminosilicates in not containing four-membered (4-MR) rings, and due to it has very interesting properties. Ferrierite is a medium-pore zeolite useful for preparation of catalysts exhibiting acid-base and redox properties. The known catalytic applications of ferrierite comprise, first of all, isomerization of butenes and NO_x removal.

Ferrierite was dealuminated by various methods and the samples obtained were examined using: XRD, BET, SEM, IR and solid-state MAS NMR (^{29}Si, ^{27}Al and ^{1}H). Additionally, studies on SBA-15 materials modified with heteropoly acid $H_3PW_{12}O_{40}$ have been carried out. The methods of ferrierite dealumination were developed, keeping the high crystallinity of the samples after modification. Small and anisotropic unit cell contraction was observed during the treatment with hydrochloric acid only. By using IR spectroscopy it was possible to examine the interactions between chosen samples and CO or NH_3. It was thus possible to study the nature of acid sites and their strength.

Transformation of alkylaromatic hydrocarbons (isomerization of *m*-xylene and *1,2,4*-trimethylbenzene) using both pulse and continuous-flow reactor were studied. The modifications of ferrierite catalysts exert significant effect on the rate of *m*-xylene isomerization, and lead to a decrease of the *m*-xylene disproportionation rate and an increase of the main reaction, i.e. *m*-xylene isomerization. In this way a product significantly enriched in *p*-xylene is formed. Moreover, a multistep dealumination by aqueous solution of hydrochloric acid was giving the catalyst exhibiting much higher *p*-xylene to *o*-xylene ratio (~50) in the products, in comparison with the unmodified catalyst.

The ratio of *1,3,5*- to *1,2,3*-trimethylbenzene has been found experimentally for various conversion level of the substrate (*1,2,4*-trimethylbenzene) as a function of the dealumination step. The shape-selectivity index as defined above was around one for the parent H-ferrierite and the sample after the first dealumination step. In other words, preponderance of the *1,2,3*-isomer was observed for these samples, far from the composition required by thermodynamic equilibrium. However, if the treatment of zeolite was more severe, the secondary mesoporous system was formed, and then the ratio between the *1,2,3*- and *1,3,5*-TMB in the products was approaching values typical for thermodynamic equilibrium (i.e., 2.3 at 700 K). The acid sites were less confined geometrically and thus more accessible due to the presence of mesopores, and the reaction was proceeding similarly to the one studied on amorphous wide-pore aluminosilicates.

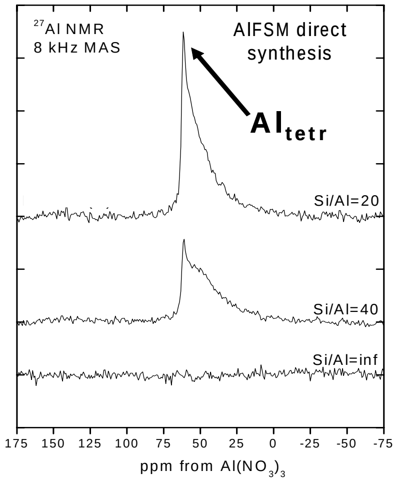
Mesoporous SBA-15 type catalysts containing heteropoly acid (*12*-tungstophosphoric acid, $H_3PW_{12}O_{40}$) were prepared. The mesoporous molecular sieves SBA-15 containing aluminum or gallium and exhibiting high surface area, were used as the supports for the *12*-tungstophosphoric acid. The catalysts were characterized by a number of techniques. The catalytic properties of the samples were studied in oxidation reaction of organic compounds in the liquid phase. The catalytic tests were performed using anhydrous hydrogen peroxide as an oxidant in dioxane. The following classes of compounds were studied as substrates: alkanes, alcohols, aldehydes and aromatics. The following substrates were chosen for catalytic studies: *1*-methylnaphtalene, *2*-methoxynaphthalene, *m*- and *p*-xylene, *4*-methoxybenzaldehyde, ethylbenzene, cyclohexene, cyclopentanol, cyclohexanol, heptanol, octanol, benzyl alcohol, *2*-methylpentan and *n*-nonan. The reaction products were analyzed by gas chromatography, and then the conversion level of the substrates and the selectivity of reactions were estimated.

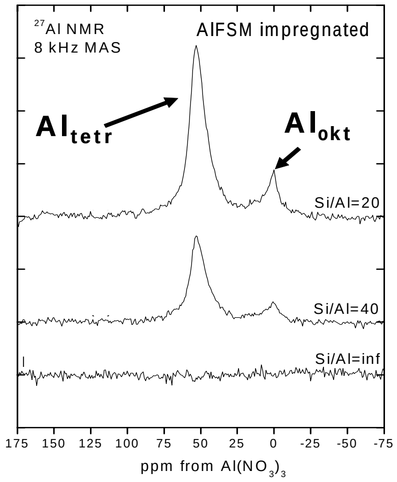
Mesoporous Molecular Sieves Derived from Layered Silicates

(Małgorzata Zimowska, Alicja Michalik, Jan Połtowicz, Wojciech Włodarczyk,
Ewa Serwicka-Bahranowska,

Mesoporous molecular sieves of the FSM type (folded sheet mesoporous material) are obtained from the layered mineral kanemite. Purely siliceous mesoporous materials are frequently modified by alumination, which is the source of acidity and cation exchange capacity. The aim of the present work was to investigate and compare two different methods of FSM alumination: direct alumination, carried out at the stage of kanemite synthesis, and postsynthesis alumination, performed via impregnation of purely siliceous FSM with Al compounds, followed by calcination (Si/Al=20, 40, 60).

Introduction of Al leads to a certain deterioration of the long range hexagonal order and lowering of the specific surface areas of the mesoporous materials, the effect being more pronounced for directly aluminated samples. ^{27}MAS NMR data show that in the directly aluminated samples aluminium exists as tetrahedrally coordinated centres, while in postsynthetically doped materials, beside tetrahedral Al also octahedrally coordinated Al can be detected, showing that incorporation of Al into the silica framework is, in the latter case, not complete





In order to determine what is the distribution of the incorporated Al between the inner pore walls and the external surface, the synthesised materials were used as supports for cationic metalloporphyrin MnTMPyP and tested in the reaction of cyclohexene oxidation with iodosobenzene. We have shown earlier, that in the case of porphyrin centres compensating Al sites on the inner pore walls the oxidation leads preferentially to the allylic products, while porphyrin species attached to the external surface catalyse epoxidation.

Catalyst	Conversion [%]	Epoxidation selectivity [%]	Allylic oxidation selectivity [%]
MnTMPyP/AlFSM40(D)	18	5	95
MnTMPyP/AlFSM40(P)	23	68	32

It was found that the distribution of Al sites depends on the type of the alumination procedure. Direct alumination favours allylic oxidation, thus pointing to the localisation of Al on the inner pore walls. Post synthesis alumination enhances formation of epoxide, which indicates that here Al is present also at the external surface of the support.

Structural and Electronic Properties of Cationic Active Sites in Nanoporous Structures – Quantum Chemical Investigation

(Ewa Brocławik, Paweł Rejmak)

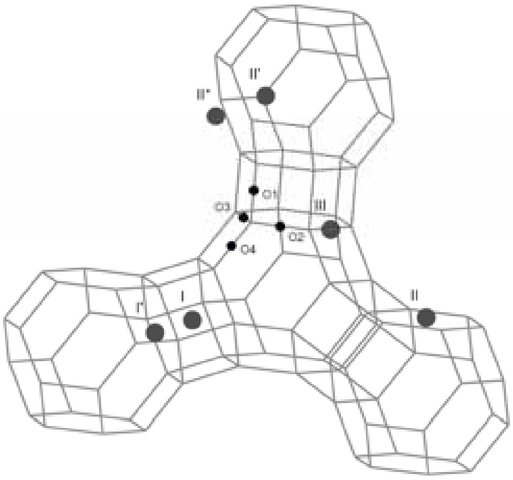
The purpose of this work was to investigate properties of the Cu(I) centres in faujsite (FAU) and explanation of the experimental spectra of adsorbed CO molecules. Calculations (geometry optimizations, harmonic frequencies) were performed using The Combined Quantum Mechanic – Interatomic Potential Functions (QMPot) method. Within this approach extended system is divided into the cluster, treated at the QM level of theory (DFT method in this case), and periodic environment, described using less computationally expensive MM level. In addition, CO frequencies were calculated with semiempirical scaling method, using linear dependency between CO bond length calculated at the DFT level and experimental frequencies in systems containing Cu(I)-CO species.

The lattice models with different Al content and clusters of different size or Al contents were used. All three main types of the Cu(I) sites were investigated.

The most stable positions are sites I’ and II. In these positions Cu(I) achieves threefold coordination to framework O atoms and lies in the plane of the 6T ring (by T atoms we mean Si or Al). For site II Cu(I) binding energies increase with the number of Al atoms in 6T ring. Cu(I) in positions III appears to be much weaker bound and has twofold coordination.

Upon CO adsorption Cu(I) tends to achieve threefold coordination to two O atoms of the same AlO_4 unit and C atom. Achieving such coordination is connected with significant structural changes in site II and migration of the cation above 6T ring plane. CO adsorption on site III is not associated with significant changes of the Cu(I) siting.

CO heats of adsorption decrease with the increase in Cu(I) binding energies. The stronger bound the CO molecule, the higher become CO stretching frequencies. Our calculations show that CO frequencies in Cu(I)-FAU are as well site–specific as depend on the number of Al atoms in the site II case. The following explanation of the CO-Cu(I)-FAU spectra is proposed: for zeolite Y (low – alumina FAU) low frequency band comes from site II with 2 Al atoms in 6T ring, high frequency band comes from site II with 1 Al in 6T ring; for zeolite X low frequency band is due to the site II with 3 Al atoms in 6T ring, while high frequency band is due to the site III.



Possible cation positions (grey balls) and different O crystallographic positions (black balls) in FAU.

Catalysis in Environmental Protection

Development of Thermally Stable Platinum Catalyst for Total Oxidation of Oxygen-Containing Organic Compounds

(Jerzy Haber, Tadeusz Machej, Janusz Janas, Robert Janik, Halina Piekarska-Sadowska)

Organic compounds containing oxygen, such as alcohols, ethers, ketones etc. are components of solvents largely used in industry. These pollutants can be easily transformed into harmless products by combustion, which can be thermal or catalytic.

Thermal combustion is carried out at high temperatures of the order of 800°C and is economically viable only if the concentration of pollutants in the flue gases is high enough for the heat of their combustion to be sufficient to maintain the high temperature of the reactor. Much lower temperature is required for a catalytic combustion. The most popular catalysts used for cleaning the flue gases are noble metals, Pt and Pd, supported on γ-Al_2O_3. Such catalyst must exhibit high catalytic activity, high selectivity to total oxidation products and long life time.

It is known from the industrial practice that the platinum catalysts are loosing selectivity to total oxidation products on time-on-stream, instead yielding partial oxidation products, e.g. aldehydes.

Different γ-Al_2O_3 (Procatalyse) were used as supports for the catalysts preparation. They were denoted as GA5, GA5 SPH, GA5/531P (beads of GA5 washcoated with alumina powder 531 P) and GA5 impregnated with cerium nitrate followed with drying and calcining at 550°C. All supports were impregnated with platinum hydrochloric acid in an amount 0.05 wt. % Pt. The BET surface area of the fresh catalysts was respectively: 300, 110, 135 and 250 m^2/g and after calcination at 550°C for 250 hrs, respectively: 140, 100, 115 and 145 m^2/g.

Total oxidation of ethyl acetate (EA) and ethanol were chosen as a test reaction. The EA and ethanol concentrations in air were 3 g/m^3.

It was found that the prolonged calcination of GA5 support results in a strong decrease of the BET surface area and an increase of the selectivity to intermediate products, ethanol and acetaldehyde (Fig. 1). This phenomenon is not observed for other catalysts.

Fig. 2 presents the light-off curves and minimum temperatures of 98.5 % conversion (Best Available Technology level) for different calcined catalysts. It can be observed that the modified catalysts operate at much lower temperature (especially GA5/Ce) and do not undergo deactivation on time-on-stream in comparison with the standard catalyst (GA5).

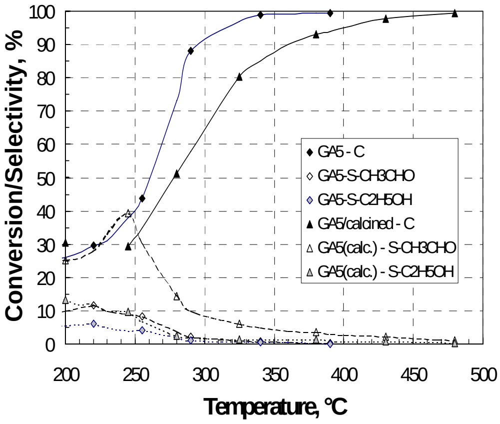


Fig. 1. Ethyl acetate conversion and selectivity to ethanol and acetaldehyde on GA catalysts

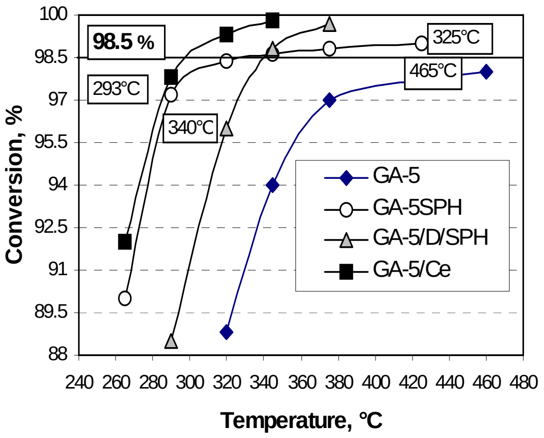


Fig. 2. The light-off curves and minimum temperatures for different calcined catalyst

Designing of Catalyst for Low-temperature Total Oxidation of Organic Pollutants

(Jerzy Haber, Tadeusz Machej, Janusz Janas, Robert Janik, Halina Piekarska-Sadowska)

Volatile organic compounds (VOCs) can be destroyed by thermal or catalytic incineration. The VOCs are burned in air, forming carbon dioxide and water in the case of VOCs containing only carbon, oxygen and hydrogen. Ideally, the heat released during the oxidation will sustain the combustion reaction. However, dilute waste stream will usually require some supplementary fuel.

Catalytic oxidation takes place at much lower temperatures than thermal oxidation. Thermal process typically requires temperatures in the range 750 – 900°C, while catalytic oxidation only in the range 200 – 500°C. Catalytic oxidation therefore becomes self-sustaining at VOC concentrations much lower than those required for self-sustained thermal oxidation and thus becomes more economic because of lower operating cost. This cost could be still redused by introducing catalysts operating in the temperature range 100 – 200°C.

It is well known that standard catalysts are not efficient below 200°C because of adosrption of the VOC and reaction product on the catalyst surface.

The aim of the work was to develop a catalyst which would work effectively at temperatures below 200°C, characterized by no adsorption of VOCs and/or reaction products, and with high conversion.

It was found in the preliminary study that a standard Pt/γ-Al_2O_3 was not active in the total oxidation of hydrocarbons, both aliphatic and aromatic whereas oxygen containing organic compounds were transformed to CO_2, H_2O and aldehydes. That is why methanol and ethanol were chosen for further studies.

Two catalysts were prepared: i) platinum (0.1 wt. %) supported on SiO_2 (4 wt. %)/ γ-Al_2O_3, ii) mixed oxides supported on γ-Al_2O_3. Oxidation of methanol and ethanol were performed in a flow reactor under G.H.S.V. = 5,000 h^{-1}. The concentration of reagents in air was 1 g/m^3. The conversion of alcohols was monitored by continuous measurement of CO_2 concentration in outlet of the reactor.

It was found that the oxidation of methanol proceeds effectively below 200°C on both catalysts.The complete oxidation of methanol and 100 % selectivity to CO_2 are observed on Pt/SiO_2/Al_2O_3 catalyst above 140°C and on MO/γ-Al_2O_3 -above 180°C. Below these temperatures the conversion of ethanol is also complete but some part of CO_2 formed is irreveribely adsorbed on the catalyst surface. Adsorbed CO_2 is desorbed abruptly on increasing the temperature while methanol and/or formaldehyde are not detected in the reaction products.

The catalytic activity of the catalyst differs in the oxidation of ethanol. The complete conversion of ethanol is observed on the MO/γ-Al_2O_3 catalyst at 180°C whereas on the Pt/SiO_2/γ-Al_2O_3 catalyst the temperature 300°C is necessary to get the same result (Fig. 1).

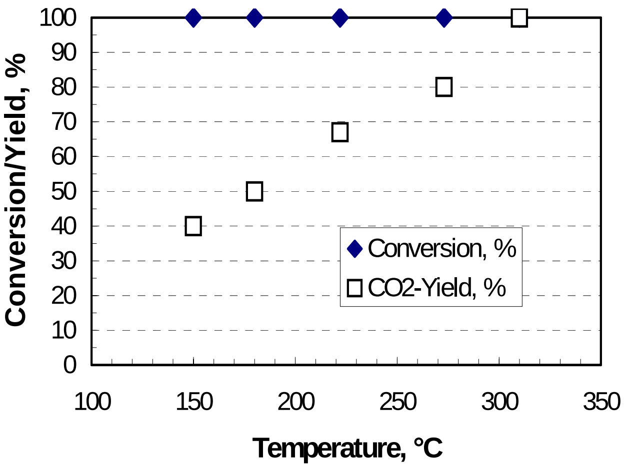


Fig. 1. Conversion of ethanol and yield of CO_2 on Pt/SiO_2/γ-Al_2O_3 catalyst. GHSV = 5000 h^{-1}

Oxidation of CO, Ethane and Propane on Gold Nanoparticles/mixed Oxide Systems

(Barbara Grzybowska–Świerkosz, Małgorzata Ruszel, Irena Gressel)

In continuation of studies on catalytic properties of Au/oxide support systems, a series of catalysts in which Au nanoparticles were dispersed on chromium spinels with various cations, was tested in oxidation reactions. The spinels have the same structure and different reducibilty, thus they seem to be a good models for studying the influence of support properties on catalytic activity of Au/oxide systems.

Earlier studies on activity of $Au/M^{II}Cr_2O_4$ where M^{II} = Co, Mn, Fe in CO oxidation, have been extended in 2005 to new supports (M^{II} = Zn, Cu, Mg). The whole series was tested in oxidation of CO (also in selective CO oxidation), and additionally in oxidation of C_3H_6, C_3H_8 and C_2H_6.

The results of catalytic activity in function of their reducibility are presented in Fig 1.

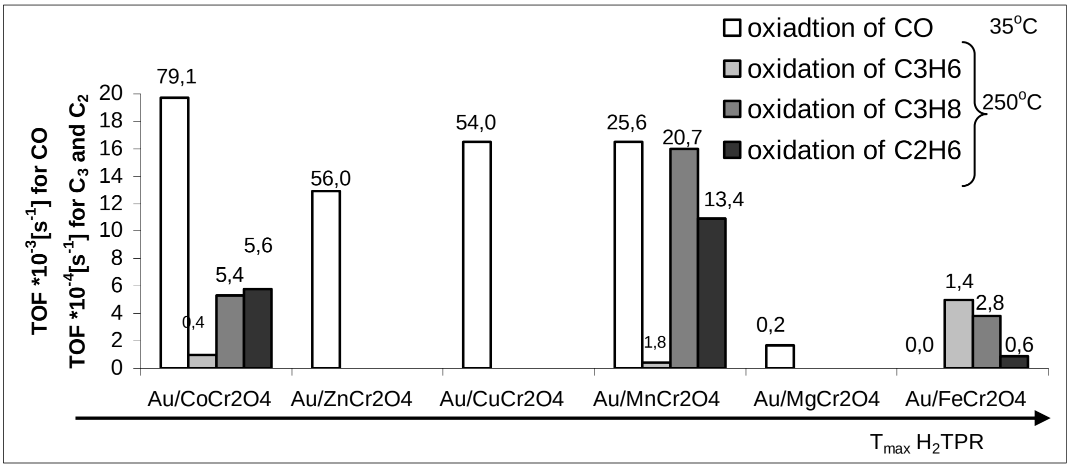


Fig. 1. Catalytic activity of $Au/M^{II}Cr_2O_4$ systems in oxidation of CO, C_3H_6, C_3H_8 and C_2H_6, numbers above the blocks are the conversion values in %.

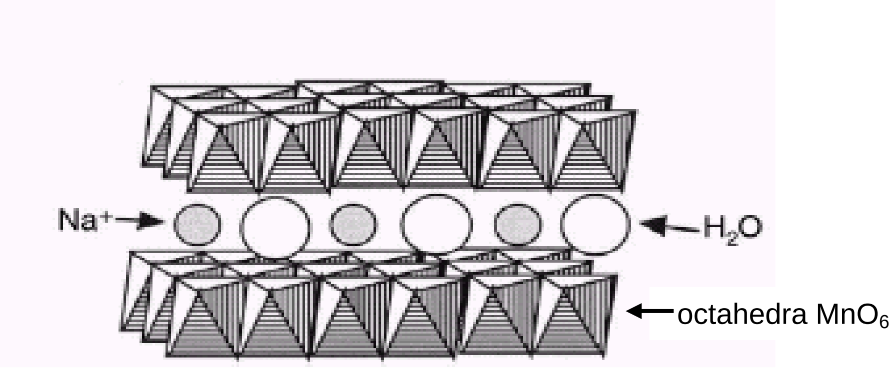
The results obtained so far on catalysts of this type lead to the following conclusions:

- $Au/M^{II}Cr_2O_4$ catalysts are active in oxidation of CO already at low temperatures, the most promising catalyst being $Au/CoCr_2O_4$ (100% CO conversion at 65°C).
- the sequence of increasing activity approximately follows the sequence of increasing reducibilty of catalysts: AuFeCr (0.0/450) < AuMgCr (4.8/350) < AuMnCr (25.6/210) < AuZnCr (56.0/140) < AuCuCr (54.0/160) < AuCoCr (79.1/100) (the numbers in brackets are CO conversion at 35°C [%]/temperature of maximal reduction [°C]), which indicates the importance of the support redox properties in controlling of the catalytic performance of Au/oxide support systems
- $Au/M^{II}Cr_2O_4$ catalysts are active in selective CO oxidation (with H_2 in the reaction mixture), complete CO conversion and 94% selectivity to CO_2 was observed for $Au/CoCr_2O_4$ at 60°C; the sequence of activity is preserved: AuFeCr (1.5/100) < AuMgCr (2.5/99) < AuMnCr (54.0/97) < AuZnCr (55.0/98) < AuCuCr (73.0/98.5) < AuCoCr (85/98) (the numbers in brackets are CO conversion/selectivity to CO_2 at 60°C in [%])
- $Au/M^{II}Cr_2O_4$ catalysts are active in oxidation of hydrocarbons: propane, propene, and ethane at higher temperatures (>200°C); the main products of the reaction are CO_x; in oxidation of ethane lower activity (conversion) as compared to C_3 hydrocarbons was observed. No correlations between reducibility of systems and their catalytic activity in these reactions were observed.

Catalysts for Combustion of VOCs Derived from Layered Manganese Compounds

*(Andrzej Mrzygłód, Roman Dula, Robert Janik, Tadeusz Machej,
Ewa Serwicka-Bahranowska)*

Birnessite is one of the layered manganese oxides. This naturally occurring compound can be relatively easily obtained in the laboratory. Ion exchange properties and susceptibility to structural transformation render birnessite an interesting object of research, in particular in the area of battery materials and molecular sieves (OMS). Catalytic systems based on birnessite were reported as active in oxidation reactions.



Structure of birnessite

Birnessite is usually synthesised in an alkaline medium, by oxidation of Mn^{2+} or reduction of MnO_4^-. In the present work the synthesis of birnessite was attempted at the surface of high surface area basic support MgO-Al_2O_3 (220 m^2/g) obtained by thermal decomposition magnesium-aluminium hydrotalcite. The nature of support precursor allows for control of the support basicity by the appropriate choice of the hydrotalcite composition. The synthetic procedure involved preparation of the support and impregnation thereof with the solution of either $Mn(NO_3)_2$ or $KMnO_4$, in the amount corresponding to 1 monolayer, followed by drying and calcination at 450°C. XRD detectable birnessite phase, visible in both dried samples, after calcination persisted only in the materials obtained from impregnation with permanganate. Birnessite is known to decompose in the temperature range 200-400°C, depending on the nature of the interlayer cations. The presence of reflections characteristic of birnessite in the material calcined at 450°C suggests that the birnessite phase, when obtained from the permanganate impregnated material, becomes stabilized at the surface of magnesia-alumina support. In the case of $Mn(NO_3)_2$ impregnation, calcination leads to the formation of a poorly crystalline magnesium-manganese aluminium spinel isostructural with $MgMn_{1.75}Al_{0.25}O_4$.

Calcined samples have been tested in the reaction of toluene combustion (flow reaktor, catalyst volume 0.5 cm^3, toluene concentration in air 2 g/m^3, GHSV 10000 h^{-1} i 30000 h^{-1}, temperature range 150-450^{0}C). Catalyst obtained by $Mn(NO_3)_2$ impregnation proved much more active than the one derived from the $KMnO_4$ impregnated material. In the first case, at space velocity of 10000 h^{-1}, 50% conversion was reached at 190°C, in the second at 310°C. At GHSV=30000 h^{-1} the temperatures of 50% conversion were 235°C and 340°C, respectively. This result suggests that the advantageous catalytic characteristics are possibly related to the formation os poorly crystalline surface phase of magnesium-manganese aluminium spinel.

Mechanisms of Biocatalytic Processes

Enzymatic Activity of Ligninolytic Enzymes in the Systems of Controlled Water Content

(Jerzy Haber, Janina Rodakiewicz-Nowak)

White-rot fungi are the most important group of the organisms capable to destroy lignin polymer in the Nature. The extracellular ligninolytic enzymes (heme containing ligninases and manganese dependent peroxidases, as well as copper containing polyphenol oxidases (laccases) are mainly responsible for this activity. The ligninolytic enzymes may be also used for oxidation of various aromatic compounds, including the toxic polycyclic aromatic hydrocarbons, phenols, chlorophenols and dyes. Many of these compounds are poorly soluble in water and their conversion needs application of organic solvents.

The aim of this work was to determine the effect of the physical and chemical parameters of the reaction medium (pH, concentration and thermodynamic activity of water, concentration and thermodynamic activity of the applied solvent, molecular properties of the solvent and substrate of the enzymatic reaction) on the stability and catalytic activity of polyphenol oxidases (laccases and tyrosinases) as well as peroxidases in the solutions of the water-miscible solvents, and water-in-oil microemulsions. The effect of physical and chemical parameters of the microemulsions (their dynamics, pH, water content) and the influence of the substrate on the catalytic activity of laccases, tyrosinases, catalase and lipoxygenase was studied also in water-in-oil microemulsions.

Various possible analytical models of the enzymatic activity and the possibility of prediction the enzymatic activity in the studied systems were also analyzed.

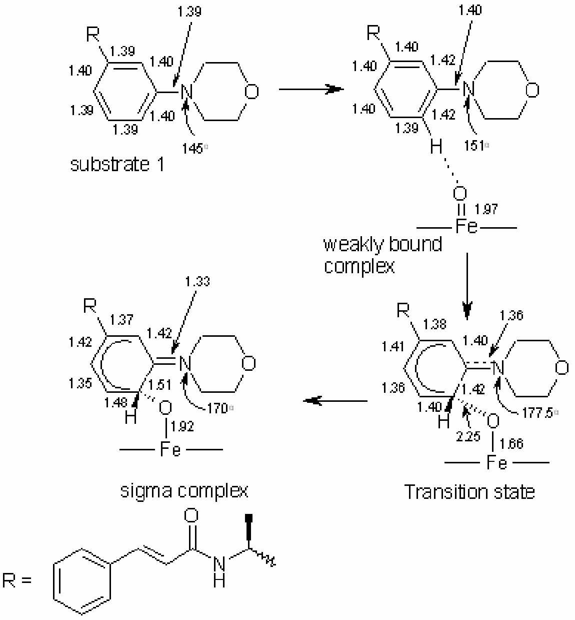
The majority of works was focused on blue laccase from various sources (*P. radiata* cultivated in the Institute) and *P. tigrinus, P. ostreatus, C. unicolor* and *C. versicolor* (in the co-operation), as well as yellow laccases from *P. tigrinus* and *P. ostreatus* (in co-operation). It was found that blue laccases are relatively resistant to the inactivation in solutions of organic solvents. It is possible to predict reasonably the catalytic activity of these enzymes towards various substrates in the presence of water-miscible organic solvents and in water-in-oil microemulsions, after some preliminary experiments. On the other hand, yellow laccases are more sensitive to the presence of organic solvents and their sensitivity depends on their history to a great extent. Moreover, it was found that these enzymes are capable to oxidize polycyclic aromatic hydrocarbons in the absence of external mediators. Water-in-oil microemulsions are a better medium for yellow laccases than solutions of organic solvents, because the enzymes keep their enzymatic activity and the presence of apolar organic solvent enhances the solubility of hydrophobic substrates.

The work was based on the co-operation with the Polish (Department of Biochemistry, M. Skłodowska-Curie University, Lublin), and foreign (Department of Physiology and Biochemistry of Plants and Microorganisms, RAS, Saratov, Department of Biochemistry of microorganisms, RAS, Puschino, ETH Zurich, Rengo and Shimadzu Co., Osaka) institutions.

Structural and Electronic Factors Determining Activity of Metal Sites in Ezymes – Quantum Chemical Investigations

(Ewa Brocławik, Mariusz Radoń - Jagiellonian University, Shaikh Abdul Rajjak - Tohoku University, Japan)

The cytochrome P450 enzymes play a central role in drug metabolism by catalyzing the biotransformation of a wide variety of xenobiotics. CYP3A4 is a major CYP450 isoform with broad substrate specificity and is estimated to be involved in the metabolism of approximately 50% drugs used in humans. (S)-N-[1-(3-morpholin-4-ylphenyl)ethyl]-3-phenylacrylamide (**1**) is the novel KCNQ2 potassium channel opener with significant activity in a cortical spreading depression model of migraine. We have studied the mechanism of arene ring hydroxylation in (1). Our work is based on the existing model of the active, oxidized form of the enzyme and focuses on the substrate transformation. DFT calculations were done for a gas phase model composed of the Compound I form of the active iron site, containing oxyferyl unit in a heme ring with a proximal cysteinate ligand ($Fe^{4+}O^{2-}(C_{34}O_4N_4H_{32})^{1-}(SCH_3)^{1-}$), and the substrate molecule (1). Stable structures in the first, rate determining reaction step (encounter complex and tetrahedral σ complex) were fully optimized. Transformation mechanism between stable structures was followed by approximate minimum energy pathway calculations based on geometrically selected reaction coordinate (C---O distance).



Initial structure in our study of this reaction step for actual bulky drug molecule **1** and Cpd I was the weak encounter complex bonded via hydrogen bond C-H---O (-21 kcal/mol). Geometrical parameters found important for the reaction coordinate at transition state with the barrier of 7.4 kcal/mol are shown in the scheme. The substrate, strongly bound in a σ-complex becomes substantially stabilized with respect to encounter complex by 8.3 kcal/mol.

The barrier for (1) is much lower than that for unsubstituted benzene and still well below those calculated for electron withdrawing or donating para substituents. Substantial height of the barrier was related to the loss of aromaticity in the benzene ring by $sp^2 \rightarrow sp^3$ rehybridisation on tetrahedral carbon. It seems clear from the structure of the transition state that rehybridisation of ortho nitrogen and making double bond to the ring carbon precede the formation of tetrahedral carbon, making this step less energetically demanding. Here we show that in the case of the nitrogen with its hybridisation flexibility the stabilizing effect is enhanced: the number of conjugated double bonds is preserved both in TS (low barrier) and in the tetrahedral complex (high stability). In conclusion we propose that the presence of an electron pair donating substituent in the ortho position to the oxidized arene site will substantially lower the energy barrier for the rate-determining σ-complex formation step in the drug metabolism. Thus enhancing or suppressing the drug metabolism should concentrate on this fragment.

Xenobiotic metabolites of methanotrophs as a subset of their metabolome - analysis of available pieces of information

(Władysław Kraus)

Results of works on whole *genome* sequencing of organisms (*genomics*) at the end of the last century stimulated development of a series of new „*-omics*"; object of their studies become whole-cell composition and location of substances making up the organisms, including proteins (*proteomics*) and metabolites (*metabolomics*) and their relationships. The process is furthered with development of new advanced technics of their separation and identification like ultra-high pressure nano-scale capillary liquid chromatography combined with Fourier transform ion cyclotron resonance mass spectrometry successfully used for analyses of some microbial systems or research approaches like *dynameomics* studying "native" features of biologically relevant and non-redundant folds of proteins (folding). Desirable are methods based on differences in physical, rather than chemical, properties of the compounds to avoid changes of *proteome* (organism compartments can have up to 10 000 different proteins expressed at once) and *metabolome* (metabolites with molecular mass up to 500 a.m.u.) during analyses. Systemic analysis of metabolite profiles and their turnover rates helps unerstanding organism functioning in environment and elucidation of gene function of its genome. Metabolic pathways of bacteria (including methanotrophs) enable them to mobilize nutrients as well as to immobilize or to detoxify substances detrimental for them, what is also realized with proteins and metabolites extreted to local environment (external proteome and metabolome). Metabolites are so numerous and very heterogeneous, that analyses of selected subsets of metabolome are usually possible. The present work deals with analysis of pieces of information of this kind distributed in literature on methanotrophs.

Methanotrophs are the group of bacteria wide-spread in upper parts of soil and waters (where concentration of oxygen is high enough), which used „one-carbon" compounds (without C-C bond in molecule, at most methane) as the sole source of carbon and energy. Enzymes of their main metabolic pathway metabolize methane, one of main gases responsible for greenhouse effect. The pathway is initiated with two forms of methane monooxygenase (MMO), the non-heme iron or copper protein (expressed depending on availability of methane and oxygen in environment) able according to existing information to oxidize chemical compouds foreign to methanotrophs (*xenobiotics*). Information on tens (closer to hundred) such compounds exists including environmentally burdensome compounds of the BTX group, methyl derivatives of pirydine and alkenes of industrial importance. In the case of other bacteria expression of that kind of enzymes could only be induced by the xenobiotics present in an environment (suitable genes could be also included to their genome with genetic engineering methods). Analysis of literature and own studies results suggests methanotrophs extrete to environment (and could absorb from it) the MMO xenobiotic metabolites and moreover environment could function as a temporary „stock" of the intermediates (they can also undergo an action of methanotroph enzymes other than MMO). Studies with DNA-array methods showed that environmental factors (technology of agriculture or fertilization) influence species composition of methanotrophs (chemical carrier of information responsible for changes could be benzoic acid derivatives) determining amount of methane assimilated by them. An influence of different ions and other compounds on reaction course (including its prevention) of xenobiotics with the enzymes of the MMO pathway and whole cells of the bacteria is recognized as well as differences found between different strains of methanotroph species. Expression of different forms of the MMO is also dependent on concentration of cupric ions in the bacteria environment. The data suggest the xenobiotics could shape methanotroph metabolome and could be its subset.

Dynamics of Dispersed and Biocolloidal Systems

Determination of the Influence of Ionic Strength on the Kinetics of Deposition of Colloid Particles on Hetereogeneous Surfaces

(Zbigniew Adamczyk, Lilianna Szyk-Warszyńska, Paweł Weroński, Barbara Siwek,
Katarzyna Jaszczółt)

Adsorption and deposition (irreversible adsorption) of colloids, proteins and other bio-materials on solid/liquid interfaces is of large significance for many practical and natural processes such as filtration, paper-making, chromatography, separation of proteins, viruses, bacteria, pathological cells, immunological assays, thrombosis, biofouling, biomineralization, *etc*. The effectiveness of these processes is often enhanced by the use of coupling agents bound to interfaces, e.g., polyelectrolytes. In biomedical applications special proteins (antibodies) attached to the surface are applied for a selective binding of a desired ligands from protein mixtures. On the other hand, many experimental studies on colloid particle adsorption have been carried out for surfaces modified by adsorption of polymers, surfactants, polyvalente ions, or chemical coupling agents (silanes), which change the natural surface charge of substrate surfaces. Appearance of such heterogeneous interfaces may exert important effects on transport of colloid particles in aqueous porous media, e.g., in soils. Because of the significance of these processes, precise experimental measurements were performed with the aim of determining mechanism and kinetics of adsorption on heterogeneous surfaces. Negatively charged polystyrene latex particles of submicrometer size range were used as model colloid system. The heterogeneous substrate bearing a controlled number of adsorption sites was produced by pre-covering mica sheets by positively charged polystyrene latex particles. The latex deposition was carried out under diffusion-controlled transport conditions and the particle coverage was determined by direct particle counting using the optical and electron microscopy. Deposition kinetics of latex particles at heterogeneous surfaces produced in this way was studied by direct optical microscope observations in the diffusion cells (under no-convection transport conditions). The role of the ionic strength (regulated by the addition of NaCl) on the kinetics of particle adsorption, structure of the self assembling monolayers, characterized in terms of the pair correlation function, and their jamming coverage was systematically studied. It was demonstrated that the ionic strength exerted a profound effect on the structure and the jamming coverage, whereas the kinetic aspect were affected to a lesser extent. With decreasing ionic strength, the structure of particle monolayers, showed less short-range ordering, and the site coordination number was also significantly reduced. It was postulated that in this case particle adsorption occurred at the top of adsorption sites only. In this way the possibility of producing random site surfaces by increasing ionic strength was clearly demonstrated. Additionally, the increase in the ionic strength reduced significantly the jamming coverage of particles. These observations were found in a quantitative agreement with theoretical predictions derived from the Monte-Carlo simulations. On the other hand, particle adsorption kinetics was quantitatively interpreted in terms of numerical solutions of the governing diffusion equation with the non-linear boundary condition derived from the available surface function. These results suggest unequivocally that by varying the ionic strength of colloid suspensions one can regulate the processes of particle transport to interfaces and taulor the structure of particle monolayers.

Influence of Roughness of Hydrophobic Surface on Kinetics of Formation of the Three Phase Contact Gas-liquid-solid

(Kazimierz Małysa, Marcel Krzan, Marta Krasowska, Jan Zawała, Marta Barańska)

Collisions of bubbles with grains and formation of the three phase contact (TPC) is a necessary condition for formation of the bubble-grain aggregates and flotation separation of various components of an ore. It is a common understanding that hydrophobicity of the grain surface is a necessary and sufficient condition for attachment to the colliding bubble, because the wetting film at hydrophobic surface is not stable, and as a result of its rupture the three-phase contact gas-liquid-solid is formed.

Phenomena occurring during the bubble collisions with a model hydrophobic solid (Teflon) of different surface roughness were studied. In our model system the experiment were carried out in a such way that probability of collision and probability that the detachment would not occur were always 100%. Thus, it was possible to determine effect of the surface roughness on time-scale of the three phase contact formation, and to evaluate a rupture thickness of the wetting films. A high-speed camera (1182 Hz) was used to record velocity variations, bouncing and time of attachment of the bubble colliding with Teflon plate positioned horizontally at the distance of ca. 300 mm above the point of the bubble formation (capillary orifice). The experiments were carried out for 5 Teflon plates having different surface roughness. Roughness of the plates was modified using different abrasive papers It was found that surface roughness had a crucial influence on the time-scale of the TPC formation by the bubble colliding with the Teflon plates. As the Teflon is a model hydrophobic surface (contact angle ca. 115^o in distilled water) one could expect that every collision should result in the TPC formation and the bubble attachment. However, it was observed that at the most smooth Teflon surfaces (called “Teflon I” and “Teflon II” and having surface roughness below ca.1 μm) there was no immediate attachment of the bubble during its first collisions. Time of contact of the colliding bubble with these solids was very short 2-3 ms, and simultaneously shape of the bouncing bubble varied rapidly within time intervals below 0.85 ms. These results indicate that during that short time of the collision the liquid layer separating the colliding bubble and the solid did not reach a critical thickness of its rupture. In distilled water four or even more “approach – bouncing” cycles could occur prior to the bubble attachment. With increasing surface roughness the time of attachment, i.e. the time period from a moment of the first collision to the TPC formation was shortened, and for the Teflon surfaces having surface roughness above ca. 30 μm the attachment occurred always during the first collision. On the basis of the determined time of the bubble contact with Teflon surface and using the Scheludko equation for the thinning of the circular plane parallel film between a solid wall (non-slip conditions) and free surface (full mobility) the average thickness of the wetting film rupture would be of an order 2 μm. Fact that surface roughness had so crucial effect on the time of the attachment and the TPC contact formation is most probably related to the following factors: i) larger asperices at more rough surface mean higher probability that critical thickness of the wetting film is locally faster attained, and/or ii) higher roughness means larger cavities and larger volumes of the air can be present at such surface, which as well can facilitate the liquid film rupture. The importance of the air presence and mechanism of air influence on the TPC formation bubble attachment are currently under investigations.

Interactions of Biologically Acticve Substances with Model Phospolipid Membranes

(Wanda Barzyk)

Penetration of three peptides into insoluble monolayers formed with phospholipids typical of biological membranes, i.e., 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) or L-α-phosphatidyl-D,L-glycerol-dipalmitoyl (DPPG), was investigated. It is a part of research conducted in co-operation with University Henri Poincaré Nancy (France) on penetration of biologically active substances to phospholipid monolayers as a model of biological membranes. Despite, the latter are bilayers containing dispersed sterols and proteins, their external phase boundary - at areas free of dispersed components - is identical in terms of molecular structure with phospholipid monolayers, on the solution side. The density range typical of biological membranes corresponds to phospholipid liquid expanded (LE) or liquid condensed (LC) phase, or their mixture - d in phospholipid monolayers with the Langmuir trough technique, in the range of $\Pi = 35 \pm 10$ mN/m.

Peptides isolated from the sequence of bovine milk proteins were investigated as the penetrants, namely: 5-residues peptide from α-lactalbumin, 16-residues peptide from α-s2 casein and 23-residues peptide isolated from component-PP3, of the molecular mass: 689, 2211 i 2683 g/mol, respectively. Tests for antimicrobial activity of the substances - performed earlier in France, showed the positive result. Because the peptides were available in small amounts, the procedure for the penetration measurements, enabling the minimum solution sample of 20 ml, was established; The phospholipid monolayer was spread - with a Hamilton syringe, at free water surface in a Petrii dish, up to reaching the desired equilibrium value of the surface pressure, Π_t, in the range 5-50 mN/m. A volume (100-1000 μl) of the peptide solution was injected beneath the surface and the subphase was stirred - without disturbing the monolayer - with a precision glass stirrer mounted at the bottom of the cell, to obtain the peptide's desired concentration in the subphase, c_o in the range $2 \cdot 10^{-7}$-$1 \cdot 10^{-5}$mol/dm^3. The penetration process was examined under the stationary diffusion conditions, by registering variations of the surface pressure with time, Π-t, and of the electric surface potential, ΔV-t, during the period of 120 min. after the injection step. The Π measurement was performed with a Wilhelmy plate, and the ΔV – with a vibrating plate, by applying the apparatus supplied by the KSV firm (Finland).

Dependence of the penetration effects was determined in relation to: i/ the initial density of the phospholipid film - characterized by the equilibrium surface pressure, Π_t, ii/ the peptide's concentration, c_o, and iii/ type of the lipid: DPPC or DPPG. In general, the penetration process caused an increase of the Π and a decrease of the ΔV, indicating increase in the intermolecular interactions in the film (increase of Π) and re-orientation of phospholipid molecules owing to the penetrant (i.e., the ΔV decrease owing to mutual compensation of molecular dipoles). The change caused by particular peptide was strongly dependent on type of the film-forming phospholipid, i.e., the Π-effect was greater for DPPC monolayer, as compared to DPPG, and quite the opposite for the ΔV-effect - it was greater for DPPC than DPPG. This differentiation is discussed in terms of structure of the phospholipid's head group, which is of purely polar character in DPPG molecule, and zwitterionic in DPPC. For all counterparts investigated: the peptide/the phospholipid, the dependences of the Π- and the ΔV-effects on density of the phospholipid's film, characterized by the Π_t, were found non-linear and showing two alternate maxima and minima. The courses indicate different penetrant's interactions with different phospholipid's 2D-phases, formed within the particular Π_t-regions, such as, liquid expanded (LE) and liquid condensed (LC) phase.

Adsorption of Biocolloid Particles on Polymer Fibre Surfaces
Stage II - Dependence of Adsorption Selectivity on Physicochemical Properties of the Adsorbent/solution/biocolloid System

(Piotr Warszyński, Jerzy Superata)

Adsorption of biological macromolecules on surfaces occurs the stronger, the better is their mutual steric and chemical compatibility with the structure of surface adsorption centres. Complementarity of chemical moieties leads to the strengthening of dipolic, hydrophobic or ionic interactions and hydrogen bond formation. The net observable effect is the significant increase of contact time or immobilization of adsorbate molecules on the adsorbent surface.
The role of liquid environment in which adsorption takes place is equally important as its composition in many ways can strengthen or weaken the interactions of a macromolecule with a surface. In order to obtain the most strongly and selectively adsorbing surface, various approaches can be applied; e.g. selection from among readily available surfaces, physical or chemical modification of existing surfaces or, alternatively, synthesis or construction of new surfaces. In the case of biocolloids their existing natural receptors or antibodies can be used as constituents of adsorption centers.

The experimental work of the present stage of the project has been devoted to searching for simple and economical ways of surface layer production in controllable manner. As model processes, the electropolymerizations of 1,2-diaminobenzene or its mixtures with modified carbon nanotubes were conducted. Subsequent cyclic voltammetric measurements revealed that diverse properties of the layers obtained depended on the electropolymerization technique applied (chronoamperometry vs. CV - Fig.1.) as well as the precursor composition (e.g. type of nanotube pretreatment - Fig.2.). General observation was that carbon nanotubes improved and stabilized electrochemical properties of the produced surface layers. The electropolymerization technique has proved to deserve further attention for its speed, reproducibility and good controllability of process parameters.

Fig. 1 CV: modified Pt microwire

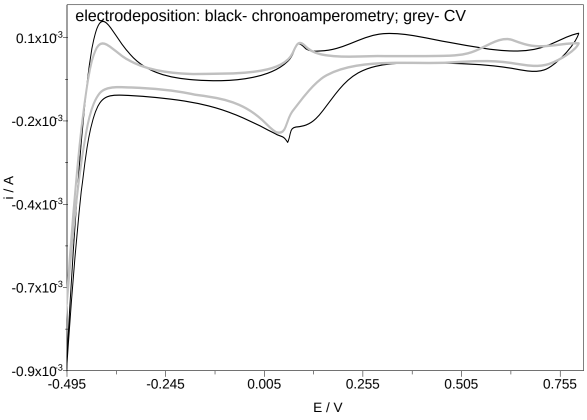
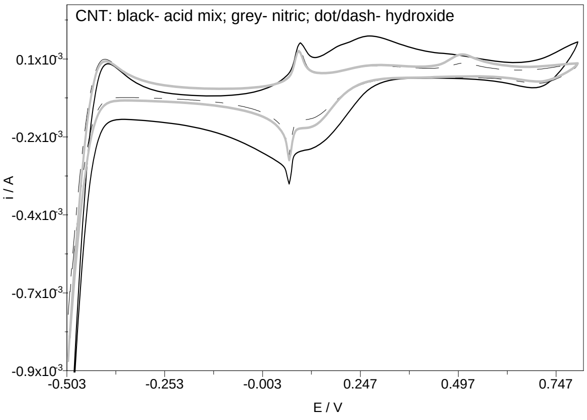


Fig.2 CV: modified Pt microwire



Moreover, preliminary experiments, involving application of molecular self-assembly processes in adsorbing surface construction, are in progress.

The previous and current research contributed to the outline of the concept of the integrated biosensor in which a selective adsorptive surface would constitute the receptor layer, and the amount of the adsorbed ligand could be transformed into change in the signal generated in the effector part. Verification of this concept is planned in next stages of the project.

Self-organizing Structures and Nanoparticles Monolayers

Determination of the Structure and Electrokinetic Properties of Adsorption Layers on Heterogeneous Surfaces

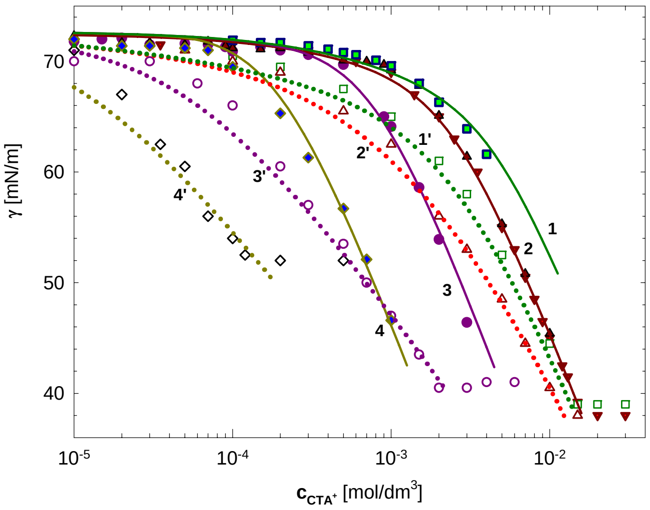
(Zbigniew Adamczyk, Maria Zembala, Aneta Michna, Barbara Jachimska, Elżbieta Porębska)

Consecutive deposition of anionic and cationic polyelectrolyte layers at solid interfaces proved an efficient method of preparing films of a desired composition and functionality. There are, however, few precise methods, which can be used for evaluating the homogeneity of such films in the micro scale. It was proposed that these properties can well be characterized by using the particle deposition technique. This is so because particle adsorption and deposition (irreversible adsorption) is exceptionally sensitive to local charge distribution at solid substrates. In addition, particle deposition studies can elucidate the mechanism of incorporation of particles and proteins into the multilayer film that is of vital interest for producing composite materials of targeted properties. In this study, deposition of negatively and positively charged latex particles on polyelectrolyte multilayers adsorbed on mica was studied experimentally by using the radial impinging–jet cell. These data were completed by streaming potential measurements in parallel– plate channel arrangement. Three types of polyelectrolytes were used: polyallylamine hydrochloride (PAH), poly (ethylene imine) PEI of a cationic type and polysodium 4-styrenesulfonate (PSS) of an anionic type. The bulk characteristics of polymers are represented by the zeta potential values obtained from microelectrophoretic mobility measurements. It was shown that the initial deposition rates of polystyrene latex onto oppositely charged polyelectrolyte layer achieved the limiting value characteristic for homogeneous surface. On the other hand, the initial deposition rate in case of similarly charged: polyelectrolyte layer and colloid particles was considerably smaller. These results correlate well with the zeta potential data of polyelectrolyte covered surfaces derived from the streaming potential method. It was observed, however, that measurable deposition rates of particles were observed for zeta potential of the multilayer having the same sign as the zeta potential of the particle. This discrepancy was interpreted quantitatively in terms of the improved theoretical model taking into account the local variations in charge distribution, similarly as for adsorption of particles on sites. Therefore, it was postulated that previous results obtained for particle adsorption on spherically-shaped sites can be used as reference states for interpretation of particle adsorption on polyelectrolytes. Besides the initial deposition rate, the long-time kinetics was determined and the jamming coverage of particles as a function of polyelectrolyte coverage. These results obtained for in the case of negatively charged latex adsorption on PAH layer showed that the jamming coverage of particles was strictly correlated with the polymer coverage. For polymer coverage larger than 0.3, the maximum deposition rate of particles became identical to the deposition rate at homogeneous surfaces. Under such conditions deposition kinetics can be well described by applying the random sequential adsorption model. The structure of the adsorbed particle layer was analyzed quantitatively in terms of the pair correlation function. It was revealed that the structure was similar to the homogeneous surface case, which excludes the possibility of macroscopic heterogeneities present on the surface. The results obtained confirmed that particle deposition method can be exploited as a sensitive tool for detecting the presence of nano-sized heterogeneities at solid/liquid interfaces.

Influence of Counterion Polarizability on Their Surface Activity in the Presence of Cationic Surfactants

(Piotr Warszyński, Grażyna Para, Ewelina Jarek, Marzena Noworyta)

We determined the influence of addition of various anions as Cl^-, Br^-, F^-, I^-, NO_3^-, ClO_4^-, CH_3COO^- on the surface tension of aqueous solution of alkyltrimethylammonium bromides; $C_{16}TABr$, $C_{12}TABr$ and $C_{10}TABr$. For the description of experimental results we applied previously developed theoretical surface quasi-twodimensional electrolyte (STDE) model. Contrary to the traditional model of surfactant adsorption, that model allows to take into account the effect of specific counterions on adsorption, and consequently, on the surface tension of solutions of ionic surfactants. A good agreement between the theory and experiment was obtained in a wide range of surfactants and added electrolytes concentrations. We found a very pronounced effect of anion specific in the dependence of surface tension on the concentration of cationic surfactants. The presence of perchloride anion led to the highest decrease of the surface tension at given surfactant concentration, while the solution in presence of fluoride ions exhibit the lowest surface activity. As an example of results obtained (Fig.1) we present the surface activity of $C_{12}TA^+$ cations which depends on the type of anion present in solution (either as a counterion or anion of added electrolyte) and follows the series $Cl^- < Br^- < I^- < ClO_4^-$. We found a very large differences in ability of various anions to facilitate adsorption of cationic surfactant which follows the order: $F^- < CH_3COO^- < Cl^- < Br^- < NO_3^- < KI^- < KClO_4^-$, which coincides with Hofmeister series of anions. We were able to correlate one of the parameters of our model, “counterion surface activity” α_c, which is a measure of penetration of the interfacial layer by ions, with their excess polarizability α_p.The obtained correlation is shown in Fig. 2. The results indicate that the anion specific effects in adsorption of cationic surfactants can be explained by different ability to penetrate the surface Stern layer by particular anion. Anions, which can easily penetrate the surface layer, neutralize more effectively the charge of adsorbed surface active cations and lower the surface potential. As the result of the surface charge neutralization more surfactant ions can be adsorbed at the interface. The phenomenon of the Stern layer penetration can be effectively described by the “surface quasi two-dimensional” model of ionic surfactant adsorption.



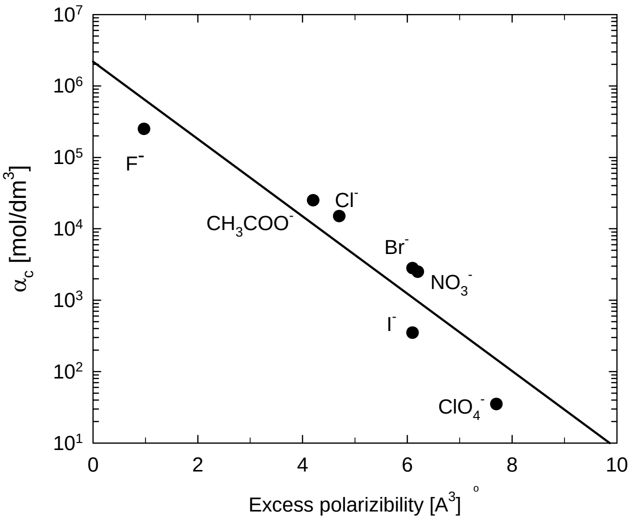


Fig.1. Equilibrium adsorption isotherms of: 1 – DTACl, 2 – DTABr, 3 – DTAI and 4 $DTAClO_4$ solutions in comparison with adsorption isotherms for DTABr solutions containing 10^{-2} M concentration of: 1’- KCl, 2’ – KBr, 3 – KJ, 4’ – $KClO_4$, lines represent results of fit of the theoretical STDE adsorption model.

Fig.2. The correlation between surface activity parameter α_c of anions and their excess polarizability α

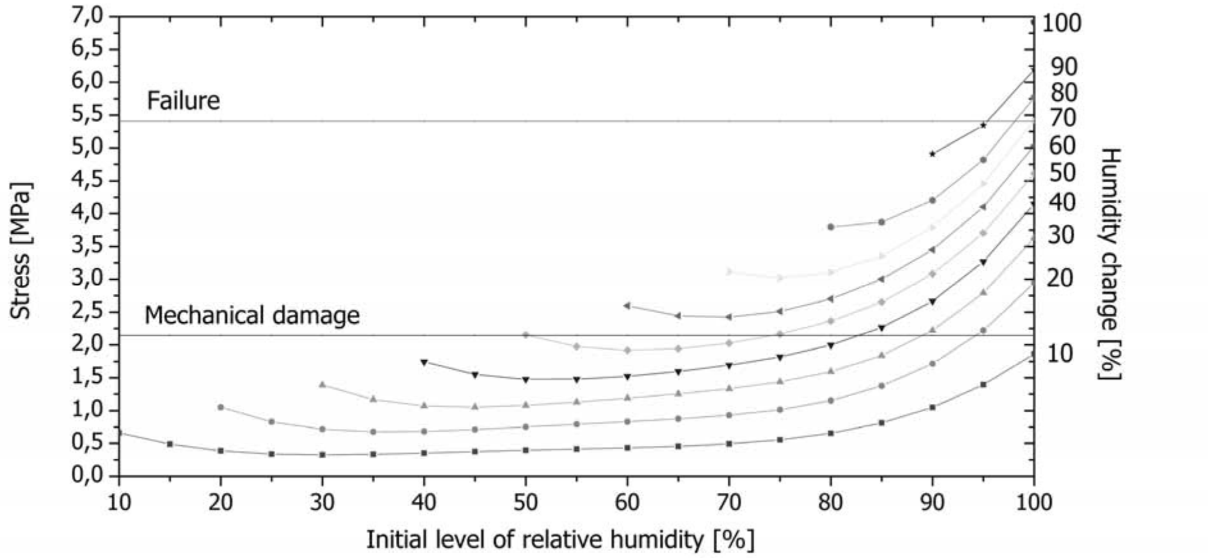
Protection of Cultural Heritage

Allowable Thresholds in Magnitude and Frequency of Fluctuations of Air Parameters in the Environment of Wooden Cultural Objects

(Roman Kozłowski, Łukasz Bratasz, Sławomir Jakieła, Antonina Kozłowska)

Development of mathematical model to calculate mechanical stress in the cross section of wooden elements subjected to fluctuations of the air climatic parameters – relative humidity and temperature was finalized. An adequate model of the moisture transport in wooden elements and objects in response to climatic fluctuations was obtained basing on adsorption and diffusion characteristics of the wood, determined in laboratory. Realistic moisture distributions in the cross sections of the wooden elements were obtained, in particular changes in the moisture content close to the surface which area is especially sensitive to fast fluctuations of the microclimate in the environment. Internal stresses resulting from this differential moisture penetration were calculated.

Using the developed model threshold levels in the magnitude of the climatic variations were established beyond which deformation and mechanical damage appears in the wood. This was accomplished by comparing stresses calculated to mechanical strength, measured in laboratory, for various species of wood occurring in historic objects. The calculations were done for a cylindrical wooden object of a diameter larger than 5 cm for fast changes of relative humidity, as under these conditions the largest stresses are engendered. The result of the researches described is a map of stresses with the areas of humidity fluctuations in air, for which a risk of damage of wood appears, marked. The map of risk for the lime wood is shown in the figure below.



RESEARCH PROJECTS
of the Ministry of Education and Science

Theoretical Description of the Temporal Evolution of Adsorption Systems with Surfaces Characterized by Energetic/geometric Heterogeneity

(*Władysław Rudziński, Tomasz Pańczyk*)

Research Project KBN 4 T09A 015 24

Within the framework of the project realization we continued the studies of the influence of structural heterogeneity of surfaces on the dynamics of adsorption/desorption processes. We are preparing an article devoted to the influence of surface defects, obtained by the laser ablation, on the dynamics of associative desorption of probe molecules. We also started the studies devoted to the influence of fractal dimension of surfaces on the frequency of collisions of probe molecules with such highly irregular surfaces. The frequency of collisions of molecules with the surface is the most fundamental factor governing the overall rate of adsorption. In the case of a flat surface, that frequency is described by a simple equation derived from kinetic theory of gases (we confine the analysis to the case of ideal gas), whereas in the case of irregular surfaces it is not clear how that frequency will be changing with pressure or fractal dimension. The studies are carried out using molecular dynamics.

We have published the article where we analyzed the accuracy of the condensation approximation (which we applied so far) used for the generalization of the kinetic equations derived from the Statistical Rate Theory (SRT), for the case of the energetically heterogeneous surfaces. We showed that in the case of very small or very high surface coverages the condensation approximation may not be sufficiently accurate. Then, one has to use full solutions which do not lead to simple analytical equations. We also showed that application of the SRT to the analysis of sorption kinetics in porous materials leads to the same agreement with experimental data as surface diffusion model. Moreover, the limiting form of the SRT equations (for the case of energetically heterogeneous as well as homogeneous surfaces) for initial times, gives the square root dependence of adsorbed amount on time, i.e. $t^{1/2}$, that is relation typical for surface diffusion model. It suggests that the linear dependence of adsorbed amount on $t^{1/2}$ is not an ultimate proof for that the process is governed by surface diffusion, which is commonly accepted assumption. The results of the above studies were published in the *J. Phys. Chem. B*, (Rudziński W., Pańczyk T., Płaziński W., *J. Phys. Chem. B* 109 (2005) 21868).

Influence of Position of Transition Metal in Heteropoly Compound Structure on Its Catalytic Activity and on Reaction Mechanism of Oxidation of Cyclic Hydrocarbons

(Katarzyna Pamin, Jan Połtowicz)

Research Project KBN 3 T09A 092 29

Heteropolyacids exhibit structures that are well characterized at the molecular level, and therefore acidity and redox properties can easily be controlled. The oxidation of saturated organic substrates, like light paraffins, is an example of catalytic reaction which requires both functions. The introduction of transition metal cations into heteropolyacid structure influences its oxidation properties. Depending on the position of metal in the heteropolyacid structure, its catalytic properties will be different.

The first stage of this work consists in the introduction of transition metals into the counter cation position of the heteropolyacids. Cobalt cations were exchanged for protons in the $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ acids. The following catalysts were synthesized: $Co_3(PW_{12}O_{40})_2$, $HCoPW_{12}O_{40}$, $H_2Co_{0.5}PW_{12}O_{40}$, $Co_3(PMo_{12}O_{40})_2$, $HCoPMo_{12}O_{40}$, $H_2Co_{0.5}PMo_{12}O_{40}$. The synthesized catalysts were characterized by means of thermal analysis and XRD. The changes observed in diffractograms and derivatograms of the studied catalysts confirm the formation of a series of cobalt salts with changing stoichiometry. The purpose of the present study is to determine the influence of the cobalt counter-cation on the redox and acid-base properties of the heteropoly compounds in the oxidation of cyclooctane with molecular oxygen. The acidic properties of the catalysts were also determined in the vapour-phase dehydration of ethanol. For comparison, the catalytic activities of HPW and HPMo were tested in both reactions. The liquid-phase oxidation of cyclooctane was performed at the optimum temperature of 120^{o}C, for 6 hours and under the pressure of 10 atm. The reaction products are cyclooctanol and cyclooctanone. The dehydration of ethanol was carried out in a conventional flow type reactor, in the stream of helium of 30 mL/min flow. Catalytic activities of the catalysts were taken for comparison at 225^{o}C. The exchange of protons for cobalt atoms results in the stepwise weakening of the acidic strength of the synthesized salts. Neutral salts, in which all protons were exchanged for metal atoms, show the lowest activity in the dehydration of ethanol. The introduction of cobalt atoms into the $H_3PW_{12}O_{40}$ has a substantial influence on the catalytic activity in the oxidation of cyclooctane. However, the presence of cobalt in the structure of $H_3PMo_{12}O_{40}$ acid improves its catalytic activity only to a small degree.

Application of Macrocyclic Complexes of the Transition Metals: Metalloporphyrins, Metallophthalocyanins and Metallosalens in Catalytic Oxidation of Propylene

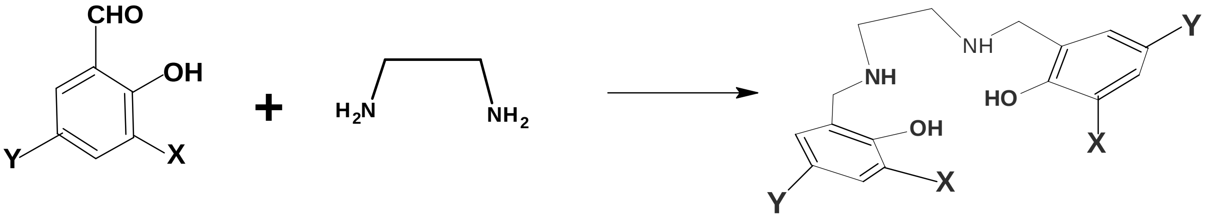
(Jan Połtowicz, Katarzyna Pamin)

Research Project KBN 3 T09B 091 29

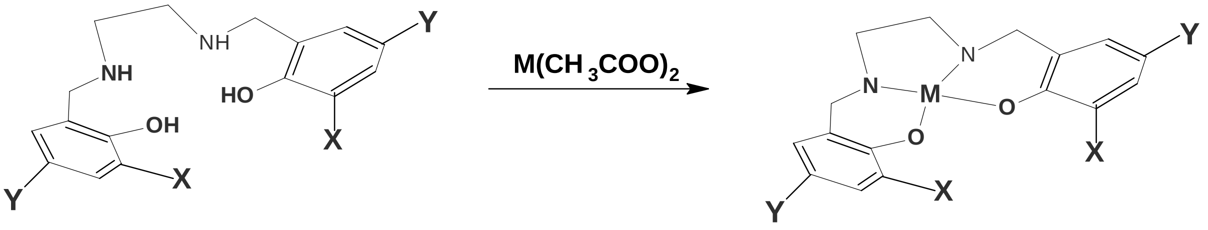
The catalytic properties of macrocyclic metallocomplexes for oxidation of hydrocarbons have became of considerable interest. Three groups of complexes: metalloporphyrins, metallophthalocyanine and metallosalen have been the subject of many studies of their potential application as selective catalysts. A lot of information has been accumulated regarding the reactivity of these complexes in particular bearing electron-with drawing substituenets at the ring macrocycle. In contrast, little is known regarding the catalytic properties of metallocomplexes with electron-donor groups.

In this work we presented our study on the synthesis of metallosalen complexes with electron-donor substituents and their catalytic activity.

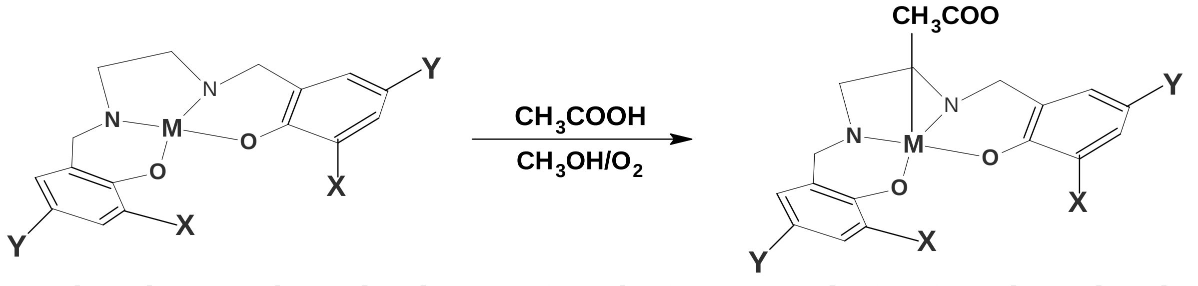
Salen ligands were obtained in the classical way in the reaction of appropriate alkylsalicylaldehyde and 1,2-diaminocyclohexane in 96% ethanol solution:



Co(II)salen complexes were synthesized from salen ligand and cobalt(II) acetate in dichloromethane/methanol solution.



The Co(II) complexes must be subjected to one–electron oxidation to produce Co(III)salenX complexes (X = acetate anion). This may be done conveniently by aerobic oxidation of metallophthalocyanine in the presence of acetic acid according to the reaction:



Four ligands were obtained: salen$(OCH_3)_2$, salen$(OC_2H_5)_2$, salen(t-Bu)$_4$ and simple salen. Metalation of these ligands with cobalt acetate gave eight cobalt complexes: Co(II)(salen), Co(III)(salen)OAc, Co(II)(salen)$(OC_2H_5)_2$, Co(III)(salen)$(OC_2H_5)_2$OAc, Co(II)(salen)$(OCH_3)_2$, Co(III)(salen)$(OCH_3)_2$OAc, Co(II)(salen)(t-Bu)$_4$ and Co(III)(salen)(t-Bu)$_4$OAc. All free salen ligands and metallosalen complexes were characterized by UV-Vis, EPR, FTIR spectroscopy and cyclic voltammetry.

Application of Fluorous Biphasic System to Catalytic Processes of Hydrocarbon Oxidation

(Jerzy Haber, Katarzyna Pamin, Jan Połtowicz)

Research Project KBN 3 T09B 122 26

One of the major problems in the field of homogeneous catalysis is the separation of the catalyst from the reaction products. The commonly used method, separation by distillation, requires elevated temperatures. Fluorous biphasic catalysis (FBC) is a relatively new concept for easy isolation of catalysts and their re-use. The catalysts with long fluorinated alkyl chains are soluble only in a perfluorocarbons. The reactants are added to an organic solvent that is immiscible with the perfluorocarbon at room temperature. On heating, the two phases form homogeneous system and the reaction occurs; on cooling, the fluorinated and organic layers separate. The organic phase can be removed and the product isolated, while the fluorinated catalyst-solvent phase can be reused.

Oxidation of hydrocarbons with molecular oxygen catalyzed by metallocomplexes is one of the most attractive transformations in organic synthesis. The major drawback which prevents progress in practical application of the macrocyclic catalysts for large scale oxidation is their recycling and re-use. One of the methods to circumvent this problem is the catalysis in biphasic system solvents, in particular in a relatively new fluorous biphase system. Thus, we have synthesized the macrocyclic compounds: metalloporphyrins with ponytails and we have applied these compounds in epoxydation of alkenes with molecular oxygen.

These compounds were characterized by UV-Vis, EPR and FTIR spectroscopy. They are soluble in some perfluorosolvents like perfluoro(methylcyclohexane), perfluorohexane or perfluorodecalin. These metallocomplexes were applied as catalysts in epoxidation of cycloalkenes in perfluorohexane/CH_3CN biphase system with molecular oxygen and sacrificial aldehyde as the reducing agent. Epoxidation reactions were carried out at room temperature under O_2 at atmospheric pressure. All synthesized metalloporphyrins were active in the investigated epoxidation reaction. The main product was epoxide. No epoxydation products have been observed in blank experiment without catalyst. The conversion of substrates and epoxide yields were high, about 80-100% for cyclooctene and cyclohexene. The macrocyclic catalysts were separated from products, recycled and re-used in epoxidation without decrease of conversion of substrate or yield of epoxide, indicating that the metalloporphyrin does not lose catalytic activity during oxidation process.

The catalytic results show that the activity of perfluorinated catalysts seems to be dependent on the character of the metal center, on the kind of the fluorous chains and on the type of substituents in macrocyclic ring.

The second part of this work was synthesis metallophthalocyanines with perfluoro alkyl tails. Iron, manganese, copper and nickel complexes were prepared by condensation of the appropriate metallophthalocyanines with perfluoroalkyl iodides. Eight complexes were obtained: simple Mn(Pc), Fe(Pc), Co(Pc),Cu(Pc) and Ni(Pc) with perfluoro chains and manganese, iron and cobalt phthalocyanines with nitro groups and perfluoro alkyl tails. All compounds were characterized by UV-Vis, EPR and FTIR spectroscopy. Synthesized metallophthalocyanines are soluble in some perfluorosolvents like perfluoro(methylcyclohexane), perfluorohexane or perfluorodecalin and insoluble in commonly used organic solvents.

Mesoporous Silica Supports as a Tool for Control of Catalysis by Macrocyclic Metallocomplexes

(Ewa Serwicka-Bahranowska)

Research Project KBN 3 T09B 066 26

In 2005 the studies concentrated on the investigation of cyclooctane oxidation with molecular oxygen over cationic manganese porphyrin deposited at the surface of aluminated mesoporous silicas of HMS, MCM-41 and SBA-15 types. The oxidation of cyclooctane was performed in a stainless steel batch reactor system at 120°C, under an air pressure of 10 atm, using 60 ml of cyclooctane, with the molar ratio of cyclooctane to oxygen set at 6.5. In each experiment the amount of the catalyst was adjusted so that the net content of the active MnTMPyP phase corresponded to 1.1 μmole. Analysis of the product distribution showed that cycloctanone was the main reaction product, cyclooctanol being produced in only small quantities. The cyclooctanone selectivities observed for the Mn(TMPyP)/AlHMS and Mn(TMPyP)/AlMCM-41 catalysts (≥94%) were much higher than for the MnTMPyP/AlSBA-15 materials and the unsupported Mn(TMPyP), for which the selectivity to cyclooctanone was always below 90%. We have explained the effect as being due to stereoselectivity imposed by the relatively small pore dimensions of the HMS and MCM-41 type mesoporous supports. Oxidation of cyclic hydrocarbons is a radical-chain reaction, initiated by the activation of hydrocarbon molecules by metalloporphyrin species to give cycloalkyl radicals. In the presence of molecular oxygen the reaction branches out to form cyclooctanone via metalloporphyrin-cycloalkylperoxo complex and/or to yield cyclooctanol via cycloalkylhydroperoxide intermediate. We propose that the latter pathway is suppressed in the confined space of narrow mesopores as the cycloalkyl radicals that are formed tend to remain trapped by the neighbouring metalloporphyrin to form the complex required for the cyclooctanone pathway rather then escape and react to give cycloalkylhydroperoxide necessary for the formation of cyclooctanol.

The activity of the catalysts increased with the increasing pore size of the support, which pointed to the existence of diffusion limitations within the pore inner space. Catalytic activity was also shown to depend on the metalloporphyrin surface density. Increase in metalloporphyrin loading above a certain optimum value resulted in reduction of the catalyst activity attributed to the lessening of site isolation effect. The supported metalloporphyrin catalysts could be reused without any significant loss of activity.

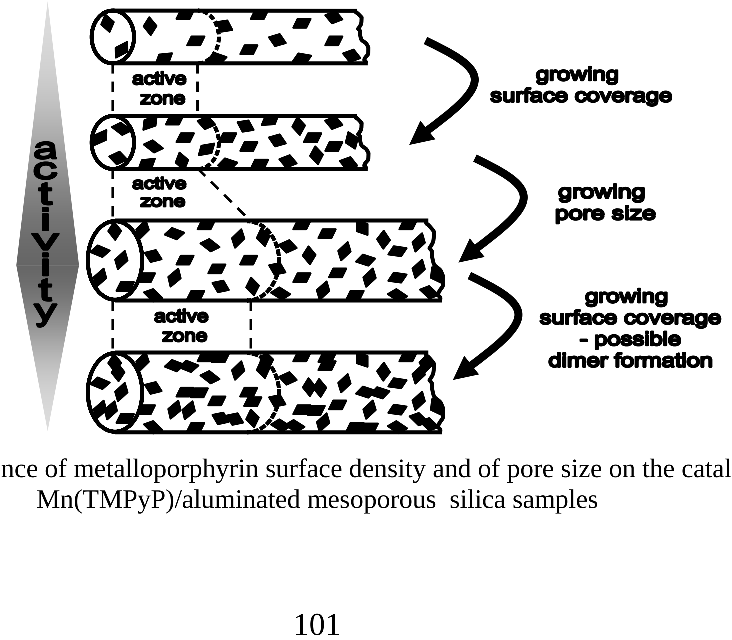


Illustration of the influence of metalloporphyrin surface density and of pore size on the catalytic activity of Mn(TMPyP)/aluminated mesoporous silica samples

Basis for the Technology of Manufacturing Complex Oxide Materials for Neutralisation of Toxic Solvent Vapours

(Alicja Michalik)

Research Project KBN 3 T08D 003 26

In view of the well known unique properties of mixed oxide phases prepared from the hydrotalcite-like precursors, an attempt has been made to synthesise such precursors containing copper and manganese, with aim to design catalysts for combustion of VOCs. Zinc and aluminium were added to the synthesised materials in order to promote formation of the hydrotalcite structure. The samples were obtained by co-precipitation at a constant pH=7 from aqueous solutions of appropriate nitrates at (Cu+Zn)/(Mn+Al) ratio equal 2. The following precursors, referred to as CuMn(7), CuZnMn(7), CuMnAl(7) and CuZnMnAl(7), were obtained: Cu:Mn=2, Cu:Zn:Mn=5:1:3, Cu:Mn:Al=6:2:1, and Cu:Zn:Mn:Al=4:2:2:1. Prior to catalytic tests the precursors were subjected to 3 h calcination in air at 673 K.Depending on the sample composition the crystalline phases identified in the precursors included hydrotalcite-like structure, layered hydroxy double salt and ZnO. Calcination led to mixed oxide phases, in which CuO of various degrees of crystallinity could be identified, as well as traces of ZnO in the Zn-containing materials. The Al- and Mn-containing phases remained amorphous.

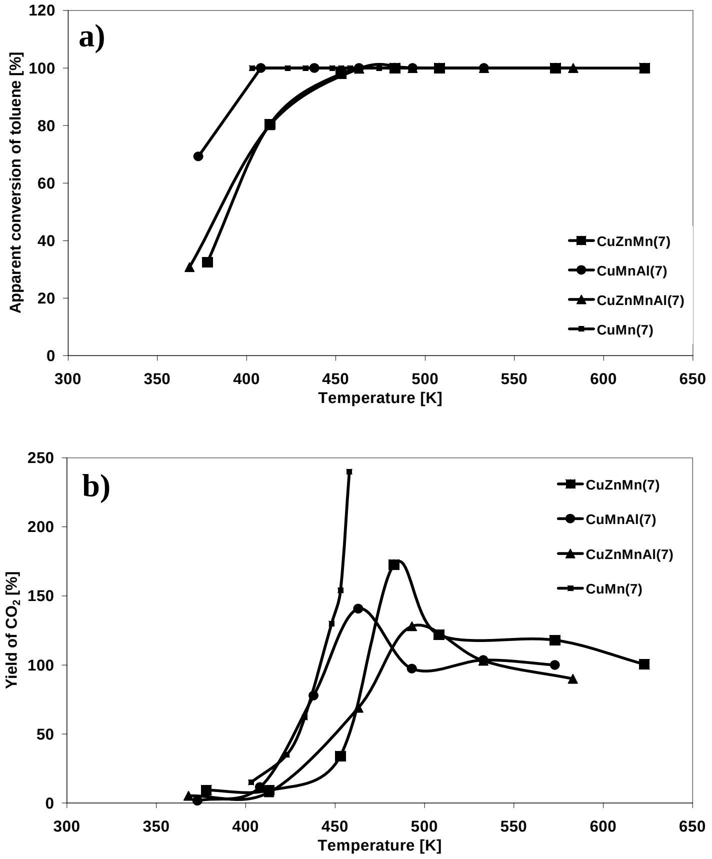


Fig. 1. Catalytic performance of mixed oxide catalysts in the combustion of toluene

All mixed oxide samples proved extremely active in the catalytic combustion of toluene. Some catalysts reached 100% conversion already at 403 K (Fig. 1a). Addition of Zn had an adverse effect on the catalytic activity, while addition of Al showed no negative influence. In the low temperature regime (below 450 K) the catalytic reaction was accompanied by strong sorption of toluene. Combustion of adsorbate at higher temperatures is responsible for the over 100% yield of CO_2 at certain temperature ranges (Fig. 1b). Analysis of the CO_2 yield curves shows that addition of Al is beneficial for the catalytic performance as it lessens the surplus CO_2 formation at higher temperatures, obviously due to the suppression of the excessive adsorption of toluene at low temperature. This feature is important as strong low temperature toluene sorption carries the danger of possible explosion.

Method of Preparation and Physicochemical Properties of the Manganese-containing Synthetic Hydrotalcite-type Compounds

(Roman Dula)

Research Project KBN 3 T09A066 27

Manganese was inserted into the structure of Mg-Al hydrotalcite-like compounds in two ways: in the form of Mn^{2+} or Mn^{3+} cations into the brucite-like layers and in the form of MnO^{-}_{4} anions in the interlayer spaces. Two types of materials: Mg-Mn-Al nitrate and Mg-Al permanganate intercalated LDHs with Mg/Mn/Al atomic ratios close to 2/0.5/1 have been prepared. Mg-Mn-Al nitrate LDH was synthesized by coprecipitation, while Mg-Al permanganate intercalated LDH was prepared by ion-exchange of the parent Mg-Al nitrate LDH precursor with MnO^{-}_{4} anion. TG analysis showed that $MgAlMnO_4$ LDH is more thermally stable – the total decomposition of the layered structure occurs at 426°C instead of 400°C observed for the MgMnAl nitrate LDH, which leads to the lower crystallinity of phases formed at higher calcination temperatures. In all mixed oxides type phases identified in samples calcined at 600°C manganese exists at its +2 and +3 oxidation states, while XPS analysis data show mainly Mn^{4+} on the surface of both calcined materials. It leads to the conclusion that in both samples Mn^{4+}-containing phases are highly amorphous, but the surface density of Mn^{4+} centres is higher for the Mn-layer doped material than for interlayer doped one.

The freshly prepared samples were converted into the mixed oxide systems by the calcination in air at 600°C for 4 h. Mixed oxide systems obtained by calcination at 600°C were characterized by XPS, TPR and BET and used as catalysts for the total oxidation of toluene. The samples derived from the LDH precursor containing Mn within the brucite layer showed higher conversion of toluene than the ones obtained from the permanganate-intercalated precursors. The catalytic activity has been correlated with the presence of Mn^{4+}-containing, easily reducible amorphous surface coat. Catalytic properties of the more active material were comparable with those of the commercial catalyst.

Mechanisms of Colloid Particle Monolayer Formation on Heterogeneous and Conductive Surfaces

(Zbigniew Adamczyk, Maria Zembala, Lilianna Szyk-Warszyńska)

Research Project KBN 4 T09A 076 25

Deposition kinetics of colloid particles one heterogeneous and modified metallic surfaces was studied experimentally. Two types of substrates were used in these studies (i) mica surface covered by polyelectrolyte multilayers (PSS of anionic type and PAH of cationic type both having molecular weight of 70 000) and (ii) titanium surface modified electrochemically. Mica sheets supplied by Dean Transted Ltd. England were used as the substrate surfaces for polyelectrolyte deposition. Thin sheets were freshly cleaved and used in each experiment without any pre-treatment. Metallic titanium (99.6% pure Ti) was supplied in the form of thin foils (dimensions 50 per 50 mm, thickness 30 μm) by Goodfellow. The foil was cut into strips of the dimensions of 10 per 50 mm. The titanium substrate were passivated electrochemically according by an anodic oxidation carried out in a phosphate buffer solution of pH =7.4 and the over-voltage of 80 V. This procedure, lasting 100 s, resulted in formation of a titania layer as confirmed by X-ray studies, having an averaged thickness of 150 nm and the micro-roughness of 17 nm. Preparing the titania layer of higher resistivity was advantageous because it prevented uncontrolled oxidation of titanium in the deposition experiments. The streaming was measured using the two Ag/AgCl electrodes using the Keithley 6512 electrometer. Knowing the streaming potential, one can calculate the apparent zeta potential of the substrates, which is of primary practical interest. Contact angle measurements have been carried out according to a two-stage procedure: first the substrate was covered by a desired number of polyelectrolyte layers by dipping the substrate into the appropriate solution of alternatively PAH and PSS of the concentration 0.5 mg/ml (500 ppm), adsorbing the polymer under diffusion controlled transport (30 minutes) and washing with water for ca. 1 minute. Then, the multilayer covered substrate was dried for 24 hours under controlled humidity conditions. Finally, wetting angle of sessile drops placed at random over the substrate surface has been determined using a home made thermostated apparatus under controlled humidity. The contact angle was determined by image analysis software exploiting a polynomial fit of the drop shape near the three phase perimeter. Particle deposition was carried out in the oblique impinging jet cell using the monodisperse suspensions of polystyrene latex particles synthesized previously. The polyelectrolytes were adsorbed according to the layer by layer method from NaCl solutions of various concentration. It was demonstrated that after completing a bilayer, periodic variations in the apparent zeta potential between positive and negative values appeared for multilayers terminated by PAH and PSS, respectively. This was in accordance with zeta potential of the polymers in the bulk measured by electrophoresis. It also was observed that streaming potential data correlated well with the contact angle characteristics of dried polyelectrolyte films. Variations in the contact angle between 70^o for PAH and 40^o for PSS were exactly in phase with the variation in the zeta potential. The stability of polyelectrolyte films against prolonged washing (reaching 24 hours) was determined using the streaming potential method. It was revealed that both for mica and titanium, the PSS layer was considerably more resistant to washing, compared to the PAH layer. These results were compared with the measurements of deposition kinetics of model colloid suspensions. It was demonstrated that the initial deposition rate of particles was strictly correlated with the zeta potential and wetting angle variations. These results enabled one to formulate a sensitive procedure of determining the presence of adsorbed species at various surfaces.

Determination of Physicochemical Mechanism Formation of Multilayers Ceramic Nanomaterials with Higher Biocompatibility

(Barbara Jachimska, Zbigniew Adamczyk)

Research Project KBN 3T08D 045 29

Polyelectrolyte has received considerable attention for the past few decades, but our understanding of their novel behavior still remains limited. One interesting phenomenon is formation specific conformation of polyelectrolyte chains in the suspension. In this note, we study a correlation between viscosity and dynamic light scattering results for flexible polyelectrolyte solutions in an attempt to better understand the conformation effects.

Two types of polyelectrolytes were used in our studies: polyallylamine hydrochloride (PAH), of a cationic type, and polysodium 4-styrenesulfonate (PSS) of an anionic type, both having molecular weight of 70 000. The bulk characteristics of polymers were determined by measuring the zeta potential, diffusion coefficient and viscosity for various pH and ionic strength. The zeta potential and diffusion coefficient of polyelectrolytes was determined by using a Zetasizer Nano ZS Malvern instrument. These measurements as well as molecular dynamic simulations of chain shape and configurations, suggested that the molecules assume an extended, worm-like shape in the bulk. Accordingly, the diffusion coefficient was interpreted in terms of a simple hydrodynamic model pertinent to flexible rods.

The dynamic viscosity of polyelectrolyte suspensions as a function of its volume concentration was measured using a capillary viscometer. Experimental data showed that the relative viscosity increased more rapidly with the volume fraction than predicted by the Einstein formula for spherical particles. This allowed one to calculation the specific conformation of polyelectrolyte chains in the suspension. It was proved that conformation of molecules was strongly influenced by the ionic strength of the solution. This finding is in accordance with Monte Carlo simulations of Stoll, who indicated that the chain extension increased significantly with the decrease in the ionic strength. The results obtaining suggest that the combination of DLS and viscosity measurements can be uses as a sensitive tools to study properties and structure of polyelectrolyte solutions.

Localized Adsorption of Colloid Particles in Processes of Formation of Multilayer Surface Coverages by "Layer-by-layer" Method

(Paweł Weroński)

Research Project KBN 3 T09A 089 27

Computer simulations of multilayer adsorption of hard (non-interacting) spherical particles were conducted using the earlier developed theoretical model. Adsorption simulations of the multilayers composed of twenty monolayers were conducted at the first monolayer surface coverage θ_1 = 0.01, 0.02, 0.05, 0.10, 0.20, and 0.30, and at the dimensionless adsorption time of the subsequent monolayers equal to $\tau = 10^4$. Based on the results obtained in the Monte Carlo simulations the multilayer structure was determined in terms of the 2D and 3D pair-correlation function. The software for calculating the multilayer density distribution was designed, too, and the density distribution was calculated for the six values of the first monolayer surface coverage. Our results suggest a strict correlation between the first monolayer coverage and the monolayer density profile. The profile exhibiting small periodical changes is relatively smooth at low surface coverage of the first monolayer. The periodical changes of the multilayer density increase with the first monolayer surface coverage. Figure 1 presents the multilayer density profile calculated at the first monolayer surface coverage $\theta_1 = 0.30$. The outer surface of the multilayer achieves its final shape with a large number of adsorbed monolayers, when the subsequent monolayers surface coverage approaches the jamming limit at a homogeneous interface, and the multilayer thickness scales linearly with the distance from the adsorption surface. The number of monolayers needed to form the final outer surface of the multilayer increases when the first monolayer coverage decreases. In our simulations the number does not exceed twenty. Apart from the computer simulations conducted in the project, the efforts were continued to include the effect of the electrostatic interaction into the RSA model of multilayer adsorption.

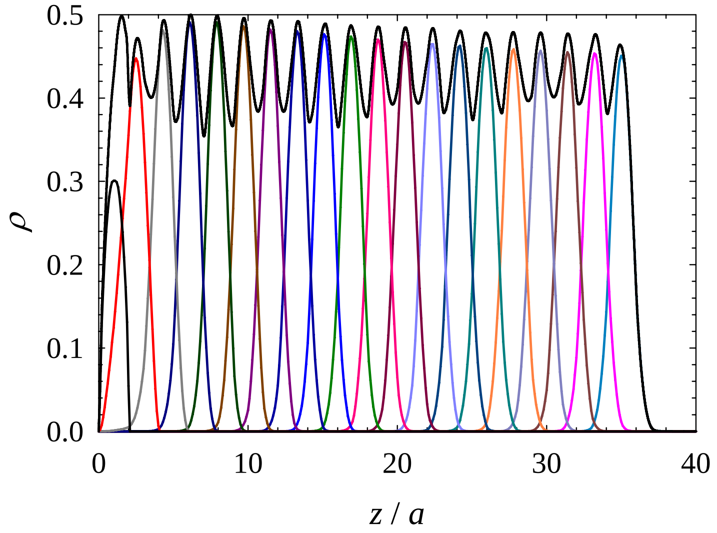


Fig. 1.Multilayer density ρ as a function of the distance from the adsorption surface *z*/*a*. Results obtained at the first monolayer surface coverage $\theta_1 = 0.30$ and the dimensionless adsorption time of the subsequent monolayers $\tau = 10^4$. The black line depicts the total density of the multilayer calculated as a sum of contributions originating from the individual monolayers (color lines).

The Effect of Molecular Structure of Surfactant Molecules on Their Adsorption and Self-organization at Liquid Interfaces

(Piotr Warszyński, Wanda Barzyk, Grażyna Para, Ewelina Jarek, Tomasz Jasiński)

Research Project KBN 4 T09A 038 24

An improved model of non-ionic surfactant adsorption needs to be elaborated to take into account the effect of surfactant molecular structure on the shape of surface tension and surface potential isotherms. Surface potential is very sensitive to conformational changes of surfactant molecules in the adsorption layer. We proposed a model of surfactant adsorption based on HFL isotherm describing non-localized adsorption of interacting hard objects (disks). In our model the distribution of areas occupied at interface by molecule in given conformations are considered. For low surface concentration of surfactant all conformation are accessible. When the surface concentration increases the probability of assuming by the molecule the conformation which occupies large area at the interface is strongly diminished. This change of probability distribution leads to the additional entropic term in the free enthalpy of adsorption, usually not accounted for in other models of adsorption of non-ionic surfactants. The results of molecular mechanics simulations using Amber99 force field in the

HYPERCHEM 7.5 package indicate, that the distribution of the areas assumed by alkanols at interface can be approximated by beta distribution. In Fig. 1. the comparison of distributions of areas taken at the interface by hexanol and decanol in various conformations obtained by simulations and approximated by beta distribution is presented. Taking into consideration the distribution of areas assumed by surfactant molecule at various conformations and using our model of non-ionic surfactant adsorption we can calculate surface tension and surface potential isotherms. Fig. 2. presents the comparison between surface potential isotherms for hexanol and decanol calculated applying our model and experimental isotherms measured with vibrating plate electrode using experimental setup previously developed by us. One can conlude that the agreement between the results of calculations and experimental date for surface potential is quite good. A very good description of surface tension isotherms by our theoretical is also achieved.

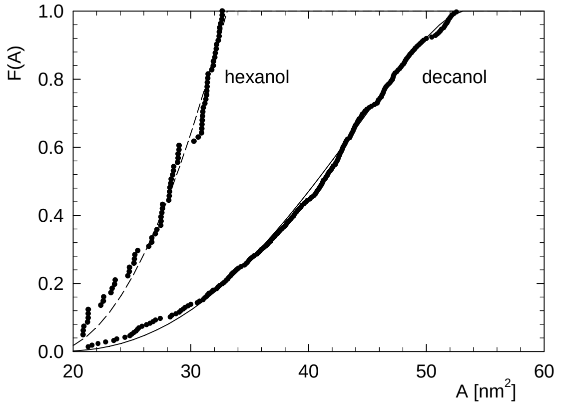


Fig. 1. Comparison of distributions of areas occupied by surfactant molecule in various conformations at interface for hexanol and decanol.

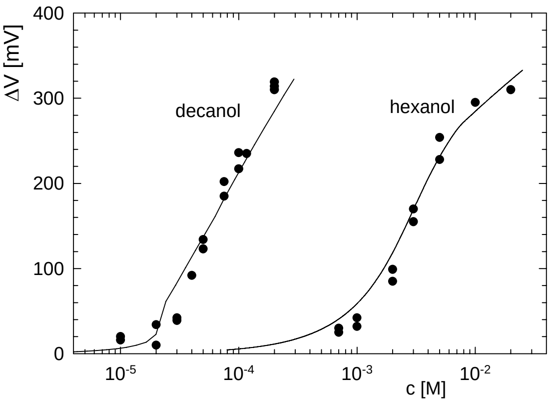


Fig. 2. Comparison of experimental isotherms of surface potential of solutions of hexanol and decanol with isotherms obtained from model calculations

Dynamic Adsorption Layer – the Influence of Surface Active Substance on Interfacial Mobility

(Kazimierz Malysa, Marcel Krzan, Marta Krasowska, Jan Zawała, Marta Barańska)

Research Project KBN 3 T09A 164 27

The aim of the project is to determine the mechanism and most important factors determining the formation of dynamic structure of adsorption layer at interface of the rising bubble. This investigation will make possible to obtain novel data on: i) mechanism of formation of dynamic adsorption layer (what is influence of type of surface active substance and the layer formation kinetics), ii) what is a minimum adsorption coverage needed to immobilization of the bubble interface and reduction of the bubble velocity, iii) whether the value of the minimum adsorption coverage needed to immobilization of a bubble surface depends on molecular structure of SAS.

The laboratory equipment planned to buy was purchased and the experimental set-up consisting digital image recording and analyzing system was modernized. The modernized experimental set-up is used to monitor and record motion of the single bubbles over the distance of 300 mm from the capillary orifice, where the bubble is formed in a well-controlled manner. To determine initial accelerations, local velocities, size and shape variations of the bubble the CCD camera Moticam 2000 cooperating with stroboscopic illumination with flash frequency 100-200 Hz was used. Every recorded image was analyzed using image analysis software Sigma Scan Pro 5.0. The local velocities as well as bubble shape deformations were determined. The local and terminal velocities as well as size and shape variations of the bubble was determined for solutions of n-alkyltrimethylammonium bromides (C8, C12, C16) and solutions of n-octyl acid, n-octanol and n-octyl-β-D-glukopiranozid. The calculations of a bubble surface coverage's as a function of solution concentration of the surfactants studied were carried out. done. The adsorption coverage's needed to full immobilization of the bubble liquid/gas interface were determined. It was found that the bubble motion (its acceleration and velocities profiles) depended on the value of a adsorption coverage and the time of formation of dynamic adsorption layer (i.e., uneven steady state distribution of the surfactant molecules over the surface of the rising bubble). It was also showed that initial accelerations of the bubbles decreased with increasing solution concentration of the surfactants studied (degree of adsorption coverage) from 930 cm/s^2 in distilled water to c.a. 500 cm/s^2 in the concentrated solutions. In the case of lower adsorption coverage's the maximum on the bubble local velocity profiles was observed for all surfactant studied. The maximum was not observed in the case of distilled water and in the highest concentration of surfactant solutions. It was showed that presence of the maximum on the local velocity profiles, its disappearance time and the terminal velocity establishment depending on type of the surface active substance and the degree of adsorption coverage on the bubble surface at the moment of bubble detachment from the capillary. The values of minimum adsorption coverage needed to full immobilization of the rising bubble interface were different for various types of SAS and in the case of n-alkyltrimethylammonium bromides vary from 25 to 1% with elongation of hydrocarbon chain from 8 to 16 carbon atoms.

Tertiary Ethers Synthesis on Dawson type Heteropolyacids as Catalysts

(Adam Bielański, Anna Lubańska, Anna Micek-Ilnicka, Joanna Poźniczek)

Research Project KBN 4 T09A 0099 23

The aim of the research project was to investigate on the example of ethyl-*tert*-butyl ether (ETBE) synthesis the course of electrophilic addition of alcohol to olefin on solid Wells-Dawson type octadecaheteropolyacid as catalyst. This type of catalyst is considered as exhibiting better catalytic properties than dodecaheteropolyacids of Keggin type on which until now most of catalytic research and application has been done. In recent years the interest in Wells-Dawson heteropolyacids (HPA) and in particular $H_6P_2W_{18}O_{62}$ is growing in the literature. The choice of ETBE synthesis from ethanol and isobutene for the investigation is due to the fact that this latter is expected to substitute at least partially methyl-*tert*-butyl ether (MTBE) as antiknocking component in automotive fuel. The use of the latter is now controversial from environmental reasons.

Classical catalytic investigation of $H_6P_2W_{18}O_{62}$, crystalline as well as supported, were supplemented by complex physicochemical studies in which thermal analysis TG/DTA, microcalorimetry, FTIR spectroscopy of catalysts and adsorbed reagents, X-ray structural analysis, scanning microscopy as well porosity measurements were applied.

All catalysts investigated in gas phase in a constant flow microreactor were highly active already at temperatures as low as 40-50°C. In polythermic tests a maximum of activity about 50°C was observed. At constant temperature (40°C) the catalysts exhibited steady activity and selectivity about 90% in the course of catalytic tests lasting up to 6 hours. An important result of the investigation on the different hydrates of $H_6P_2W_{18}O_{62}$ was the demonstration of the effect of crystallization water on the activity. Water molecules formally not participating in the reaction $C_2H_5OH + C_4H_8 = C_2H_5\text{-}O\text{-}C_4H_9$ play the role of a factor modificating the secondary structure of heteropolyacid crystallites.

In the case of supported $H_6P_2W_{18}O_{62}$ catalysts catalytic activity related to the heteropolyacid mass is higher than that of unsupported HPA. This increase of activity is due to the dispersion of catalytically active mass. Heteropolyacid is present on the support in the form nanocrystallites (of the order of several nm) which are easily penetrated by the absorbed ethanol molecules while ethanol migration in the crystallites of unsupported HPA (of the order of 10μm) appears slower. Some differences in the behavior of catalysts on SiO_2 and TiO_2 are due to the different capillary properties of both supports.

Structure and Enzymatic Activity of Clavaminate Synthase: Theoretical Study on the Enzymatic Reaction Mechanism

(Ewa Brocławik, Artur Góra, Marcin Król – Uniwersytet Jagielloński, Tomasz Borowski - Stockholm University, Waldemar Szczepanik – Uniwersytet Jagielloński

Research Project KBN 2 P04A 042 26

Calculations carried out in the group are continuation of the project which aimed at the elucidation of the molecular mechanism of clavaminic acid biosynthesis. The reaction is catalysed by trifunctional enzyme – clavaminate synthase (CS, α-ketoglutarate (α-KG) dependent non-heme Fe enzyme). The main effort is focused on reproducing available spectra (obtained and published by Solomon and co-workers) – native form of the enzyme, with bounded co-substrate (α-KG) and with substrate in the presence of α-ketoglutarate. The best models which properly reproduce registered spectra (especially two-three crucial bands) will be further used in the modeling of catalytic reaction mechanism. At the same time are carried out investigations over mimicks, simple and small models containing iron cations having different oxidation states and ligands which cause behavior of the system similar to active sites in the real enzymes (reproducing UV-VIS and Raman spectra, isotopic shift).

Calculations have been performed using modern and innovative approach, the subsystem formulation of density functional theory. The total system is divided into two subsystems - ρ_a treated usually with high accuracy and ρ_b which describes environment modifying properties of the crucial fragment denoted as ρ_a. All the terms representing interactions between subsystems are functionals of electron density (Kohn-Sham orbitals describing different subsystems are not mutually orthogonal (Cortona, *Phys. Rev. B,* 44 (1991) 8454, Wesolowski and Warshel *J. Phys. Chem.*, 97 (1993) 8050).

For simulations of electronic spectra of different forms of the enzyme simplified version of LR-KSCED (Linear Response Kohn-Sham Equations with Constrained Electron Density) was employed i.e. dynamic response of the environment was neglected (M. Casida and T.A. Wesolowski, *Int. J. Quantum Chem.* 96 (2004) 577-588). The importance of static relaxation seems to be very small; however it will be evaluated in case of more significant effect. LR-KSCED approach allows for very accurate description of the environment. Moreover squeezing TDDFT calculations (Time Dependent Density Functional Theory) just for crucial fragment improves accuracy (for instance results in block diagonalization of smaller matrices, it causes smaller error) and timing (less excitations must be calculated).

Present work is dedicated mainly for searching of the optimal size of the subsystems describing active center and protein environment (it means that the smallest possible model will be built properly reproducing electronic spectra; that is excitation energies and oscillator strengths must be close to the values corresponding to big models). The biggest model is sphere-like of radius 8-10 Å. Despite of many approximations used in the implementation of KSCED (especially not accurate non-additive kinetic energy term, not perfect exchange-correlation functionals) the accuracy of obtained results is unreachable for competitive QM/MM approaches which are usually used in similar investigations (in KSCED both subsystems are treated fully at quantum level).

In situ Synthesis of Zeolite Coatings on Metal Substrates and Their Physicochemical Characteristics

(Bogdan Sulikowski, Ewa Włoch, A. Gil, M. Homa, A. Stawiarski, M. Lekka)

Research Project KBN 4 T08C 036 25

Manufacturing of an active catalyst working under demanding conditions of the NOx abatement process requires developing the technology of preparation of zeolite coatings on a proper substrate. Analysis has shown advantages when using for this process a monolithic catalyst. On the other hand, taking into account mass and heat transfer, and the technology of catalyst production, metals and their alloys were selected as materials to be coated by zeolite layers. The objective of this project is to study the conditions of synthesis and properties of zeolite coatings prepared by in situ hydrothermal synthesis on metallic substrates. Physicochemistry of zeolites, their synthesis on metal substrates, interaction occurring between the zeolite coating and the substrate, and the properties of the metal support itself after oxidative treatment are the main topics of the present project.

Studies carried out previously by us revealed that aging of a gel at temperatures well below the temperature of hydrothermal synthesis has a significant influence on the amount of zeolite deposited on a metal support. These studies, as well as influence of nucleation on forming and crystal size of ferrierite, were pursued in 2005. The properties of metal supports after oxidation in air and in SO_2 were also studied. The conditions allowing preparation of smaller ferrierite crystals in the coating were developed. The mechanically stable ferrierite coatings prepared by vapour-phase transport of a template, in the presence of steam, were synthesized. The basic material for synthesis of zeolite coating was a FeCrAl foil.

Optimization of ferrierite crystallization method was studied at temperature range 60-160 ^{o}C, by changing the gel aging time and a way of temperature increase in autoclaves. Of paramount importance is the mechanical stability of zeolite coating, therefore the conditions leading to smaller ferrierite crystals in the coating, giving rise to more stable catalyst, were studied. Three different manners, affecting zeolite crystallization: time of synthesis, synthesis under rotation of autoclave and changing the composition of a gel, were accomplished. Zeolite crystals size was estimated by scanning microscopy and laser diffraction techniques. The conditions giving much smaller crystals (up to 70% decrease) than produced by a standard synthesis were arrived upon.

Adhesion of ferrierite crystals towards metal substrates was estimated using atomic force microscopy. The adhesion was measured as a maximum on a Gaussian curve obtained from above 100 measurements.

Finally, in order to obtain coatings with better mechanical properties, syntheses in organic template vapour were carried out. Thus, a gel prepared by the previously elaborated method was deposited on a substrate, dried and placed in an autoclave. The zeolite synthesis was performed in the presence of steam and the template vapour. Deposition of gel onto the substrate was made by a dip-coating method. The ferrierite coatings obtained in this way were 5-25 µm thick, and surface loading was up to 31 m^2/g. By modifying the procedure of a gel deposition surface loadings of 45-161 m^2/g were obtained, with thickness 25-100 µm. The zeolite crystals size was controlled by changing the way of gel preparation before its deposition on the substrate (gel ageing, preliminary hydrothermal synthesis).

Zeolite Membranes (MFI, BEA, FAU) as New Nanomaterials for Separation of Hydrocarbon Mixtures

(Mirosław Derewiński, Maria Zembala, Elżbieta Bielańska, Joanna Kryściak-Czerwenka, Adam Węgrzynowicz)

Research Project KBN 3 T09A 029 29

The main goal of new project is to determine the conditions of synthesis required for a successful preparation of stable and defect free zeolite membranes. The project proposes using zeolites of various sizes and architecture of pores (MFI, BEA, FAU type zeolites). The hydrothermal growth of polycrystalline, thin zeolite films, starting from a monolayer of seeds with initial random orientation (*secondary growth technique*) will be carried out. For this purpose, colloidal suspensions containing zeolite nanocrystals will be prepared and subsequently used for the deposition on surface of porous supports. The parameters of synthesis influencing the quality of membranes (continuity of zeolite film, absence of defects/cracks, thickness of membranes, grain boundary structure and orientation of crystals forming the film layer) will be determined. Permeation tests for selected gases (CO_2, N_2) will be used to distinguish between membranes of poor or high quality. The performance of prepared zeolite membranes – permeance and separation factors in separation of light hydrocarbon mixtures (olefins/paraffins) will be determined.

Ph.D. RESEARCH PROJECTS

of the Ministry of Education and Science

Comparison of Catalytic Properties of Metalloporphyrins and Their μ-Oxo Complexes in Hydrocarbons Oxidation

(Jerzy Haber, Edyta Tabor)

Ph.D. Research Project KBN 3 T09A 167 29

Series of syntheses of porphyrines which in their *meso* positions contained phenyl rings bearing substituents with different electron afinity were performed. Substituents in *meso* positions of porphyrin rings influence the electronic structure of metaloporphyrins which is decisive for their catalytic activity in charge transfer reactions. These substituents have either electron-donating or electron-withdrawing effect to the porphyrin ring.

The simpliest obtained porphyrin ligand was tetraphenylporphyrin (TPP) with hydrogens as substituents on phenyl rings. Furthermore, porphyrines containing different electron-donating (T(p-Cl)PP, T(p-CF_3)PP, TPFPP) or electron-withdrawing (T(p-OCH_3)PP, T(p-CH_3)PP, TTP, TMP) substituents on phenyl rings were synthesized.

In the following part of the work metaloporphyrins of manganese, iron and cobalt were prepared using the ligands described above. As the source of transition metal ions their respective inorganic salts – $Mn(CH_3COO)_2 \cdot 4H_2O$, $FeCl_2 \cdot 4H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ – were used.

The physicochemical and catalytic properties of metaloporphyrines are influenced not only by the structure of the porphyrine ligand and by the type of the central metal ion but also by the type of the axial ligand, if present. The axial ligand plays the crucial role in the processes of the oxidation of the organic compounds. In this study, chlorine was choosed as an axial ligand. Due to the creation of the chemical bond between the metaloporphyrine and the axial ligand the oxidation state of transition metal ions was changed from (II) to (III).

UV-VIS spectroscopy was used to verify the results of the syntheses of ligands and to prove the successful complexation of the transition metal ion into the porphyrine. Moreover, the infrared spectroscopy (FT IR) was employed to check the structures of obtained metaloporphyrine catalysts.

Effect of Additives to VO_x/oxide Support Catalysts on Their Physicochemical and Catalytic Properties in Oxidative Dehydrogenation of Lower Alkanes

(Barbara Grzybowska-Świerkosz, Anna Klisińska-Kopacz)

Ph.D. Research Project KBN 4 T09B 108 25

The PhD thesis, under the above title, has been terminated and subjected to public defence (July 2005). The thesis (in English, 220 pp) was evaluated by the Referees and the PhD Commission as exceptional.

The main conclusions of the thesis:

The additives (A) of transition metal ions of different electronegativity (Ni, Cr, Nb, Mo) and of main group elements (P, alkali metal ions {K, Rb, Li, Na}, introduced to VO_x/SiO_2 (VSiA) and VO_x/MgO (VMgA) catalysts do not affect markedly the catalysts' structure, but modify their acido-basic properties, reducibility, and catalytic performance in oxidative dehydrogenation of propane and ethane.

The character and magnitude of the effect of the additives depend on the type of the catalyst and on the alkane nature.

1. For VSiA catalysts which: ➢contain V_2O_5 as a main component**,** ➢exhibit both Lewis and Brönsted acid sites, ➢show prevalence of acid sites over basic sites:

a) all the transition metal ion additives increase the total specific activity in both ODH of propane and ethane, the presence of the K and other alkali and alkaline earth metal ions leads to the decrease in the activity. The activity increases with the electronegativity of the additives' ions and with the concentration of acid sites an,
b) all the additives with the exception of P increase the selectivity to propene, the highest effect being exerted by alkali metals, in particular by potassium,
c) selectivity to propene in ODH of propane increases: ➢with the decrease in the strength and number of Lewis and Brönsted acid sites (decrease in electronegativity of the additives ions) ➢with the decrease in reducibility,
d) practically no effect of additives on the selectivity to ethene in the ODH of ethane was observed,
e) the selectivities to ethene are generally higher than those to propene.

2. For VMgA catalysts which: ➢contain magnesium orthovanadate $Mg_3V_2O_8$ as an active phase, ➢exhibit Lewis acid sites, ➢show prevalence of dehydrogenation (basic) sites over acidic sites:

a) all the additives decrease the specific activity in the propane ODH: no correlations between activity and acido-basic properties are observed,
b) additives of alkali metal ions (K, Li, Na, Rb) decrease the selectivity to propene, whereas transition metal ions (Ni, Cr, Nb, Mo) and alkaline earth metal ions (Ca) increase it or have no effect (P). No clear correlations between selectivity and acido-basic properties are observed, selectivity increases however with the decrease in the reducibility,
c) all transition metal ions increase slightly the selectivity to ethane,
d) the selectivities to ethene are generally lower than those to propene.

3. The opposite effect of K on selectivity to propene observed for VSiK (increase) and VMgK (decrease) catalysts, in spite of the decrease in the acidity in both catalysts, indicate, that different catalyst properties control the selectivity: ➢acido-basic in the case of VsiK, ➢properties of catalyst oxygen including reducibility, and probably the type of oxygen species (more of electrophilic forms) in the case of VMgK.

Au Nanoparticles on Oxide Supports as Catalysts for Oxidation of CO and C_3 Hydrocarbons

(*Barbara Grzybowska–Świerkosz, Małgorzata Ruszel*)

Ph.D. Research Project KBN 4 T09B 066 27

The aim of the PhD work is (among others) the determination of the effect of support on catalytic properties of Au/oxide support systems in oxidation of CO (also in selective oxidation of CO with H_2 in the reaction mixture), and in oxidation of C_3 hydrocarbons.
In 2005 the studies were concerned with:

a) $Au/M^{II}Cr_2O_4$ catalysts – a continuation of earlier studies (results described in detail in part entitled "Oxidation of CO, ethane and propane on gold nanoparticles/mixed oxide systems")
b) Au/MgF_2 and Au/MgO catalysts – aim: to elucidate the role of oxide support in activation of O_2 on Au-based catalysts. The results of preliminary studies show: 1) low interaction of Au-precursor with non-oxidic MgF_2 support, 2) low activity of Au/MgF_2 catalyst as compared with Au/oxides in CO oxidation, 3) decrease of activity after pretreatment of Au/MgF_2 in H_2 (in contrast to Au/oxide supports). The studies will be continued.
c) Au/Ti-SBA-15 catalysts –aim: check their activity in CO oxidation (also selective or preferential in the mixture with H_2). The latter process, consisting in oxidation of CO without oxidizing H_2 can be applied for purification of H_2 from traces of CO for fuel cells. Preliminary studies were performed on Au/Ti-SBA-15 catalysts of 2 different concentration of Ti (0.26 and 2.6 wt. %). It has been found that activity in CO oxidation depends on Ti content; high conversion of CO being observed on the sample of low content of Ti. The catalysts are active also in preferential CO oxidation with the selectivities of ~90%.

The results of preferential CO oxidation on Au/Ti-SBA-15 catalysts are presented on Fig.1. Selectivity to CO_2 is estimated as the percent of O_2 used for CO oxidation.

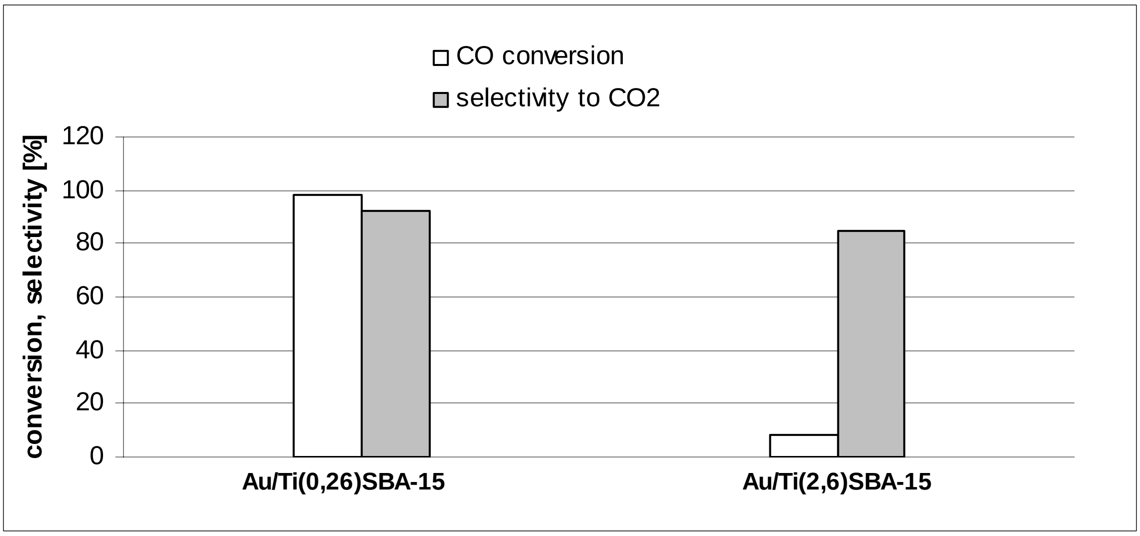


Fig. 1. Selective oxidation of CO on Au/Ti-SBA-15 catalysts at 50°C.

In further studies the range of samples will be extended (different concentration of Ti, between 0.1-3 wt. %), and the samples will be characterized by various techniques (in particular for determination of structure of TiO_x centres).

Oxidative Dehydrogenation of Isobutane on Vanadium and Chromium Oxide Systems with Additives, Dispersed on Different Support

(Barbara Grzybowska-Świerkosz, Katarzyna Samson)

Ph.D. Research Project KBN 4 T09B 115 25

The work is a part of studies on ODH of lower alkanes on oxide catalysts.
In 2005 the studies related with PhD thesis of the above title included:

a) preparation (by impregnation) of two series of catalysts containing CrO_x and VO_x (1-1.5 theoretical monolayer = 10at Cr or V/nm^2 of support) as the active phases dispersed on next commercial supports: CeO_2 (Fluka), Al_2O_3 (Merck) and SiO_2 (Aerosil); the same systems with addition of potassium were also synthesized (K/Cr or V = 0.1), [symbols CrS, or CrSKwhere S is a cation of a support,

b) physicochemical properties of the catalysts: their specific surface area (determined with BET method), analysis of the surface composition by XPS, measurements of acido-basic properties using decomposition of isopropanol as a probe reaction, reducibility (TPR H_2) of the selected catalysts and Raman spectra (in collaboration with Institute of Catalysis and Petroleochemistry CSIC)

c) catalytic activity measurements in oxidative dehydrogenation, ODH, of isobutane in temperature range 280-450^{o}C.

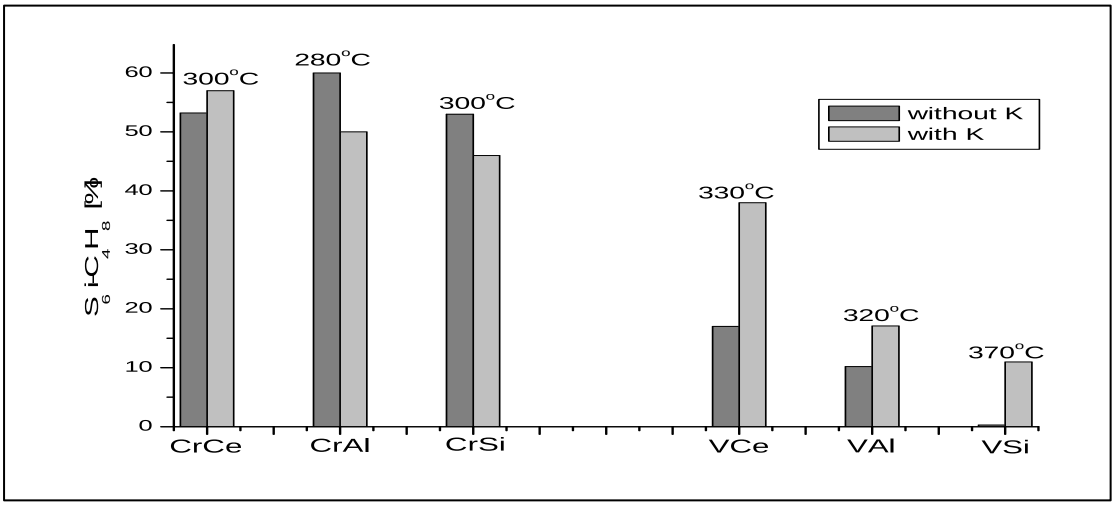
It has been shown:

a) chromium oxide dispersed on supports CeO_2, Al_2O_3 and SiO_2 is more active and selective to isobutene in ODH of isobutane than supported vanadia catalysts; the best catalyst CrAl attained 60% selectivity to isobutene at ~6% conversion of isobutane and at the reaction temperature of 280^{o}C

b) potassium clearly decreases specific activity in tested reaction for both CrS and VS catalysts (with the exception of CrAlK and VAlK samples)

c) the effect of potassium promoter on selectivity to isobutene depends on the nature of the active phase: for VSK the increase in selectivity has been found, for CrSK the decrease in the selectivity, or no influence have been observed.

Fig.1 presents the comparison of the influence of potassium additive for two series of supported catalysts: CrO_x and VO_x on catalytic activity (temperature of 6% conversion of isobutane, T_6, placed above the blocks), and selectivity to isobutene.



At present the catalytic data are being correlated with the physicochemical properties of the catalysts.

Novel Catalytic Materials: Composites of Layered Minerals and Heteropolyacids

(Ewa Serwicka-Bahranowska, Aleksandra Pacuła)

Ph.D. Research Project KBN 4 T08D 051 24

In the final year of the project the experimental work encompassed synthesis and intercalation with heteropolyanions of two series of hydrotalcites: magnesium-aluminium and zinc-aluminium, both as nitrate forms. The intended values of the degree of substitution $x=M^{3+}/M^{2+}+M^{3+}$ were $0.166 < x < 0.5$. It was found that the range of x at which rentgenographically pure hydrotalcite phases could be obtained was much higher for the magnesium-containing systems ($0.169 \le x \le 0.357$) than for the zinc-based materials ($0.323 \le x \le 0.345$). In the Mg-Al hydrotalcites the degree of crystallinity increased with the increase of Mg/Al ratio, while in the Zn-Al systems the increase of Zn/Al ratio resulted in poorer crystallinity of the precipitated hydrotalcite. Heteropolyacid $H_4SiMo_{12}O_{40}$ was chosen as a source of anions for intercalation, because of its relatively weak acidity (as compared to other hereropolyacids), and potentially lesser destructive influence on the structure of essentially basic hydrotalcites. Experiments were carried out both with the $SiMo_{12}O_{40}^{4-}$ anion and its electrochemically reduced form $SiMo_{12}O_{40}^{6-}$.

It was established that the major factors determining the efficiency of intercalation procedure are: charge of the heteropolyanion, crystallinity of the hydrotalcite matrix and the nature of the divalent cation in the brucite layer. When unreduced $SiMo_{12}O_{40}^{4-}$ anion was used, only in the case of poorly crystalline zinc-based matrices a phase with the interlayer distance corresponding to the size of heteropolyanion could be detected. Electrochemical reduction was shown to be a convenient tool of adapting the charge on the heteropolyanion to the requirements of the intercalation. Intercalation with reduced by 2 electrons $SiMo_{12}O_{40}^{6-}$ anions was quick and efficient for the majority of employed Mg-Al hydrotalcites and all members of the Zn-Al series, resulting in the appearance of hydrotalcite phases with interlayer distance typical of intercalated Keggin anions. In all cases the desired product was accompanied by certain amounts of by-products such as hydrotalcite phase intercalated with smaller, partially depolymerized heteropolyanions, heteropolysalt of metals dissolved from the brucite layer as a result of treatment with heteropolyacid solution, or hydrotalcite matrix which did not undergo anionic exchange. In Mg-Al matrices the anion exchange was complete, while in the Zn-Al materials part of the starting material remained unexchanged. Thermal stability of intercalated $SiMo_{12}O_{40}^{6-}$ anions is similar as in the bulk heteropolyacid.

The chemical nature of the hydrotalcite matrix determines the acidic and basic/redox properties of the intercalation products, as indicated by the test reaction of isopropanol decomposition. The acidity of the heteropolyanion-intercalated matrices is much lower than that of bulk heteroplyacid, the decrease being stronger for the more basic magnesium-aluminium hydrotalcite. The latter material is characterized by pronounced basic/redox properties. Both heteropolyanion-intercalated hydrotalcites show significant activity in the oxidation of cyclooctane.

Irreversible Adsorption of Colloid Particles at Heterogeneous Surfaces

(Zbigniew Adamczyk, Katarzyna Jaszczółt)

Ph.D. Research Project KBN 4 T09A 034 26

The possibility of producing surface clusters of colloid particles of well-defined structure was analyzed theoretically and experimentally. Theoretical results were derived by performing Monte-Carlo type simulations according to the generalized random sequential adsorption (RSA) mechanism. The first step of these simulations was covering a homogeneous surface by adsorption sites of controlled density and structure, characterized in terms of the pair correlation function. The second step of simulations was a quasi 3D adsorption on sites by considering their true topology. In these simulations the available surface function and the jamming coverage of particles adsorbing irreversibly on spherical sites was determined as a function of the particle to site ratio size ratio λ. It was revealed that by properly choosing λ a targeted site coordination can be achieved, e.g., there can be one, two, three etc. particles attached to one site. The structure of the heterogeneous clusters produced in this way was described in terms of the pair correlation function. It was predicted that the extent of ordering within surface clusters was diminished with the increased concentration of sites. These theoretical predictions were checked by performing deposition experiments of negatively charged polystyrene latex particles (averaged diameter 0.9 μm) under the diffusion-controlled transport regime. As the substrate surface in these experiments, mica sheets precovered by positively charged polystyrene latex (averaged diameter 0.45 μm and 1 μm) were used. Positive latex (site) deposition also was carried out under diffusion-controlled transport conditions. Both the concentration of sites and adsorbed particles was determined by direct particle counting using the optical microscopy. It was found, in a quantitative agreement with theoretical simulations, that the structure of surface clusters produced in this way exhibits a considerable degree of short-range ordering. It also was proven experimentally that clusters containing a targeted number of colloid particles, between one and six could be produced by the deposition procedure. It was suggested that these results derived for model colloid particles can used as reference results for polyelectrolyte multi-layer formation, which cannot be studied by direct observation methods.

Mechanism of Interaction of Colloid Particles with Heterogeneous Surfaces Determined by Adsorption and Electrokinetic Measurements

(Zbigniew Adamczyk, Aneta Michna)

Ph.D. Research Project KBN 3 T09A 145 29

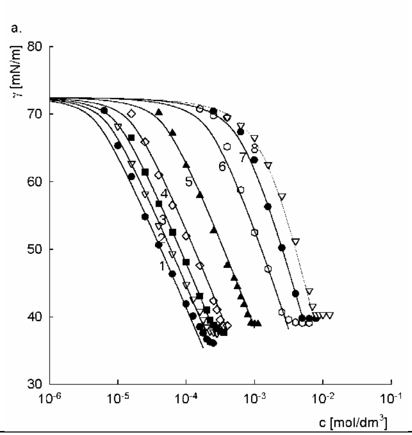
The aim of the preliminary works within this research project was developing a new cell for streaming potential measurements of heterogeneous surfaces formed by adsorption of polyelectrolytes and colloid particles. Precise measurements of the streaming potential and in consequence zeta potential of surfaces, has a major significance because it allows one to determine surface coverage of adsorbed species with the accuracy exceeding any other method. Usually the streaming potential measurements have been carried out using traditional cells in the form of a parallel-plate channel. This type of construction excluded the possibility of regulating the distance between plates. This in turn, limits severely the accuracy of measurements because of the appearance of the surface conductivity effect. This disadvantage was largely eliminated in the new cell, whose construction was elaborated in this project. The possibility of regulating the distance between plates in a gradual way was created by using a rectangular piston motion. A four electrode system was used in this cell with one pair exploited to measure the streaming potential and the second pair of electrode used for the electric conductivity measurements. The electrolyte flow in the cell was provoked by the gradient of the hydrostatic pressure which was measured in the inlet and outlet compartment using a piezo electric pressure sensors. Because of the appearance of the electric double layer at the substrate surfaces under study (mica plates) the electrolyte flow generated an electric potential difference between the inlet and the outlet part of the cell, which was measured by the silver chloride electrodes. Using the new cell preliminary experiments have been carried out for mica sheets whose surface properties have been determined previously using a traditional cell. It was proven that because of increased precision the new cell broadens significantly the range of measurements. In this way measurements of streaming and zeta potential for much higher ionic strength became feasible using the new cell.

Adsorption of Ionic and Nonionic Surfactant Mixtures at the Liquid Interfaces Fluid/air

(Piotr Warszyński, Ewelina Jarek)

Ph.D. Research Project KBN 3 T09A 061 26

We proposed the theoretical model of adsorption of ionic-nonionic surfactant mixtures and applied it for the description of surface behavior of systems being a mixtures of nonionic sugar derivatives: n-dodecyl-β-D-maltoside or n-dodecyl-β-D glucoside and ionic surfactants such as sodium dodecyl sulfate or dodecyltrimethylammonium bromide. The sugar derivatives belong to a relatively new class of surface active compounds. They can have large potential applications because they are non-toxic, biodegradable and possess good surface properties. The surface activity of such mixtures depends very strongly on their relative composition. Using our approach we were able to calculate theoretical isotherm of adsorption with the same set of parameter for various composition of such mixtures. The values of model parameter were established on the basis of fitting procedure for pure ionic and nonionic surfactant only. We obtained a good agreement with experimental data in the whole range of investigated compositions of surfactant mixtures (Fig.1). By solution of equations of adsorption given by our model, we can obtain directly the values of surface excess of all component (surfactant ions, counterions and nonionic surfactants molecules) (Fig.2), which are presented in the investigated system. Moreover, the parameters of our model could be correlated with molecular properties of components presented in solution like molecular size of hydrophilic head group, polarizability of counterions and molecular structures. The model, also take to account the effect connected with ionic charges of surfactants. These features of the proposed theoretical model allow to understand better the adsorption mechanism of surfactant mixtures comparing with models existing in the literature derived from Gibbs-Duhem equation (for example Motomura's theory). The latter allow only for indirect evaluation of the composition of mixed monolayers and its determination relies on a fit of the polynomial to the experimental surface tension isotherms. The coefficients of this polynomial cannot be directly correlated with characteristic physicochemical features of the investigated system.



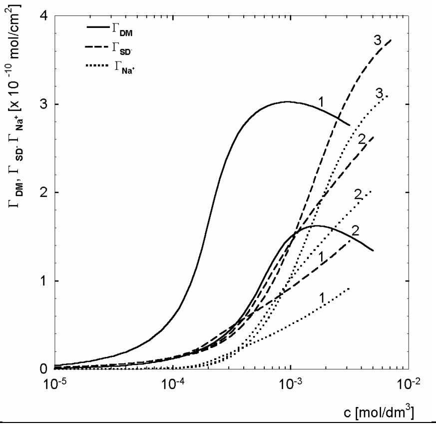


Fig.1 The surface tension of N-dodecyl-β -D-maltoside (DM) and Sodium dodecyl sulfate (SDS) mixtureswith various composition as a function of total concentration of surfactants in the solution: 1-X_{DM} =1, 2 -X_{DM} =0.7, 3 -X_{DM} =0.5, 4 -X_{DM} =0.3, 5 - X_{DM} =0.1, 6 -X_{DM} =0.02, 7 -X_{DM} =0.005, 8 - X_{DM} =0 where X_{DM} - mole fraction of DM	Fig.4 The surface excess concentration as a function of total concentration of surfactants in the solution for different composition of solution 1- X_{DM}= 0.02, 2 - X_{DM}= 0.005, 3 - X_{DM}= 0 . Solid line – for nonionic surfactant (DM), dashed line – for ionic surfactant (SD^-), doted line – for counterion (Na^+).

Surface and Electric Properties of Ployelectrolyte Multilayers Covered on Macroscopic Surfaces

(Piotr Warszyński, Marta Kolasińska)

Ph.D. Research Project KBN 3 T09A 085 27

Polyelectrolyte multilayers (PEMs) obtained via sequential adsorption of oppositely charged polyions from their solutions were studied by ellipsometry. As the support material silicon wafers were used. The aim of our studies was to determine the influence of the first, anchoring layer on the structure of the whole multilayer system. For that purpose we examined the properties of model PAH/PSS systems and its analogues, built-up on first PEI layer. The effect of molecular weight of PEI was also considered. We determined thickness of given multilayer structures, focusing on changes in properties introduced by PEI layer. Measurements were carried out in auto-nulling mode with PCSA configuration (PCSA acronym standing for sequence of ellipsometer optical elements, i.e. polaryzator-compensator-sample-analyzator) using single wavelength multiangle imaging ellipsometer EP3, Nanofilm. Refractive index, needed for thickness determination was found by performing multiple angle of incidence analysis and it was equal to 1.55.

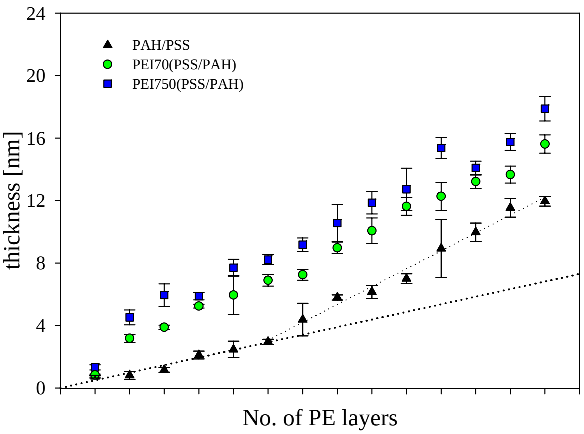


Fig. 1 Film thickness vs. number of PE layers

Figure 1 illustrates the dependence of ellipsometric thickness of PE multilayer films on the number of deposited layers. The presented results demonstrate that films with given number of layers built up on PEI anchoring layer are thicker than structures having the same number of PE layers but consisting of PAH/PSS only. One can observe the increase of PAH/PSS film thickness with the number of layers (slope of regression lines in Fig.1) is smaller for first six PE layers than for subsequent ones (0.5 nm/layer vs. 1.1 nm/layer). Both PAH and PSS are linear polyelectrolytes. PAH adsorbed at solid surface of Si-SiO2 wafer assumes predominantly flat conformation. Moreover, the adsorbed layer is very heterogeneous having many voids. Second PSS layer is formed on the adsorbed PAH. When PAH is deposited during formation of third PAH layer, voids started to be filled in, and consequently high degree of interpenetration can be observed. With the increase of number of layers surface of the film becomes more uniform. In contrast PEI/(PSS/PAH) films exhibit uniform growth starting from the first layer amounting to c.a. 1.1 nm/layer that is to the value of thickness increment observed for (PAH/PSS) films thicker than 6 layers. The ellipsometric thickness of studied multilayers was found to be little dependent on molecular weight of PEI. Films built on the anchoring layer of 750 kDa were 1-2 nm thicker than ones built on 70 kDa PEI layer but they exhibit almost identical thickness increment per adsorbed layer (c.a. 1.1 nm/layer). Branched PEI used as a first layer acts as a uniform anchoring network for the consecutive layers' formation, therefore the uniform layer growth can be observed and the resulting PE films are more homogeneous.

The images of the surfaces of studied multilayer films obtained by ellipsometric imaging mode were used to determine thickness profiles of the samples and their roughness. It was found that films terminated with polyanion were less rough then those having polycation as the outermost layer.

Influence of Surface Active Substance on Kinetics of Formation of the Three Phase Contact Gas/liquid/solid

(Kazimierz Małysa, Marta Krasowska)

Ph.D. Research Project 3 T09A 092 27

The study aims at determination of the role of surface active substances and mechanism of their action in formation of the three phase contact gas/liquid/solid during the bubble collisions with solid surfaces. Bubble arriving at the solution surface forms a symmetric (gas/liquid/gas) foam film, while at the liquid/solid interface an asymmetric (gas/liquid/solid) wetting film is obtained. Properties of such film (stability) depend mainly on properties of the solid surface and presence of surface active substances, their type and concentration, and also the solution pH and ionic strength. It is rather well known, that for the three-phase contact formation the solid surface needs to be hydrophobic because the wetting films on hydrophobic surfaces are of low stability and can be ruptured easily.

The equipment and software were purchased and the experimental set-up and image analyzing system were modernized. Measurements of the local velocities and shape pulsations of the bubbles colliding with surfaces of different solids in n-pentanol, n-hexanolu i n-oktanol solutions were carried out. Influence of concentration and degree of adsorption coverage at surface of the rising bubbles on kinetics of formation of the three phase contact gas/liquid/solid was studied. In distilled water the bubble colliding with hydrophilic solid surface bounces a few times and 4-5 “approach-bounce” cycles were observed. Simultaneously, shape of the colliding bubble started to pulsate rapidly within time intervals shorter than 0.85ms. With each “approach-bounce” cycle the bubble velocity was lowered as a result of the energy dissipation. However, in the case of the hydrophilic solid surface (glass plate) even after the bubble stopping the three phase contact was not formed because the liquid film (wetting film) was stable enough and did not rupture. In the case of hydrophobic solid surfaces the wetting films are unstable and it is commonly expected that here each collision should result in formation of the three phase contact and the bubble attachment. Nevertheless, it was found that even in the case of such hydrophobic solid as Teflon the bubble attachment did not occur at first collision when the Teflon surface was smooth and a few “approach-bounce” cycles were observed, similarly as for the hydrophilic solid surface. However, when the bubble was stopped the three phase contact was always formed, the bubble was attached to Teflon surface and the time of its attachment was 84ms. In solutions of the surface active substances (SAS) studied an increase of rate of the three-phase contact formation was observed with increasing SAS concentration. Bubble rising velocity is lowered in solutions of surface active substances as a result of diminished fluidity of the gas/liquid interface due to adsorption there of molecules of the surface active substance (surface tension gradients). When the bubble arrives at the liquid/solid interface with a lower velocity the time of the contact between bubble and solid is prolonged. Longer the contact time the higher probability that the three phase contact will be formed. According to our studies an adsorption coverage as low as a fraction of percent (0.4%) lowered velocity of the rising bubble and the coverage of an order of a few percent diminished the bubble velocity by over 50%. Presence of surface active substance can modify also properties of the liquid film separating the colliding bubble from the solid surface and also in a such way can facilitate the three phase contact formation and the bubble attachment.

Biocatalytic Oxidation of Ethylbenzene and Its Derivatives

(Małgorzata Witko, Maciej Szaleniec)

Ph.D. Research Project KBN 3 T09A 062 28

The biochemical and physicochemical characterization of the enzyme yielded following results:

- Heme activity staining of SDS-polyacrylamide gels with purified EBDH showed a stained band specifically co-migrating with the γ-subunit, but not with the other subunits of the enzyme. Since the α- and β-subunits are predicted to bind the molybdopterin and the [Fe4S4] clusters, the specific association of heme with the γ-subunit indicates that this subunit may actually contain the heme b cofactor. Although heme b is not covalently attached to the protein, it is known that some heme b proteins retain enough of the cofactor after SDS-PAGE to react positive in heme staining
- The thermodynamic study of ethylbenzene oxidation by EBDH was conducted with Isothermal Titration Calorimetry. The whole reaction cycle enthalpy was studied in 20 and 30 centigrade yielding ΔH=-143 and -153 kJ/mol respectively. This shows that reaction is exothermic. The measurements of half reaction cycle (ethylbenzene oxidation and enzyme reduction) indicate that the heat effect is endothermic.
- The influence of hydrogen peroxide on EBDH UV-vis spectrum was established. It shows decrease in absorption iron-sulphur centers as a result of oxidation and possible decomposition. The spectra of oxidized and reduced enzyme were also recorded and are depicted in figures below.

The plans of anaerobic glow-box constructions were laid. The air-lock system as well as electrical connection system was designed. The preparative steps for glow-box construction were undertaken.

The substrate spectrum was characterized. From potential EBDH substrates following compounds had following relative (ethylbenzene – 100%) activity: 1,4-diethylbenzene 35%, n-propylbenzene 14%, 2-ethyltoluene 3.8 %, 3-ethyltoluene 10 %, 4-ethyltoluene 28 %, 2-ethylnaphtalene 9.3 %, 4-fluorethylbenzene 15%, 2-ethylfenol 56.14±5.98 %, 3-ethylfenol 19.39±1.71 %, 4-ethylfenol 259.01±17.93 %, 2-ethylaniline 94.53±3.59 %, 4-ethylaniline 136%, 3-ethylpyridine 16.94±0.75%, 2-ethylfuran 134.05±6.13%, 2-ethylthiophene 242.92±16.60%, 2-ethylpyrrol 234.63±4.40%.

RP-HPLC separation protocol was established for ethylphenols reaction mixture and ethylbenzene reaction mixture. Additionally stoichiometry tests were conducted (Table 1). Chromatographic analyses showed that product fractions are more polar than substrates. Stoichiometry shows that 2 ferricenum tetrafluoroborates equivalents are used per ethyl group, which point out at two electron oxidation.

Table 1. Stoichiometric tests

substrate	**$FCBF_4$: substrate ratio**
ethylbenzene	2,2 ± 0,2
2-ethylfenol	2,5 ± 0,03
3-ethylfenol	2,3 ± 0,1
4-ethylfenol	2,3 ± 0,2
1,4-diethylbenzene	4,9 ± 0,2

CO Adsorption on a Au/Fe_3O_4(001) - Structure and Morphology of Surface

(Józef Korecki, Jakub Barbasz, Nika Spiridis)

Ph.D. Research Project KBN 4 T08A 004 25

It is known from TPD measurements that, for nanometer gold clusters, CO adsorption does not depend on the oxide support used. CO desorption spectra are reported in literature for example for (111) oriented magnetite surface. The present work is aimed to analyze influence of surface termination on CO adsorption/desorption on Au/Fe_3O_4(001).

An UHV TPD system constructed recently has been optimized to enhance the ratio of the desorption signal from the sample to a background level. It has been achieved by a differential pumping of the mass spectrometer volume.

Test measurements were performed using metal desorption from a vicinal W(540) surface, which has 6.3^o misorientation relative to (110). STM images indicated that, contrary to the W(110) case, iron does not grow pseudomorphically on W(540). To test the thermal stability of this new system we measured iron TPD spectra for films from a submonolayer to several atomic layers (AL's) thickness. TPD spectra revealed two distinct peaks: a low temperature one (at about 1000 K) dominating for coverages up to 1 AL, and a second that showed up for thicker layers. It is opposite to what is known for Fe/W(110), where the pseudomorphic monolayer is stable for temperatures considerably exceeding desorption temperature of thick films. Adsorbate-substrate interaction must be strongly modified by the presence of high density substrate steps.

Test TPD measurements were also done for Au/W(540) and Co/Au/W(540), proving expected sensitivity and selectivity of the method.

First CO adsorption/desorption measurements on Au/Fe_3O_4(001) were performed for Au clusters with average diameter of 3 nm. No desorption peak was observed after CO adsorption at 170 K for gold clusters on a magnetite surface with tetrahedral Fe rich termination.

Optimization of the sample holder will allow us to lower the sample temperature to 100 K during adsorption and to make comparative studies for magnetite surfaces with different terminations.

Along with the TPD studies, detailed analysis of the magnetite surface structure and Au adsorption was performed using STM data. Corresponding sections of the PhD thesis have been accomplished.

The Mechanism of Rhodium Catalyst Operation for Nitrous Oxide Decomposition in the Gases Emitted to the Environment

(Jerzy Haber, Małgorzata Nattich)

Ph.D. Rresearch Project KBN 3 T09D 010 28

Removal of N_2O from industrial gases is an important problem in the environment protection. The most efficient method is the catalytic decomposition of N_2O in which Rh supported on industrial γ-Al_2O_3 is used as a catalyst. The industrial Al_2O_3 contains usually some amount of sodium. The question arises what is the influence of alkali metal ions on the catalytic activity. The study was undertaken to evaluate the influence of Li, Na, K, Cs in Al_2O_3 on catalytic activity of Rh/γ-Al_2O_3 catalyst. Commercial γ–Al_2O_3 (Procatalyse, Spheralite 531), containing trace amount of Na_2O (0,006w/w%).was used as a support studies. Alumina was impregnated with different amounts of lithium, sodium, potassium and cesium carbonates followed by drying at 120°C for 2 h and then calcining at 550°C for 5 h. Supports prepared in this way were impregnated with an aqueous solution of rhodium nitrate. The samples, after drying, were activated in reducing atmosphere at 550°C for 1h. The resulting catalysts contained 0.1 w/w % Rh and 0.033-0.099 mol.% of appropriate alkali oxide.

The catalytic tests were performed in the flow reactor at G.H.S.V = 4000 h^{-1} with nitrogen as a carrier gas. The concentration of N_2O in nitrogen was 1.0 v/v % and N_2O decomposition was studied in the temperature range 200 - 500°C.

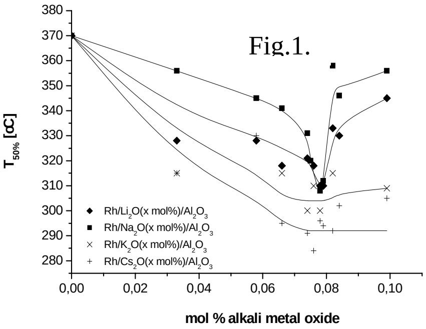


Fig.1.

The results of the studies of catalytic activity of samples, doped with different amounts of the four alkali metal cations are summarized in Fig.1, in which, the activity, expressed in terms of the temperature of 50% conversion, is plotted as a function of the concentration of dopant for the whole series of alkaline metal oxides. It may be seen that a sharp maximum of catalytic activity (minimum of $T_{50\%}$) is attained at the concentration of about 0.08 mol.% for lithium and sodium containing samples, whereas in the case of the potassium and cesium containing samples a plateau is attained around this concentration. The measurements of BET surface area, which is practically that of alumina as a support, have shown that it has similar value for all samples and is not affected by doping.The study of hydrogen adsorption on above described catalysts has been performed to evaluate the dispersion of of rhodium on the catalyst surface (Fig.2.) as a function of the concentration of dopant. It has been stated that alkali metal ions present on the surface of alumina cause the increase of rhodium dispersion. Comparison of Fig.1 with Fig.2 shows, that the changes of catalytic activity follow in general the changes of the Rh dispersion.

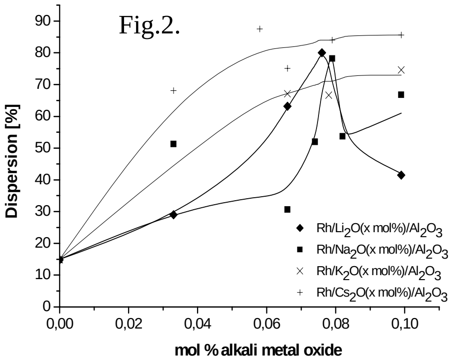


Fig.2.

The result of the study leads to the conclusion that technical Al_2O_3 isn't good support for Rh catalyst.

SCIENTIFIC NETWORK

of the Ministry of Education and Science

Nanomaterials as Catalysts for New Environmentally Friendly Processes

(Małgorzata Witko)

Ministry of Education and Science Scientific Network

Update of the database of the network members

The address database of the Network members was recently updated, supplemented and linked to the web-page of the International Scientific Network at the ICSC PAS server (http://atom.ik-pan-krakow.pl/siec/index.html). The web-page includes all the information concerning the different thematic groups and their activities within the Network. There are details on aims, action plans and meetings of the Network.

Organisation of scientific events

The Catalytic Network co-organised the 37th Polish Conference on Catalysis, which was held on March 15-18, 2005 in Cracow. There were 225 participants. 8 plenary lectures and 1 invited lecture were delivered and 24 oral presentations and 194 posters were presented. Registration fee for young scientists was covered from the Networks funds. The platform for dissemination of the conference results is a book 'Book of abstracts 37th Polish Conference on Catalysis' (Materiały XXXVII Ogólnopolskiego Kolokwium Katalitycznego ISBN 83-920331-2-4) which is an annex to this report.

The Catalytic Network also co-organised an international symposium „*Catalysis on oxide-type materials. Theory and experiment: share needs and capabilities*", which was held on November 17-19, 2005. There were 120 participants. 9 lectures and 20 oral presentations were delivered and 29 posters were presented. Registration fee for young scientists was covered from the Networks funds. The platform for dissemination of the conference results is a book of abstracts '*Catalysis on oxide-type materials: Theory and experiment: share needs and capabilities'* (ISBN 83-920331-7-5) which is an annex to this report.

Meetings of the network participants

The meeting of the Network participants was held on March 16, 2005. During the meeting the Network activities in 2004 were reported. The Network Coordinators' meeting was held on November 19, 2005. The meetings on the thematic groups took place including: the group led by Professor R. Dziembaj - Natural and synthetic layered minerals as basis for catalytic nanostructures, the group led by Professor B. Grzybowska-Świerkosz - Monomolecular and macroclustered nanoparticles of chemical compounds (oxides, sulphides) on supports and in matrixes, the group led by Professor M. Ziółek - New nano- and microporous materials and the group led by Professor W. Bartczak - Catalyst design basing on different theoretical approaches.

The activities of some of the Network's scientific teams resulted in a solicited project granted on December 12, 2005 by the Minister of Education and Science (decision number K124/T09/2005) entitled 'New catalytic materials for eco-friendly chemical processes'.

The scientific teams of the Polish Catalytic Network are active in EC Framework Programmes:
CONCORDE 'Nanostructured Catalytic Oxides Research and Development in Europe' (CA)
TOK-CATA 'Transfer of Knowledge in Design of Porous Catalysts' (ToK)
ACENET 'ERA-NET for Applied Catalysis in Europe' (ERA-NET)
IDECAT 'Integrated Design of Catalytic Nanomaterials for a Sustainable Production' (NoE)

EU 5th FRAMEWORK PROGRAMME PROJECTS

Centre of Excellence – Cracow Research Centre of Molecular Catalysis and Soft Matter Chemistry

(Piotr Warszyński)

UE CoE Project CATCOLL G5MA-CT-2002-04024

Year 2005 was the last year of the activities of the Centre of Excellence financed by the EC project. Their main aim was to strengthen role of the Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences as a leading research centre in molecular catalysis, surface chemistry and colloid science in Europe and integrate it within European Research Area. The specific objective of our activities was broad participation of the Institute in the projects of 6th European Framework Programme. During three years of CATCOLL activity the number of proposals for the projects 6th Framework Programme of European Commission were submitted (3 – IP, 6 – NoE, 14 – STRP, 2 – CA, 3 – SSA). Out of this number five proposal was submitted last year. The success rate of the proposal was close to 30% and currently nine 6th FP projects are running (1 NoE, 3 – STRP, 2 – SSA, 2 – CA, 1 – MC ToK), four of them are coordinated by ICSC. To strengthen links of the Centre with European Research Area (ERA) number of visits of researchers of the Centre in the leading European Scientific Institutions were organized. The alternative action was to participate in high ranking international meetings. The purpose was to establish as many links as possible having in mind the perspective of the 7th Framework Programme. During this reporting period the Centre hosted number of visitors from EU countries, or Associated States, who either took part as the invited speakers in conferences and workshops organized by the Centre or they had special lectures directed to the scientific staff and PhD students of the Institute. Networking at the national level the Centre has been equally successful. The Institute is currently coordinating two national networks: "Nanomaterials as Catalysts for New, Environmentally Friendly Processes" and "Surfactants and Dispersed Systems in Theory and Practise - **SURUZ**" and is actively participating in three other national networks and cooperating with other Polish Centres of Excellence. It is also one of the founders of the "National Research Laboratory of Surface Sciences". As a proof of recognition of the Institute high position in colloid and interface science it was granted organization of the prestigious conference of European Colloid and Interface Society in 2008.

Eight study visits, financed entirely or co-financed by the Centre, for PhD students were organized in leading European scientific centres. Altogether seventeen PhD students participated in the top scientific conferences and workshops. Representatives of PhD students participated in the workshops devoted to scientific mobility in the frame of Marie Curie actions and other international fellowships opportunities.

International Symposium "Particles and Polyelectrolytes at Interfaces" was organized by the Centre in May 2005. The symposium gave the opportunity to meet together 65 scientists from various European countries, specializing in various aspects of adsorption of polyelectrolytes and colloid particles at macroscopic surfaces. The scientific programme included: 11 invited keynote lectures and 25 oral presentation. The book of abstracts from the symposium was published. The second scientific event was the **International Symposium "Catalysis on oxide-type materials. Theory and experiment: share needs and capabilities"** organized jointly by CATCOLL, CONCORDE EC programmes and Polish Network on Catalysis. The main aim of the meeting was to enhance contacts between "theoreticians" and "experimentalists" in the field of catalysis on oxide-type materials, to profit from both approaches for understanding catalysis phenomena.

Friendly Heating: Comfortable to People and Compatible with Conservation of Art Works Preserved in Churches

(Roman Kozłowski, Łukasz Bratasz, Sławomir Jakieła, Antonina Kozłowska)

UE STREP Research Project FRIENDLY HEATING EVK4-CT-2001-00067

Most historic churches are heated during the cold season sporadically when used. The short-term abrupt falls in the air relative humidity, bring about evaporation of moisture contained in the materials and shrinkage of such objects as polychrome wood. The aim of the FRIENDLY HEATING project was to develop a novel, prototype heating system which would supply heat locally in the areas where people are, with no disturbance of the conditions in the environment of the elements of historic church furnishing. During the 3 years of the project's implementation, the research team of the institute has done measurements of the dimensional changes of sculpted elements of a historic wooden altarpiece in the church in Rocca Pietore in Italy in response to fluctuations of the temperature and relative humidity in its environment caused by various heating systems. A systematic numerical modelling of the mechanical stress engendered by these fluctuations was also done and their allowable critical levels above which damage of wood appears were determined.

In 2005, the last year of the project, direct measurements of the level of stress in wood were done using the acoustic emission method to validate experimentally the results of the numerical simulations. It has been shown that acoustic signals due to damaging fluctuations of relative humidity occur at a characteristic frequency of 100-300 kHz, which makes possible distinguishing and filtering off acoustic effects due to temperature and external noise. The acoustic emission signals have been recorded for wooden elements subjected to fluctuations of the air parameters first in the controlled laboratory conditions and then in situ in the church of Rocca Pietore. A correlation was established between the amplitude of the fluctuations of relative humidity and the energy of acoustic emission pulses. In particular the acoustic emission goes to zero when the fluctuations are below the allowable threshold. The obtained results have confirmed that the acoustic emission signal, when properly calibrated, can become an excellent indicator of risk of the environmental damage to wooden objects which can be successfully used in monitoring museums and historic sites.

At the end of the project, a two-day national workshop disseminating its results in Poland was organised. The workshop took place in the National Museum in Warsaw on April 13-14. The programme of the workshop comprised 9 presentations by the project team as well as a panel discussion with the introductory contributions from three local experts and voices from the audience. The workshop was attended by close to 100 participants – representatives of authorities and offices - both state and church - responsible for the care of built heritage, conservators, teaching staff and students of art schools, engineers and enterprises working in the field of heating churches.

Roman Cement to Restore Built Heritage Effectively

(Roman Kozłowski, Grzegorz Adamski, Łukasz Bratasz,
Antonina Kozłowska, Dariusz Mucha, Bogna Napruszewska)

EU STREP Research Project ROCEM EVK4-CT-2002-00084

Roman cements – natural hydraulic binders – were key materials to decorate façades of buildings during the nineteenth and early twentieth centuries due to their very short setting time, decorative colour and excellent durability. The material is no longer available on the market. The aim of the project is to re-establish their manufacture and use in conservation of the built heritage. The institute is a coordinator of the project. The research tasks implemented by the institute during the reporting period (3d year of the project) were:

- gaining information on primary aesthetic appearance and execution techniques of the facades of buildings decorated in the Roman cement technology

In Cracow, a survey of 12 municipal schools built between 1879 – 1914 and decorated with Roman cement mortars was carried out as a joint activity with the Municipal Conservator of Monuments. For each object, historic information was collected, available archival materials were studied, photographic documentation was prepared, as well as technological and microscopic investigations were done. Varied grain textures and thicknesses of technological layers were revealed. The Roman cement mortars were often combined with cement-lime, or lime mortars, and the entire renders were usually coated with a pure Roman cement wash to produce a uniform aesthetic effect.

- establishing criteria of the technological compatibility between the historic and new repair mortars

The unperturbed transport of water through the interface between historic substrate and repair mortar was identified as the key compatibility criterion. Barriers in moisture movement lead to zones of damage due to ice and salt crystallization. The Nuclear Magnetic Resonance imagining was used to determine moisture distribution across the combinations of substrates and mortars during drying. The studies have revealed that the brick-mortar interface in samples collected from historic facades does not perturb the flow of water. This was further confirmed by the SEM-images which pointed to an excellent adhesion of the render but also to the presence of large pores in the render making water and water vapour transfer easy.

- manufacturing larger quantities of high quality Roman cements

Large-scale calcinations of marls collected from two geological sources in Poland and Austria, selected in the previous year of the project, were carried out. 2 cements differing in colour and early mechanical strength, immediately after hardening, were obtained. Both cements produced were passed to conservation partners who undertook practical experimentation.

EU 6th FRAMEWORK PROGRAMME PROJECTS

Dynamics in Nano-scale Materials Studied with Synchrotron Radiation

(Józef Korecki, Nika Spirids, Tomasz Ślęzak, Kinga Freindl)

UE STREP Research Project DYNASYNC NMP4-CT-2003-001516

The following deliverables were realized in the frame of DYNASYNC project in 2005:

1. Ultra high vacuum Kerr spectrometer – Prototype. The task was accomplished in cooperation with AGH University of Science and Technology and first results concern magnetization structure in Fe films on W(110) (comp. 8)
2. Growth and diffusion in thin iron layers on a stepped W(110) surface. Nuclear resonance scattering of synchrotron radiation was performed at ESRF Grenoble using a UHV instrument constructed during the first year of the project. The model of surface diffusion by ad-atom diffusion was postulated.
3. Growth kinetics of metallic nanoclusters on oxide substrates. The growth of gold nanostructures on a magnetite surface was characterized using STM and grazing incidence small angle X-ray scattering (GISAXS). Kinetics of Fe cluster formation on MgO(100) was studied using combined GISAXS and conversion electron Mössbauer spectroscopy (CEMS) measurements.
4. Oxidation and internal oxidation at Fe(001) surface and Fe(001)/MgO(001) interface. Phase analysis of early oxidation stages at surfaces and interfaces in Fe(001)/MgO systems was done using ^{57}Fe probe layer CEMS measurements.
5. Comparison of vibrational density of states (DOS) for planar Fe films and islands with a capping layer on W(110) and Mo(110). Vibrational density of states for Fe nanostructures on W(110) and Mo(110) capped with a silver layer were determined by nuclear inelastic scattering of synchrotron radiation. The phonon transport across different interfaces (Fe/W(110), Fe/Mo(110) and Fe/Ag) was compared.
6. Thickness and temperature dependence of the vibrational DOS in ultrathin Fe films and nanostructures on W(110), and/or Mo(110), Cr(001). Using the UHV instrument constructed at ID18, ESRF Grenoble, the impact of size effects on phonon spectra in ultrathin Fe films on W(110), ranging from a monolayer to 50 atomic layers, was analysed. Transition from 3-dimensional to quasi 2-dimensional behaviour was seen as pronounced phonon softening and marked anisotropy of the partial DOS's along highly-symmetric crystallographic directions.
7. Magnetization structure of Fe on W(110) or Mo or Cr. In plane spin reorientation transition was compared for flat and stepped Fe films.

As the project coordinator we realized also numerous management tasks. The most important were:

1. Preparation of the annual management and technical reports and 18. months interim activity report.
2. Preparation of the project Mid-Term Assessment.
3. Distribution of the second prepayment from the EC.
4. Preparation of the project meetings, both management and scientific. Four project meeting took place in 2005, two of them of purely scientific character.

The annual report was approved by the Commission after minor revisions. The project successfully passed the mid-term assessment procedure.

Transfer of Knowledge in Design of Porous Catalysts

(Ewa Serwicka-Bahranowska)

EU ToK Project TOK-CATA MTKDCT-2004-509832

TOK-CATA is a transfer of knowledge project which started on October 1, 2005 and will take place until September 30, 2008. The Institute of Catalysis and Surface Chemistry is the host institution of the project. The Institute is responsible for all the scientific and organisation activities, which include: recruitment of the foreign experts and organisation of their stay in Poland, development of detailed work programmes for the employed experts, providing access to or creation of necessary research infrastructures, recruitment of scientists with a vast experience, who would be able to supervise the implementation of research tasks, enabling information exchange and dissemination of results through organisation of workshops and meetings, taking part in conferences, publications in scientific journals, development of patents, project management, focusing on effective communication with the partner organisations and the European Commission.

The intention of the project is to provide paths for combining a longstanding tradition of the studies on porous materials in the host institute with the expertise of researchers from other organisations interested in intelligent design of porous catalysts. The project focuses on the following key areas of research on porous materials:

- design, synthesis and optimisation of porous materials based on zeolites, modified layered silicates and ordered mesoporous structures;
- control of the catalyst texture, grain morphology and insertion of active sites, targeted at application in processes of fine chemicals synthesis and abatement of air pollutants;
- creation of a progressive connection between theoretical simulation modelling of porous structures and catalyst design.
- In the framework of this research project the Institute established research contacts with partner organisations:
- Professor Ewa Serwicka-Bahranowska began the research activities in the UK at the University of Nottingham, School of Chemistry, which will bring a highly specialized know-how in tailoring and morphological control of mesoporous silicates.
- Associate Professor Bogdan Sulikowski began the collaboration with the University of Stuttgart, Department of Chemistry, Germany, which will provide access to advanced NMR equipment, to study working catalysts *in situ* under batch and continuous flow conditions. Moreover, dr Rafał Rachfalik begun his stipend at the University of Stuttgart.
- Associate Professor Bogdan Sulikowski began the collaboration with the Institute of Catalysis and Petrochemistry, Madrid, Spain, which will provide access to excellent equipment for characterisation of catalysts *in situ* as well as bring its expertise in designing equipment for catalytic testing.
- Dr Dorota Rutkowska-Żbik concluded the research activities at Lund University, Department of Theoretical Chemistry, Sweden, which will provide advanced theoretical methods combining semi-classical approach and advanced quantum chemistry.

The Institute recruited 4 scientists from abroad experienced in the abovementioned research field. Dr Leszek Góra, dr Dorota Duraczyńska and dr Helena Palkova were employed for 1 year. The Institute began the collaboration with Professor Michael Hunger from the University of Stuttgart.

Scientific Network – Surfactants and Dispersed Systems in Theory and Practise

(Kazimierz Małysa)

EU SSA Project SURUZ INCO-CT-2003-003355

The main objective of the “SURUZ” project coordinated by ICSC PAS is to build a network of scientific institutions in Poland, dealing with various aspect of colloid and interface science. The network brings together 24 research group from 14 various scientific institutions in Poland. The organization of the network is going to facilitate exchange of the personnel, information and dissemination of scientific results. It contributes to optimisation of use of research infrastructure available to the members of the network, prevents fragmentation and/or overlap of the research topics and favours cooperation especially among PhD students and young scientists.

To achieve the main objectives the “SURUZ” project it has been configured in five main activities (WP - workpakages). First activity (WP1 “*Kick-of-meeting*”) was accomplished in 2004. Second activity (WP2) “*Networking*” was initiated immediately after kick-off meeting. Within the reporting period (August 1, 2004 – July 31, 2005) 63 scientists visited and got familiar with Labs and equipment available in institutions of the SURUZ Network Partners. There was 14 lectures presented by visiting scientists on seminars in partner institutions. Total number of employees and Ph.D. Students visits in the partners labs., attending workshops, conferences and cluster meetings organized and/or co-organized by SURUZ Network was 564. Within the frame of third workpakage (WP3 - “*Thematic workshops for young scientists*”) Three workshops for young scientists were organized during the first reporting period. Two of them “SURUZ Workshop for Young Scientists” (9 November 2004, attendance 37 persons) and „Technologies for Characterization of Liquid and Solid Interfaces” (18-19 May 2005, attendance 48 persons) were organized by ICSC and the workshop “Nano- and Microdispersed Systems” (22 April 2005, attendance 19) was organized by CUT. A special session devoted to participation PhD and some undergraduate students was organized during “SURUZ” Conference in Polanica (1-3 June 2005).Every thematic cluster (WP4 - “C*luster workshops*”) organized its annual meeting. Workshop of Cluster A – “Interfaces, Surfactants and Dispersed Systems” was organized by UMCS (12-14 April 2005, attendance 62), Cluster B – by WRUT (1-2 April 2005, attendance 23), Cluster C – “Emulsions for Food, Cosmetics, Pharmaceutical and Household Use” (19-20 June 2005, attendance 35) – organized by GUT, Cluster D – was arranged by WRUT (31.03.2005 - 01.04.2005, attendance 23). Within the frame of the workpakage WP5 - “*Network conferences*” - three scientific conferences were organized with financial support of the project. Large scale (over 130 participants) network “SURUZ” conference was organized on 31 May – 4 June 2005 in Polanica and chaired by prof. K. Wilk of WRUT. The second major conference (120 participants) organized with the financial support of the project was “Oils & Environment International Conference” (20-23.06.2005 by prof. Jan Hupka of GUT. The third (smaller) conference (38 participants) - “Separation processes in dispersed systems” - was organized in Poznań (21-22 April 2005) by teams of Poznan University of Technology. The WP6 – “*Coordination*” tasks were carried out by prof. K. Malysa (coordinator), prof. P. Warszynski (deputy coordinator) and dr. L Szyk-Warszynska (secretary). They delivered series of lectures during cluster workshops and network conferences on objectives and current state of the project to increase awareness both members of the Network research groups and scientists outside the consortium. The project devoted website: ***www.cyf-kr.edu.pl/~ncmalysa/,*** has been build and permanently updated on server of ICSC PAS. The 1st Intermediate Report was prepared and accepted (with congratulations). The EU prepayment for the next period was received and the funds allocated to all partners were transferred to their bank accounts by ICSC PAS in December 2005.

Annual Polish Conferences Are Setting Up a New Platform for Dissemination of Knowledge in the Field of Catalysis

(Bogdan Sulikowski)

EU SSA Project POL-CAT NMP3-CT-2004-510318

The objective of this project is to promote and disseminate the newest knowledge and development in the field of catalysis, setting an efficient forum for exchange of relevant information and experience between scientists, research institutions and industry.

To address these topics, organization of the national conferences on catalysis in Kraków is suggested. This will enable to form new and exxtend the currently existing contacts between the Polish scientists and experts from the European Union, the EU associated countries, and also, if required, from outside Europe. Thus, three conferences on catalysis will be organized by the ICSC at Cracow on an annual basis, in the years 2004 to 2006.

The second of the conferences planned was held in Kraków on March 15-18, 2005; it was the 37th Polish Conference on Catalysis. Polish and foreign scientists, in all 240 registered participants, were attending the meeting. The following tasks have been carried out to organize the conference:

- the Scientific Committee was formed
- the topics were chosen in co-operation with this body
- the WEB page was formed containing pertinent information on the conference
- the national and foreign speakers were chosen and invited to Kraków
- materials required to realize the project were purchased
- the program of the conference was printed, announced in internet and sent to participants
- the conference materials were edited and printed (392 pages, 250 copies)
- the 37th Polish Conference on Catalysis was organized
- contributions obtained were selected and prepared for editing a special volume of the *Catalysis Today* “Nano-Structured Materials for Catalysis”, comprising a choice of the delivered as well as invited papers (B. Sulikowski – Guest Editor).

In 2005, a special issue of the *Catalysis Today* entitled ”Oxide-Based Materials in Catalysis” was published (vol. 101, issue 2, 30 March, 2005; ISSN 0920-5861). Guest Editor: B. Sulikowski. In this volume the presentations delivered at the 36th Polish Conference on Catalysis in Kraków (2004) were published.

Nanocapsules for Targeted Controlled Delivery of Chemical

Studies of the attachment of microcapsules to stainless steel surface and permeability of microcapsule shells

(Piotr Warszyński, Lilianna Szyk-Warszyńska, Mqria Zembala, Marta Kolasińska, Anna Trybała)

UE STREP Research Project NANOCAPS NMP4-CT-2003-001428

The main aim of the "NANOCAPS" project is to develop new technologies based on micro-encapsulation to solve industrial problems related to controlled release of chemicals. The technical objectives are to develop nano-materials and nano-composite coatings for cost-efficient production of nano-capsules and to validate the technical and economical feasibility of the knowledge acquired in the fields of biomedical (anti-proliferating and anti-allergic agents) and metal plating (self-repair) applications. The attachment of microcapsules to external surface and formation of permanent coverages in the fluid flow conditions is one of the important problems for these specific applications. We studied the problem of deposition of microcapsules at a model mica surface and the surface of stainless steel used to production of stents. In our experimental investigation we used "oblique impinging jet cell", which allows direct observation of deposition process on non-transparent surfaces. As model capsules we used polystyrene latex particles of 1 μm covered with polyelectrolyte (PE) shells of various thickness. The PE shells were constructed by sequential adsorption of polycationic and polyanionic layers (LbL technique) and model polyelectrolytes PAH/PSS as well as chitosan/alginate i.e. natural polyelectrolytes were used to construct the shells. Thickness of the respective PE layers were established by ellipsometric measurements. The procedure of the shell construction was established with the intermediate rinsing step performed by ultrafiltration (instead of previously used centrifugation) giving monodispersive suspension of microcapsules. Figure 1. presents the dependence of the reduced microcapsules' flux to the silanized mica surface (positively charged) being a measure of the deposition rate on the flow intensity (expressed in terms of Reynolds number) and number of (PAH/PSS) layers. The results show that irrespective of the shell thickness the deposition rate is close to maximum one obtained for barrier-less electrostatically driven deposition as the PSS terminated shells are negatively charged. The result show that deposition is irreversible as no capsule detachment was observed either during experiment or prolong flushing under high flow conditions.

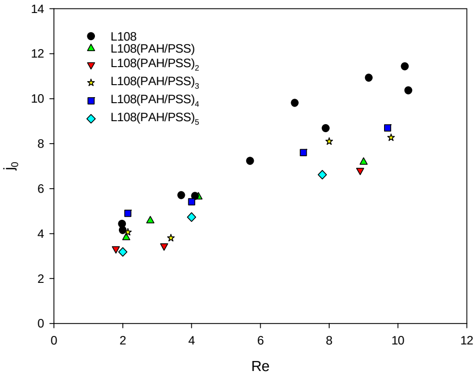


Fig.1. Microcapsules' deposition rate

The method of monitoring of the release of encapsulated material was also elaborated. The method is based on the direct observation in the "oblique impinging jet cell" of the release of fluorescent dye from the capsule attached to the surface. The development of the fluorescent intensity profile around the microcapsule attached to the surface is monitored by the system consisting of fluorescent microscope, camera and image analysis system. The example of the image obtained during monitoring of the release of fluorescein from the chitosan/alginate covered capsule is shown in Figure 2.

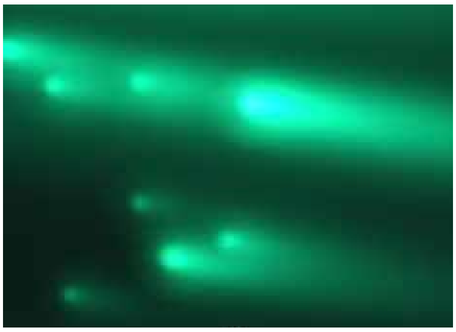


Fig. 2. Release of fluorescein from microcapsules with CHIT/ALG shells

Global Climate Change Impact on Built Heritage and Cultural Landscapes

(Roman Kozłowski, Łukasz Bratasz, Sławomir Jakieła)

EU STREP Research Project NOAH’S ARK SSP1-CT-2003-501837

The aim of the project has been establishing meteorological parameters and variations which will affect in a critical way the material heritage environment in the coming 100 years, as well as development and dissemination of strategies mitigating the resulting threats. The activities of the research team of the institute within the project has focused on development of risk indices for historic materials sensitive to moisture and temperature, like wood or clay containing sandstones, which would describe relative potential of a climate to promote the material decay.

The main research task for the reporting period was developing a new improved climate risk index for historic wooden structures exposed to the outdoor weather. The deterioration mechanism involves growth of wood destroying fungi when the availability of the moisture for exploitation by fungi has exceeded critical levels. It was assumed that precipitation and temperature are dominating elements of climate making the growth of fungi possible and that the relation between the growth rate to temperature was linear above the bottom limit of 2°C.

The index developed took into account the real moisture penetration depth and resulting real infestation volume. The water transport into 3 species of wood, favoured in the past by builders and craftsmen in Europe, was measured using an NMR imaging. A moisture content profile across wood was determined as a function of duration of the precipitation wetting the external surface. A model of two-stage infiltration, interpretable in terms of very rapid transport through the capillary vessels with a simultaneous slower infiltration into the denser material surrounding them was used. As the result, a profile of moisture penetration into wood could be numerically simulated for any precipitation event. The profile was expressed in terms of time when the moisture content at a given distance from the external surface was above the critical level of 20%. The critical level corresponds to the moisture content above which the fungal growth appears. The events were agglomerated into the monthly moisture penetration profiles corresponding to a cumulative product of the volume in which, and time during which, the decay by fungi was possible.

The final form of the Climate Risk Index for Cultural Heritage (CRI_{CH}) was:

$$CRI_{CH} = \sum_{Jan.}^{Dec.} \left(T - 2\right) \int_{0}^{D_{\max}} t_{crit}(D)\, dD$$

where: T is the mean monthly temperature in ^{o}C, $t_{crit}(D)$ is monthly time when moisture content at distance D from the wood’s surface exceeded the critical level. D_{max} is the maximum distance at which infiltration of water produces moisture contents above the critical magnitude, D_{max} is specific for each species of wood and is determined experimentally. The index is normalised to make it fall within the range 0 to 100.

Co-ordination of Nanostructured Catalytic Oxides Research and Development in Europe

(Vicente Cortés Corberán, Bogdan Sulikowski)

EU CA Project CONCORDE NMP2-CT-2004-505834

Institute of Catalysis and Surface Chemistry (ICSC) is carrying out the EU project entitled as above and scheduled for 27 months (2004-2006). The objective of the project is to coordinate research and development activity in the leading European laboratories, working on nanostructured metal oxides with redox properties, and also on other multifunctional materials, which are effective catalysts of the chemical processes. The protection of natural environment and sustainable development are in focus of the project. A project consortium is composed of 42 partners (7 industrial; and 3 from small and medium enterprises) from 16 European countries. The topics comprise a field of catalysis, starting from fundamental research (theory, advanced techniques and methods of catalysts preparation, reaction mechanisms) and ending on applied aspects (reactors design, process control, studies on catalyst life etc.).

In 2005, the following meetings of the Steering Committee were held: at Louvain-la-Neuve (Jan. 25), at Berlin (Febr. 27-March 1), at Sofia (August 28), and at Kraków (November 16). During the meetings current project topics were addressed, the plans for future activities were discussed and set (people and samples exchange, a “white book”, cooperation and co-ordination of plans within the five subtasks). The five working groups are co-ordinated by the following scientists: V. Rives (USAL), B. Weckhuysen (UU), A. Brückner (ACA), X. Verykios (UPATRAS) and A. Lemonidou (CERTH). The questionnaires prepared by prof. Hodnett were filled out.

In 2005 the following scientists were involved in the people exchange scheme of Concorde: K. Samson, MSc, A. Klisińska, PhD - two weeks in Madrid (catalysis, Raman spectroscopy); U. Filek, MSc - 2 wekks in Berlin and 3 weeks in Bucharest (*in situ* measurements, UV-Vis, Raman, ESR, catalysis); Ł. Mokrzycki, MSc - 3 weeks in Utrecht (XRD, XRF, IR). The stays were devoted to oxide and zeolite catalysts studies. Both MSc and PhD scientists were involved, as the project has a significant pedagogical aspect.

The first conference of CONCORDE on “Understanding the dynamic and transient behaviour of oxide catalysts in working conditions and the relationships with their catalytic performances”, was held at Louvain-la-Neuve in January 26-28, 2005. About 100 scientists participated, including five persons from ICSC.

Due to the support of the project five scientists from ICSC were participating at EuropaCat-VII conference in Sofia (28.08-2.09.2005). In November 17-19 ICSC has organized the international conference on ”Catalysis on oxide-type materials. Theory and experiment: share needs and capabilities”.

The 4th Workshop to be held in Kraków in February 24-25 is now being organized by ICSC, The other forthcoming events are: the international conference at Thessaloniki (26-28.01.2006), and the final conference closing the CONCORDE project at Sevilla in May 2006.

ERA-NET for Applied Catalysis in Europe

(Ewa Serwicka-Bahranowska, Małgorzata Witko)

EU ERA-NET Project ACENET ERAC-011784

The objective of ACENET as an ERA-NET project is cooperation and coordination of research activities carried out at national and regional level in the Member States and Associated States. ERA-NET projects enable networking activities and mutual opening of research programmes. The project involves 10 partners from 9 countries: Netherlands Organisation for Scientific Research, the Netharlands; Bundesministerium fuer Bildung und Forschung, Germany; Centre National de la Recherche Scientifique, France; Ministerstwo Edukacji i Nauki, Poland; Fundacao para a Ciencia e a Tecnologia, Portugal; Ministero dell'Istruzione della Universita e della Ricerca and Consorzio Reattivita e Catalisi, Italy; General Secretariat for Research & Technology, Ministry of Development, Greece; Ministerio de Educacion y Tecnologa, Spain; Forschungszentrum Juelich GmbH, Germany; Engineering and Physical Sciences Research Council, UK. The Institute of Catalysis and Surface Chemistry represents in the project the Polish Ministry of Education and Research, because the project refers to applied catalysis. The project started on September 1, 2004 and will take place until August 30, 2008.

It is foreseen to open within the project a joint call for proposals in the field of applied catalysis, which would be based on the priority areas identified in the Strategic Research Agenda developed in the Technology Platform on Sustainable Chemistry. The partners believe that the joint programme should be formulated as soon as possible, so that the call for proposals could be opened in 2007. A detailed analysis of the responsibilities, competences, decision procedures of all the partners was carried out. Profound understanding of the differences between the partners was especially important. The working team created a questionnaire, which enabled receiving all the necessary information from the partners. Data on the applied catalysis funding figures, application procedures, priorities, strategies and preparation of strategies as well as decision making bodies were collected. The partners presented information concerning the initiation, definition and establishment of research programmes, role of industry, criteria for funding, possibilities of funding abroad and considerations for jointly funded research programmes. Data was also collected on different programmes in the frames of which research projects are being funded. Each programme was described in detail concerning its objectives, size of funds, eligibility of expenses and applicants, application processing and content, evaluation of the proposals, decision-making and follow-up of projects. On the basis of the above information the participants agreed on best practices and chose model procedural steps, which will be used for the management of 'case study programmes' carried out at a later stage of the project.

Parallel to the efforts to open a joint call for proposals it is the aim of the project to create a framework for Joint Training and Education Programme. The main part of this Programme will be an Integrated Course on Catalysis. The course can be organised differently in different countries. It will have a common obligatory scientific programme and an examination in English following a common standard. On the basis of the examination it will be possible to find a few best students who will take part in the Educational Centre of Excellence in Catalysis. Moreover, the programme envisages a school on catalysis and Continuous Professional Development courses, which will be based on the UK experience.

Integrated Design of Catalytic Materials for a Sustainable Production

(Małgorzata Witko)

UE NoE Project IDECAT NMP2-011730-2

The objective of IDECAT a Network of Excellence is to strengthen research on catalysis creating a coherent framework, know-how and training between various catalysis communities (heterogeneous, homogeneous and bio-catalysis). This objective will be achieved when a lasting integration between the main European institutions in the area will take place. The Institute of Catalysis and Surface Chemistry is one of the 17 partners of the project which is coordinated by the Department of Industrial Chemistry and Material Engineering at the University of Mesina in Italy. The partners in the project are 37 laboratories from 17 institutions: Consorzio Interuniversitario per la Scienza e Tecnologia dei Materiali, Italy; Ghent University, Belgium; Katholieke University Leuven, Belgium; J. Heyrovsky Institute of Physical Chemistry, Czech Republic; Helsinki University of Technology, Finland; Centre Nationale de la Recherche Scientifique, France; Max-Planck-Gesellschaft, Germany; Leibnitz Institute of Organic Catalysis, Germany; Technische University Munchen, Germany; Consiglio Nazionale delle Ricerche, Italy; NRSC-Catalysis, the Netherlands; Instytut Katalizy i Fizykochemii Powierzchni, Poland; Consejo Superior de Investigaciones Cientificas, Spain; Stockholm University, Sweden; University St. Andrews, UK; University of Southampton, UK; Ecole Polytechnique Federale de Lausanne, Switzerland. The project started on April 1, 2005 and will last until March 31, 2009.

The official kick-off meeting of the project took place on July 15, 2005 in Florence. During the meeting the leaders of the 13 Workpackages presented the work plan for the coming year. The Workpackages are divided into 4 groups of activities: Joint Programme of Integration, Joint Programme of Research, Joint Programme of Spreading Excellence and Management.

The Joint Programme of Integration foresees the establishment of juridical structure and Internet tools which will enable the integration of the laboratories taking part in the project, pooling of equipment and best practices as well as continuing education and mobility. The final objective of IDECAT is the creation of an European Research Institute of Catalysis The Institute of Catalysis is the co-leader of the e-IDECAT Workpackage. There is a web site of the project being created in the Institute in the frames of this Workpackage. The Institute's staff has also taken part in a few conferences organised within the project.

The Joint Programme of Research focuses on four research tasks: 1) creating and mastering nano-objects and nano-organisation, 2) creating and designing new multifunctional and nano-structured materials, 3) bridging the gap in multi-disciplinary approaches, 4) eco-processes and sustainable energy and production. The abovementioned tasks are parallel to the field of research of some of the research groups in the Institute. Those groups have started to establish scientific contacts with the other partners of the project so as to come up with common research topics which would be possible to develop within the project.

The Joint Programme of Spreading Excellence foresees two areas of activities. The first one focuses on new forms of teaching like e-learning, or multi-institution PhD studies. The second one includes promotion of science. The Open Days of the Institute were organised within the second field of activities.

OTHER EU PROJECTS

Catalytic Cleaning of the Gases from Chlorinated Hydrocarbons

(Tadeusz Machej, Ewa Serwicka-Bahranowska, Janusz Janas, Robert Janik, Halina Piekarska-Sadowska, Wojciech Włodarczyk)

Research Project EUREKA E! 3454 CHLORCAT

The project is the cooperation between Katalizator Sp. z o.o. and Institute of Catalysis and Surface Chemistry PAS in Poland, and Elcom Ekotechnika s.r.o., and Vysoka Škola Chemicko-Technologicka in Czech Republic as a result of a long term mutual relationship in the field of the environmental protection.

Chlorinated hydrocarbons may be destroyed by thermal combustion at 1270 – 1470 K. Such process demands a lot of energy and may result in dioxins formation. A high-tech way to handle this problem is to use a catalyst. The catalyst shall be able to convert these compounds to harmless products, i.e. carbon dioxide, water and HCl easy to remove by caustic scrubbing and shall be resistant to deactivation by HCl. The catalyst shall have, depending on an application, a monolith/honeycomb structure or pellets form.

The aim of the project is to develop a technology of a catalyst manufacturing for total oxidation of chlorinated hydrocarbons. The catalyst was designed in the Institute of Catalysis and Surface Chemistry in the laboratory scale. The method of its preparation is a subject of two patent applications (P-362181 and P-362182). Palladium, active component of the catalyst, is supported on natural montmorillonite modified with titanium.

The present research is concentrated on transferring the technology from the laboratory scale to the industrial one.

The montmorillonite used in this study was sodium-exchanged less than 2 μm particle size fraction of Milowice bentonite (Na-mt). Titania-pillared clay was prepared by adding $TiCl_4$ solution and HCl (6 mmol Ti^{4+}/ 1 g Na-mt) to a water suspension containing about 14 g/l of bentonite. The mixture was allowed to age for 5 hrs at 293 K under continuous stirring. The resulting material was centrifuged, washed free chlorine ions and dried at 363 K.

The dried Ti-exchanged bentonite was added to a water suspension of γ-Al_2O_3 and then continuously stirred overnight. A cordierite honeycomb monolith was washcoated by dipping it into the prepared slurry. The excess of slurry was removed with compressed air. The monolith was then dried at 373 K and calcined at 773 K. The monolith will be impregnated with palladium nitrate and then an activity of resulting catalyst will be checked in a pilot plant in the next stage of the research.

EU STRUCTURAL FUNDS

Implementation of the Roman Cement Technology into the Practical Conservation of Historic Buildings

(Roman Kozłowski, Grzegorz Adamski, Łukasz Bratasz, Antonina Kozłowska, Dariusz Mucha, Renata Vyskocilova)

Sectorial Operational Programme Project – Growth of the Competitiveness of Enterprises, WKP_1/1.4.1/1/2005/8/8/222/2005/U

The aim of the project is to introduce novel materials into the conservation practice which would posses characteristics of the mortars based on Roman cements originally used during the nineteenth and early twentieth centuries. This will make possible a proper conservation of the vast urban built heritage of the period. The project is implemented by a consortium of the conservation enterprise AC Konserwacja Zabytków Piotrowski, Kosakowski Spółka Jawna and the institute.

The main research task carried out in the reporting period was obtaining Roman cements of varied properties such as setting time, colour and early mechanical strength. The calcinations were carried out for two different raw materials – calcitic marls of required chemical composition - gained from the quarries in Folwark, Poland and in Lilienfel, Austria. The calcinations were carried out in a large electric kiln with the capacity of 300 kg of raw material. Temperature and time of calcination were varied between 830 – 1060 ^{o}C and 300 – 1500 minutes. The phase composition of cements obtained was determined using X-ray diffraction. The raw materials were found suitable for the production of high quality Roman cement in the relatively broad range of temperatures and times of calcination. A fast method to assess the capacity of cements to reach early mechanical strength after mixing with water was developed. It involved determination of the content of hydrated aluminate phases, responsible for this strength, using X-ray diffraction. The setting time was found to be very short – 30 to 120 seconds. Therefore a number of methods extending the setting time were tested. The optimum method proved to be the addition of citric acid in the amount of 0,4% per weight of dry cement.

The cements manufactured and information on recipes have been passed to the conservation partner for experimentation and practical investigations.

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PARTICIPATION IN SCIENTIFIC CONFERENCES

PLENARY AND INVITED LECTURES

1. Z. Adamczyk, K. Jaszczółt, B. Siwek "Irreversible Adsorption – Kinetic and Structural Aspects", Scientific Conf. Surfactants and Dispersed Systems in Theory and Practice SURUZ, Polanica Zdrój 2005

2. Z. Adamczyk "Adsorption on Surfaces with Controlled Heterogeneity", Symp. Interfacial Phenomena, Surfactants and Dispersed Systems, Lublin 2005

3. A. Bielański, A. Lubańska, A. Micek-Ilnicka, J. Poźniczek "Catalytic Synthesis of Tertiary Ethers on Heteropolyacids", 16th Cracow-Jena Seminar on Physical Chemistry, Jena 2005

4. E. Brocławik, “Iron Sites in CYP450 Enzymes: Quantum Chemical DFT Modeling", 16th Cracow-Jena Seminar on Physical Chemistry, Jena 2005

5. A. Chumakov, P. T. Jochym, J. Korecki, J. Lazewski, K. Parliński, R. Röhlsberger, R. Rüffer, B. Sepioł, M. Sladecek, T. Ślęzak, N.Spiridis, S.Stankov, G.Vogl "Nano-scale Systems: Dynamics", Symp. on Nuclear Resonant Scattering, ESRF, Grenoble 2005

6. A. Chumakov, P. T. Jochym, J. Korecki, J. Lazewski, K. Parliński, R. Röhlsberger, R. Rüffer, B. Sepioł, M.Sladecek, T.Ślęzak, N.Spiridis, S. Stankov, G. Vogl "Vibrational Density of States in Ultrathin Fe Films on W(110) from Nuclear Inelastic Scattering of Synchrotron Radiation", 23rd European Conf. on Surface Science, Berlin 2005

7. M. Derewiński "Not Only Breck Award", "Donald W. Breck Award" for Professor A. Corma Conf., Instituto de Tecnologia Quimica UPV-CSIC, Valencia 2005

8. B. Grzybowska-Świerkosz "Nano-Au/oxide Support Catalysts in Oxidation Reactions: Provenance of Active Oxygen Species", 1st Conf. of the Coordination Action 'CONCORDE' Understanding the Dynamic and Transient Behaviour of Oxide Catalysts in Working Conditions and Relationships with Their Catalytic Performances, Louvain-la-Neuve, Belgium 2005

9. B. Grzybowska-Świerkosz, M. Witko. R. Tokarz-Sobieraj "Oxide Catalysts: What We Know, and What We Would Like to Know", Int. Symp. Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities, Kraków 2005

10. J. Haber "Electronic Factor in Heterogeneous Catalytic Oxidation Revisited", 5th World Congr. on Oxidation Catalysis, Sapporo 2005

11. B. Jachimska "Metoda Dynamicznego Rozpraszania Światła (DLS), czyli jak odkryć świat koloidów"6. Studenckie Spotkania Analityczne, Kraków 2005

12. J. Korecki "Epitaxial Nanostructures – Characterization and Growth", MDN & DYNASYNC Workshop on Dynamics in Nanoscale Systems, Raach am Hochgebirge 2005

13. J. Korecki "Dynamics in Nano-scale Materials Studied with Synchrotron Radiation", Science and Art in Europe, session 'Catalysis: Nanotechnology with a Past', Berlin 2005

14. J. Korecki, A. Chumakov, P. T. Jochym, J. Lazewski, K. Parliński, R. Röhlsberger, R. Rüffer, B. Sepioł, M. Sladecek, T. Ślęzak, N. Spiridis, S. Stankov, G. Vogl "Studying Nanostructures with Nuclear Resonance Scattering of Synchrotron Radiation", Joint Meeting of the German Vacuum Soc. and the Polish Vacuum Soc. 'Vacuum Based Science and Technology' & 4thAnnual Meeting of the German Vacuum Soc., Kraków 2005

15. A. Kowal, J. Czyżniewska, L. Pavlovic, M. Pavlovic, C. Gutierrez "Ti/SnO_2(Sb) Electrodes Used for Decomposition of Organic Pollutants in Water", Symposium 'Wodowody i Kanalizacja', Herzeg Novi 2005

16. W. Kraus "'Chemia i Inżynieria Ekologiczna' – Material for Bibliometric Rating of the Journal", 10th Int. Scientific Conf. Metal Ions and Other Abiotic Factors in the Environment, Krakow 2005

17. T. Machej "Current Trends in Development of Catalysts for VOC Emission Abatment", Konf. 'Emise organických látek z technologických procesů a metody jejich snižování', Pardubice 2005

18. T. Machej "Catalytic System – SWINGTHERM", Konf. 'Emise organických látek z technologických procesů a metody jejich snižování', Pardubice 2005

19. W. Rudziński, T. Pańczyk "Quantative Analysis of the Thermodesorption Spectra from Catalyst Surface Based on the Statistical Rate Theory Approach", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

20. E. M. Serwicka "Mesoporous Molecular Sieves as Hosts for Catalytically Active Organometallic Macrocycles", Science and Art in Europe, session 'Catalysis: Nanotechnology with a Past', Berlin 2005

21. R. Tokarz-Sobieraj "DFT Cluster Model Studies of Molybdenum Based Catalysts", 1st Int. Symp. on Methods and Applications of Computational Chemistry, Kharkiv 2005

22. R. Tokarz-Sobieraj "DFT Description of Molybdenum Based Catalysts", CatColl Meeting and SURUZ Young Scientists Workshop, Kraków 2005

23. P. Warszyński "Adsorption of Surfactants; Route from Molecular Modeling to Adsorption Isotherms", Scientific Conf. Surfactants and Dispersed Systems in Theory and Practice SURUZ, Polanica Zdrój 2005

24. P. Warszyński "Some Dynamic Aspects of Surfactants and Colloid's Adsorption", 19th Conf. European Colloid and Interface Soc., Geilo 2005

25. M. Witko, P. Hejduk "Teoretyczne badania powierzchni katalizatorów", 48. Zjazd PTChem i SITPChem, Poznań 2005

26. M. Witko "Surface Modification of Oxide Catalysts – Quantum Chemical Modeling", Conf. Catalysis and Adsorption in Fuel Processing and Environmental Protection, Kudowa-Zdrój 2005

27. M. Witko "Theoretical Studies on Heterogeneity of Surfaces of Oxide-Based Calatysts", Symp. on the Role of Vacancies, Disorder, and the Relationship between Surfaces and Bulk Structure in Selective Oxidation Catalysis, Irsee 2005

28. M. Witko "Theoretical Studies on Heterogeneity of Oxide Surfaces", Science and Art in Europe, session 'Catalysis: Nanotechnology with a Past', Berlin 2005

29. M. Witko "Oxygen at V_2O_5 Surface – Quantum Chemical Studies", 2nd Concorde Workshop In situ Characterization and Modeling of Oxide Catalysts", Belfast 2005

30. M. Witko, R. Tokarz-Sobieraj, R. Gryboś "Heterogeneity of Surface of Oxide-Based Catalysts. Cluster DFT Studies", 7th Congr. of the World Association of Theoretically Oriented Chemists, Cape Town 2005

LECTURES AND ORALS

1. Z. Adamczyk "Understanding Hetero System (Adsorption): Can It Be Achieved?", Int. Symp. "Particles and Polyelectrolytes at Interfaces", Kraków 2005

2. Z. Adamczyk "Colloids for Targeted Drug Delivery", 'NanoDrugs' Consortium Meeting, Athens 2005

3. Z. Adamczyk, K. Jaszczółt, B. Siwek "Irreversible Adsorption – Kinetic and Structural Aspects", Scientific Conf. Surfactants and Dispersed Systems in Theory and Practice SURUZ, Polanica Zdrój 2005

4. Z. Adamczyk, A. Michna, P. Warszyński, M. Zembala "Polyelectrolyte Multilayer Probing by Streaming Potential and Particle Deposition Measurements – New Data and New Problems", Int. Symp. "Particles and Polyelectrolytes at Interfaces", Kraków 2005

5. G. Adamski, Ł. Bratasz, N. Mayr, D. Mucha, R. Kozłowski, M. Stilhammerova, J. Weber "Roman Cement – Key Historic Material to Cover the Exteriors of Buildings", RILEM, TC 203-RHM: "Repair mortars for historic masonry", Delft 2005

6. J. Barbasz, N. Spiridis, J. Korecki "Wpływ terminacji powierzchni Fe_3O_4(001) na adsorpcję złota", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

7. W. Barzyk "Electric Surface Potential Study of Orientation Changes in Monolayers at the Air/solution Interface", Scientific Conf. Surfactants and Dispersed Systems in Theory and Practice SURUZ, Polanica Zdrój 2005

8. M. Bazarnik, M. Zimowska, E. Serwicka, K. Bahranowski, A. Gaweł, Z. Olejniczak "Syntetyczny kanemit jako prekursor mezoporowatych materiałów krzemionkowych", 6. Międzynarodowa Konf. Doktorantów i Młodych Pracowników Nauki, Miękinia-Herlany 2005

9. A. Bielański, A. Micek-Ilnicka, A. Lubańska "Solid Heteropolyacids as the Catalysts for Alcohol to Olefin Addition (Case Study)", Int. Symp. Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities, Kraków 2005

10. Ł. Bratasz, S. Jakieła, R. Kozłowski "Allowable Thresholds in Dynamic Changes of Microclimate for Wooden Cultural Objects: Monitoring in-situ and Modelling", 4th Triennial Meeting ICOM Committee for Conservation, The Hague 2005

11. A. Bratek, Z. Adamczyk, B. Jachimska "Wpływ siły jonowej na lepkość roztworów polielectrolitów", SURUZ Cluster Meeting, Pawłowice-Wrocław 2005

12. A. Bratek, Z. Adamczyk, B. Jachimska "Wpływ pH i siły jonowej na lepkość roztworów polielectrolitów", Mikrosympozjum "Stabilność układów dyspersyjnych", 48. Zjazd PTChem i SITChem, Poznań 2005

13. A. Bratek, Z. Adamczyk, B. Jachimska "Determining the Structure of Polyelectrolytes by Dynamic Viscosity Measurements", SURUZ Young Scientists Workshop, Kraków 2005

14. E. Brocławik "Reaction Mechanism for the Metabolism of Antimigraine Drugs on Iron Site in Cytochrome P450 Enzymes: A DFT Study", Workshop on Modeling Interactions in Biomolecules, Prague 2005

15. E. Brocławik, K. Chiba, Y. Sasaki, H. Tsuboi, M. Koyama, M. Kubo, K. Akutsu, M. Hirota, M. Kitada, H. Hirata, A. Miyamoto "First-Principles and Tight Binding Quantum Chemical Molecular Dynamics Approach to Vibrationally Excited States Dynamics of Water", 229th American Chem. Soc. National Meeting, San Diego 2005

16. E. Brocławik, A. Rajjak Shaikh, M. Ismael, H. Tsuboi, M. Koyama, M. Kubo, C. A. Del Carpio, A. Miyamoto "Metabolism of Arene Substrates on Iron Site in Cytochrome P450: Quantum Chemical DFT Modeling", Int. Conf. of Computational Methods in Sciences and Engineering, Loutraki 2005

17. N. Carmona, A. Kowal, J. Rincon, M. Villegas "AFM Assessment of the Superficial Nano/microstructure on Chemically Damaged Historical and Model Glasses", 10th EuCheMS, Rimini 2005

18. S. Cohen-Addad, R. Höhler, M. Krzan, M. Marinic, B. Herzhaft "Rigidity Percolation in Particle Laden Foams", 58th Annual Meeting of the Division of Fluid Dynamics, American Physical Soc., Chicago 2005

19. C. Dejugnant, G. Para, P. Warszyński "Preparation of PAH/PSS Microcapsules by Membrane Emulsification", Int. Symp. "Particles and Polyelectrolytes at Interfaces", Kraków 2005

20. M. Derewiński, K. Góra-Marek, P. Sarv, J. Datka "Relationship between Thermal Stability and Acidity of Mesoporous Alumina and Aluminosilicates", 21eme Réunion du GFZ, Sevrier 2005

21. R. Dula, R. Janik, T. Machej, P. Olszewski, J. Stoch, E. M. Serwicka "Hydrotalcite-derived Mn-Containing Mixed Oxides as Catalysts for Removal of VOCs", Int. Symp. Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities, Kraków 2005

22. R. Dula, R. Janik, T. Machej, E. M. Serwicka, J. Stoch "New Mn-Containing Catalytic Materials for the Total Combustion of Toluene", Int. Symp. on Air Pollution Abatement Catalysis, Kraków 2005

23. P. Dyshlovenko, P. Warszyński "Numerical Study of Electrostatic Colloidal Interaction at Charged Interface", Int. Symp. "Particles and Polyelectrolytes at Interfaces", Kraków 2005

24. S. Dźwigaj, I. Gressel, B. Grzybowska, K. Samson "Oxidative Dehydrogenation of Propane pn VSiβ Catalysts", 12. Forum Zeolitowe, Ciążeń 2005

25. K. Freindl, N. Spiridis, T. Ślęzak, M. Zając, W. Karas, J. Korecki "Hyperfine Fields in Nano-dispersed Magnetite", MDN & DYNASYNC Workshop on Dynamics in Nanoscale Systems, Raach am Hochgebirge 2005

26. A. Gomułczak, K. Wieczorek-Ciurowa, J. Rakoczy, J. Stoch "Ocena skutków mechanicznej aktywacji tlenków V_2O_5-Cr_2O_3 jako prekursorów katalitycznych", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

27. R. Grabowski "Modelowanie kinetyki utleniającego odwodornienia alkanów na katalizatorach wanadowych", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

28. R. Gryboś, M. Witko "Vanadium Oxide on Anatase Surface. Theoreticians View", Int. Symp. Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities, Kraków 2005

29. J. Haber, J. Janas, J. Kryściak, T. Machej, H. Sadowska "The Role of Support in Catalysts for Oxidation of Nitromethane", Int. Symp. on Air Pollution Abatement Catalysis, Kraków 2005

30. J. Haber, J. Stoch, V. A. Zazhigalov "Transition Metal Promoted VPO Catalysts in Selective Oxidation of Propane, n-Butane and n-Pentane", Int. Symp. Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities, Kraków 2005

31. P. Hejduk, M. Witko, K. Hermann "Kwantowo-chemiczne badania struktury elektronowej niewysyconej powierzchni $V_2O_5(001)$", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

32. P. Hejduk, M. Witko, K. Hermann "Theoretical Approach to Invastigate Into Active Sites at Undercoordinated Vanadium Oxide Surfaces by Hydrogen: Ab inito DFT Cluster Studies for V_2O_5 (001)", 2nd Int. School - Conference on Catalysts Design for Young Scientists, Novosibirsk-Autai, 2005

33. P. Hejduk, M. Witko, K. Hermann "Hydrogen Adsorption at V_2O_5: DFT Cluster Stidies for Saturated and Unsaturated Surfaces", Int. Symp. Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities, Kraków 2005

34. S. Jakieła, K. Cieślar, Z. Olejniczak, Ł. Bratasz "Measurement of Moisture Transport in Wood Using Low Field 1D-MRI", 38. Ogólnopolskie Seminarium na Temat Magnetycznego Rezonansu Jądrowego i Jego Zastosowań, Kraków 2005

35. E. Jarek, P. Wydro, M. Paluch, P. Warszyński "Surface Properties of Mixtures of Surface Active Sugar Derivatives with Ionic Surfactants. Theoretical and experimental investigations", SURUZ Young Scientists Workshop, Kraków 2005

36. T. Jasiński, P. Warszyński "Molecular Mechanics Simulations of Adsorption of Single Hydrocarbon Chain Surfactants at the Air/water Interface", Symp. Interfacial Phenomena, Surfactants and Dispersed Systems, Lublin 2005

37. T. Jasiński, P. Warszyński "Molecular Mechanics Simulations of Adsorption of Single Hydrocarbon Chain Surfactants at Air/water Interface", Symp on Theoretical and Experimental Studies of Interfacial Phenomena and Their Technological Application, Wólka Milanowska 2005

38. K. Jaszczółt, Z. Adamczyk, B. Siwek "Surface Clusters of Colloid Particles Produced by Deposition on Sites", Int. Symp. Particles and Polyelectrolytes at Interfaces", Kraków 2005

39. V. Jovanović, A. Kowal "Characterization of Silver Particles Spontaneously Deposited on Glassy Carbon", YUCOMAT 2005, Herzeg Novi 2005

40. A. Klisińska, K. Samson, A. Kotarba, I. Gressel, B. Grzybowska-Świerkosz "The Opposite Effects of Potassium Additive on the Catalytic Performance in Oxidative Dehydrogenation of C_2-C_4 Alkanes over VO_x/Oxide Support Catalysts", 7th European Congr. on Catalysis EuropaCat-7, Sofia 2005

41. A. Klisińska, K. Samson, A. Kotarba, I. Gressel, B. Grzybowska-Świerkosz "The Positive and Negative Effects of Potassium Additive on Catalytic Properties in Oxidative Dehydrogenation of Lower Alkanes on VO_x/oxide Supports Satalysts", 2nd Int. School - Conference on Catalysis for Young Scientists, Novosibirsk-Autai, 2005

42. W. Kobyzewa, M. Derewiński "Transformacja mezo- i makroporowatych glinokrzemianów zeolitowych materiały zawierające domeny mikrokrystaliczne zeolitu Y", 12. Forum Zeolitowe, Ciążeń 2005

43. M. Kolasińska, P. Nowak, A. Trybała, P. Warszyński "Characteristics of Polyelectrolyte Multilayers: Compasison of PAH/PSS and Chitosan/Alginate Systems", Int. Symp. "Particles and Polyelectrolytes at Interfaces", Kraków 2005

44. M. Kolasińska, R. Krastev, P. Warszyński "Characteristics of Polyelectrolytes Multilayers, Effect of PEI Anchoring Layer and Post-treatment after Deposition", 19th Conf. European Colloid and Interface Soc., Geilo 2005

45. M. Kolasińska, A. Trybała, P. Warszyński "Ellipsometric Study and Wetting Properties of Polyelectrolytes Multilayers. Comparison of PAH/PSS and Chitosan/Alginate Systems", 17th European Chemistry at Interfaces Conf. ECIC XVII, Loughborough 2005

46. M. Kolasińska, P. Warszyński "Properties of Polyelectrolyte Films Deposited on Macroscopic Surfaces", Symp. Interfacial Phenomena, Surfactants and Dispersed Systems, Lublin 2005

47. J. Korecki, N. Spiridis, T. Ślęzak, M. Zając, K. Freindl "Growth and Oxidation of Nanostructures at the Metal Oxide Interface", DYNASYNC Mid-term Assessment Meeting, Grenoble 2005

48. A. Kowal, P. Olszewski, D. Tripković, R. Stevanović "Nanoscale Topography of GC/Pt-C and GC/Pt-Ru-C Electrodes Studied by Means of STM, AFM and XRD Methods", YUCOMAT 2005, Herzeg Novi, 2005

49. M. Krasowska, K. Małysa "Role of Gas Presence at Hydrophobic Solid Surface in Formation of the Three-phase Contact", Scientific Conf. Surfactants and Dispersed Systems in Theory and Practice SURUZ, Polanica Zdrój 2005

50. M. Krasowska, K. Małysa "Gas Nucleation and Formation of the Three Phase Contact at Hydrophobic Solid Surface by the Rising Bubble", Symp. Interfacial Phenomena, Surfactants and Dispersed Systems, Lublin 2005

51. M. Krzan, S. Cohen-Addad, R. Höhler "Rheology and Stability of Particle Laden Foams", 17th European Chemistry at Interfaces Conf. ECIC XVII, Loughborough 2005

52. M. Krzan, J. Zawała, M. Krasowska, K. Małysa "Bubble Motion as Method of Detection of Organic Contaminations in Water", Proc. 4th Int. Conf. "Oils and Environment" AUZO 2005, Gdańsk 2005

53. A. Kubacka, E. Włoch, Z. Olejniczak, V. Cortés Corberán, R. X. Valenzuela, A. Fuerte, B. Sulikowski "Functionalisation of Propane on Mesoporous Molecular Sieves", 7th European Congr. on Catalysis EuropaCat-7, Sofia 2005

54. M. Kubo, Y. Sasaki, K. Chiba, P. Qiang, S. A. Rajjak, H. Tsuboi, M. Koyama, E. Brocławik, K. Akutsu, M. Hirota, M. Kitada, H. Hirata, A. Miyamoto "Tight Binding Quantum Chemical Molecular Dynamics Approach to the Formation Dynamics of Hydrogen by the Chemical Reactions of Vibrationally Excited Water on Si Surfaces", 229th American Chem. Soc. National Meeting, San Diego 2005

55. K. Małysa "Scientific Network SURUZ – Aims and Current State", Scientific Conf. Surfactants and Dispersed Systems in Theory and Practice SURUZ, Polanica Zdrój 2005

56. K. Małysa "Dynamics of Bubble Collision with Different Interfaces", Symp. Interfacial Phenomena, Surfactants and Dispersed Systems, Lublin 2005

57. K. Małysa, M. Krzan, M. Krasowska "Dynamic Effects in Formation of the Disspersed Systems", 17th European Chemistry at Interfaces Conf. ECIC XVII, Loughborough 2005

58. P. Nowak, R. P. Socha "Metal Sulfides’ Oxidation in Flotation Wastes – the Fate of Sulfide Sulfur”, Konf. Fizykochemiczne Problemy Mineralurgii, Wisła 2005

59. A. Pacuła, K. Pamin, A. Kozłowska, J. Komorek, E. M. Serwicka "Montmorillonit – naturalny minerał warstwowy jako nośnik heteropolikwasów", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

60. A. Pacuła, K. Pamin, J. Kryściak-Czerwenka, Z. Olejniczak, R. Dula "Montmorillonite as Supports for Heteropolyacids", Int. Symp. Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities, Kraków 2005

61. K. Pamin, J. Połtowicz, J. Haber "Cycloalkanes Oxidation with Molecular Oxygen Catalysed by Encapsulated Metallosalen Complexes", 7th European Congr. on Catalysis EuropaCat-7, Sofia 2005

62. K. Pamin, J. Połtowicz, E. Tabor, J. Haber "Cycloalkanes Oxidation with Molecular Oxygen Catalyzed by Encapsulated Metallosalen Complexes", Séminaire Hors-Ville en Chimie 1, Villars sur Ollon 2005

63. K. Pamin, J. Połtowicz, D. Mucha, J. Haber "Effect of Cobalt Counter-cation on Catalytic Properties of Tungstophosphoric and Molybdophosphoric Acids", 48. Zjazd PTChem i SITChem, Poznań 2005

64. T. Pańczyk, W. Rudziński "Współczynnik przyklejenia w świetle Statystycznej Teorii Transportu Międzyfazowego", 48. Zjazd PTChem i SITPChem, Poznań 2005

65. G. Para, E. Jarek, P. Warszyński "Hofmeister Series Effects in Adsorption of n-Alkyl Trimethyl Ammonium Bromide Cationic Surfactants at Fluid Interfaces", 19th Conf. European Colloid and Interface Soc., Geilo 2005

66. G. Para, E. Jarek, P. Warszyński "Hofmeister Series of Anions and Adsorption Cationic Surfactants at Fluid Interfaces", 3rd Thermodynamics Polish-French Days, Carry le Rouet 2005

67. K. Parliński, P. T. Jochym, J. Lazewski, A. M. Oleś, P. Piekarz, M. Sternik, J. Korecki "Ab initio Phonon Calculations on Multilayers, Crystal Surfaces and Crystals with Heavy Elements", PSIK 2005, Schwäbisch Gmünd 2005

68. J. Połtowicz, K. Pamin, J. Haber "Fluorous Biphase Catalysis-Macrocyclic Complexes with Fluorous Ponytails as Catalysts in Epoxidation of Alkenes", Séminaire Hors-Ville en Chimie 1, Villars sur Ollon 2005

69. J. Połtowicz, K. Pamin, E. Tabor, J. Haber "Pernitrometalloporphyrins with Fluorous Ponytails as Catalysts in Epoxidation of Alkenes", Int. Symp. on Fluorous Technologies, Bordeaux 2005

70. J. Połtowicz, K. Pamin, E. Tabor, J. Haber "Fluorowa kataliza dwufazowa – Metaloporfiryny kobaltu jako katalizatory epoksydacji olefin", 48. Zjazd PTChem i SITChem, Poznań 2005

71. A. Pomianowski "Open Systems", Scientific Conf. Surfactants and Dispersed Systems in Theory and Practice SURUZ, Polanica Zdrój 2005

72. J. Poźniczek, A. Micek-Ilnicka, A. Lubańska, A. Bielański "Synteza ETBE na katalizatorach: $H_6P_2W_{18}O_{62}$ / TiO_2 i $H_6P_2W_{18}O_{62}$ / SiO_2", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

73. R. Rachwalik, Z. Olejniczak, B. Sulikowski "Transformacje węglowodorów alkiloaromatycznych na modyfikowanych ferierytach", 12. Forum Zeolitowe, Ciążeń 2005

74. R. Rachwalik, Z. Olejniczak, B. Sulikowski "Właściwości katalityczne modyfikowanych ferierytów w procesach transformacji węglowodorów alkiloaromatycznych", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

75. S. A. Rajjak, M. Ismael, H. Tsuboi, M. Koyama, M. Kubo, C. A. Del Carpio, E. Brocławik, K. Nishijima, T. Terasaki, A. Miyamoto "Interaction of Antimigraine Agents with Cytochrome P450 3A4: Modelling Biotransformation Reactions by Combined QM/MM Methods" 125th Annual Meeting of Pharmaceutical Society of Japan, Tokyo 2005

76. J. Rodakiewicz-Nowak "Biosensors – the Future of Medical Analysis", SURUZ Cluster Meeting, Pawłowice-Wrocław 2005

77. J. Rodakiewicz-Nowak "Catalytic Activity of Ligninolytic Enzymes in Water in Oil Microemulsions", Scientific Conf. Surfactants and Dispersed Systems in Theory and Practice SURUZ, Polanica Zdrój 2005

78. M. Ruszel, B. Grzybowska, I. Gressel, A. Klisińska "$Au/M^{II}Cr_2O_4$ Spinels as Catalysts in Oxidation of CO and C_3 Hydrocarbons", 2nd Int. School - Conference on Catalysts Design for Young Scientists, Novosibirsk-Autai, 2005

79. M. Ruszel, B. Grzybowska, A. Palej, M. Łaniecki, M. Wójtowski "Oxidation of CO and C_3H_6 on Au/Ti-SBA-15 Catalysts", 12. Forum Zeolitowe, Ciążeń 2005

80. D. Rutkowska-Żbik, M. Witko, G. Stochel "DFT Studies on Ligand Binding Properties of Cobalamins", Workshop on Modeling Interactions in Biomolecules II, Prague 2005

81. P. Sarv, M. Derewiński, I. Heinmaa "Active Site Reinsertion and Redistribution in B,Al-Beta Zeolite Effected by Boron Removal", 3rd FEZA Conf. Prague 2005

82. E. M. Serwicka "Educational Opportunities in the Field of Catalysis in Poland", ACENET ERA-NET Meeting, Kraków 2005

83. C. Simon, P. Petitjean, J. Beylich, C. Dejugnant, G. Para, P. Warszyński "Preparation of PAH/PSS Microcapsules by Membrane Emulsification", Int. Symp. Particles and Polyelectrolytes at Interfaces", Kraków 2005

84. N. Spiridis "Fe Growth on W(110)", DYNASYNC Meeting, Budapest 2005

85. N. Spiridis, J. Barbasz, K. Freindl, J. Korecki "Gold Adsorption on Fe_3O_4(001)", MDN & DYNASYNC Workshop on Dynamics in Nanoscale Systems, Raach am Hochgebirge 2005

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177. J. Zawała, M. Krzan, M. Krasowska, K. Małysa "Influence of the Molecular Structure of Surfactant on Bubble Local Velocities", 17th European Chemistry at Interfaces Conf. ECIC XVII, Loughborough 2005

178. V. Zazhigalov, J. Stoch, A. Kowal, M. Mikołajczyk, S. Kirilov, I. Romanova "Aktywność katalizatorów Cu-Ce-O w utlenianiu tlenku węgla", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

179. V. Zazhigalov, J. Stoch, A. Kowal, M. Mikołajczyk, J. Podobiński "Activity of Ce-Cu-O Catalysts in Carbon Monoxide Oxidation" Int. Symp. Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities, Kraków 2005

180. V. Zazhigalov, Y. Zaitsev, D. Brazhnyk, I. Bacherikova, J. Stoch, A. Kowal, V. Strelko "The Peculiarities of H_2S and CO Oxidation on Carbon Catalysts Containing Nanoclusters of Vanadium and Cobalt Oxides on Their Surface", Int. Conf. on Carbon, Gyeongju 2005

181. A. Zikánova, P. Hrabánek, L. Brabec, K. Kovandová, M. Kočiřik, B. Bernauer, V. Krystl, M. Derewinski "Transport Related Texture Characteristics of Composite Zeolite Based Membranes", Int. Symp."Catalytic Processes on Advanced Micro- and Mesoporous Materials", Nessebar 2005

182. M. Zimowska, M. Bazarnik, K. Bahranowski, A. Michalik, E. M. Serwicka, Z. Olejniczak "Synteza i właściwosci strukturalne aluminowanych mezoporowatych sit molekularnych typu FSM", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

183. M. Zimowska, J. Camra, B. Borzęcka-Prokop, J. Wagner, J. Dziedzic, M. Najbar "Ewolucja powierzchni katalizatora 2% wag. Rh/Al_2O_3, otrzymanego metodą zol-żel, w czasie obróbki termicznej w warunkach utleniających i redukujących", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

184. M. Zimowska, R. Dula, R. Janik, A. Michalik, T. Machej, E. M. Serwicka "Układy typu mieszanych tlenków Cu-Mn jako katalizatory w reakcji całkowitego spalania toluenu", 37. Ogólnopolskie Kolokwium Katalityczne, Kraków 2005

185. M. Zimowska, R. Dula, A. Michalik, R. Janik, T. Machej, E. M. Serwicka "Cu-Mo Oxides Derived from Layered Inorganic Precursors as Catalysts for the Complete Oxidation of Toluene", 7th European Congr. on Catalysis EuropaCat-7, Sofia 2005

186. M. Zimowska, A. Michalik, R. Janik, T. Machej, E. M. Serwicka "Catalytic Combustion of Toluene over Mixed Cu-Mn Oxides", Int. Symp. on Air Pollution Abatement Catalysis, Kraków 2005

187. M. Zimowska, A. Michalik-Zym, R. Janik, T. Machej, E. M. Serwicka "Cu-Mn Mixed Oxide Systems for Removal of VOCs: from Precursors to Catalysts", Int. Symp. Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities, Kraków 2005

188. M. Zimowska, A. Michalik-Zym, I. Stefanowicz-Pięta, R. Janik, T. Machej, Z. Czuła, E. M. Serwicka "Highly Efficient Cu-Mn Mixed Oxide Catalysts for Total Oxidation of Toluene", 48. Zjazd PTChem i SITPChem, Poznań 2005

LECTURES IN SCIENTIFIC INSTITUTIONS AND SOCIETIES

1. Z. Adamczyk "Colloids as Universal Systems for Studying Adsorption", (Universite de Geneve)

2. M. Derewiński "Siting and Distribution of Al in TON and BEA Zeolites", (Laboratoire SIEN, CNRS 7142, Universite Pierre et Marie Curie, Pari VI)

3. M. Derewiński "Catalytic Cracking", (Laboratoire de Materiaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 ENSCM/CNRS, Montpellier)

4. J. Haber, T. Machej, J. Kryściak, J. Janas, H. Sadowska "The Role of Support in Catalysts for Oxidation of Nitromethane", (Université Pierre et Marie Curie, Paris VI)

5. J. Korecki "Fonony w nanostrukturach" (Seminar of Solid State Physics, Technical University AGH, Kraków}

6. A. Kowal "Application of STM and AFM Techniques for the Investigation of Corrosion Processes and Materials Protection", (CENIM-CSIC, Madrid)

7. A. Kowal "Badania nanostruktur na powierzchni metali i tlenków metodą AFM, STM i XRD", (Central Laboratory of Batteries, Poznań)

8. A. Kowal "STM and AFM Observations of Metal Corrosion" (Serbian Society of Electrochemistry, Belgrade)

9. A. Kowal, N. Matić, T. Vidaković, D. Mucha, M. Kopczyk "Nickel Electrodes with Deposited Ag Clusters (Ni/[Ag]cl) Characterized by Means of AFM, STM, XRD and Electrochemical Methods" (Electrochemistry Group, Brookhaven National Laboratory)

10. P. Nowak "Pyrite Oxidation in Aqueous Environment – Can We Avoid the Formation of Sulfates?" (Geological Survey of Finland, Laboratory of Mineral Processing, Outopumpu)

11. P. Nowak, R. P. Socha "Flotation Wastes as a Potential Source of the Environment Contamination – Column Tests of the Zn-Pb Wastes", (Institute of Orogen Mechanics PAS, Kraków)

12. W. Rudziński, T. Pańczyk "Pożegnanie XX-wiecznych teorii kinetyki adsorpcji" (Lublin Branch of Polish Physical Society, Lublin)

13. E. M. Serwicka "Mesoporous Supports as a Tool for Controlling Catalytic Performance of Metalloporphyrins" (School of Chemistry, University of Nottingham)

14. E. M. Serwicka "Hydrotalcite-derived Catalysts in Environmental Catalysis" (School of Chemistry, University of Nottingham)

15. P. Weroński, Z. Adamczyk, B. Siwek, K. Jaszczółt "Monte Carlo Random Sequential Adsorption" (Center for Nonlinear Studies, Los Alamos National Laboratory)

16. P. Weroński, Y. Jiang, S. Rasmussen "Molecular Dynamics Study of a Small PNA Molecule in a Lipid-Water System", (Center for Nonlinear Studies, Los Alamos National Laboratory)

17. M. Witko "Oxygen at V_2O_5 Surface- Quantum Chemical Studies" (Institute of Catalysis Siberian Branch RAN, Novosibirsk)

18. M. Zimowska "Research Profile of Institute of Catalysis and Surface Chemistry, Research Group Clays, Mesoporous Oxides, Nanostructures" (Institute of Chemical and Engineering Sciences, Singapore)

LECTURES FOR STUDENTS AND Ph.D. STUDENTS

1. E. Brocławik "Applied Quantum Chemistry", lectures in the cycles "New Materials" and "Theoretical Chemistry and Numerical Mathods", Faculty of Chemistry, Jagiellonian University, 30 hours

2. E. Brocławik "Quantum Material Science", lectures for M.Sc. students, Department of Applied Chemistry, Tohoku University, Sendai, 30 hours

3. M. Derewiński "Introduction to Infrared and Raman Spectroscopy", lectures for Ph.D. students of International Postgraduate Studies ICSC PAS, 4 hours

4. A. Drelinkiewicz "Inorganic Chemistry", lecture and seminars for second course students, Faculty of Chemistry, Jagiellonian University, 90 hours

5. B. Grzybowska-Świerkosz "Fundamentals of Heterogeneous Catalysis" lectures for Ph.D. students of International Postgraduate Studies ICSC PAS, 25 hours

6. J. Gurgul "Electron Spectroscopy for Chemical Analysis", lectures for Ph.D. students of International Postgraduate Studies ICSC PAS, 2 hours

7. B. Jachimska " DLS Method for Colloidal Particle Dimension Measurements", lectures in the cycles "Instrumental Analytic Methods", lecture for fourth course students, Faculty of Materials Engineering and Ceramics, Technical University AGH, 2 hours

8. B. Jachimska "Laser Doppler Velocimetry – Measurements of Electrophoretic Mobility of Colloidal Particles", lecture for fourth course students, Faculty of Materials Engineering and Ceramics, Technical University AGH, 2 hours

9. J. Korecki, didactic pensum, Technical University AGH

10. J. Korecki, lectures for Ph.D. students of International Postgraduate Studies ICSC PAS

11. A. Kowal, seminar and laboratory "AFM and STM Techniques", Institute of Electrochemistry ICTM, University of Belgrade, 36 hours

12. P. Nowak "Current Problems in Electrochemistry", lecture for students, Faculty of Chemistry, Jagiellonian University, 15 hours

13. P. Nowak "Chemistry" and "Environmental Chemistry", lecture for students, School of Environment Protection, Radom (Miechow Branch), 40 hours

14. E. M. Serwicka "Elektron Paramagnetic Resonance", lecture and laboratories for Ph.D. students of International Postgraduate Studies ICSC PAS, 6 hours

15. B. Sulikowski "Solid State Chemistry: Outlines of Physicochemistry of Aluminosilicates and Zeolites", lecture and exams for fourth course students, Faculty of Engineering and Chemical Technology, Technical University, Kraków, 10 hours

16. B. Sulikowski "Physical Chemistry", lectures for Ph.D. students of International Postgraduate Studies ICSC PAS, 44 hours

17. M. Witko – seminars for Ph.D. students of International Postgraduate Studies ICSC PAS, 32 hours

SCIENTIFIC SEMINARS IN THE INSTITUTE

LECTURES OF INVITED GUESTS

1. S. Bem (Nitrogen Works S.A., Tarnów) "Kierunki działalności rozwojowej w Zakładach Azotowych w Tarnowie-Mościcach S.A."

2. V. Cores Corberan (Institute of Catalysis and Petroleochemistry CSIC, Madrid) "Bimodal Mesoporous Catalysts for Selective Oxidation of Isobutane" [lecture of CatColl Centre of Excellence]

3. U. Domańska-Żelazna (Faculty of Chemistry, Warsaw University) "Ciecze jonowe – nadzieja nowych technologii"

4. M. Ekiel-Jeżowska (Institute of Fundamental Problems of Technics PAS, Warsaw) "Oddziaływania hydrodynamiczne a współczynniki transportu zawiesin"

5. J.-B. d'Espinose de Lacaillerie (Ecole Supérieure de Physique et de Chimie Industrielles) "Surface Modifications of Alumina During the Preparation of Molybdenum Based Catalysts: a Local Approach by Solid-state NMR"

6. J. Heider (Institut für Microbiologie und Genetic, Darmstadt) "New Biochemical Principles from Anaerobic Metabolism of Ethylbenzene and Toluene" [lecture of CatColl Centre of Excellence]

7. J. Hennel (Institute of Nuclear Physics PAS, Kraków) "Teoria falek i jej zastosowanie do redukcji szumów i kompresji danych"

8. M. Hunger (University of Stuttgart) "Basic Principles and Applications of Solid-state NMR. Part I" [lecture of EU Project ToK-Cata]

9. M. Hunger (University of Stuttgart) "Basic Principles and Applications of Solid-state NMR. Part II" [lecture of EU Project ToK-Cata]

10. M. Hunger (University of Stuttgart) "In situ Spectroscopy in Heterogeneous Catalysis"

11. G. Koper (Delft University of Technology) "Slip and Friction in Liquid Flow over Solid Surfaces" [lecture of CatColl Centre of Excellence]

12. R. Krastev (Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Potsdam) "X-Ray and Neutron Reflectometry in Studies of Interfaces" [lecture of CatColl Centre of Excellence]

13. H. Lyklema (University of Agriculture, Wageningen) "Colloid Interaction Beyond DLVO: Gouy-Stern Layers, Regulation and Hetero-Interactions" [lecture of CatColl Centre of Excellence]

14. H. Lyklema (University of Agriculture, Wageningen) "On the Interpretation of Electrokinetic Potentials" [lecture of CatColl Centre of Excellence]

15. J. A. Mielczarski (Institut National Polytechnique de Lorraine, Nancy) "Composition and Structure of Surface Layers in Naniscale"

16. E. Mileva (Institute of Physical Chemistry BAS, Sofia) "Amphiphiloic Nanostructures in Fluid Media" [lecture of CatColl Centre of Excellence]

17. J. Nalaskowski (University of Utah, Salt Lake City) "Application of Atomic Force Microscopy in Fundamental Studies of Flotation Separation Systems"

18. R. Olindo (Technische Universität, Munich) "Butane Isomerization on Sulfated Zirconia: Reaction Mechanism and Key Component for Active Sites" [lecture of CatColl Centre of Excellence]

19. M. W. Radny (University of Newcastle, Australia) "Atomowe domieszkowanie powierzchni Si(001) – praktyka STM i Symulacja DFT" [lecture of CatColl Centre of Excellence]

20. M. Rogalski (University of Metz) "Thermodynamic Properties of Nanoparticles Containing System" [lecture of CatColl Centre of Excellence]

21. M. Stadler (Veeco Instruments, Germany) "New Developments in SPM" [lecture of CatColl Centre of Excellence]

22. D. Stępiński (Polish Society of Arterial Hypertension) "Profilaktyka nadciśnienia tętniczego i chorób układu krążenia"

23. A. Witko (Papal Teological Academy, Kraków) "Boże Narodzenie w sztuce" [Christmas lecture]

LECTURES OF INSTITUTE STAFF

1. A. Drelinkiewicz "Układy Pd-polimery, własciwosci fizykochemiczne i katalityczne"

2. R. Dula, R. Janik, T. Machej, E. M. Serwicka, J. Stoch "New Mn-Containing Catalytic Materials for the Total Combustion of Toluene"

3. L. Góra "Zeolite Membranes in Catalytic Applications" [lecture of EU Project ToK-Cata]

4. W. Łasocha "Nowe metody dyfraktometrii proszkowej – metoda czy konieczność?"

5. G. Para "Adsorpcja jonowych związków powierzchniowo aktywnych na swobodnej powierzchni roztworu w obecności elektrolitów"

6. R. Tokarz-Sobieraj "DFT Description of Molybdenum Based Catalysts" [lecture of CatColl Centre of Excellence]

7. P. Weroński "Modelowanie nieodwracalnej adsorpcji koloidów z zastosowaniem techniki MCRSA"

8. P. Warszyński "Life after CatColl" [lecture of CatColl Centre of Excellence]

LECTURES OF "OPEN DAY" OF THE INSTITUTE

1. Z. Adamczyk "Małe jest piękne, czyli co mogą koloidy"
2. A. Bielański "Wodór - przyjazne dla środowiska paliwo przyszłości"
3. J. Haber "Chemia – przekleństwo czy błogosławieństwo ludzkości?"
4. J. Korecki "Czy można zobaczyć atomy?"
5. D. Rutkowska-Żbik "O Albercie Einsteinie, czyli jak jeden naukowiec, w jeden rok zrewolucjonizował wiedzę o świecie"
6. M. Szaleniec "1000 sposobów na nieśmiertelność"

POPULARIZED SCIENTIFIC LECURES

1. J. Korecki "Promieniowanie synchrotronowe", obóz dla dzieci szczególnie uzdolnionych, Warszawa-Świder 2005
2. R. Kozłowski "Cement romański – tajemnice krakowskich kamienic", Festiwal Nauki, IKiFP PAN, Kraków 2005
3. E. Serwicka "Goethe – poeta czy naukowiec?", Festiwal Nauki, IKiFP PAN, Kraków 2005
4. M. Szaleniec "Alchemia - wiedza tajemna, magia, czy nauka?", Festiwal Nauki, IKiFP PAN, Kraków 2005
5. J. Szaleniec, M. Szaleniec "Język Alchemii", Krakon 2005, Kraków 2005
6. P. Warszyński "Nano- i mikrocząstki w naszym otoczeniu", Otwarty Uniwersytet Techniczny AGH
7. M. Zembala "Koloidy, czyli fascynujący świat małych cząstek", Festiwal Nauki, IKiFP PAN, Kraków 2005

SCIETIFIC DEGREES AND TITLES AWARDS

DOCTORS

1. R. Gryboś "Influence of Dopants and Support on Catalytic Properties of Vanadium Pentoxide. Quantum Chemical Modelling"
2. A. Klisińska "Effect of Additives to VO_x/Oxide Support Catalysts on Their Physicochemical and Catalytic Properties in Oxidative Dehydrogenation of Lower Alkanes"

3. R. Rachwalik "Transformacje węglowodorów alkiloaromatycznych na modyfikowanych katalizatorach zeolitowych"

4. D. Rutkowska-Żbik "Ligand-Binding Properties of Selected Transition Metal Tetrapyrrolic Complexes. Implications for Catalysis and Bioinorganic Chemistry"

SCIENTIFIC CONFERENCES ORGANIZED BY THE INSTITUTE

1. ACENET ERA-NET Meeting, Kraków, February 16-17, 2005 (E. M. Serwicka)

2. 37. Ogólnopolskie Kolokwium Katalityczne, Kraków, March 15-18, 2005 (B. Sulikowski)

3. KSV Instruments Ltd, CATCOLL and SURUZ Workshop "Technologies for Characterization of Liquid and Solid Interfaces", Kraków, May 18-19, 2005 (P. Warszyński)

4. International Symposium "Particles and Polyelectrolytes at Interfaces", May 22-25, 2005 (P. Warszyński)

5. SURUZ Network Meeting, Kraków, July 15, 2005 (K. Małysa)

6. DYNASYNC Mid-Term Assessment, Grenoble, September 20-24, 2005 (J. Korecki)

7. ACENET ERA-NET Meeting, Kraków, October 26, 2005 (E. M. Serwicka)

8. DYNASYNC Scientific Meeting, Kraków, November 8-9, 2005 (J. Korecki)

9. "The Last CATCOLL Meeting" and SURUZ Young Scientists Workshop, Kraków, November 14-15, 2005 (P. Warszyński, K. Małysa)

10. International Symposium "Catalysis on Oxide-type Materials. Theory and Experiment: Share Needs and Capabilities", Kraków, November 17-19, 2005 (B. Grzybowska-Świerkosz, M. Witko)