JERZY HABER INSTITUTE
OF CATALYSIS
AND SURFACE CHEMISTRY
POLISH ACADEMY OF SCIENCES

DETAILED RESEARCH REPORT

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Statutory research

Nanotechnology as the Basis of New Catalytic Materials

Textural and Structural Properties of Molecular Sieve Nanoparticles

(Assoc. Professor Mirosław Derewiński DSc, Katarzyna Onik MSc, Jerzy Podobiński MSc)

Steric constraints to diffusion and/or access of reactants molecules to the active sites confined in micropores, as well as formation and/or diffusion of the target products is a main reason of exclusion molecular sieves (zeolites) as effective catalyst for chemical transformation of larger molecules and for processes carried out in a liquid phase. In order to overcome mass transport limitations in zeolites several strategies have been developed. One of the routes proposed to synthesize more open hierarchically structured materials (micro/meso/macroporous) is assembly of zeolites nanocrystals (zeolite seeds, protozeolitic species, zeolite precursors). The ultra fine zeolite seeds are the species which are formed during the very first stages of synthesis of zeolites. Knowledge about conditions required for their formation, about their real structure, nature and strength of active sites, dependence of their properties on the size and chemical composition of the parent gel and about mechanism of their formation are of fundamental importance for understanding the mechanism of the zeolite crystal formation.

The synthesis of protozeolitic nanoclusters builded with joined Si and Al tetrahedra was carried out in the mild conditions (temperature below 50^{o}C) in presence of teterapropyl- (TPA^+) and tetraethylammonium (TEA^+) cations as templating agents. Conditions ensuring formation of ultra small, XRD amorphous, nanoparticles (below 10 nm) have been determined. The DLS and SEM and TEM techniques were used to determine their size and morphology. The obtained colloidal suspensions are stable and no aggregation of nanoparticles was observed during weeks. NMR studies of the early stages of synthesis confirmed that all Al atoms in nanoparticles are bonded to Si tetrahedra, thus can be involved in formation of acid centres. When Fe was used instead of Al as T atom isomorphously substituting silicon in the silica framework of the nanoparticle, more severe conditions were required for the formation of the zeolite nanoseeds. As a result of higher temperature applied, bigger nanoparticles were formed (c.a. 15 nm). The size of Al containing nanoparticles synthesized in the same conditions is c.a. 100 nm. Moreover, it has been found that a significant number of Fe atoms are not tetrahedrally coordinated, thus can not contribute to the formation of acid sites (Fe-OH-Si type). The structure of the organic template (TPA^+ or TEA^+) used did not influences significantly both size as well as morphology of the formed nanoparticles.

Structural Properties and Dynamics in Epitaxial Oxide and Metal Nanostructures Studied with Microscopic and Spectroscopic Techniques Radiation

(Professor Józef Korecki DSc, Nika Spiridis PhD, Jacek Gurgul PhD, Robert Socha PhD,
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[in cooperation with AGH University of Science and Technology])

Oxide and metallic nanostructures on W(110) imaged with LEEM. Low Energy Electron Microscope (LEEM) is a perfect tool to study in nano- and mesoscale surface processes such as nucleation or growth, adsorption/desorption and surface reaction. In contrast to scanning imaging techniques, LEEM offers real time imaging possibility connected with relatively large field of view (up to 150 μm) and high lateral spatial resolution (down to 3nm in the present instrument). Moreover, images and movies can be acquired 'live' at temperatures as high as 1200 ºC, both in real and reciprocal (diffraction) space, giving access to the kinetics of the studied process. First investigations using our new Elmitec LEEM III instrument included different nanostructure systems on W(110).

A. High temperature oxidation of the W(110). We studied formation of WO_2 oxide layers grown on the W(110) surface when the sample is annealed between 1000 K and 1500 K in oxygen atmosphere at 1×10^{-6} mbar oxygen pressure. Temperature induced structural phase transitions and the phase domain morphology was for the first time directly imaged for tungsten oxide both in real and reciprocal space (Fig.1). Domains of the row-like structures stabilized on the WO_2/W(110) surface can serve as a patterned template for the growth of iron nanostructures. Using LEEM, formation of such Fe-nanostructures was documented and their growth conditions were optimized.

B. Iron nanostructures on the W(110) surface. Ultrathin Fe films on W(110), if annealed at sufficiently high temperatures, form three dimensional islands with unusual magnetic properties, which might be related to a specific structure. We studied islands formed either by depositing or annealing Fe films (1.5, 2.5 and 5.0 ML) at elevated temperatures (300ºC – 700ºC). Selected area analysis revealed quantum size effects in reflectivity vs. energy dependence as a function of island lateral and vertical dimensions. The islands grow through the Ostwald ripening enhanced at high step density areas.

TiO_2 nanostructures on W(001)

Nanostructures were prepared by the oxidation of pre-deposited Ti layers at 600 ºC under controlled O_2 atmosphere and characterized by STM (Fig. 2), LEED and XPS. The system is an excellent material for model catalysts.

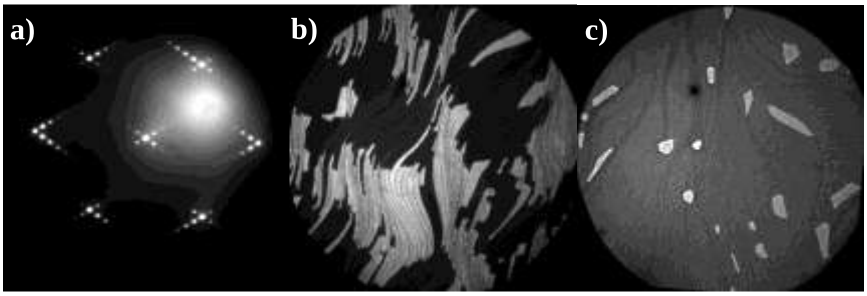


Fig.1. WO_2/W(110) imaged with LEEM: a) diffraction, b) dark field for a selected domain. FOV 10 μm. c) Islands formed by annealing of 1.5 ML Fe film.

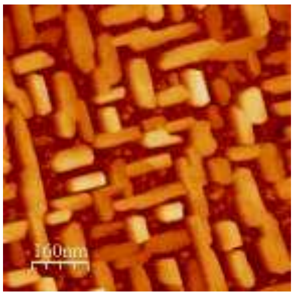


Fig.2. STM image of TiO_2 nanostructures on W(001). Average islands height is 3.5 nm

Nanomaterials Based on Layered Minerals

(Professor Ewa Serwicka-Bahranowska DSc, Małgorzata Zimowska PhD,
Alicja Michalik-Zym PhD, Roman Dula PhD, Elżbieta Bielańska PhD, Daria Napruszewska MSc)

Recently, we have synthesized and thoroughly characterized Laponite-based porous clay heterostructure (PCH-Lap). PCH-Lap is a high surface area (600-800 m^2/g) composite obtained from the synthetic layered silicate Laponite $Na_{0.7}[Si_8Mg_{5.5}Li_{0.3}O_{20}(OH)_4]$ and tetraethoxysilane (TEOS) as a silicon precursor, in the presence of surfactants as structure-directing agents. The aim of the present work was to generate acidic properties in such a material, in order to broaden the scope of its applications in catalysis. The method frequently used to introduce acidic function into the silicate structures is alumination, i.e. substitution of part of Si sites with Al. In this work two alumination procedures were employed: a) direct alumination, at the stage of PCH-Lap synthesis, by addition of appropriate amount of Al isopropoxide to TEOS, and b) post-synthesis alumination, by impregnation of PCH-Lap with an aluminium source (isopropoxide or nitrate) followed by calcination. For each method and each Al source samples of Si/Al = 40 and 10 were obtained. ^{27}Al MAS NMR spectra demonstrated that Al is present predominantly as tetrahedrally coordinated species, which confirmed the efficiency of the adopted alumination procedures. Investigation of the nitrogen adsorption/desorption at 77 K revealed qualitative differences between the isotherms of PCH solids aluminated by different methods. Post-synthesis aluminated PCHs are characterised by isotherms of IIb type and H3 hysteresis loop, i.e. are similar to the isotherm of the starting PCH-Lap. Impregnation with Al causes a fall of specific surface area, the more pronounced the more Al has been introduced. Direct alumination results in a change of the isotherm character to IVb type and H2 hysteresis loop, pointing to a different networking of pore system. The efficiency of alumination procedures as means of generating acidity was confirmed by the studies of ammonia TPD, which revealed the presence of acid centres not existing in the reference PCH-Lap material. The content of these centres grew with increasing Al substitution. The presence of Brønsted acidity was also demonstrated by FTIR study of pyridine adsorption and catalytic tests of ethanol conversion. In the latter, an increase of ethylene yield was observed for increasing degree of alumination.

Proton Ceramic Conductors Containing $BaCeO_3$ as Electrolytes for Solid Oxide Fuel Cells (SOFC)

Assoc. Professor Paweł Nowak DSc, Michał Mosiałek PhD, Grzegorz Mordarski PhD, Magdalena Dudek PhD [AGH University of Science and Technology])

The possibility of forming ceramic shapes from $BaCeO_3$ and $BaZr_{0.9}Y_{0.1}O_3$ based electrolytic materials by gel-casting method was investigated.

$BaCeO_3$, $BaCe_{0.9}Sm_{0.1}O_3$, $BaZr_{0.9}Y_{0.1}O_3$ (BZY), $Ca_{0.05}Ba_{0.95}Zr_{0.9}Y_{0.1}O_3$ (C5BZY), $Mg_{0.05}Ba_{0.95}Zr_{0.9}Y_{0.1}O_3$ (M5BZY), powders were prepared by a polymer complex method with the use of EDTA. The starting aqueous solutions were prepared by dissolving appropriate amounts of nitrates in distilled water according to required stoichiometry then the ammonium versenate solution was introduced. Further evaporation led to the formation a very porous, solid body. The prepared precursors were calcined at 600ºC, then at 1000ºC. The powders were ground in a rotary-vibratory mill, then shaped to the form of rods by gel casting method and sintered at 1500-1600°C for 2h.

Electrical and electrochemical properties of $BaCeO_3$, $BaCe_{0.9}SmO_3$, $Ba_{0.95}Mg_{0.05}Zr_{0.9}Y_{0.1}O_3$, $Ba_{0.95}Ca_{0.05}Zr_{0.9}Y_{0.1}O_3$ and $BaZr_{0.9}Y_{0.1}O_3$ electrolytes were examined by chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). At the experimental conditions relevant to the intermediate temperature solid oxide fuel cell the process of oxygen reduction at the interface metallic microelectrode|ceramic proton conducting electrolyte revealed complicated character. The conductivity of an investigated sample as a function of temperature and composition of the gas mixture is depicted in Fig. 1 and Table 1 below. The samarium doped $BaCeO_3$ reveal better electrical properties than undoped one. The chemical stability of $BaCeO_3$ based electrolytes in gas atmospheres involving H_2, CO, CO_2 is rather limited.

Measured electrical conductivity of C5BZT and M5BZT was higher than BZT. Prepared samples of electrolytes were tested in SOFC. The measured power density for SOFC with Ca or Mg doped BZT electrolytes were higher than for SOFC with BZY as an electrolyte. The results of the measurements showed that $Ba_{0.95}M_{0.05}Zr_{0.9}Y_{0.1}O_3$, M=Ca, Mg shapes formed by gel-casting method have better electrical and electrochemical properties than BZY to be applied as components in solid oxide fuel cells.

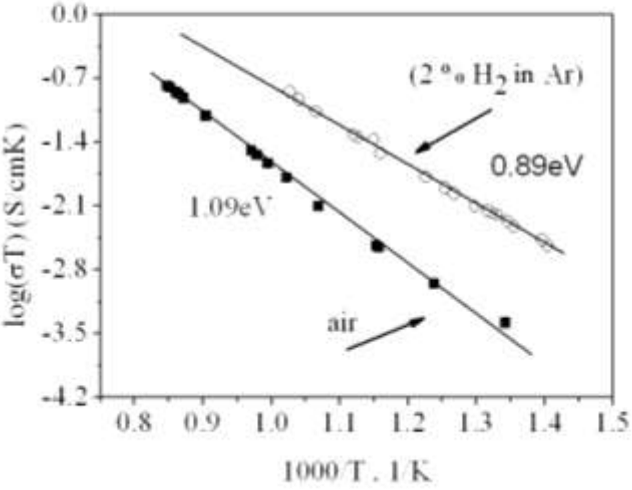


Fig. 1. Arrhenius plots for $BaCeO_3$ sample in different atmospheres.

Table 1. Conductivity and activation energy of examined electrolytes: A – Air, H – gas mixture of 98% Ar and 2% H_2

Material	σ (S/cm) 600°C	Ea, eV
$BaCeO_3$	$5.1\cdot10^{-6}$ (A) $1.2\cdot10^{-5}$ (H)	1.09 (A) 0.89 (H)
$BaCe_{0.9}Sm_{0.1}O_3$	$1.8\cdot10^{-3}$ (A) $7.1\cdot10^{-3}$ (H)	0.74 (A) 0.67 (H)

Composites Containing Nickel Compounds and Carbon Nanotubes Prepared with the Use of Synthetic Layered Minerals as Potential Electrode Materials for Direct Methanol Fuel Cells (DMFC)

(Assoc. Professor Paweł Nowak DSc, Aleksandra Pacuła PhD)

The object of the project was the synthesis of composites containing nickel compounds and carbon nanotubes and characterization of their physicochemical and electrocatalytic properties. The composites were prepared by heating synthetic hydrotalcite-like material containing Ni and Al (Ni/Al=2 or 3) at the temperatures of 600, 700 or 800^{o}C under the flow of argon saturated with CH_3CN. During synthesis both substrates were decomposed to metal oxides and carbon deposit. Moreover, nickel oxides were partially reduced to metallic nickel which catalysed the formation of carbon nanostructures. As-prepared composites were then treated with acid to remove partially metal/metal oxide component giving a series of acid-treated composites. Newly prepared composite materials were characterized by means of X-ray diffraction (XRD), thermal analysis (TG), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Electrocatalytic activity of the composites in the reaction of methanol oxidation were examined by cyclic voltammetry only in alkaline medium (0.1 M KOH) because the composites in acidic medium were. In the electrochemical measurements a glassy carbon electrode coated with the studied composite acted as a working electrode, whereas the $Ag/AgCl/KCl_{sat}$ electrode was used as a reference electrode.

The main part (60-67%) of the prepared composite consisted of metal/metal oxide material which contained crystalline particles of Ni, $NiAl_2O_4$ and amorphous Al_2O_3. The remaining part of the composites (33-40 %) was the carbon-rich material containing mainly carbon nanotubes. The composites derived from hydrotalcite-like material with Ni/Al=2 showed lower degree of crytallinity than those obtained with the use of hydrotalcite-like material with Ni/Al=3. Treating composites with acid lowered metal/metal oxide component content to 15-24%.

Among two series of composites, the most active catalysts for methanol oxidation reaction were as-prepared composites especially those derived from hydrotalcite-like material with Ni/Al=2. The samples prepared at lower temperature (600^{o}C) containing metallic nickel particles with smaller size, dispersed on more porous support were more active than those prepared at higher temperatures (700 and 800^{o}C), containing less dispersed nickel species. Treating as-prepared composites with acid resulted in lowering metallic nickel content and therefore diminished their electrocatalytic activity. Acid-treated composites in comparison to as-prepared composites had higher specific surface area showing higher specific capacitance.

Statutory research

Catalytic Processes for Sustainable Development

New Peroxo-compounds of Mo(VI), W(VI) i V(V) – Synthesis, Crystal Structure, and Physico-chemical Investigations

(Professor Wiesław Łasocha DSc, Dariusz Mucha PhD, Anna Szymańska MSc,
Katarzyna Luberda-Durnaś MSc, Marta Grzesiak MSc)

Our recent research are related to synthesis and structural studies of new peroxy compounds of Mo, W and V. Results obtained in the recent period, can be briefly summarized as:

1. Due to the observation that studied peroxo-molybdates of nicotinic acid, often contain the N-oxide groups (as a building blocks), series of syntheses using nicotinic acid N-oxide, as a substrate, were performed. It was found that such syntheses will be more reproducible and much shorter.
2. The crystal structure refinement of monoclinic: aqua-oxo-diperoxo-(pyridine-3-carboxylato-O)-molybdenum has been completed (single crystal study).
3. A number of syntheses of new peroxo compounds of Mo, W and V with 2,6-dicarboxypiridine acid have been performed. So far, we failed to isolate pure new phase in the larger quantities, the dominant product is the $[NH_4]_4\,[O\,(VO\,(O_2)_2\,(H_2O)_2)]$.
4. We have undertaken several attempts to obtain new diperokso-vanadates of **a**mino**p**ropane: 1-**ap**, 1,3-di**ap**, 1,2-di**ap**. The resulting compounds are investigated now by powder diffraction methods.
5. We have performed a number of attempts to synthesize new oxodiperoxovanadates of Li, Na, Rb and Cs. In the case of Rb we obtained orange-yellow crystals, which are now in the process of structural studies (single crystals), other compounds are studied by XRPD methods (powder diffraction). It was noted that factor disrupting synthesis process, was the impact of CO_2. Therefore, further crystallizations were performed in the desiccators, over the excess of strong bases, which significantly improved the purity of the phases obtained.
6. For peroxo-compounds of nicotinic acid, tests of catalytic oxidation have been initiated, they will carried out in the IC&SCh PAS.

Figure below shows the refined asymmetric unit (a), and the projection of the structure (**b**) of monoclinic compound: 'aqua-oxo-diperoxo-(pyridine-3-carboxylato-O)-molybdenum'

a) **b**)

Transformations of Aromatic and Terpene Hydrocarbons on Molecular Sieves of Different Acidity

(Professor Bogdan Sulikowski DSc, Ewa Włoc, PhD)

Growing demands of better catalysts (activity & selectivity) for the fine organic synthesis require detailed knowledge of physico-chemistry of systems used for contacts preparation. In our team we study therefore various zeolites, including composite materials. One of the zeolites exhibiting very interesting properties is ferrierite (FER), manufactured on an industrial scale. This aluminosilicate is useful for preparation of acidic and, as we have shown earlier, also redox type catalysts. Ferrierite has high topological density of framework T-sites (where T=Si, Al) and its structure consists of numerous 5- and 6-membered rings, giving rise to its high stability.

Two commercially available ferrierite type zeolites of different origin (Tosoh Corp. and Zeolyst Intern.) were studied. The catalysts were characterized by several methods, including NMR and IR. Ferrierite was transformed into a hydrogen form. The H-forms of ferrierite were characterized further, and particularly the type and amount of acid centres was assessed (quantitative NMR and IR), while their strength was estimated by sorption of CO. Acid sites on zeolites catalyze many reactions, e.g. isomerization, transalkylation and cracking. Transformations of α-pinene and limonene were chosen for our catalytic tests.

Terpenes encompass a large number of hydrocarbons with various structures. α-Pinene is one of the important monoterpene hydrocarbons used for the synthesis of raw materials as camphene, limonene and *p*-cymene. Limonene is one of the α-pinene transformation products. Catalytic transformation of α-pinene is nowadays carried out industrially using acidic TiO_2 contacts. The process has, however, some disadvantages, such as the low reaction rate coupled with corrosion of the equipment. We have therefore decided to develop other viable zeolite catalysts, containing acid sites and exhibiting micro- and mesoporous regular architecture. Our earlier studies led to the selection of a few zeolites for this purpose.

Transformations of α-pinene and limonene on H-forms of ferrierite from Tosoh and Zeolyst companies were studied. The process was carried out under mild conditions ($T<100^oC$) in the liquid-phase under atmospheric pressure. Camphene and limonene were the main products of α-pinene isomerization. Isomerization of α-pinene proceeded smoothly on the ferrierite catalysts, giving however different selectivity. Such behaviour was rationalised taking into account the course of the reaction of pure limonene and the different acidic properties of the catalysts studied. Finally, it was shown that the initial rates of α-pinene transformations over FER-type materials exceeded those observed earlier for other catalytic systems, comprising sulphated zirconia and 12-tungstophosphoric heteropoly acid supported on silica.

Carbon Nanotubes as the Support for Heteropolyacid Catalysts

(Professor Adam Bielański DSc, Anna Micek-Ilnicka DSc, Urszula Filek MSc)

The aim of the research was to obtain and test the catalysts containing heteropolyacid $H_3PW_{12}O_{40}$ (HPW) supported on multiwalled carbon nanotubes (CNT). For this purpose dodecatungstophosphoric acid has been chosen as the strongest Keggin type heteropolyacid. Besides CNT dioxides of silicon and titanium were used as the supports. The supports were covered with the amounts of heteropolyacid corresponding to coverage with either 0.25 or 1.0 of monolayer. The symbols of prepared catalysts, the content of heteropolyacid (wt.%) and their specific surface areas (m^2/g) are given in the Table.

Supports specific surface area (m^2/g)	Catalysts HPW/layer/support	HPW content (wt.%)	Catalyst specific surface area (m^2/g)
SiO_2 517 m^2/g	HPW / 0.25 / SiO_2 HPW / 1.0 / SiO_2	38.0 62.0	222 110
TiO_2 264 m^2/g	HPW / 0.25 / TiO_2 HPW / 1.0 / TiO_2	24.0 0,56.0	14 12
carbon nanotubes 138 m^2/g	HPW / 0.25 / CNT HPW / 1.0 / CNT	14.2 39.3	78 52
---	pure HPW	100.0	6

The acid strength of the supported heteropolyacids was characterized by the enthalpy of irreversible sorption of ammonia $\Delta H_{irrev.}$ This enabled to propose the following sequence of heteropolyacids:

$$\text{HPW} > \text{HPW/0.25/SiO}_2 \cong \text{HPW/0.25/TiO}_2 > \text{HPW/1.0/CNT} > \text{HPW/0.25/CNT} \quad \text{(I)}$$

$$[-\Delta H_{irrev}] \quad 235 > 172 \cong 171 > 147 > 78 \text{ kJ(mol NH}_3)^{-1}$$

The lowest acid strength was exhibited by the catalysts supported on CNT, the highest one those unsupported and silica supported.

As catalytic test reaction gas phase dehydration of ethanol has been used. Below 90°C no catalytic reaction was observed. In the temperature range 90-130°C all catalysts behave in the same way independently of the support; at and above 150°C the conversion of ethanol was higher on the CNT supported catalyst than on the not supported heteropolyacid. Two products of ethanol dehydration were observed: diethyl ether, exhibiting highest selectivity at lowest investigated temperatures, and ethylene the concentration of which increased with the increasing temperature. At 190°C the following activities sequence of the catalysts was obtained:

$$\text{HPW/0.25/SiO}_2 > \text{HPW/0.25/CNT} > \text{HPW/0.25/TiO}_2 > \text{HPW}$$

It is seen that the highest activity (conversion) was exhibited by the silica supported catalyst. This fact suggests that it is the specific surface area of the catalyst which plays the predominant role in the series of investigated catalysts. Carbon nanotubes do not appear to be the best supports for heteropolyacids catalytically active.

Acidic Component Influence on Catalytic Properties of Hybrid Catalysts for Dimethyl Ether Synthesis

(Assoc. Professor Ryszard Grabowski DSc, Michał Śliwa PhD, Katarzyna Samson PhD, Małgorzata Ruggiero-Mikołajczyk PhD, Jan Mizera MSc)

The commercial montmorillonite K10 (K10) was used as an acidic component of bifunctional catalyst. The copper based catalysts were used as a metallic component. The modification of the montmorillonite by one monolayer of $H_3PW_{12}O_{40}\cdot 23.5\ H_2O$ tungstophosphoric acid (TPA) deposition was carried out by wetness impregnation method. The prepared acidic function is designated as TPA-K10. The bifunctional catalysts were obtained by physical mixture of the metallic functions and the acidic functions with the volume ratio equal to 2/1 and the grain size 0.64-1mm.

The montmorillonite modification with TPA changes the BET surface area of the support and pore distribution. Before modification, the BET surface area of montmorillonite K10 is 248 m^2/g while after TPA deposition its surface decreases to 95 m^2/g. In the both samples, the mesopores dominates with the maximum for the pores of 38 Å. The decrease in BET surface for TPA-K10, in comparison with montmorillonite K10, results from the decrease in pores amount and their volume. It can be stated that TPA deposition on the montmorillonite K10 surface leads to a small pores blockage and limits the availability of the pores with higher diameters.

Based on the UV-VIS analysis, the experimental amount of the deposited TPA was determined. For the both: pure TPA and TPA-K10 two absorption bands at 222 and 265 nm are visible in the UV-VIS spectra. The former one is due to charge transfer from terminal oxygen to tungsten in W=O and the latter one is assigned to charge transfer from bridge oxygen to tungsten in W-O-W. The presence of the same UV-VIS adsorption bands, in the case of pure TPA and TPA-K10 proves that TPA has been successfully deposited on the surface of the montmorillonite K10. The experimental amount of TPA, deposited during impregnation, was determined. It was revealed that total amount of TPA is sufficient to cover the surface of montmorillonite K10 only with 0.8 monolayer. This suggests uneven coverage by TPA what leads to the formation of TPA blocks of different height.

The acidity of montmorillonite K10, TPA-K10 and pure TPA was evaluated by FTIR measurements with pyridine (Py) adsorption as a probe molecule. The modification of montmorillonite K10 with TPA leads to the increase in the intensity of band at 1545 cm^{-1} and its position shift toward lower wave numbers. From the other hand, the band at 1454 cm^{-1} stays unaltered after deposition of TPA on the surface of the montmorillonite K10. The reason of these changes is that TPA exhibits only acidity of Lewis type and there is no band in area assigned for pyridine coordinately bonded with the aprotic sites for TPA. The increase in the intensity assigned to pyridine adsorbed on Brønsted acidic sites for TPA-K10 in comparison with montmorillonite K10 proves that acidity of TPA-K10 is higher than for the support. The increase in the acidity for TPA-K10 results from the higher concentrations of Brønsted acidic sites and higher strength as well.

The activity of hybrid catalysts can be enhanced by tuning of the acidic strength and the number of the acidic centers of acidic component. In the case of hybrid catalysts for which high concentration of unreacted methanol are observed in the by-products of STD process, the substitution of montmorillonite K10 with TPA-K10 leads to the increase in DME yield.

Ceramic Foam Catalysts

(Tadeusz Machej PhD, Łukasz Mokrzycki PhD)

This report is focused 1) on a ceramic foam catalyst carrier synthesis and 2) obtaining an active phase of a catalyst by microemulsion method, that can be used with the ceramic foam carrier.

Ceramic foams (reticulated ceramics) are three dimensional cellular structures with high porosity (80-90% void space). This class of materials has been developed as impurities filters but nowadays their application also as catalyst carriers is investigated. Ceramic foams posses some advantages when compared to honeycomb monoliths: i) wide range of foams' shapes is possible, ii) more torturous nature of porosity which improves reactant mixing and iii) better radial transport.

Here, the ceramic foam catalysts were prepared by a classic route proposed by Schwarzwalder. In this approach polyurethane foam is used as a skeleton/template (green body) which is being removed in a heating process. The polyurethane foams were provided as a free sample by INTERCHEMALL Co. The foams F10 and F20 (with 10 and 20 cells per square inch) were chosen for thIS synthesis procedure.

The inorganic substrates used in the synthesis procedure are: PURALOX (activated γ-Al_2O_3), silica (SiO_2, POCh), kaolin clay (Aldrich), Disperal S, phosphoric acid (POCh), water glass (POCh) and distilled water. Several samples with different kaolin, Puralox and/or Disperal S contents were prepared. The synthesis procedure consists of following steps: a) preparing a ceramic slurry, b) coating an open cell polymer foam with the slurry, c) removing excess of the slurry, d) drying coated foam at room temperature and then at 100°C, e) burning out the organics and sintering. The sintering process has been carried out under flow of air at 1050°C. The examples of polyurethane foam coated with dried ceramic slurry and ceramic foam after sintering are presented on Fig. 1.

Fig. 1. Polyurethane foam coated with ceramic slurry and dried at RT (left) and sintered ceramic foam (right)

The next element of the research task was the preparation of mixed oxide catalyst nanoparticles by water-in-oil microemlusion method. In this method three components are used in general. First is a water phase solution (chosen metal salt solution), next an oil phase (cycloheksane) and surfactant together with cosurfactant (Triton-X, heksanol). Three samples were obtained: a) ceria CeO2, b) ceria doped with 10% of manganese, and c) ceria doped with 5% of copper and 5% of manganese. The physicochemical characterization was accomplished by means of XRD, SEM and EDS techniques. In order to investigate the catalytic activity toluene combustion tests were performed in a gas flow reactor. It was proven that copper and manganese additives have increased the catalytic activity of samples studied.

Catalytic Activity and Physicochemical Properties of Anionic Macrocyclic Metallocomplexes on Liposomes

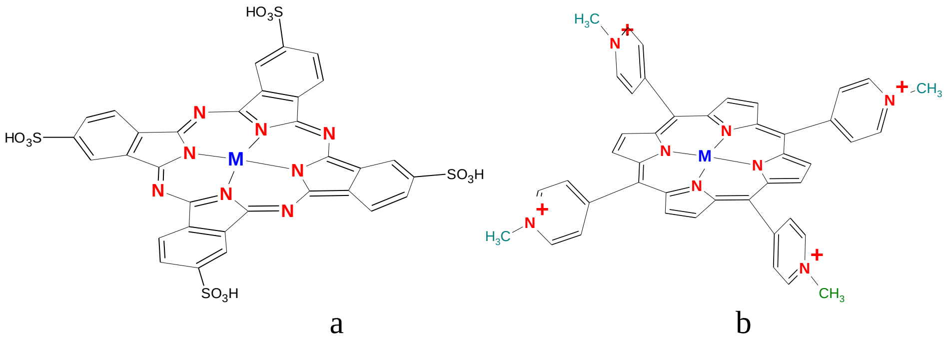
(Katarzyna Pamin PhD, Jan Połtowicz Połtowicz PhD, Robert Karcz MSc)

Synthetic metalloporphyrins and their analogues like metallophthalocyanines with polar groups such as sulfonic, carboxylic, amino, or ammonium groups are widely used as active and selective catalysts in olefins epoxidation and hydrocarbons hydroxylation.

Heterogenization of metallocomplexes substantially modifies the properties of these systems. In many cases it has been already shown that supported metallocomplexes can be more reactive and selective than unsupported ones. Liposomes are good candidates to immobilize macrocyclic metallocomplexes providing biomembrane properties and the specific hydrophylic/lipophilic environment. They are formed by amphiphilic molecules like phospholipids. Under certain physical conditions phospholipids form a lipid bilayer in the shape of the sphere which are hollow inside and contain liquid in which they were formed.

Synthesized metallocomplex-liposome hybrids were characterized using several methods: UV-Vis spectroscopy, zeta potential and Dynamic Light Scattering (DLS) measurements, optical and fluorescence microscopy.

The main goal of our work was to design and to synthesize metallocomplexes immobilized in/on liposomes in order to study their catalytic activity in the epoxidation of cyclohexene by NaOCl as oxygen donor. The following anionic metallophthalocyanines MnPcS, FePcS, CoPcS, NiPcS, CuPcS, anionic metalloporphyrins MnTPPS, FeTPPS, CoTPPS (Fig. 1) and these metallocomplexes immobilized in/on liposomes were applied as catalysts.



a

b

Fig. 1. The structure of studied catalysts: a. MPcS, where M=Mn, Fe, Co; b. MTPPS, where M=Mn, Fe, Co, Cu, Ni

Three reaction products: cyclohexene epoxide, 2-cyclohexen-1-one and 2-cyclohexen-1-ol, were obtained in the epoxidation of cyclohexene with NaOCl in the presence of phthalocyanine and porphyrin metallocomplexes. The most active catalyst among metallophthalocyanines was CuPcS complex and the following order of activity for metallophtalocyanine was established:

CuPcS > MnPcS > FePcS > CoPcS > NiPcS

All three metalloporphyrins demonstrated quite similar activity with each other which was approximately half of the activity of the most active metallocomplexes. Immobilization of metallocomplexes on liposomes resulted in the substantial increase of the catalytic activity for all the tested catalysts.

Statutory research

Adsorption and Catalytic Processes Modeling

Structural and Electronic Factors in Catalytic Activity of Metal Sites in Nanoporous Materials: Quantum Chemical Investigations

(Professor Ewa Brocławik DSc,
Mariusz Radoń PhD [PhD student of Jagiellonian University, until May 2011])

Charge transfer between the active site and a substrate results from delicate balance in individual electron transfer processes. We apply new electron density analysis (ETS-NOCV) with flexible strategy of dividing multicomponent system (zeolitic active site) into fragments. It decomposes total electron transfer upon adsorbate bonding, into independent channels, showing various impact on substrate bonding and activation. Two alternative fragmentation schemes of three-component embedded cluster models of Cu(I) and Ag(I) sites in zeolites hosting ethene, ethyne or formaldehyde, provided insight into charge transfer between the substrate and a site or between framework oxygens and a cation. In this report we present NOCV cross-analysis based on DFT modeling of charge transfers between the substrate, the cation and framework oxygens. It is focused on the influence of zeolite (treated as an electron reservoir) on donation/backdonation processes, supposed to tune properties of embedded cation and thus the activity of the Me(I) site.

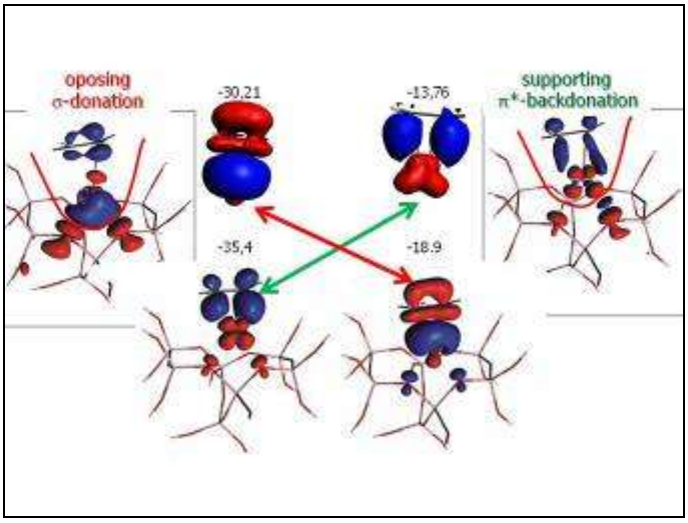


Fig. 1. Electron transfers between ethene and either Cu^+ or Cu(I)-ZSM-5 (up/down); red and blue represent electron outflow/inflow. Left and right insets illustrate the role of framework oxygens.

Insets in Figure 1 illustrate two dominant electron transfer channels from framework oxygens to Cu(I) cation: opposing σ-donation of ethene bonding electrons and supporting π*-backdonation to antibonding ethene orbitals (shown in main window). While the latter enhances substrate activation (evidenced by IR red-shift), the former weakens activation ability of the cation upon embedding in zeolite framework. Thus the activity of a cationic site must be viewed as resulting from framework effect on a sensitive balance between concurring electron transfer channels.

Detailed cross-analysis for the three substrates shows that activation decrease due to reduction of σ-donation is outweighed by the increase in π*-backdonation for Cu(I) but not for Ag(I). Our results indicate clearly that zeolitic framework regarded as an electron reservoir may either support (Cu^+) or impair (Ag^+) electronic processes underlying catalysis. Therefore enhancing effective activity of zeolitic cationic sites requires designed tuning of as well its σ-donation as π*- backdonation ability by intelligent modification of framework properties.

The Dynamics of Oscillatory Heat Evolution in the Sorption of Gaseous Hydrogen in Metallic Palladium as a Function of an Inert Gas Present in a Reaction Mixture and on the Palladium Surface

(*Erwin Lalik PhD*)

The year 2011 saw the continuation of research into the thermokinetic oscillations in the sorption of gaseous hydrogen in metallic palladium, and the Microscal gas flow-through microcalorimeter combined with gas spectrometer continued to be used in the experiments. The crucial condition necessary for the oscillations to occur is an addition of small amount of inert gas to either hydrogen or deuterium prior to its flowing through the microcalorimetric cell. The inert gases used in the experimentation to date included N_2, He, Ne, Ar, and Kr. The kind of the gas used turned out to be highly consequential, as the oscillation frequencies were found to be a function of atomic parameters of the gases. A linear relation of the normalized frequency and the first ionization potential of the inert gas used to induce the oscillations has been found empirically, indicative of a role that must be played by the inert gas adsorption on the Pd surface in inducing the oscillations. The research conducted in 2011 was focused on finding a way to extend the scope of techniques that may be applied *in situ* to study the oscillatory sorption.

A problem that must be solved before using any technique other than microcalorimetry for research into the oscillatory sorption is to find an alternative way for detection of the oscillatory time series representing the process. It has been found that pressure variations within the system may likely be used for the purpose. The pressure variations can be detected and recorded concurrently with the thermokinetic oscillations using pressure transducer. It turns out, that not only the frequencies of pressure variations correspond closely to the thermokinetic frequencies, but also they show the same dynamic character as the latter, either periodic or quasiperiodic (cf. Fig. 1). In contrast to the microcalorimeter, of which the principal parts (the heat sink and the thermistors) must be physically in contact with the sample for measurements of heat evolution, leaving no room for other detectors, the pressure transducer can be located conveniently as far as 1 or 2 meters away from the sample, effectively allowing the sample itself to be located within any other instrumental space. Hence, it may be concluded, that the monitoring of pressure can be proposed as an alternative method of detecting and recording of the oscillatory time series in the sorption of hydrogen in Pd, allowing for a concurrent application of other techniques *in situ* to study the mechanism of oscillations.

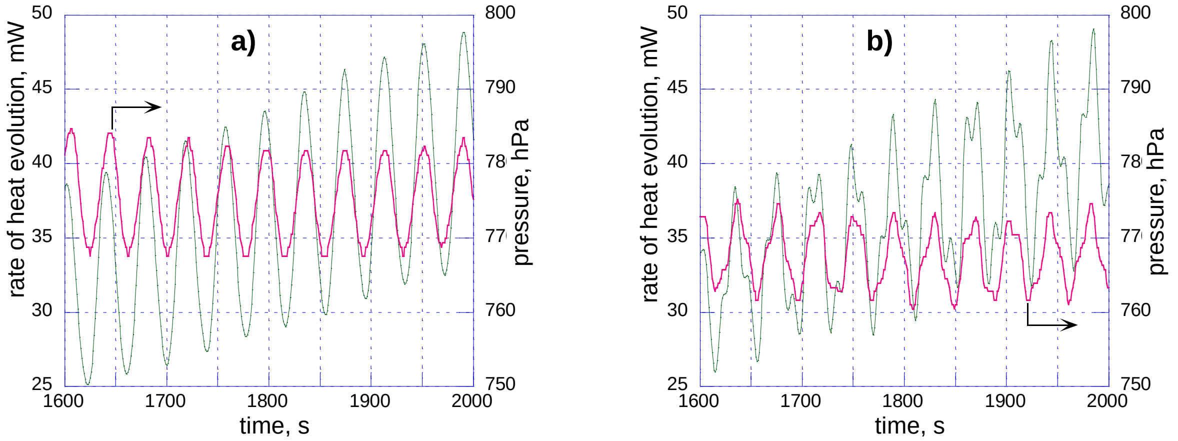


Fig. 1. The concurrence of the thermokinetic oscillations (green, solid line) and the oscillations of pressure (magenta, dashed line) in sorption of a mixture of H_2 + Ar in Pd: (a) periodic, (b) quasiperiodic.

Comparison of Properties of Modified Heteropolyacids and Oxides Systems

(Assoc. Professor Renata Tokarz-Sobieraj DSc, Professor Małgorzata Witko DSc,
Piotr Niemiec PhD)

The goal of the presented project was to determine similarities and differences in the properties of active centers present in the transition metal oxides (MoO_3, V_2O_5) and in molybdenum heteropolyacids (HPA), with Keggin structure in which vanadium was introduced in the position of the addenda atoms ($PV_xMo_{12-x}O_{40}^{-3-x}$). Crystallographic structures of these systems are composed of metal-oxygen octahedra arranged in various configurations. In structures of transition metal oxide and heteropolyacids different types of metal and oxygen centers (with various coordination and various neighbors type) are present, the common elements are oxygen sites singly coordinated with metal centers (Mo/V) and oxygen sites bounded two metal centers.

Description of the properties of active sites was performed by DFT calculations, using gradient corrected PBE functional. For all cluster calculations the package Turbomole was applied. For all investigated structures spectra of the density of states and IR spectra were produced. Besides electronic population analysis (Mulliken's, ESP see Table below) of active centers as well as character and energy of boundary orbital were calculated. On top of these, energy of H adsorption was determined.

	$Mo_{15}O_{56}H_{22}$ (MoO_3)	$V_{10}O_{31}H_{22}$ (V_2O_5)	$PMo_{12}O_{40}^{-3}$ (HPMo)	$PV_1Mo_{11}O_{40}^{-4}$ (HPVMo)	$PV_2Mo_{10}O_{40}^{-5}$ (HPVMo)
Mo/V	1.37 / -	- / 1.32	1.02 / -	0.99 / 0.80	1.02 / 0.80
Mo=O	-0.23	-	-0.37	-0.41	-0.45
V=O	-	-0.28	-	-0.45	-0.48
Mo-O-Mo	-0.41	-	-0.36; -0.42	-0.38; -0.44	-0.40; -0.45
Mo-O-V	-	-	-	-0.34; -0.38	-0.35; -0.36
V-O-V	-	-0.59	-	-	-0.34

The spectra of the density of states show that in all investigated compounds valence band (around the Fermi's level) is dominated by the orbital of bridging oxygen atoms connected with two addenda metals, while the central part of the band is characterized by orbitals of singly coordinated oxygen. Conduction band is described through metal atoms (Mo/V).

The results of population analysis (Mulliken) indicate that the charge on the metal centers (the same formal oxidation state in both types of systems) is higher in the oxide systems than in the HPA. In oxide systems the differences between oxygen ions singly and doubly coordinated with the metal is greater than in the HPA. Addition of vanadium increases nucleophilicity of oxygen centers.

Covalent character of metal-oxygen bonds, measured by the values of Mayer bond order indexes (BO), is slightly higher in the HPA systems than in oxides (e.g., Mo=O in the HPA BO=1.72, in MoO_3 BO=1.67).

In oxide systems singly coordinated oxygen centers (Mo=O, V=O) seem to be energetically preferred for H adsorption while in HPA there are doubly coordinated oxygen sites. Theoretical IR spectra shows that the frequency of vibration of different types of active centers in the oxide systems are shifted towards higher energy compared to the same types of oxygen in systems heteropolyacids (eg. Mo-O-Mo 993 cm^{-1} in MoO_3 and 931 cm^{-1} in HPMo).

Mechanisms of Enzymatic Reactions - Computational Studies

(Assoc. Professor Tomasz Borowski DSc, Anna Wójcik MSc, Anna Miłaczewska MSc)

One research project concerned the catalytic reaction mechanism of Cu-dependent oxygenase catalyzing oxidation of phenol groups to catechols, i.e. tyrosinase. Two previous studies on the mechanism of tyrosinase had given quite conflicting results. In a QM-only study using a rather small model, a mechanism was suggested in which the tyrosine proton is removed before catalysis. This was followed by catalytic cycles where a superoxo ligand attacks the phenolate ring. In another, more recent study, at the QM/MM level including the entire protein in the model, a quite different mechanism was instead advocated where a bridging O_2H ligand was homolytically cleaved. That mechanism was rejected in the earlier QM-only study as having a prohibitively large barrier for O–O bond cleavage. In the present study, this discrepancy between the previous studies was investigated by new QM-only and QM/MM calculations and it was found that the most likely explanation for the discrepancy is that the previous QM/MM geometry optimization converged to an incorrect reactant state (high energy local minimum).

Another research project focused on the mechanism of O_2-dependent aliphatic carbon-carbon bond cleavage, as catalyzed by Ni(II)-dependent acireductone dioxygenase. The reaction of the anion $[PhC(O)C(OH)C(O)Ph]^-$, which is a synthetic model for natural acireductone, with O_2 was studied with DFT methods and the results support a hydroperoxide mechanism wherein the first step is a redox process that results in the formation of 1,3-diphenylpropanetrione and HOO^-. In subsequent steps trione and HOO^- react to form a 5-membered cyclic peroxo species, which decomposes with the release of CO and two equivalents of $PhCOO^-$. Alternative reaction path engaging triplet dioxygen and acireductone radical anion, which was previously found to be the preferred mechanism for natural acireductone, turned out to involve substantially higher barrier.

The last research problem we tackled in 2011 concerned the mechanism for the reaction between an intradiol dioxygenase and a hydroperoxy compound that served the role of a mechanistic probe molecule in previous experimental studies. The product of O-OH bond cleavage was observed in the previous studies and this fact was interpreted as evidence for the formation of Fe(IV)=O species. In the present computational study five different models of the complex between iron cofactor and the probe were considered and used to model the reaction. The most important conclusion we drew from the results is that the critical O–O bond cleavage, leading to the alkoxyl radical intermediate, most likely does not yield the reactive oxoferryl species. Instead, in the preferred reaction channel the O–O cleavage leads to the ferrous complex with one of the tyrosine ligands oxidized to the tyrosinate radical.

Molecular Modeling of the Selected Poly- and Oligosaccharides, Their Structural Features and Interactions with Metal Ions

(Professor Władysław Rudziński DSc, Wojciech Płaziński PhD)

The study was focused on the poly- and oligosaccharides composed of α-L-guluronic acid (G) and β-D-mannuronic (M) acid. These two carbohydrate units are constituents of the unbranched natural biopolymers, alginates. They both contain carboxyl moieties, thus, can be considered as anionic or neutral species, depending on the pH of the environment. Two distinct aspects were considered: (1) the interactions of calcium ions with deprononated forms of alginates (the infinite poly(G) chains and the octamers consisting only G units were considered); (2) the interactions of poly(G) and poly(MG) chains (both protonated and deprotonated forms were taken into account) with the selected phenolic compounds (i.e. phenol, *o*-chlorophenol and *p*-chlorophenol). The first part of the studies included the parameterization of the GROMOS96 force field with respect to interactions between negatively charged uronate residues and calcium ions. The second part allowed for identification of the interactions types responsible for the binding of phenolic compounds by the alginate chains.

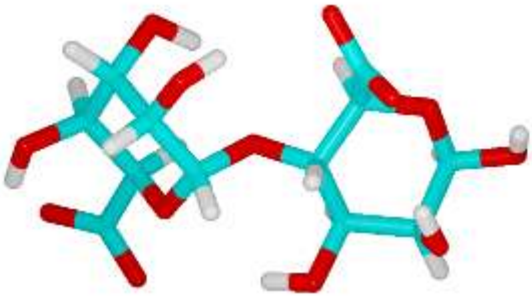


Fig. 1. The structure of disaccharide composed of the G (left) and the M (right) units after geometry optimization at the PM3 level.

Theoretical Studies of Structural Transformations Occurring under External Magnetic Field in Systems Composed of Carbon Nanotubes and Magnetic Nanoparticles

(Assoc. Professor Tomasz Pańczyk DSc)

Coupling of a carbon nanotube with a magnetic nanoparticle by an alkane chain leads to a macromolecule which structure is determined by a balance between dispersion interactions, magnetic interactions and parameters of bonds in alkane chains. Thus, properties of the resulting system cannot be predicted from general knowledge about individual components of the macromolecule.

Therefore, extensive calculations have been performed in order to study how some key parameters of the system affect its structure in normal conditions and under external magnetic field. The calculations were performed using Monte Carlo simulations and an original force field composed of the Dormann-Bessais-Fiorani potential (interaction between magnetic dipoles), Hamaker potential (dispersion interactions between nanoparticles and carbon nanotube), Yukawa potential (interaction between charged colloidal nanopartices), stretch-torsional potential (alkane chain) and standard Jennard-Jones potential.

Large energetic barriers were found to exist for configurational changes corresponding to a transfer of nanoparticle between the sidewall and the tip of carbon nanotube. Moreover, the magnitude of those barriers changes strongly depending on mutual configuration of anchoring points of alkane chains and carbon atoms within the nanotube tips, as well as on mutual spatial configuration of magnetic moments of nanoparticles (Fig. 1).

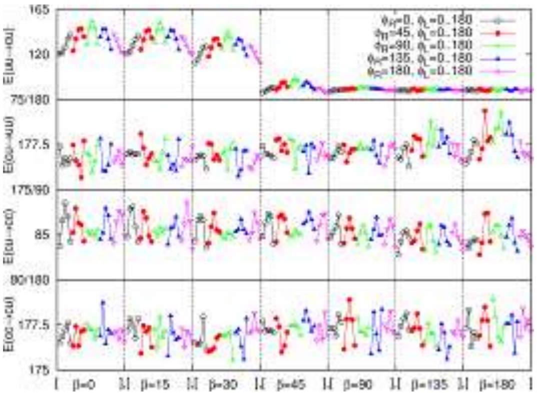


Fig. 1. Activation barriers found for a system composed of (45,0) nanotube and nanoparticles of diameter 90Å as functions of configuration of anchoring points and magnetic moments

It was found that a spontaneous transformation of the system structure might occur only in one direction and only for a few combinations of system parameters. Namely, this spontaneous transition is possible only from the nanotube sidewall to the tip, however, this process is never fast. Reverse transition is not possible without an extra energy gain. It was found that exposition to an external magnetic field might be a source of that extra energy. However, another condition must still be obeyed, i.e. the magnetic nanoparticles must exhibit some specific spatial configuration of magnetic moments.

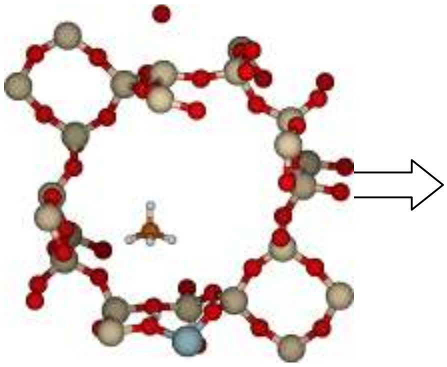
Mechanism of Reaction of NO and CH_4 Molecules on Pd Centres in Mordenite

(Robert Gryboś PhD)

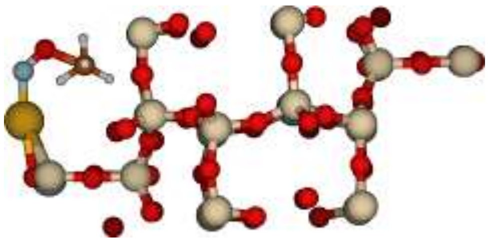
Quantum-chemical simulations within periodic DFT were performed, using VASP code with GGA functional and PAW pseudopotentials.

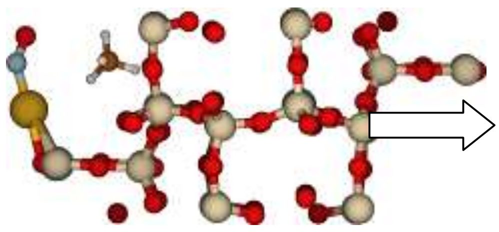
Due to the highest C-H bond energy among hydrocarbons, activation of methane is a very demanding process. Despite large effort, it was not possible to reach stable adsorption of methane on palladium centres or on acid sites (of both Brønsted and Lewis type) present in mordenite. Lack of adsorption, which serves as an activation precursor, made direct search for the transition state impossible.

One of the pathways of methane activation is creation of a carbenium cation CH_5^+. Attempts create the carbenium cation by placing methane in close vicinity of the Brønsted centre were unsuccessful - methane did not react with the acid site. Also, placing a pre-optimized CH_5^+ in the centre of the main channel did not yield positive results - the cation migrated to the nearest Al site, detached a proton and desorbed back into the main channel of the zeolite.



Attempt to simulate the reaction between methane and nitric oxide according to the Langmuir-Rideal mechanism, i.e. putting the CH_4 molecule from the gas phase in contact with NO adsorbed on a metallic centre, also did not yield positive results. Methane does not interact with the activated NO molecule and simply moves away in the direction of the main zeolite channel.





Suggestions for further research include:

1. methane activation on zeolite framework defects – requiring a separate study of how and where the framework defects are formed in mordenite,
2. high-temperature methane activation according to Langmuir-Rideal mechanism – requiring long simulations using Molecular Dynamics techniques.

Studies on the Coordination Properties of Chlorophyll in Organic Solvents

(Professor Małgorzata Witko DSc, Dorota Rutkowska-Żbik PhD)

The research aimed at the elucidation of ligand binding properties of chlorophylls towards selected organic solvents: acetonitrile (ACN), imidazole (Im), methanol (MeOH), dimethylformamide (DMF) and pyridine (Py). Our motivation for the studies is the fact that naturally occurring chlorophyll may be converted to yield derivatives with different metal ions, which may be of interest of pharmaceutical industry. It is found that the rate of metal exchange depends on the organic solvent used for the transformation.

The present studies are done within quantum-chemical method based on Density Functional Theory (DFT) within the non-local gradient-corrected Becke-Perdew functional, with Ri approximation for coulomb integral fitting. All electrons are described by Gaussian-type basis set of def-TZVP quality. The studied systems are characterized by geometry parameters (bond lengths, valence angles) and ligand binding energies. Additionally, the theoretical UV-VIS spectra were computed using time-dependent Density Functional Theory.

The obtained results (see: Table) indicate, that in all five-coordinate complexes magnesium ion is considerably pulled out of macrocycle plane and forms relatively long bond with the solvent molecule. Binding of the sixth ligand (being the second solvent molecule) results in the insertion of Mg^{2+} ion into the tetrapyrrolic plane and further elongation of magnesium-solvent bond. Imidazole is the strongest bound ligand, while acetonitrile is the weakest. The latter does not tend to form six-coordinate complexes, what is due to the low contribution of dispersion to the interaction between ACN and the rest of the system, as shown by SAPT(DFT) method. DFT calculations explain experimentally observed batochromic shifts in UV-VIS spectra of the studied compounds under high-pressure. They are due to the elongation of metal-ligand bond, and not to the insertion of Mg^{2+} into the macrocycle ring.

Table. Computed Mg-L bond lengths - r [Å], Mg^{2+} out of plane displacement d [Å], and ligand binding energies E in [kcal/mol].

L 1	**L 2**	**r1**	**r2**	**d**	**E1**	**E1**
ACN	-	2.24	-	0.32	-13.1	-
Im	-	2.20	-	0.38	-18.8	-
DMF	-	2.11	-	0.27	-13.5	-
MeOH	-	2.15	-	0.30	-14.3	-
ACN	ACN	2.38	2.37	0.00	-2.6	-4.4
ACN	Im	2.46	2.28	0.00	-1.6	-7.2
Im	Im	2.34	2.33	0.00	-6.3	-6.5
MeOH	MeOH	2.24	2.24	0.00	-7.1	-7.7
DMF	DMF	2.24	2.25	0.00	-5.8	-5.8
Py	Py	2.43	2.39	0.00	-5.1	-5.3

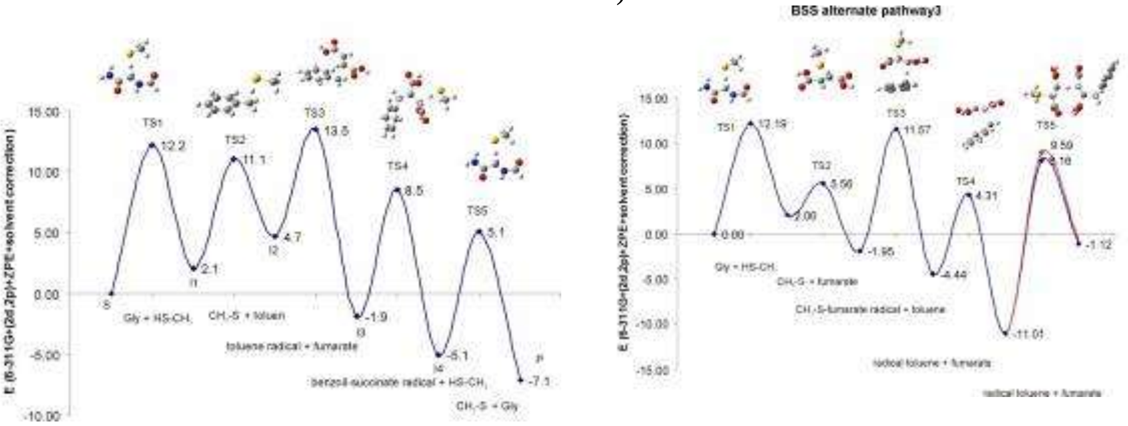
Small Models Theoretical Studies of Benzylsuccinate Synthase Reaction Mechanism

(Professor Małgorzata Witko, Maciej Szaleniec PhD)

Quantum chemical modeling with models have been conducted in order to study potential reaction pathways catalyzed by the glycyl radical enzyme **benzylsuccinate synthase (**BSS). The model included reactants and model residues of amino acids involved in the reaction. The aim of the study was to facilitate the interpretation of kinetic and spectroscopic (EPR) results obtained in the cooperation with a group of Prof. Johann Heider from Marburg University.

The applied method is based on the investigation of elementary reaction steps for individual pairs of reagents, calculation of energy of substrates, products and transition states *in vacuo* and in a model solvent (eps=4). The geometry optimization, vibration analysis and solvent corrections were conducted by DFT (B3LYP functional) in 6-31g(d,p) basis set. The final energies were calculated in a high TZV basis set TZV (6-311+g(2d,2p)).

As a first step, a classical reaction pathway was addressed, which is initiated by transfer of the radical from Gly to Cys and subsequent radical activation of toluene, followed by addition to fumaric acid, which leads to a benzylsuccinyl radical intermediate that reacts with Cys to the product benzylsuccinate with concomitant radical transfer and final restoration of the glycyl radical. This process exhibits the highest rate-limiting barrier for the reaction of the benzyl radical with fumaric acid (13.5 kcal/mol) and is energetically favorable ((Δ(E+ZPE)=-5.1 kcal/mol). An **alternate pathway 1** was calculated, with initial addition of fumarate to the Cys radical, followed by toluene activation by the resulting cysteinylsuccinate radical and finished by the recombination between the benzyl radical and cysteinylsuccinate to the product. However, that pathway exhibited too high energy barrier for the last elementary step (35 kcal/mol). A further **alternate pathway 2** implying release of fumaric acid after activation of toluene was also excluded (barrier 55 kcal/mol). Similarly it was possible to exclude **alternate pathway 3,** which implied reaction of the activated benzyl radical with a second molecule of fumaric acid and further reaction of the cysteinylosuccinate with the radical benzylsuccinate leading to the product and the restoration of the radical (barrier 20 kcal/mol) - see Figure 1. Therefore, the originally proposed reaction pathway still seems to be the most probable route for the mechanism of BSS.


a)

b)

Fig. 1. BSS reaction pathways: a) classical pathway,. b) alternate pathway 3

Additional calculations for reactivities of enzyme substrates and inhibitors are on the way to complement spectroscopic and biochemical investigations on BSS. These calculations will be a valuable aid in interpreting the biochemical data and in experimental validation of the reaction mechanism of BSS.

Statutory research

Dynamics of Nanoparticle and Colloid Systems

Electrostatic Interactions of Nanoparticles with Charge Surfaces Including Many Body Effects

(Professor Piotr Warszyński DSc)

Advanced numerical methods allow modeling of electrostatic interaction in complicated systems of nanoparticles with nonuniform distribution of surface charge. In particular it applies to proteins. For instance α-chymotrypsin at pH 8.6 is near the isoelectric point. However, it has the permanent dipole moment, 480 D, which value does not vary in the concentration range of 2 to 12 mM of monovalent salt solution and is weakly dependent on pH. Size of proteins (or other nanoparticles) in the range of nanometers is usually, in aqueous environment, comparable or smaller than the Debye screening length, therefore the approximate methods of solution of the Poisson-Boltzmann equation cannot be applied and numerical solution needs to be used. The aim of the work in year 2011 was to apply the numerical algorithms based on the finite element method in order to evaluate the electrostatic interactions between nanoparticle with dipolar charge distribution and uniformly charged surface. More complicated systems of interactions of two and three nanoparticles were also considered.

Figure 1 illustrates example of the distribution of the electric potential around deposited particles with dipolar charge distribution being the result of the final element method calculations with COMSOL software package.

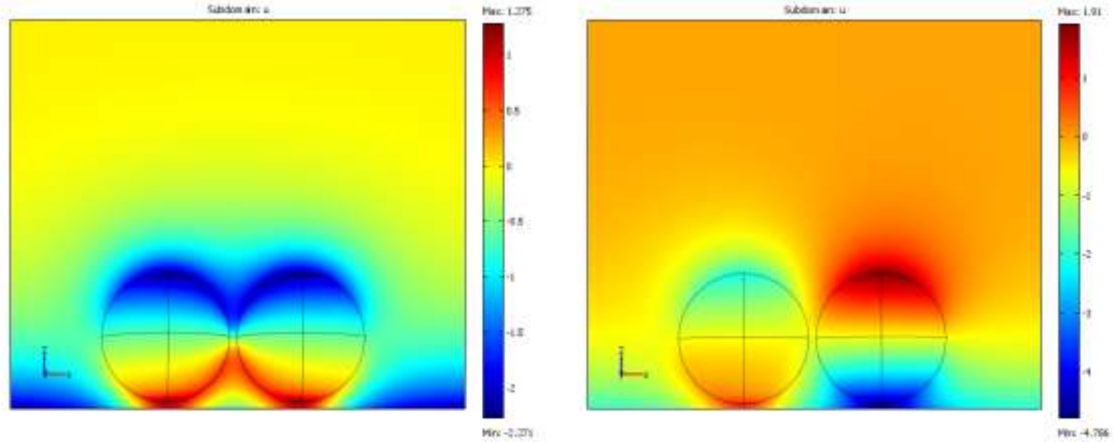


Fig. 1. Example of the distribution of the electric potential around particles with dipolar charge distribution deposited on charge surface in parallel and antiparallel orientations

We found that presence of charge surface modifies lateral interactions between nanoparticles when the thickness of the electric double layer is comparable or larger than their size. We calculated the dependence of the interaction force on the mutual orientation of particles.

These theoretical predictions were used for the interpretation of the experimental, literature data for the adsorption and desorption kinetics of α-chymotrypsin at mica surface. We found that they can be well explained in terms of profile of interaction energy between protein and surface, taking into account the electrostatic interactions. Our results can provide theoretical background for formation of nanoparticle or protein layers at surfaces with controlled charge density.

Physicochemical Background of the Colloid Enhancement Method for Protein Monolayer Detection at Solid/Electrolyte Interfaces

(Professor Zbigniew Adamczyk DSc, Małgorzata Nattich-Rak PhD, Marta Sadowska MSc, Monika Wasilewska MSc, Jakub BarbaszPhD)

An efficient experimental method aimed at detecting protein monolayers at solid interfaces was elaborated. The method, shown schematically in Fig. 1, is based on non-specific (driven by electrostatic interactions) or specific (driven by chemical covalent bound formation) interaction of colloid microparticles with protein layers. The number and distribution of colloid particles deposited on protein monolayers surfaces can be determined in a convenient way by optical or fluorescent microscopy. The method, referred to as the colloid enhancement (CE), can be used for a quantitative determination of the surface coverage of adsorbed protein. Besides the coverage, the CE method allows one to determine the charge distribution within adsorbed protein layers and their apparent zeta potential as a function of pH (isoelectric point), ionic strength, etc. This has a major practical significance given the problems with determining isoelectric points of proteins in the bulk using the traditional microelectrophoretic methods. Knowing the surface coverage of proteins one can determine accurately the protein bulk concentration as low as 0.01 ppm (10 ppb). This is a precision superior to traditional methods, e.g., spectrometric measurements. In order determine the range of applicability of the CE method a series of calibrating measurements was performed for fibrinogen monolayers on mica. These monolayers of a controlled coverage and structure were produced by diffusion-controlled adsorption of this protein from solutions of various bulk concentration. Afterwards, negative and positive latex particles (800 nm in diameter) were deposited and their coverage was determined as a function of the fibrinogen monolayer density for various pH and ionic strength. It was demonstrated that the latex coverage increased abruptly with fibrinogen coverage Θ_f attaining its maximum value for Θ_f=0.10 (10%). Hence, the slope of this relationship was very high, which confirms the utility of the CE method for a precise determination of protein monolayer coverage. These experimental data were quantitatively interpreted in terms of the fluctuation theory developed in this work whereas the commonly used DLVO theory proved inappropriate. This was so because of a considerable heterogeneity of charge distribution within adsorbed fibrinogen layer. It can be, therefore, concluded that the results obtained in this work have significance for basis colloid and protein sciences. Practical aspects are also important since a reliable protocol for a precise determination of protein bulk concentration can be devised.

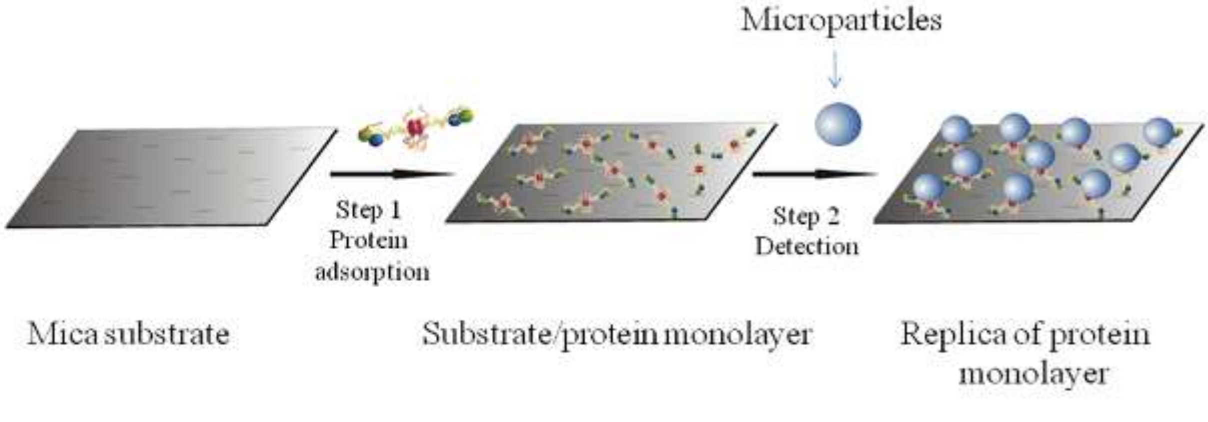


Fig. 1. Schematic view of the colloid enhancement of protein layers

Influence of the Liquid Film Size on Time of the Bubble Coalescence at the Liquid/Gas Interface

(Professor Kazimierz Małysa DSc, Jan Zawała PhD, Mariusz Krzan PhD, Dariusz Kosior MSc, Anna Niecikowska MSc)

The study aims at description the mechanism and most important parameters determining the outcome of the bubble collisions with the liquid/gas interface (coalescence and/or bouncing). Effect of the bubble impact velocity and size of the liquid films, formed during the collisions, on the bubble coalescence and/or bouncing was studied. The bubble impact velocity (kinetic energy) was tuned either by: i) changing the bubble diameter (bubble size affects its terminal velocity), or ii) adjustment the distance between the bubble formation point and the water free surface (at the acceleration stage the bubble velocity depends on distance from the capillary).

It was found that the bubble bouncing and the coalescence time, i.e. the time from the moment of the bubble first collision to its rupture, increased with the impact velocity. The coalescence time varied from few up to 120 ms when the bubble impact velocity was changed from 8 to 36.7 cm/s. The bubble impact velocity affects strongly size of the thin water film separating the colliding bubble from gas phase and therefore determines probability of the bubble bouncing from the water free surface. Figure 1 presents photos of the bubble colliding with the water surface with different impact velocities. As seen the horizontal diameter of the colliding bubble, which determines size of the thin liquid film formed, increases with the bubble velocity and is substantially larger under dynamic conditions. Thus, higher impact velocity means larger deformations of the bubble shape and larger radius of the liquid film formed between the bubble and the free water surface. In turn, larger radius of the liquid film formed means prolongation the time of the film syneresis to its critical thickness of the rupture. When the film syneresis time is longer than the collision time (ca. 5ms) the bubble bounces backwards. During the collisions the kinetic energy associated with the bubble motion is transferred into surface energy of the deformed water/air interfaces (bubble and free surface). As a result of the energy dissipation the bubble impact velocity during its second and subsequent collisions is diminishing. It means that size of the water film formed is decreasing and velocity of the film syneresis is increasing. It was showed that the film formed by the colliding bubble ruptured when its radius R_F<0.28mm.

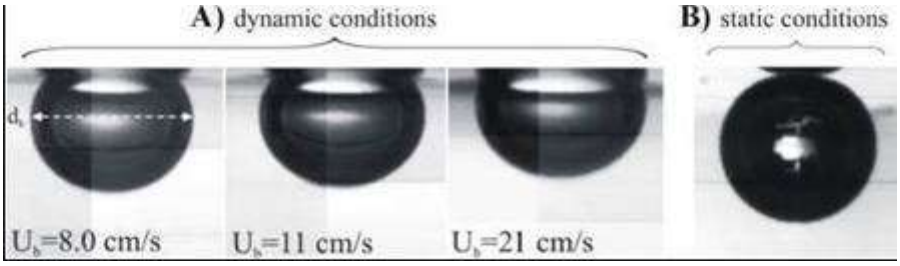


Fig.1. Photos pf the bubble of R_b=0.74mm; A) - colliding with different impact velocities with the water/air interface, B) - captured motionless beneath the mica plate

Statutory research

Self-Organized Structures and Nanoparticles Monolayers

Synergistic Effects in the Photocatalytic Degradation of Organic Pollutants in Water with the Simultaneous Action of Oxidant

(Professor Piotr Warszyński DSc, Assoc. Professor Paweł Nowak DSc, Justyna Dziedzic MSc)

The aim of our work in 2011 was to determine the effect of oxidants ($Na_2S_2O_8$ and H_2O_2) in the photocatalytic degradation of model compounds - humic acids in the presence of TiO_2 suspensions in solution with the main emphasis to achieve the synergistic effect between several methods, which consequently would lead to improving the efficiency of removal of natural organic matter (NSO) from water. We observed that addition of oxidants in the photocatalytic decomposition of humic substances significantly improved the efficiency of whole process in comparison with the process only in the presence of the catalyst or oxidant itself. Oxidant - sodium persulphate - was encapsulated in various matrices (wax capsules, organic resin capsules and silica capsules with polyelectrolyte surface modification) and the effect of persulphate released from the capsules on the process of photocatalytic oxidation of humic species was studied. Detection of the distribution of humic acids was performed using spectrophotometry in the UV-VIS range (analytical wavelength 254 nm) and additionally compared with the parameter COD-Mn.

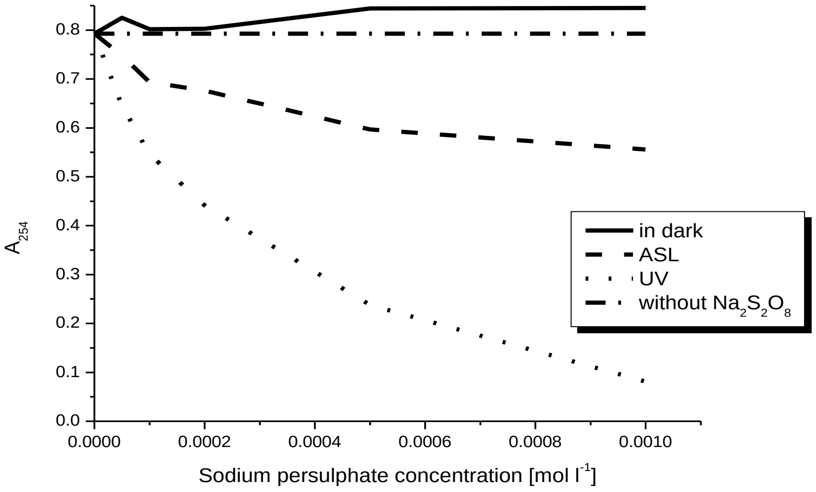


Fig. 1. The effectiveness of the oxidation of humic acid by simultaneous action of UV or VIS radiation, TiO_2 and sodium persulphate. Irradiation time: 60min, concentration of HA: 40 mg l^{-1}, concentration of TiO_2: 100 mg l^{-1}, UV radiation intensity: 48.8 mW*cm^{-2}, ASL radiation intensity: 68.8 mW*cm^{-2}

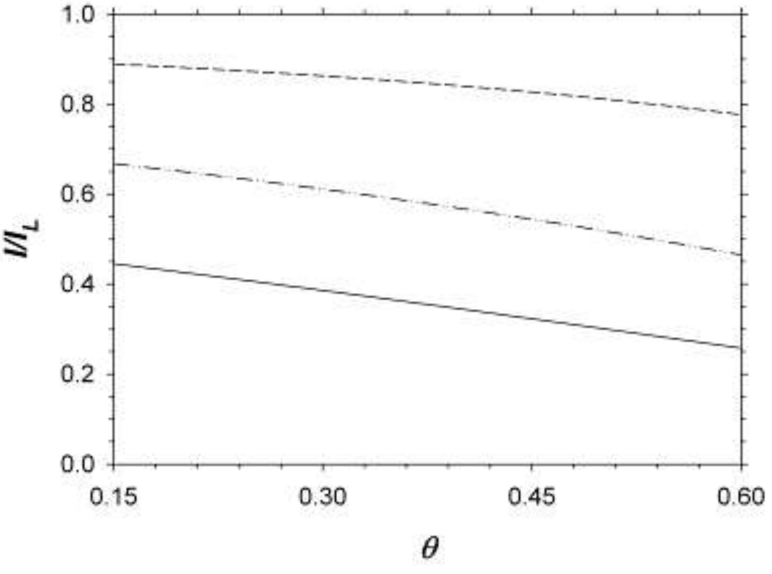
We observed that more than 50% of humic acid may be removed from the aqueous solution by photocatalytic decomposition if the concentration of TiO_2 in suspension is high enough. Addition of oxidant - sodium persulphate - greatly enhances the activity of TiO_2 in the decomposition process of organic substances. More than 90% conversion of HA was obtained when $1x10^{-3}$ mol l^{-1} sodium persulphate was used. It confirmed that synergistic effect occurred when TiO_2 and $Na_2S_2O_8$ were used for decomposition of humic acid. Similar effect was observed when the oxidant was used in the encapsulated form.

Modeling the Adsorption of Nanoparticles - Multiscale Theoretical Description of the Adsorption Kinetics of Spherical Particles on the Homogenous Surface

(Assoc. Professor Paweł Weroński DSc, Magdalena Nosek MSc, Piotr Batys MScEng, Michał Skoczek MScEng)

We have derived the equation for the limiting diffusion current at the rotating disk electrode (RDE) with a layer of particles, from the model developed by Gough and Leypoldt in 1979. They considered steady-state mass transfer of a solute that was consumed at the surface of the RDE covered by a homogenous gel membrane. Using the method of Levich and assuming no convective flow within the membrane they found the equation of the diffusion current in the case of membrane-covered RDE. In our system the RDE has been covered by a porous layer of spherical particles instead of a homogeneous gel membrane. Considering that flow penetrates the porous medium only when its solid volume fraction is less than 0.1, we can neglect the convective flow within the particle layer if the surface coverage θ >0.15. The effective diffusion coefficient in porous media depends on the porosity and tortuosity. For the simple geometry of spherical particle layer, we have calculated the tortuosity using the method of Lanfrey et al., as the average ratio of the actual path length and the straight line trajectory of the solute molecule.

In the Figure below, we show the results obtained with the equation of the limiting diffusion current at the RDE with an adsorbed layer of particles. The figure presents the limiting diffusion current I, normalized by Levich current I_L, as a function of θ. The curves correspond to the ratio of the adsorbed layer thickness to the diffusion boundary layer thickness equal η=0.1, 0,4, and 1.0 (from top down). The limiting diffusion current decreases with the growth of surface coverage, when the porosity of the layer, and thus effective diffusion coefficient in the layer, decrease. This effect is more significant at high rotation rates, when the thickness of the porous layer of adsorbed particles becomes comparable to the diffusion boundary layer thickness. However, even at a relatively thin porous layer, at η=0.1, the limiting diffusion current is still reduced by more than 10%.



We have found a good agreement between the theoretically predicted limiting diffusion current and experimental results at medium and high surface coverages of the rotating disk electrode.

Statutory research

Physical Chemistry in the Protection of Cultural Heritage

Modeling of the Response of Historic Polychromed Wooden Objects to Changes of the Ambient Environmental Conditions

*(Professor Roman Kozłowski DSc, Łukasz Bratasz PhD, Michał Łukomski PhD,
Bartosz Rachwał MSc)*

The task consisted in the refinement of the finite element analysis (FEA) to model the water vapour diffusion, strains, and stresses in multilayer structure of decorated wood in response to changing climate conditions. The aim was to reproduce with FEA accurately 'real time' responses of cultural artefacts. Unrestrained single panel of lime wood 10 mm thick coated with a gesso layer 1 mm thick was accepted as a standard object in the modelling. The water vapour diffusion coefficients, the surface emission coefficients, the water vapour sorption and dimensional change isotherms, as well as the mechanical properties of the wood and gesso were determined experimentally in earlier research. A specimen of wooden panel coated with gesso was prepared using the same specifications and exhibited in one of the galleries of the National Museum in Krakow. Its structural response - expressed in terms of panel's deflection - to real-world climatic variations was monitored for a year. A very good agreement between the measured and calculated values was obtained after a careful parametric refinement of the model, as illustrated in Figure 1.

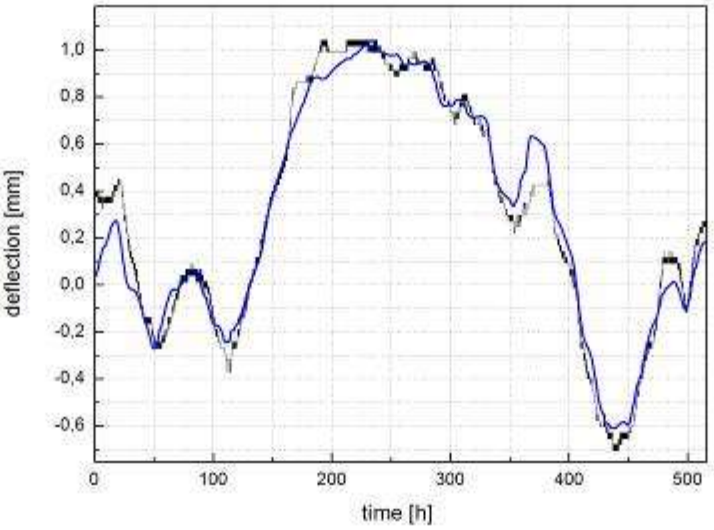


Fig. 1. Deflection of an unrestrained wooden panel coated with a layer of gesso calculated using the refined FEA model (blue curve) and measured in a gallery of the National Museum in Krakow (black curve).
The measurements were done for the period starting on July 15, 2010.

The following parameters were optimised to obtain the agreement between the observed and predicted results: thickness of the gesso layer to reproduce non-uniform distribution of gesso in real objects, calculation of the intermediate (scanning) swelling isotherms - an outcome of the hysteresis in the dimensional response of wood when subjected to alternating processes of adsorption and desorption, as well as tangential wood orientation in the centre of the panel again reflecting the anatomy of real objects.

Research projects
of the Ministry of Science and Higher Education

Complexes of Cationic Surfactants of Complicated Structure with Ionic Polymers as Elements of Nanostructures

Research project N N204 248634 [2008-2011]
(project leader: Grażyna Para PhD)

Interaction of oppositely charged surfactants and polyelectrolytes usually results in formation of nanosize surfactant-polyelectrolyte complexes. Depending on the properties and relative concentration of the surfactant/polyelectrolyte pair, such complexes can be used as cores for encapsulation of various active components. The aim of our work in 2011 was to investigate the surfactant polyelectrolyte systems at liquid/air and liquid/liquid interfaces and to develop the method of preparation of loaded nanosize capsules based on the encapsulation of surfactant-polyelectrolyte complex by sequential adsorption of polyelectrolytes. Using various types of cationic surfactants: N-dodecyl-N,N,N-trialkyl-ammonium bromides [DDTEABr], and N,N,N',N'-tetramethyl-N,N'-di(ndodecyl)-alkylene-diammonium bromides [d(DDA)HBr], and polyanion: poly(sodium-4-styrene sulfonate [PSS], surfactant-polyelectrolyte bulk complexes were formed. These negatively charged cores (complexes) were encapsulated by layer-by-layer adsorption of polyelectrolytes, polycation polydiallyl-dimethyl-ammonium chloride [PDADMAC] and polyanion PSS. We used the saturation method for formation of the consecutive layers and we determined the optimal conditions concerning concentration of surfactant and polyelectrolytes to form stable capsules. Obtained nanocapsules were characterized by dynamic light scattering (DLS) and ζ-potential measurements. Average size of capsules was in range 80-100 nm. To demonstrate possibility of encapsulation of a hydrophobic compound, we enclosed oil-soluble fluorescent dye, Cumarine-6.

Figure 1 illustrates a typical zigzag dependence of the zeta potential of obtained capsules on the adsorption of subsequent PDADMAC and PSS layers.

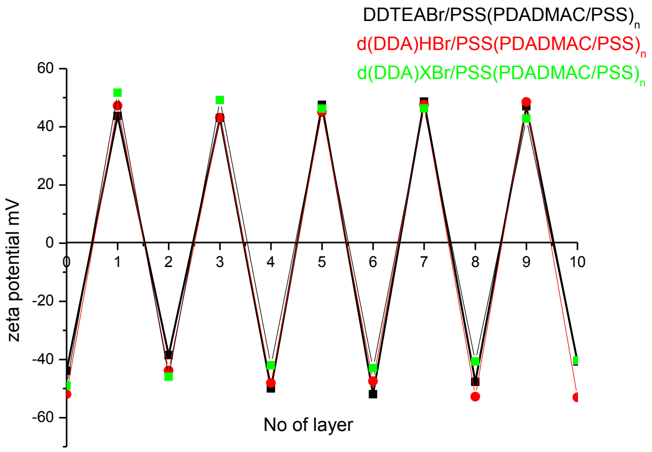


Fig. 1. Layer-to-layer variations of zeta-potential of polyelectrolyte coated complexes with the number of PDADMAC/PSS layers for: DDTEABr /PSS(PDADMAC/PSS) (solid lines), d(DDA)HBr/PSS(PDADMAC/PSS) (dotted lines) and d(DDA)XHBr(PDADMAC/PSS) (green line) systems

The Study on the Application of Heterogenized Chiral Ruthenium Complexes in Enantioselective Hydrogenation of Ketones

Research project N N204 249034 [2008-2011]
(project leader: Dorota Duraczyńska PhD)

In the course of this project three new ruthenium complexes containing chiral phosphine DuPhos ligand (Fig. 1A-C) and one with chiral amine TMBA ligand (Fig. 1D) were synthesized.

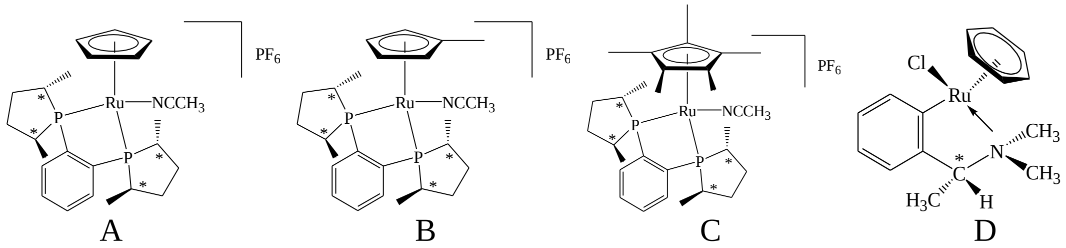


Fig. 1. The structures of new ruthenium complexes

These compounds were characterized by the following techniques: NMR (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}), IR, UV-Vis. For complexes A and C the X-ray quality crystals were obtained and their structure resolved accordingly.

Moreover, they are stable in contact wit air and in solution enabling convenient handling and processing without the use of Schlenk's line.

Compounds A-C were immobilized on aluminated molecular sieves HMS(Si/Al=20) by means of ion exchange method of the cationic ruthenium (II) complexes. Mesoporous silicas can acquire cation exchange properties by partial substitution of Si^{4+} ions with Al^{3+} in the framework. Different type of carrier e.g. gel-type methacrylate-styrene resin containing COOH groups was tested as well. Neutral compound D was "trapped" on Al_2O_3 support via wet impregnation method. The heterogenization of organometallic complexes on solid supports constitutes a very convenient way of combining the advantages of the homogeneous catalyst with those of heterogeneous ones such as ease of recovery and recycling.

The heterogenized catalysts were characterized by electron microscopic studies (SEM), high-resolution transmission electron microscopy (HRTEM), infrared spectroscopy (FTIR), UV-Vis spectroscopy, X-ray diffraction (XRD), solid state NMR (^{27}Al, 2^9Si). The textural properties were determined from nitrogen adsorption at 77K.

New catalysts were tested in catalytic hydrogenation of ketones such as acetophenone and acetol (hydroxyacetone) to the appropriate secondary alcohols. Those reactions were conducted in methanol under different hydrogen pressure (up to 50 bar) and temperature (up to 70ºC). Unfortunately, the prepared catalysts were not active in the reactions of interest. The GC analysis of reaction mixture detected only starting materials.

Exchange-bias Effect in the Epitaxial Systems Obtained by Deposition of the 3d and 4f Metals on Polar and Non-polar Transition Metal oxide Substrates

Research project N N202 248535 [2008-2011]
(project leader: Jacek Gurgul PhD)

The magnetic interactions in Fe/MnO system were studied in parallel to the investigation of Fe/CoO interfaces. At first stage, some approaches were applied in synthesis of epitaxial MnO system on polished and cleaved MgO(001) monocrystals by molecular beam epitaxy (MBE). Detailed characterizations of physical and chemical surface properties were performed using photoelectron spectroscopy (XPS), Auger spectroscopy (AES) and LEED diffraction on every stage of forming and modifying of thin films. We used different procedures to obtain epitaxial layers of metallic Mn and Fe, Mn_xFe_{1-x} alloys, MnO and $Mn_xFe_{1-x}O$ oxides. The magnetic properties of the selected systems were determined. It was found that layered Fe/MnO system shows exchange-bias effect at low temperatures in contrast to the oxidized $Mn_xFe_{1-x}O$ thin films.

The studies of metal/oxide systems prepared on non-polar substrates were compared to the ones on polar substrates. The solution of the physical and theoretical problems with thin films on polar substrates is nontrivial due to its poor stabilization but, on the other hand, it is very interesting because of the unusual electronic states on such surfaces. The experiments with polar surfaces were performed in two ways. On one hand, the metallic monocrystals of W(110) and Pt(111) were used, and on the other hand, the polished MgO(111) was tested. The experiments were begun with W(110), which was used as a substrate for preparation of well-defined and very flat Ag(111) buffer layer. After that, on such system one can deposit thin films of Fe(111), FeO(111) or CoO(111) with good epitaxial quality. However, our experiments were not successful and we have concentrated on experiments leading to the epitaxial layers of FeO(111) on Pt(111) and MgO(111) monocrystals. In both cases, we have obtained thin FeO layers (16 ML on MgO(111) and 17 ML on Pt(111)) by consecutive layer-by-layer oxidation of epitaxially deposited monolayers of Fe. The structure, magnetic and electronic properties were characterized by LEED, AES, Conversion Electron Mössbauer Spectroscopy (CEMS), Vibrating Sample Magnetometry (VSM) and Inelastic Neutron Scattering (INS) measurements. The results manifested extremely interesting properties. They showed significant differences between physical and chemical properties of FeO(111) deposited on both polar and non-polar substrates.

Moreover, we have prepared Fe/CoO(111) thin films on MgO(111) substrate. This system was characterized in details by VSM measurements and showed that exchange-bias field H_{EB} at low temperatures is more then 10-times stronger then H_{EB} in similar system prepared on MgO(001). This result suggests that thin films prepared on polar substrates can be basis for new materials, in which expected magnetic properties are enhanced when the other system properties are preserved.

Molecular Mechanisms Determining Product Specificity of 2-Oxoglutarate Dependent Oxygenases

Research project N N301 093036 [2009-2011]
(project leader: Professor Ewa Brocławik DSc)

In this project (initiated in April 2009) research on two groups of 2-oxoglutarate (2OG) dependent oxygenases: halogenases represented by SyrB2 and histone protein demethylases JMJD2. These proteins bind Fe^{2+} ion in their active site and utilize red-ox potential difference between 2OG and O_2 to carry oxidative transformation of basic substrates. These are the following reactions: demethylation of lysine groups in N-end fragment of histone protein H3 for JMJD2, and chlorination of threonine side chain for SyrB2. Both processes are of great importance since they participate in controlling gene expression (demetylazes) and antibiotics syntheses (SyrB2).

Determining of methylation level of lysine groups in histone proteins was of first importance as one of epigenetic markers, controlled by synergy of enzymes responsible for binding or elimination of methyl groups. The family of demethylases JMJD2 specializes in elimination of methyl groups from lysines 9 and 36 in histone protein H3. Particular enzymes in this family differ significantly in substrates spectrum: JMJD2A demethylyzes tri- and dimethyl derivatives H3-K9, while JMJD2D, differing from JMJD2A solely by two aminoacids in active site vicinity, is effective also for monomethyl derivative H3-K9.

In order to identify factors responsible for widening substrate spectrum between JMJD2A and JMJD2D (double mutation: S288A, T289I) classical molecular dynamics simulations were performed for the complex enzyme-Fe^{2+}-2OG-(fragment of H3-K9 with monomethylated K9). Force-field parameters (amber03-type) for iron co-factor were extracted from harmonic vibrational analysis (B3LYP/lacvp) for the co-factor model. For 2OG GAFF force-field was used, fully compatible with amber03. After initial equilibration under constant volume (heating up to 300 K) and under constant pressure (stabilization of system density), simulation run was carried out for 20 ns, with structure collecting within 1 ps intervals.

The analysis of obtained trajectories showed that the influence of double mutation on the active site structure was very subtle but substantial. Especially interesting was H-bonding system involving amino groups of lysine K9 and 2-oksoglutarate. Slight loosening of protein structure (mutation eliminates 2 hydrogen bonds: Ser288 --- Ile197, Thr289 --- Thr173) causes increase in incidence rate of H-bond between NH_2 from lysine K9 and side oxygen from Asn290 (from 57 to 65%). Oxygens from 2OG carboxylic group being the source of CO_2 for molecular oxygen activation, change their preferences for H-bond formation between OH group from side chain of Ser196: the oxygen bound with iron forms such bond in 43.9% for native form while in a doubly mutated structure such H-bond is observed for 58.0% structures. These effects though subtle and still under study, may substantially influence energetics for oxygen activation, being the key effect in the catalytic cycle. Our results allowed to propose the hypothesis about the impact of examined mutations on the active oxoferryl group formation. This may be further transformed into the substrate specificity of the given type of enzymes.

Developing of the Methods of Formation Biologically Active Multilayers Contained Polyelectrolytes, Proteins and Dendrimers

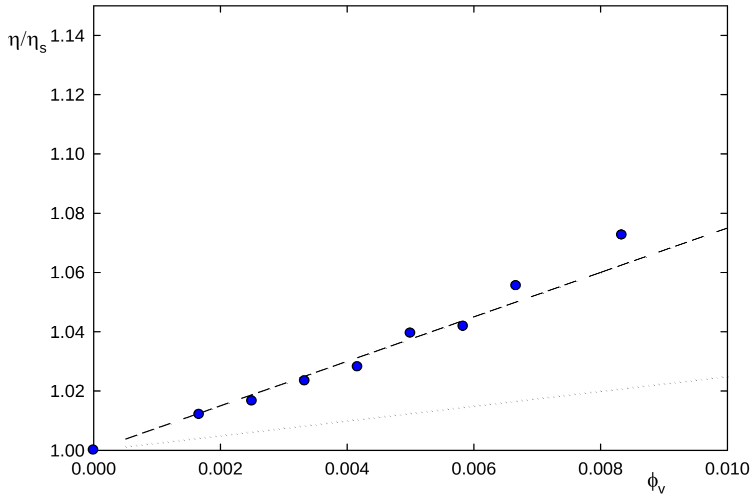
Research Project N N204 028536 [2009-20012]
(project leader: Barbara Jachimska PhD)

It has been demonstrated experimentally that the relative viscosity of dilute poly (amido amine) dendrimer (PAMAM) suspensions in electrolyte solutions increases more rapidly with the volume fraction than the Einstein formula predicts. This deviation could not be explained in terms of the primary electroviscous effect because of the small thickness of the electric double-layer in the salt solutions. The anomalous viscosity behaviour was successfully interpreted in terms of the core/shell dendrimer particle model.

The electrophoretic measurements performed at various pH levels and ionic strengths allowed for a simple and direct way of determining the number of uncompensated (electrokinetic) charge on PAMAM dendrimer molecules under various ionic conditions. This charge was found to be considerably smaller than the theoretical value predicted based on the stoichiometric structure of the dendrimer. For the first time, we have shown experimentally that the isoelectric point of PAMAM dendrimers is located at pH=9.9.

Combined electrophoretic mobility and QCM measurements enabled us to gain reliable information about the mechanism of dendrimer swelling. These measurements clearly demonstrate the essential role of pH and ionic strength on the swelling of dendrimer molecules due to the adoption of an extended conformation upon the protonation of the amine groups.

Our results also have practical merit because they indicate that dendrimers may behave as stimulus-responsive drug delivery systems. Trapped compounds can be released by inducing a conformational transition in the dendrimers' charge, which can be tuned by pH or the ionic strength of the solution.



New Nanostructured Carbon Materials, Oxide Materials and Their Composites as Components of Capacitors

Research project N N507 269936 [2009-2012]
(project leader: Aleksandra Pacuła PhDEng)

1. Two series of composites were synthesized via chemical vapour deposition (CVD) route. CVD experiments were carried out in a horizontal tube furnace. The composites were heated for 30 minutes under a flow of argon saturated with acetonitrile (CH_3CN) vapour. The first set of composites was prepared at temperatures of 600, 700, 800^oC with the use of hydrotalcite-like materials containing the following metals Co and Al or Ni and Al (Co/Al=3, Ni/Al=3). The second set of composites was prepared at temperatures of 600 and 700^oC with the use of hydrotalcite-like materials containing Co, Ni and Al with various M^{2+}/M^{3+} atomic ratio equals 2 or 3 and different cobalt to nickel atomic ratio, e.g. Co:Ni=3:7, 5:5, 7:3.
2. A series of carbon materials were obtained from the composites via treatment with acid. The carbon materials were extracted from the composites with the use of hydrochloric acid during 24-hour process enhanced by 30-minute sonication.
3. Several techniques including X-ray diffraction (XRD), thermal analysis (TG), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and volumetric nitrogen sorption were employed to describe phase composition, structure, morphology and specific surface of newly prepared materials.
4. Electrode properties of the composites and the carbon materials were examined by cyclic voltammetry in alkaline medium. The electrical double layer capacity was measured and the electrocatalytic performance was tested for oxygen reduction reaction and methanol oxidation reaction.
5. The main part (60-67%) of the composites derived from cobalt-aluminum hydrotalcite-like material (Co/Al=3) consisted of metal/metal oxide material, which contained Co, CoO, $CoAl_2O_4$ and Al_2O_3. The remaining part of the composites (33-40%) was the carbon-rich material containing mainly carbon nanotubes. Similarly for the composites derived from nickel-aluminum hydrotalcite-like material (Ni/Al=3), their main component (60-64%) consisted of consisted of metal/metal oxide material and contained Ni, $NiAl_2O_4$ and Al_2O_3. The remaining part of the composites (36-40%) was the carbon-rich material containing mainly carbon nanotubes The composites derived from hydrotalcite-like material with Co/Al=3 showed lower degree of crytallinity than those obtained with the use of hydrotalcite-like material with Ni/Al=3. Treating composites with acid lowered metal/metal oxide component content to 16-26% for the samples containing Co and Al species or 16-22% for the samples containing Ni and Al species.

Acoustic Emission for Monitoring Museum Objects as a Universal Method of the Preventive Conservation

Research project N N105 278536 [2009-2012]
(project leader: Łukasz Bratasz PhD)

The third year of the project implementation was devoted to continuation of research program which has started in the second year.

Measurements of the acoustic emission (AE) were carried out on wood and stucco samples together with monitoring of their deformation during controlled changes of microclimate parameters in their vicinity.

Obtained results indicated that acoustic emission emitted during mechanical loading of wooden samples has the same character as emission recorded when samples were subjected to sudden changes of relative humidity of significant amplitude. However, those signals have different character than signals recorded during small relative humidity variations, which are safe for objects. This proofs finally, that measurement of acoustic emission is an adequate indicator of damages induced by microclimate stimulus. It was found that critical amplitude of humidity variation causing damage is 15-20%, independently on kind of wood species used during tests. This value is consistent with results of computer simulations.

Investigations aiming at better determination of AE characteristic frequencies and development of AE Atlas were continued. For this reason the most spectrally flat sensor available on the market was purchased and implemented in tests of historic samples subjected to mechanical loading.

Very important task for the practical point of view was development and application of calibration procedure allowing for determination of relations between most adequate AE parameter (energy of acoustic emission) and macroscopic damage. Developed procedure was also implemented to determination of sensitivity of the method, which is the smallest damage which can be detected with AE method. Dependently on wood species this value differs from 5 to 30 μm^2.

Last phase of the project was focused on application of AE method to monitoring of real objects from the National Museum in Krakow collection. For this purpose two objects exhibiting damages caused by inappropriate microclimate were chosen: 18th century wooden wardrobe with visible cracks and 19th century gypsum cast with corroding steel reinforcement disintegrating object structure. The monitoring campaign has started and is continued.

Controlled Adsorption as a Method of Protection against the Environment Contamination Caused by the Oxidation of Metal Sulfides

Research project N N523 451336 [2009-2011]
(Assoc. Professor Paweł Nowak DSc)

Metal sulfides are present in the environment as natural components of the lithosphere, on waste depository places of mining and metallurgical industries as well as in the places of abandoned metallurgical works. Oxidation of metal sulfides leads to the contamination of the environment by metal ions and acidification of the environment due to the formation of sulfuric acid (when iron disulfide FeS_2, pyrite, is present in the wastes). In turns, acidification of the environment causes sequent emission of metal ions due to the leaching of the minerals by the sulfuric acid formed in pyrite oxidation.

The object of the research was the elucidation of the influence of adsorption of different surface active compounds on the oxidative dissolution of metal sulfides and the selection of the compounds which might be used as potential inhibitors of that process. The metal sulfides selected for the investigations were natural minerals: galena (PbS), pyrite (FeS_2) and non-stoichiometric copper sulfide $Cu_{2-x}S$ as well as synthetic lead sulfide and copper sulfide. Several compounds were selected that were used either as model compounds or as possible inhibitors: sodium oleate, sodium dodecylsulfate, sodium hexadecylsulfate, sodium bis-(2-ethylhexyl)-phosphate, dodecyltrimethyl-ammonium chloride, N-dodecylpyridinum chloride, n-octanol, polyvinyl alcohol, humic acid sodium salt, 2-mercaptobenzothiazole, potassium ethylxanthate, sodum phosphate and sodium silicate. Adsorption of the above-mentioned compounds was investigated using IR, XPS and electrochemical methods (cyclic voltammetry, impedance spectroscopy) as well as by the measurements of the abstraction from solution. The influence of adsorption on the oxidative dissolution of metal sulfides was investigated by measuring the leaching rate of the mineral samples previously treated with the solutions of selected compounds.

It was stated that physical adsorption does not lead to the formation of adsorption layers strongly bound to the surface and does not exert inhibiting effect on the dissolution of metal sulfides. Adsorption layers strongly bound to the surface are formed in electrosorption, however this process requires relatively high concentration to occur. Strong and stable in time inhibition was observed in the case when the insoluble and resistive to the action of aggressive agents' product was formed on the surface of a sulfide due to the reaction with the solution of investigated compound. The example is sodium oleate which forms insoluble and hydrophobic metal oleates with the metal ions originating from the dissolution of metal sulfides. That compound was selected for further studies on the influence of adsorption on the emission of metal ions from the wastes.

Three types of wastes, representative for the Polish mineral industry were selected for further studies: the deposit from the settling pond from the "Gliwice" coal mine which already finished the production, the deposit from the flotation pulp settling pond in the lead-zinc flotation plant in ZGH "Bolesław" and the deposit obtained by sedimentation of the flotation pulp directly from the copper ore flotation plant in KGHM ZWR "Lubin". Wastes were placed in specially constructed columns, treated or not with the solutions of sodium oleate and washed with water. The composition of eluents was investigated using ICP atomic absorption spectrometry and the other analytical methods. Measurements confirmed the inhibiting action of the sodium oleate solution on the oxidative dissolution of metal sulfides in the case of the wastes from the ZGH 'Bolesław'.

Theoretical and Experimental Analysis of Porosity of Multilayer of Spherical Colloidal Particles

Research project N N204 347737 [2009-2012]
(project leader: Assoc. Professor Paweł Weroński DSc)

We have conducted computer simulations of the layer by layer self-assembling process of colloidal particles. We have generated the multilayer structures of spherical particles according to a generalized model of random sequential adsorption of hard spheres. We have compared transport properties of several multilayers of the same average thickness, obtained by adsorption of subsequent particle layers at various coverages. We have calculated the porosity and tortuosity distribution of the porous films. We have also determined the entrapment ratio of spherical test particle in the layer as a function of its diameter. We have computed the root-mean-square roughness of the multilayers and presented their outer surface topography.

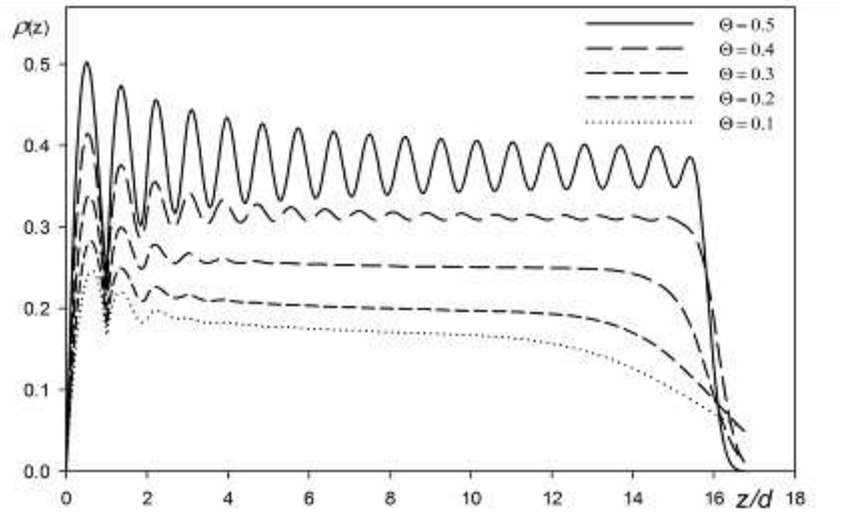
To obtain more precise information on particle distribution in each layer, we have also calculated the particle volume fraction as a function of the distance *z* from the interface using the formula:

$$\rho_i(z) = \frac{\mathrm{d}v_i(z)}{\mathrm{d}v} = \frac{\sum_{j=1}^{N} S_{ij}(z)}{S},$$

where: N is the number of single-layer particles, S is the adsorption surface area, $\mathrm{d}v_i = \mathrm{d}z\sum_{j=1}^{N} S_{ij}(z)$ is the infinitesimal volume of particles from the layer number i in the volume element $\mathrm{d}v = S\mathrm{d}z$ (having the infinitesimal thickness d*z*), and $S_{ij}(z)$ is the cross-section area of the particle j from the layer number i at the distance z from the adsorption surface. The overall particle volume fraction $\rho(z)$ is given by

$$\rho(z) = \sum_{i=1}^{l} \rho_i(z).$$

In the figure below we present overall particle volume fraction for multilayers of the average thickness of 16 particle diameters and different single-layer coverage *Θ*.



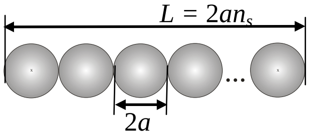
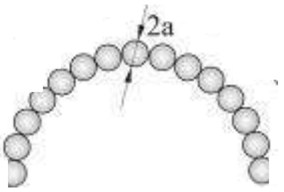
Our results suggest that the coverage of 0.3 is optimal for producing a uniform multilayer with constant porosity in a minimum number of adsorption cycles.

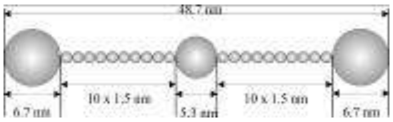
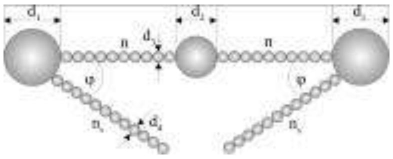
New Method of Evaluating Colloid Particle and Protein Interactions with Interfaces Based on Streaming Potential Measurements

Research project N N204 026438 [2010-2013]
(project leader: Professor Zbigniew Adamczyk DSs)

The knowledge of hydrodynamic mobility tensors and intrinsic viscosity has an essential significance for predicting conformations of proteins in electrolyte solutions for determining kinetics of aggregation processes, and mechanisms of their interactions with interfaces leading to mono- and multilayer adsorption. Because of complicated shapes of proteins, deviating significantly from the spherical shape, theoretical calculations are very tedious. Thus, the aim of this work was elaborating a new, efficient hydrodynamic model of proteins, based on the bead concept. According to this model, the real shape of the molecule is replaced by a constellation of beads of various sizes, having the same volume as the molecule. Using this model, extensive calculations were carried out, aimed at determining the hydrodynamic resistance matrix, the diffusion tensor and the intrinsic viscosity of proteins. Our calculations were based on the linear Stokes equations describing fluid velocity fields. The no-slip boundary conditions were applied on solid surfaces, the ambient flow was assumed to be zero and the fluid was assumed unbounded. Using the formalism of induced forces, and the Oseen tensor as the Green's function for the infinite system geometry, the Stokes equations are transformed into a set of boundary integral equations at the surfaces of all spheres. These equations are next projected onto a complete set of spherical multipole functions. Contrary to previous approaches, the hydrodynamic resistance, the diffusion tensors and intrinsic viscosities were evaluated by taking into account the coupling between translation and rotation of protein molecules. The hydrodynamic radius R_H for various particle aggregates calculated according to this scheme of calculations is shown in Table 1. This parameter was also determined for the fibrinogen molecule whose shape was approximated in terms of two different models: model A - without considering the presence of side arms and model B - considering the presence of side arms forming an arbitrary angle with the main body of the molecule (Table 1). It was shown that our theoretical calculations obtained for model B adequately describe experimental data obtained by the DLS method for fibrinogen solutions. This allows one to unequivocally determine conformations of this protein in electrolyte solutions.

Table 1. Hydrodynamic radii for particle of various shapes (theoretical values)

Particle shape	R_H expression	Remarks, Ref.
 Solid sphere linear aggregate	$R_H = \frac{n_s}{(\ln 2n_s - 0.253)} a$	Analytical interpolation valid for $10 \le n_s \le 450$ (1% precise) for $2 \le n_s \le 450$ numerical solution Ref.[1]
 Half circle made of n_s spheres	$R_H = \frac{n_s}{0.95\ln 2n_s + 0.02} a$	Analytical interpolation valid for $10 \le n_s \le 450$ (3-1% precise) for $10 \le n_s \le 450$ numerical solution Ref.[1]

 Circle (ring) made of n_s spheres	$R_H = \frac{n_s}{\frac{11}{12}\ln 2n_s + 0.67} a$	Analytical interpolation valid for $10 \le n_s \le 450$ (3-1% precise) for $10 \le n_s \le 450$ numerical solution Ref.[1]
 Fibrinogen Model A	$R_{H_0} = 8.54\,\text{nm}$	numerical solutions, this work
 Fibrinogen Model B	$R_H = R_{H_0} +$ $\left(R_{H_\infty} - R_{H_0}\right)\sin\left(\frac{\varphi}{82.5^\circ}\right)$ $R_{H_\infty} = 11.1\,\text{nm}$ $R_{H_0} = 8.67\,\text{nm}$	numerical solutions, this work

Remarks: The average translation diffusion coefficient of a particle is given by: $D = \frac{kT}{6\pi\eta R_H}$

[1] Z.Adamczyk, K.Sadlej, E.Wajnryb, M.L.Ekiel-Jeżewska, P.Warszyński, J.Colloid Interface Sci. 347, 2010, 192

Modeling of Kinetics and Equilibrium of Heavy Metal Ion Sorption by Materials of Biological Origin

Research project N N204 291238 [2010-2012]
(Professor Władysław Rudziński DSc)

The metal ions/biosorbent systems were studied from the point of view of the surface-heterogeneity-related effects and their transposition into the concept of the ion-exchange constant. The dispersion of the ion-exchange constant is strongly dependent on: (i) the nature of dispersion of affinity constants toward metal ions and protons; (ii) the existence or the lack of correlation between the values of affinity constants toward metal ions (K_{M}) and protons (K_{H}). When the strong correlations are assumed, the dispersion of the ion-exchange constant is smaller (or, in the limiting case, the same) in comparison to those of affinity constants. On the other hand, when no correlation is assumed, the dispersion of the ion-exchange constant is greater than those corresponding to any of the affinity constants. Furthermore, the approximation proposed for the systems with discrete distributions of K_{M} and K_{H} and based on replacing several affinity constants by only one (average) ion-exchange constant is exact for pHs lower than the lowest value of pK_a and for the systems in which only the monodentate binding mechanism exists.

The problem of interpretation of the experimental data related to the thermodynamics of metal ions binding by alginate-based biosorbents was studied. When considering the thermodynamic parameters (i.e., changes in the enthalpy and entropy values; ΔH and ΔS, respectively), one can observe large discrepancies between their values even if the considered systems have very similar features. It appears that both numerous "technical" (e.g., pH, ionic strength) and model-related (e.g., monodentate vs. bidentate binding models) parameters can seriously influence the obtained values of thermodynamic parameters. The significance of these two types of factors was discussed in qualitative and quantitative manners. The proposed methods of distinguishing between the "apparent" and the "real" ΔH and ΔS values can be also related to other types of sorption/adsorption systems.

Biocatalytic Synthesis of Chiral Alykaromatic and Alkylheterocyclic Alcohols with Ethylbenzenee Dehydrogenase- Theory and Experiment

Research project N N204 269038 [2010-2013]
(project leader: Maciej Szaleniec PhD)

Research conducted within task 1 (Application studies) has focused on finding an effective way of immobilization of ethylbenzene dehydrogenase. Two complementary approaches have been applied: covalent immobilization to the modified silica carrier and adsorption to the synthetic hydroxyapatite (BioRad).

In the first stage, enzyme was immobilized by covalent bonding to the functionalized silica SBA-S. N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane (AEAPTS) was used to functionalize silica surface and glutaraldehyde as a connecting factor. Activity of the immobilized enzyme was determined by chromatographic measurements of concentration of the reaction product ((S)-1-phenyloethanol). Reactions were carried out in tubes with a magnetic mixer simulating conditions of a batch reactor.

Studies have show, that unfortunately covalently immobilized EBDH is characterized by low operational stability. Activity of the immobilized EBDH is ten times lower than the homogenous one and the conversion of substrates is three times lower in comparison with the native enzyme. However, the immobilized enzyme stored at 0°C in the oxidizing environment (ferrocenium tetrafluoroborate solution in TRIS/HCl, pH 7.5) stays active for about 32 days, although the enzyme activity is continuously decreasing. The reference native enzyme stored at 0°C loses 90% of its catalytic activity after 10 days.

The second approach to immobilization was a non-covalent adsorption of protein on the hydroxyapatite powder (HAp). Activity of the immobilized protein was determined by the spectrophotometric assay and HPLC measurements of the concentration of reaction product. After the immobilization the enzyme activity was determined at 12% of the activity of native protein. The obtained results show that within 10 days of storage of the immobilized EBDH at 0°C and in an oxidizing environment, immobilized protein loses 100% of the activity.

Research conducted within task 2 has focused on the calculation of reaction energetic profile with QM:MM approach. The model comprised of a whole α subunit with a crystallization water. The QM part contained beside fragments of molybdenum cofactor residues of Asp^{223}, His^{192} and a substrate molecule (ethylbenzene). The modeling was conducted with either mechanical or electrostatic embedding.

The results of calculations show a profound influence of the embedding method (present or absent polarization of QM part by MM part) on the process of second electron transfer. For electronic embedding pathway high degree of electrostatic stabilization of carbocation is observed for intermediate product enzyme complex (E-I) as well as for transition state associated with OH transfer (TS2).

Functional Nanostructures of Manganese Oxides Doped with Other Metals

Research project N N204 269238 [2010-2013]
(project leader: Robert Socha PhD)

Low dimensional structures of manganese oxides (II-VII) have found growing interest due to their morphologic, electronic and magnetic properties. Only few approaches to synthesis epitaxial structures of manganese oxides (mainly MnO and Mn_3O_4) have been undertaken recently. This gives an opportunity for synthesis new systems of interesting properties, different that the ones existing in nature and leading to dispersed forms of higher catalytic selectivity.

In our studies we concentrated on application of different synthesis methodology to obtain mixed manganese (II) iron (II) oxides.

The synthesis was performed by two different methods i.e. oxidation of intermetallic Fe_xMn_{1-x} alloy or annealing of metallic layer deposited on manganese oxide (II). MgO(001) annealed at 820 K was used as a substrate. Deposition of manganese and iron was performed from the effusion cells. The composition and electronic states of elements in the studied systems were analyzed by AES, XAES and XPS. Additionally, application of ^{57}Fe allowed Mössbauer Spectroscopy (MS). Every step of synthesis was structurally characterized by LEED.

It was found that oxidation of metallic manganese led to MnO(001) in broad range of oxygen pressures ($2\cdot10^{-7}$-$1\cdot10^{-6}$ mbar) and temperatures (423-673 K). The thickness of stoichiometric MnO approached 6 nm. Oxidation of manganese above 673 C led to increase in concentration of Mn^{3+} and Mn^{+4} ions although Mn^{2+} was still the main manganese oxide component.

In first synthesis route, the manganese layer of 20 nm in thickness was covered by 2 nm of ^{57}Fe and annealed to obtain bimetallic layer isostructural with metallic manganese one. Annealing was performed in the temperature range of 373-673 K, which resulted in iron dissolution in the manganese bulk. The resulting alloy was oxidized in oxygen ($1\cdot10^{-7}$-$5\cdot10^{-6}$ mbar) leading to the mixed $Fe_xMn_{1-x}O$ oxide isostructural to MnO(001).

In second synthesis route, a layer of MnO(001) was prepared by oxidation of manganese layer (20 nm). Then metallic ^{57}Fe (2 nm) was deposited at the MnO surface at 295 K resulting in sharp (1 monolayer of FeO confirmed by MS) Fe/MnO interface. Annealing of this interface at 673 K resulted in $Fe_xMn_{1-x}O$ oxide formation.

Independently of the applied synthesis method, metallic iron was found at the oxide surface suggesting incomplete surface oxidation. Additionally, XPS measurements showed oxygen deficiency at the MnO/Mn interface.

Both applied methods resulted in similar composition of obtained $Fe_xMn_{1-x}O$ oxides, where manganese (II) and iron (II) were the main chemical components (XPS, AES). The surface structure was the same as determined by LEED.

Composite Cathodes for Solid Oxide Fuel Cells (SOFC) Working at Temperature 600°C and Lower Containing Silver

Research project N N507 616638 [2010-2013]
(project leader: Michał Mosiałek PhD)

Solid oxide fuel cells (SOFCs) are considered as promising environment-friendly next generation electric power sources because of their high efficiency. Considerable efforts were made in recent years to reduce the operating temperature of SOFCs to the intermediate temperature range 500-700°C. Nowadays the cathode is still the limiting component to make a further step forward. One of the possible solutions of that problem may be the reduction of the ovepotential of the oxygen reduction step by adding silver to the cathode material. Our investigations were focused on the possibility of applying metallic silver as a material for composite cathodes in the temperatures up to 600°C.

The first stage of the project titled "The development of the containing silver electrode materials formation. The characteristics of obtained materials (phase composition, porosity, microstructure)" was continued at 2011. The $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-d}$ (LSCF) cathode material and $Sc_{0.09}Zr_{0.91}O_{2-d}$ (9ScSZ), $Gd_{0.2}Ce_{0.8}O_{1.9}$ (20GDC) were obtained and characterized by XRD, SEM, EDS and XPS. Dense discs were formed then sintered from these materials. The LSCF disk was cut into long needles to observe point electrode behavior. The second stage of the project titled "Electrochemical measurements on connections Ag|oxide electrolyte (SDC, GDC, ScSZ) to describe oxygen reduction reaction (ORR)" began. Electrochemical Impedance Spectroscopy (EIS) measurements on Ag|GDC oraz Ag|ScSZ in various temperatures and oxygen concentrations were performed. The third stage of the project titled "Electrochemical measurements on connections composite cathode material containing Ag |oxide electrolyte to describe oxygen reduction reaction" also began.

Porous $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) and composite Ag/SSC electrodes on 8YSZ and 20GDC were produced by three methods. EIS measurements in various temperatures and oxygen concentrations were performed. $Ag/Sm_{0.5}Sr_{0.5}CoO_3$|20GDC|Ni and $Sm_{0.5}Sr_{0.5}CoO_3$|20GDC|Ni cells were tested. Electrodes with introduced silver have lower ORR resistance and gave higher power density in tested fuel cells.

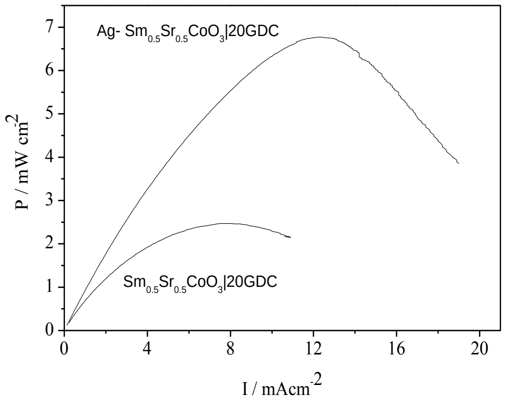


Fig. 1. Power density in $Ag/Sm_{0.5}Sr_{0.5}CoO_3$|20GDC|Ni and $Sm_{0.5}Sr_{0.5}CoO_3$|20GDC|Ni cells

New Methods for Powder Diffraction Studies of Structural Materials, Partially Amorphous, Disordered and of Reduced Dimensionality

Research project N N204 546439 [2010-2012]
(project leader: Professor Wiesław Łasocha DSc)

Many interesting materials such as zeolites, layered or fibrous materials, crystallize in the form of polycrystalline samples, often of poor quality. These materials can be valuable catalysts and composites with interesting physical properties. Their structural studies are extremely difficult due to very bad quality (and poor, in the classic sense, in the structural information) diffraction images.

Within the project, the following activities were carried out:

- Modernization and upgrading of the research facility (X'Pert Pro MPD diffractometer) in the Ag lamp with a set of filters, tests measurement were carried out. Suitable measuring programs were prepared.
- Undertaken were research on the determination of lattice parameters for the unusual specimens, including a very high texture, as well as cases of significant differences in the size of the lattice parameters.
- Some research were performed on the use of both classical (global optimization) as well as new methods, including the 'charge flipping', to the structural study of 'nonstandard' specimens. The object of the study were samples of liquid crystals, greasy layered sediments and salts of carboxylic acids with long chains.
- Some work was conducted on an independent verification of the structure models by non-diffraction methods. Support for the powder diffraction methods are supplied by computational methods, including the method DFT (Density Functional Theory). Calculations of this type were performed for a number of halogeno-anilines polymolybdates.
- In the final stages, we plan structural studies conducted on the basis of the PDF formalism (**p**air **d**istribution **f**unction). Their goal is not only putting the hypotheses regarding the ‘raw construction’ of ‘building blocks’, but also the quantitative verification of the created models by their refinement in a manner similar to the Rietveld method.

The project objectives can be defined as "to adopt and supplement existing procedures (for measurements and computation) by the essential elements (X-ray Ag tube, CHARGE FLIPPING, PDF or DFT methods), allowing wider use of powder diffraction methods to the structural characteristics of new materials exhibiting a high degree of disorder, the presence of nano-phase or partially amorphous phases, based on a laboratory X-ray sources". These objectives are realized, the work is carried out according to schedule.

Stability, Functionality and Mechanism of Creating Polymer-Casein Multilayer Structures

Research project N N204 546639 [2010-2013]
(project leader: Lilianna Szyk-Warszyńska PhD)

The main aim of this project is determination of the mechanism of formation and stability of the multilayer polyelectrolyte films with embedded casein and verification of its bioactivity, i.e. ability to bind the calcium ions

In year 2011 we investigated formation of polyelectrolyte multilayer films containing α- and β-casein. Since in neutral pH casein is negatively charged it was used as a polyanionic layer for the film build-up with poly-L-lysine, arginine and chitosan as polycations. The sequential adsorption of polyelectrolytes (layer-by-layer technique) was applied to form films at surface of silicon wafers and quartz crystals. Afterwards, thickness of the films was determined by ellipsometry and QCM. We investigated dependence of thickness of casein containing films on the ionic strength of the polyelectrolyte solution and exposure to solutions of various composition and pH. The optimal conditions for film formation were at I 0.15 M NaCl (films had maximum thickness). Films were not resistant to solutions of pH 2 due to charge reversal of casein and pH 11 due to neutralization of PLL. At the isoelectric point of casein, pH 4.5, only films containing α-casein were stable. Similarly, in neutral conditions, these films were more stable than ones with β-casein, when contacted with the solutions with various composition. We determined that films build-up with arginine were much thicker (around 80 nm) than that with poly-L-lysine (30 nm). Unfortunately, we could not achieve satisfactory results for films build with chitosan. The maximum thickness of these films was only 6 nm. That can be explained by the low positive charge of chitosan in the pH range above the isoelectric point of casein.

Studies of Structure and Properties of a Magnetically Triggered Molecular Nanocontainer

Research project N N204 546639 [2011-2014]
(project leader: Assoc. Professor Tomasz Pańczyk DSc)

Properties of a molecular nanocontainer composed of a carbon nanotube linked to magnetic nanoparticles by alkane chains depend strongly on a choice of materials used for its construction. Properties of carbon nanotubes are, at least in this case, not critical but the choice of nanoparticle material is crucial for a proper function of the nanocontainer as e.g. drug delivery vehicle. A key factor is a magnitude of the saturation magnetization of the nanoparticle material. It must be as large as possible because the energy of interaction with external fields should be enough to overcome the activation barriers accompanying the uncapping process. Another strict conclusion coming from our studies is that nanoparticles should be large as it facilitates the ferromagnetic ordering and enhances magnetic anisotropy constants.

Many important experimental observations suggested that the original model of the nanocontainer needs extension, particularly concerning the description of magnetic nanoparticles. Normally, such nanoparticulate systems are not uniform and, in order to improve their stability and avoid agglomeration, protective shells are created. Therefore, a new model for description of magnetic nanoparticles has been developed which accounts for the core-shell architecture of the nanoparticles. A few combinations of the core and shell materials have been studied. As the core material metallic cobalt is used due to its high value of the saturation magnetization whereas as the shell materials alumina and silica have been studied. A few other materials have been discussed qualitatively in terms of the results obtained for silica and alumina. Other parameters which turned out to be very important are the alkane chain length and thickness of the oxide shell.

As a result, it was found that a functional nanocontainer can only be build of nanoparticles which protective oxide shells are possibly thin and exhibit the Hamaker constants in the range $4\text{-}20\cdot10^{-20}$ J and the alkane chains should be short. Figure 1 compares some illustrative results concerning the probability of observation of the capped/uncapped states of the nanocontainer as a function of the magnetic field strength.

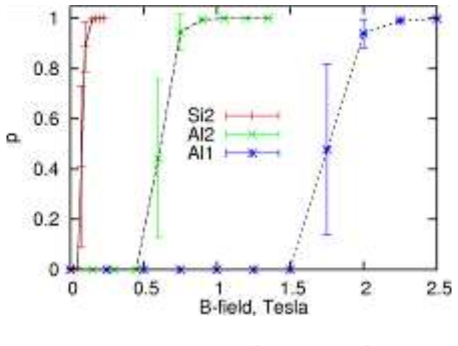


Fig. 1. Probability of finding the nanocontainer in capped/uncapped states as a function of the magnetic field strength for: Al1 - alumina shell and 1 CH_2 segment; Al2 - alumina shell and 2 CH_2 segments; Si2 - silica shell and 2 CH_2 segments.

Influence of Micro- and Nano-bubbles at Hydrophobic Surfaces on Kinetic and Mechanism of the Three Phase Contact Formation in Milliseconds Timescale

Research project N N204 133640 [2011-2014]
(project leader: Jan Zawała PhD)

The aim of the project is to investigate influence of (i) roughness of the hydrophobic surface and (ii) presence of sub-microscopic air bubbles at these surfaces on kinetics of the three-phase contact (TPC - gas/liquid/solid) formation and the bubble attachment. During the reporting period the kinetics of the bubble attachment to the hydrophobic Teflon surfaces of controlled roughness in distilled water as well as solutions of α-terpineol and n-octanol (frothers) were investigated. The roughness of the Teflon plates was varied within the range of 1-100 μm. The collisions of the bubble of radius R_b=0.74 mm with Teflon plates was monitored using high-speed camera of frequency 1040 Hz. The distance between the bubble formation point and the liquid/solid interface was chosen in such a way that the bubble impact velocity was equal to its terminal velocity (34.7 cm/s). The influence of surface roughness and concentration of the frothers studied on time of the TPC formation (t_{TPC}) was determined from analysis of the movies recorded. It was found that at low α-terpineol and n-octanol concentrations the t_{TPC} values were shorter than in distilled water. However, at higher frothers concentrations a rather unexpected effect of elongation of the t_{TPC} values was observed (see Fig. 1). As can be observed there, for example for the Teflon plate of roughness 40-60 μm (T600) the t_{TPC} values were longer by even 20-30 ms when the α-terpineol and n-octanol concentration was increased to $1 \cdot 10^{-3}$ M. The results obtained indicate that the effect of elongation of the time of TPC formation in high concentration of the frothers studied is related to presence of air in form of nano- and micro-bubbles at the hydrophobic Teflon surfaces. As the affinity to air is a common feature of highly hydrophobic solids (Teflon) so air can be entrapped in scratches and irregularities of the Teflon surfaces during the plate immersion into the aqueous phase. Prolongation of the t_{TPC} values at high α-terpineol and n-octanol concentrations is a confirmation that air is present at Teflon surface because stability of foam films increases with concentration of surface active substances. Increased stability of local foam films formed between sub-microscopic bubbles attached to the Teflon surface and the colliding macro-bubble caused prolongation of the t_{TPC} values at high α-terpineol and n-octanol concentrations.

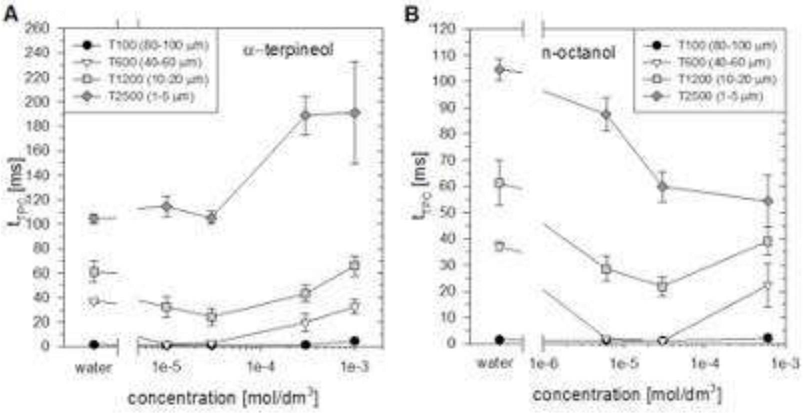


Fig. 1 Time of the TPC formation during the bubble collision with Teflon surfaces of different roughness

Quantum-chemical Studies on the Mechanism of Transmetallation Reaction of Porphyrin and its Selected Derivatives

Research project N N204 439640 [2011-2014]
(project leader: Professor Małgorzata Witko DSc)

The present research aimed at the elucidation of the mechanism of transmetalation of porphyrin by copper(II) ions. On the one hand, the studied process is considered as a model reaction for substitution of magnesium by copper in chlorophylls, which takes place in plants growing on heavy-metal polluted soils. On the other hand, it is one of the established methods of metalloporphyrin synthesis.

The present studies are done within quantum-chemical method based on Density Functional Theory (DFT) with the non-local gradient-corrected Becke-Perdew functional, with Ri approximation, as implemented in Turbomole program suite. The studied systems are characterized by geometry (bond lengths, valence angles) and electronic (charges) parameters as well as total energy changes accompanying each of the reaction steps.

First, the sixth coordinate magnesium porphyrin complex with two acetonitrile molecules (MeCN) as axial ligands is characterized. This models the solvated species found in magnesium porphyrin solution in acetonitrile (a common sovent), which are considered as the initial structure for the considered reaction. The possible adducts, which may be formed when acetate is added to the solution, are considered. The bonding between the central metal and various ligands is additionally examined by SAPT(DFT) method, to fully understand its nature.

Next, the mechanism of metalation by copper is elucidated. Based on the performed theoretical and experimental studies it is proposed that transmetallation proceeds through the following steps:

1. atack of an acetate ion on Mg^{2+} in porphyrin, dissociation of the MeCN ligand,
2. tetrapyrrole ring deformation and association of Cu ion - binding to the nitrogen from porphyrin ring,
3. formation of so called "sitting atop" complex in which two metal ions are coordinated by tetrapyrrole ligand,
4. dissociation of chelated Mg^{2+}, insertion of Cu^{2+} into tetrapyrrole cavity.

The New Multi-layered Systems with Controlled Architecture and Functionality

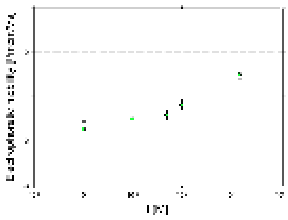
Research project N N204 439040 [2011-2014]
(project leader: Jakub Barbasz PhD)

The project was implemented according to schedule. Layer formation model has been studied by parallel adsorption algorithms based on RSA and molecular dynamics.

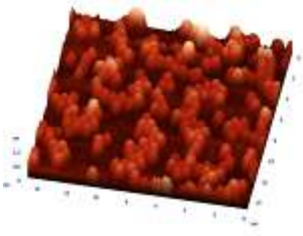
Developed a model of the kinetics of formation of a layer which is in good agreement with experimental results.

Considered the volumetric characteristics of polystyrene latexes and proteins (HSA and fibrinogen).

Determined: size, surface charge, electrophoretic mobility (example) and the stability of solutions depending on the concentration and ionic strength.



Example – Electrophoretic mobility of HSA (Human Serum Albumin, 99% agarose gel electroforesis; fatty acid<0.007%)



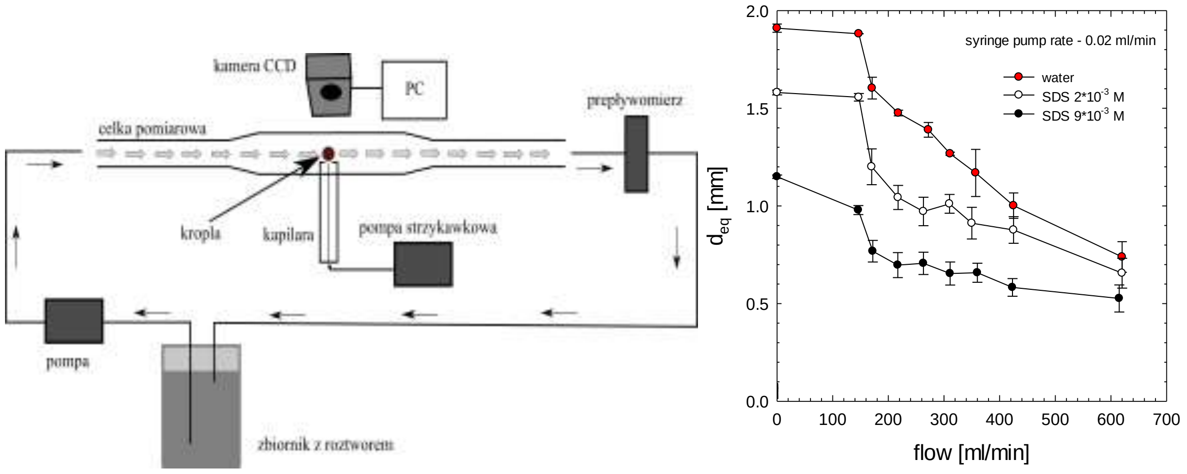
The AFM 3D image of latex particles mixture adsorber on a mica substrate.

Application of Membrane Emulsification for Formation of Nano- and Microcapsules' Cores

Research project N N204 757340 [2011-2014]
(project leader: Professor Piotr Warszyński DSc)

The main aim of the project is to develop the scientific background of effective method of preparation well defined emulsions using membrane emulsification method. Such emulsions will be used as cores in encapsulation process. Membrane emulsification method is low energy consumption process which allows controlling size of the obtained emulsion droplets by right selection of membrane material, their porosity, average pore size, concentration of surfactants. Apply of the membrane method to the formation of nanocapsules should allow production of the nanocapsules on an industrial scale.

In 2011 we were focused on the development of the theoretical model and simulation of the process of growth of single droplet on single pore in surfactant solutions in the presence of a specific shear force ("single pore"method) and on validation of the theoretical predictions by experimental results. The theoretical work consisted of formulation of the droplet growth model taking into account dynamic interfacial tension, buoyancy force and hydrodynamic force on the drop, resulting from the shear flow. The model was verified based on experimental results obtained in the single pore method. The study consisted of measuring the influence of shear force and surfactant concentration on the size of a single droplet of oil formed in a well-defined and controlled conditions. Droplets were formed on a capillary with a given diameter and the process of their formation and the moment of detachment from the capillary was monitored using a CCD camera in the system shown in Figure 1a. Figure 1b shows dependence of the size of the droplets on the flow of dispersing phase for the dodecane-SDS-water system.



a) b)

Figure 1a) Scheme of the single pore setup b) dependence of the size of the droplets on the flow of dispersing phase for the dodecane-SDS-water system

Ph.D. research projects
of the Ministry of Science and Higher Education

Influence of Modification of Electron Density of Catalysts Active Centre on Its Activity in Hydrocarbons Oxidation

PhD research project N N205 018934 [2008-2012]
(Professor Ewa Serwicka-Bahranowska DSc, Robert Karcz MScEng)

Heteropoly acids form a wide group of nanosized metal-oxygen cluster anions, which may be represented by the general formula $[X_xM_mO_y]^{q-}$ ($x \leq m$), where X is the central atom (e.g. Si^{4+}, P^5+, As^{5+}, Ge^{4+}) and M is metal ion, usually molybdenum or tungsten in their highest oxidation states. The main reason which makes these compounds particularly attractive from the point of view of catalysis is the possibility of tailoring their acid-base and redox properties by an appropriate choice of chemical composition.

In the present research Keggin type tungstophosphoric and molybdophosphoric acids were modified by exchange of protons for transition metal cations or by the formation of lacunary anions followed by incorporation of transition metal cations into the lacunary position. In the former case, samples with various content of Co(II) replacing acidic protons were prepared. The lacunary compounds, substituted with Co(II), Mn(II) or Fe(III), were prepared as tetrabytulammonium salts to improve their solubility in the organic media. The synthesized catalysts were characterized by XRF, ICP-OES, XRD, DSC-TG, FTIR and UV-Vis spectroscopy. Results of physicochemical studies confirmed that the solids possessed desired structures and compositions. The obtained heteropoly compounds were applied as catalysts for the liquid phase oxidation of phenol, cyclooctane, and cyclohexene. In the reported period the acid and/or redox properties of the catalysts were probed in the test reaction of ethanol conversion.

The observed pathways of ethanol transformation over the investigated heteropoly compounds confirmed the expected higher acidity of the 12-tungstophosphoric series of cobalt salts, as compared to the analogous 12-molybdophosphoric series. Dehydration pathway was controlled by the presence of acidic protons compensating the heteropoly anion charge, and by protons generated by dissociation of water coordinated to cobalt cations. The oxidative dehydrogenation pathway, whose occurrence depended on the redox properties of the heteropoly anion, appeared only in molybdenum-based heteropoly acid and its salts, and was associated with the redox properties of Mo centres. Oxidative dehydrogenation was only indirectly affected by the presence of cobalt cations in the secondary structure. Ethanol decomposition over tetrabutylammonium salts of transition metal substituted tungstophosphoric acid occurred chiefly via dehydration to ethylene, irrespective of the nature of the substituting transition metal. The acidic properties were attributed to the presence of protons compensating the anion charge along with the tetrabutylammonium cations.

Conformations of Selected Globular Proteins in Aqueous Solutions and on Interfaces of Controlled Heterogeneity

PhD research project N N204 166336 [2009-2011]
(Professor Zbigniew Adamczyk DSc, Monika Wasilewska MSc)

Extensive measurements of the kinetic of adsorption and conformations of fibrinogen (Fb) on mica surface have been performed. This protein, one of the most important in serum, plays an essential role in blood clotting. In order to select the optimum parameters for adsorption kinetic measurements, bulk characteristics of Fb suspensions were carried out including the diffusion coefficient and the electrophoretic mobility for various ionic strength and pH. In this way the number of uncompensated (electrokinetic) charges on protein surfaces was determined. The electrophoretic mobility data were also converted to the zeta potential values, which allowed one to determine the isoelectric point (i.e.p.) of Fb, which was found to be at pH=5.8. Hence, for pH<5.8 the Fb acquired a positive charge reaching the maximum value of 34 elementary charges for pH=3.5. This important finding suggested that a significant adsorption in the side-on orientation of the molecule can take place on negatively charged substrate surfaces, e.g., mica, whose electrokinetic properties also were determined using the streaming potential method. Afterwards, extensive kinetic measurements of Fb on mica were performed for pH=3.5 and 7.4 under diffusion-controlled transport using the direct AFM method working in the semi-contact mode. A typical fibrinogen monolayer on mica acquired by AFM is shown in Fig. 1. By determining the dependence of the surface concentration of Fb on the adsorption time, one can evaluate in a quantitative and direct way the kinetics of adsorption of this protein also shown in Fig. 1. This enables one to determine, using the appropriate theoretical formula, the bulk concentration of the protein below 0.1 ppm, which is not possible by commonly used chemical methods. It should be also mentioned that the AFM measurements enabled one to determine not only the surface concentration of adsorbed molecules but also their conformations and dimensions of molecules (length and diameter).

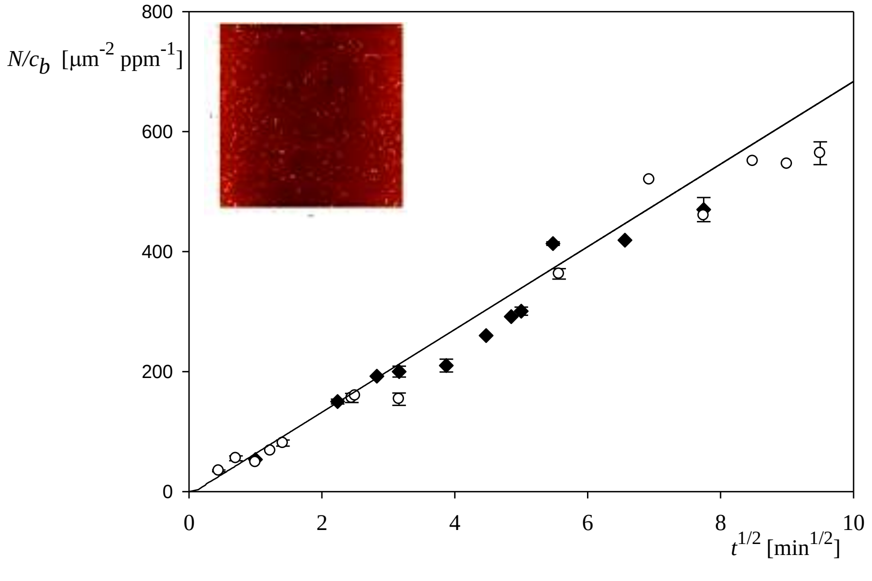


Fig. 1. The dependence of the reduced surface concentration of fibrinogen N/c_b [μm^{-2} ppm^{-1}] on the square of adsorption time $t^{1/2}$, $I = 10^{-3}$ M. The solid points denote experimental results obtained by a direct AFM enumeration for pH 3.5 (various bulk concentrations of fibrinogen) and the hollow points denote results obtained for pH 7.4. The solid line shows exact theoretic results obtained using the RSA model. The inset shows the fibrinogen monolayer on mica imaged by AFM.

Physicochemical Properties and Catalytic Activity of Hybrid Catalysts for the Direct Synthesis of Dimethyl Ether from Syngas

PhD research project N N204 279937 [2009-2011]
(Assoc. Professor Ryszard Grabowski DSc, Michał Śliwa MSc)

The activity of bifunctional catalysts in syngas to dimethyl ether process consisting of metallic function (Cu/Zn/Al/X, Cu/Zn/Zr/X, where X = Mn, Ga) obtained by the carbonate and citric method and of montmorillonite K10 as acidic function has been determined. These two components were combined by physical mixing in volume ratio metallic to acid function equal to 2:1. The physicochemical studies of the metallic functions revealed that the carbonate method leads to the metallic functions of higher copper dispersion (D_{Cu}), higher copper surface area, lower CuO crystal sizes and lower reduction temperature in comparison with metallic functions obtained by the citric method. It has been revealed that addition of the promoters enhance the copper dispersion. The acidic properties of the montmorillonite K10 were tuned by $H_3PW_{12}O_{40}\cdot 23.5H_2O$ tungstophosphoric acid (TPA) deposition of one monolayer. This modification causes the significant increase in dimethyl ether (DME) yield with no light olefins formation. Additionally, the activity of the bifunctional catalysts was correlated with the copper dispersion (D_{Cu}) in the metallic functions. Characterization of the obtained hybrid catalysts was made basing on the following analytical techniques: XRD, BET, TPR, SEM/EDS, FTIR, N_2 adsorption, ICP-AES

The CuO phase ($2\Theta=35{,}5^o$ and 39^o) dominates in the all metallic samples. ZnO ($2\Theta=32^o$) is the second phase which is distinguished in the catalysts. The absence of the characteristic reflections for ZrO_2, MnO, Ga_2O_3 and Al_2O_3 can be explained either by their low concentration (MnO, Ga_2O) or by the amorphous state (ZrO_2, Al_2O_3) in which these oxides are present in the catalysts. The CuO crystal size and dispersion depends on the promoters' presence (Mn, Ga) and in case of metallic components containing zirconium instead of gallium additionally on weight ratio between zirconium and promoter (Zr/P). For the catalyst from both series, the linear correlation between CuO crystal sizes in fresh catalysts (before reduction) and sizes of the metallic Cu^o crystals, which are present on the surface of the catalysts after reduction, is observed

The UV-VIS analysis revealed that the total amount of TPA is sufficient to cover the surface of montmorillonite K10 only with 0.8 monolayer. This suggests uneven coverage by TPA what leads to the formation of TPA blocks of different height. The increase in the intensity IR bands assigned to pyridine adsorbed on Brønsted acidic sites for TPA-K10 in comparison with montmorillonite K10 proves that acidity of TPA-K10 is higher than for the support. The increase in acidity for TPA-K10 results from the higher concentrations of Brønsted acidic sites and higher strength as well

All tested hybrid catalysts shows maximum yield to DME in the temperature range 280-300^{o}C.

Mechanisms of Irreversible Adsorption of Nanoparticles and Selected Proteins on Interfaces Determined by Electrokientic Methods and the AFM

PhD research project N 204 137537 [2009-2011]
(Professor Zbigniew Adamczyk DSs, Maria Dąbkowska MSc)

The goal of this study was to determine the range of applicability of the new theoretical model, enabling calculations of the streaming potential for surfaces covered by nanoparticles, polymers and proteins. This has an essential significance for elaborating of an sensitive method of determining protein adsorption and desorption kinetic under *in situ* conditions. In this work experimental measurements were performed for human serum albumin (HSA) using the four-electrode, microfluidic streaming potential cell. From these streaming potential measurements the zeta potential of HSA monolayers on mica was calculated. In Fig. 1 results of these measurements are show, carried out for pH=3.5 and the ionic strength of 10^{-2} M NaCl. These experimental data were interpreted in terms of two theoretical approaches (i) the Gouy-Chapman model, which neglects the heterogeneity of charge distribution due to adsorbed protein molecules. As can be seen (dashed-dotted line in Fig. 1) this model proved inadequate. However, the experimental data were properly reflected by (ii) our model postulating a monolayer particle-like adsorption of albumin (solid line in Fig. 1). Hence, the results shown in Fig. 1 unequivocally indicate that the streaming potential method applied in this work enables precise determination of the albumin coverage. This is especially valuable for the lower range of albumin coverage where other, mostly indirect methods, become inaccurate.

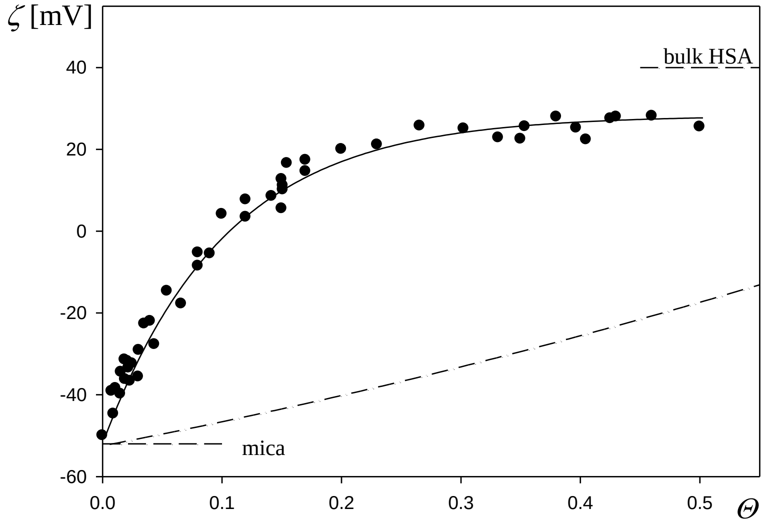


Fig. 1. The dependence of the zeta potential of mica ζ on the coverage of human serum albumin (HSA). The points denote experimental results obtained from the streaming potential measurements for pH=3.5, $I=10^{-2}$ M. The solid line denotes exact theoretical results calculated from the three-dimensional adsorption model developed in this work and the dashed-dotted line denotes the theoretical results calculated from the Gouy-Chapman model [M.Dąbkowska, Z.Adamczyk, J. Colloid Interface Sci. 366, 2012, 105]

Influence of Cationic Surfactants and pH on Kinetics of the Three-phase Contact Formation at Solid Surfaces of Low Hydrophobicity

PhD research projekt No: N N204 179439 [2010-2012]
(Professor Kazimierz Małysa DSc, Anna Niecikowska MScEng)

The project aim was to determine the mutual importance of electrostatic interactions and hydrophobicity of solid surface on kinetic of the three phase contact (TPC) formation (gas/liquid/solid) under dynamic conditions at surfaces of low hydrophobicity. Measurements were carried out for hydrophilic and hydrophobised (θ_{adv}=40^o), by adsorption of octyltrihydrosilan (OTHS), titanium dioxide films deposited at glass slides. Isoelectric point (IEP) of smooth titania surface is at pH=4.7. As the bubble surface isoelectric point is at pH_{IEP}=2 so attractive electrostatic interaction can operate between the TiO_2 and gas bubble surfaces within the range 2<pH<4. The measurements were carried out at pH 3.5; 4 and 5.8. At pH 5.8 both the bubble and titania surfaces are negatively charged and there are repulsive electrostatic interactions. Whereas, at pH 3.5 and 4.0 the bubble and TiO_2 surfaces are oppositely charged - the electrostatic interactions are attractive. Measurements of kinetics of the TPC formation at the TiO_2 surfaces were carried out for the bubbles of diameters: 0.4, 0.98 and 1.48 mm. The bubbles of the smallest diameters were generated using microfluidic chip with T-junction. The bubbles of diameters 0.98 and 1.48 mm were formed at the capillaries of different inner diameters (0.025 and 0.075 mm). Time of the TPC formation was measured from the moment of the bubble first collision with titania surface till the film rupture and the TPC formation. For each bubble size we found that the time of the TPC formation was prolonged at pH 5.8 (see Fig. 1), that is, at the pH where the lrepulsive electrostatic interactions acted in the thin liquid films. For example for d_{bubble}=1.48 mm the t_{TPC}=92.2±4.6 ms in pH=3.5, t_{TPC}=229.4±32.3 ms in pH=4 and t_{TPC}=462.0±31.0 ms in pH=5.8. Moreover, as can be observed in Fig. 1, the time of the TPC formation at weakly hydrophobic TiO_2 surface was strongly increasing with the bubble size. As size of the liquid film formed is proportional to the bubble diameter so these data show that kinetics of the thin liquid drainage was responsible for increase of the t_{TPC} values with the bubble size. The results obtained show that in the case of weakly hydrophobic solids the electrostatic interactions between liquid/gas and liquid/solid interfaces can affect significantly the kinetics of the TPC formation. This is due to the fact that for formation of the TPC (gas/solution/solid) the wetting film, which stability dependences on the electrostatic interactions, has to be ruptured.

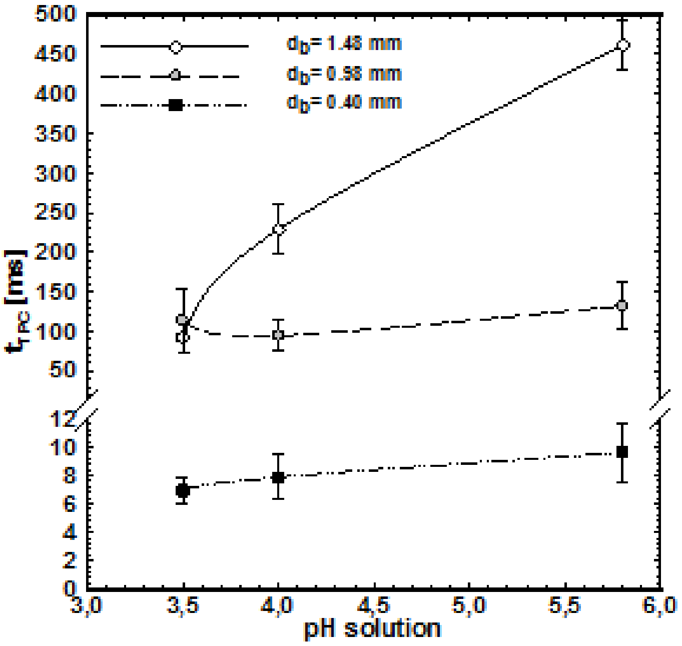


Fig.1. Time of the TPC formation at hydrophobised (θ_{adv}=40°) titania surface as a function of pH and bubble diameter

Structural Response of Roman Cement Mortars Due to Drying

PhD research project N N105 429140 [2011-2012]
(Professor Roman Kozłowski DSc, Dariusz Wilk MSc MA)

Roman cements were key materials to easy and economic manufacture of renders and decorations on façades of buildings during the nineteenth and early twentieth centuries. The formation of cracking is one of the important barriers preventing broader acceptance of Roman cements as a cultural heritage material by the contemporary conservation sector. The main aim of research doctoral project is explanation of cracking mechanism in Roman cement mortars and pastes.

The key research task, accomplished in the reporting period, was microscopical examination of shrinkage cracking pattern in Roman cement pastes, using optical and scanning electron microscopy. The investigations confirmed that cracking occurs in the matured pastes, i.e. cured for 28 and 90 days, while structure of young pastes is not damaged during the drying shrinkage. The investigations revealed two zones in the specimens, clearly differing in the intensity of cracking - an external zone showing relatively little cracking and the core zone showing high concentration of cracks, as illustrated in Figure 1. The interpretation of the observed crack pattern assumes two phases in the drying process. In the first phase, the maximum tension stress is built in the external layer of the material resulting from its drying shrinkage restrained by wet core underneath. The core zone, in turn, experiences the maximum compression stress which apparently produces a permanent plastic deformation in this zone. In the second phase, when the core zone dries, the reverse of the stress state is produced: the material in the core zone experiences tension due to the shrinkage restrained by the dried outer zone which leads to fracturing in the central portion of the material. The core zone however experiences now a considerably higher relative dimensional change, because during the first phase it has been effectively shortened (compressed), so in effect, reinitialized to a new condition. Therefore, the physical damage is much more intensive than it would be the case during uniform drying of the specimen. The interpretation is currently verified by measurements of compressive mechanical parameters of the materials.

Furthermore, a comparative study of structural response due to drying was initiated for several binders which can be used in restoration works. The research will be focused on Roman cements which are currently produced, French natural cement Prompt and natural hydraulic lime (NHL5). Composition of the pastes and mortars was determined according to constant flow which was recognized as an important variable for restorers in the practical works.

Fig. 1. Optical microscopy in transmitted light for 28-day paste cured at 100% relative humidity. High concentration of cracks is visible in the inner zone.

Iuventus Plus programme projercts of the Ministry of Science and Higher Education

Molecular Mechanism of Catalytic Oxidation of Hydrocarbons by Manganese Porphyrins in Solution and on Support

Iuventus Plus research project IP2010 036270 [2010-2011]
(project leader: Dorota Rutkowska-Żbik PhD)

The present research aimed at (1) the elucidation of the molecular mechanisms of hydrocarbon oxidation (mainly propene and cyclohexene, which may be oxidized to epoxide, alcohol and/or ketone), catalyzed by manganese porphyrins in homogeneous systems with different solvents and supported on a solid and (2) the determination of parameters (type of solvent, presence of support) which may modify the activity of the studied compounds.

The present studies are done within quantum-chemical method based on Density Functional Theory (DFT) with the non-local gradient-corrected Becke-Perdew functional, with Ri approximation, as implemented in Turbomole program suite. The studied systems are characterized by geometry (bond lengths, valence angles) and electronic (charges) parameters as well as total energy changes accompanying each of the reaction steps.

First, the molecular mechanisms for cyclohexene oxidation to epoxide, alcohol and ketone were elucidated - all intermediate structures were characterized and heights of energy barriers were calculated. The main effort was on determination of the reaction profile of ketone formation as this process is the least studied and there is not many data available in literature regarding its mechanism. Performed studies show that ketone is formed from cyclohexene radical, which reacts with oxo group of the active form of the catalyst. C-H bond, which is located in α position with respect to the double C=C bond is then activated - H atom migrates towards O atom (from oxo group). In the next step, the formed OH group is bound to C atom. The resulting protonated ketone loses proton in contact with oxygen-donor species or other catalyst molecule.

Next, a number of other (than oxo group) ligands, which may activate hydrocarbons was tested. All studied oxygen-containing ligands (OOH^-, HOOH, OCl^-, OH) exhibit high nucleophilicity (total negative charge, accumulated mainly on oxygen atoms). They may then actively participate in C-H bond activation through insertion into C-H and formation of bonds with C and H atoms. Moreover, it is found that HOOH may be bound to manganese and subsequently decomposed to yield the active oxo group of catalyst, without noticeable energy barrier. Additionally, the participation of Cl^- ligand in hydrocarbon activation was elucidated. Chlorine ligand may bind to hydrogen atom (from hydrocarbon molecule) and form neutral HCl molecule, which dissociates from the catalyst active site. Its nuclephilic properties might be lower that those of other studied ligands (containing oxygen atoms).

Finally, the influence of solvent on catalytic properties of manganese porphyrins was studied. It is found that polar environment facilitates epoxidation of cyclohexene (the main process catalyzed by manganese porphyrins) through lowering of reaction barriers.

Multilayer Polyelectrolyte Films with Catalytic Activity for Biomedical Applications

Iuventus Plus research project [2010-2011]
(project leader: Ewelina Jarek PhD)

The aim of the project, completed this year was to develop a methodology for obtaining functional polyelectrolyte films with embedded protein - an enzyme with catalytic activity preserved. Multilayered polyelectrolyte films are the scaffold and the matrix for protein, and their properties and internal structure should provide proper functioning of the enzyme and protect it against loss of biological activity. Increasing stability of enzymes and other biologically active substances is of great importance due to the potential industrial and biomedical applications.

For the studies, the α-chymotrypsin (EC 3.4.21.1.), digestive enzyme from the group of serine proteases secreted by the pancreas as model protein was chosen. Polymers used as polyanions: poly-sodium-styrene sulfonate - PSS and λ-carrageenan, a natural polysaccharide extracted from seaweed. Conditions of formation of polymer-protein films were optimized in such a way, as to maximize the content and stability of the enzyme in layers. It is known from the literature that acidic environment conducive to maintaining the biological properties of proteins during storage as solutions, zeta potential measurements showed that at pH=3 protein has a positive charge of about 40 mV and can be treated as polycation. By using the sequential adsorption method (layer-by-layer) on the cleaned silicon wafers, modified by poly-ethyleneimine iodide - PEI, films with alternating layers of polyanion and chymotrypsin at pH=3 (0.001 M HCl), pH=5.4 (water) and under optimal conditions for the action of the enzyme (TRIS buffer solution pH=7.8) were created. For layers imposed from water and buffer solutions the growth of thickness was not satisfactory (Fig. 1).

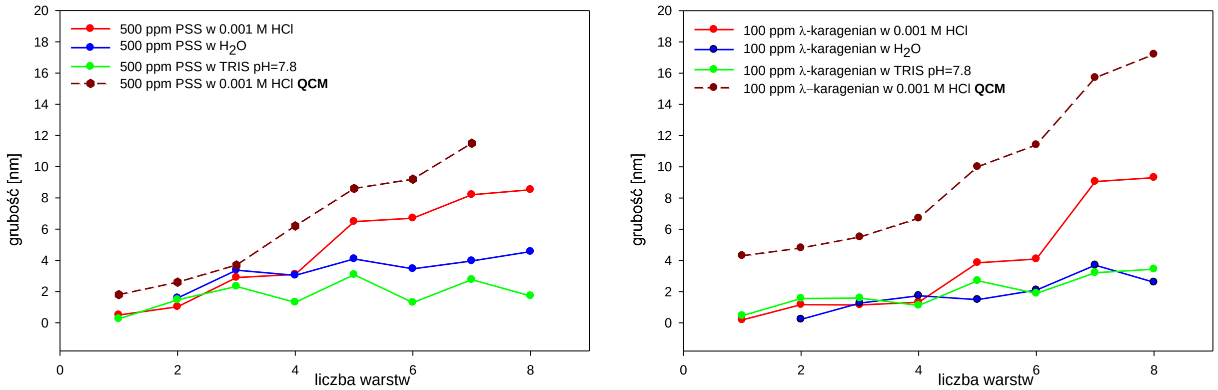


Fig.1. The elipsometric tickness of polielectrolyte films with embedded α-chymotrypsin in dependence on number of layers and conditions of imposing (solid lines) and thickness calculated on the basis of viscoelastic model
in Quartz Cristal Microbalance (QCM) experiments (dashed lines).

The experiments by using a quartz crystal microbalance (QCM) for films with the greatest ellipsometric thickness were also performed. Both methods showed qualitatively consistent results. Analysis of the results obtained by QSM indicates the compact and rigid structure of films created at pH=3, changing the environment to slightly alkaline (Tris, pH 7.8) results in stratification of the film probably related to a change in conformation of the enzyme. The catalytic activity of protein embedded in polymer film in the reaction of cleavage of the synthetic substrate was checked spectrophotometrically.

Molecular Basis of Interactions between Calcium Ions and the Selected Uronic Acids

Iuventus Plus research project IP 2010 032370 [2010-2011]
(project leader: Wojciech Płaziński PhD)

Based on the results of the molecular dynamics and ZINDO-1/Monte Carlo study the new structural model describing the Ca^{2+}-guluronate interactions was proposed. The model is very similar to the shifted egg-box one proposed by Braccini and Pérez when considering the network of inter- and intrachain hydrogen bonds as well as the distance between Ca^{2+} ions. It differs significantly, however, with regard to the Ca^{2+} coordination pattern. According to our study, the single Ca^{2+} cation is coordinated by four carboxyl oxygens (two from each chain) and by four water oxygens. The number of sugar units per number of bound calcium ions is four, in the analogy to the egg-box-like models. The large contribution of hydrogen bonds suggests that the interchain hydrogen bonding is an important driving force leading to the formation of Ca^{2+}-guluronate complexes. Furthermore, this study emphasized the significance of taking into account water molecules which play a crucial role in the above-mentioned process. The obtained results are meaningful also for other systems containing polyuronates and divalent metal cations.

Determination of Factors Affecting Stability of Liquid Films Formed during Collision of Gas Bubble with Various Interfaces

Iuventus Plus research project IP2010 049070 [2010-2011]
(project leader: Jan Zawała PhD)

The aim of the project is to determine main factors influencing stability of liquid films formed at various interfaces under dynamic conditions. The experiments were focused mainly on bubble collisions with liquid/gas interfaces. The bubble collisions were monitored using high-speed camera (~1000 fps). The experimental set-up used allowed observing the bubble collision with liquid/gas interface: (i) being at rest, when the camera was set perpendicular to the path of the rising bubble, (ii) being at rest, when the camera was directed at the liquid surface from above, to observe moment of the liquid film formation and (iii) vibrated interface, with applied surface waves of well-known frequency and amplitude.

It was found that in pure liquids the stability of liquid films formed under dynamic conditions, during the bubble collision with the interface, was determined mainly by the radius (size) of the film, i.e. the size of the thin liquid layer separating the bubble surface from liquid/gas interface. It was also found that the film radius was strongly dependent on the kinetic energy associated with the bubble motion - with increasing energy the radius of the film formed, at the moment of the bubble collision, increased. During the bubble collision with liquid/gas interface the coalescence takes place when the radius of the film is sufficiently small and there is a chance for the film to drain to its critical thickness of rupture ($h_{critical}$) within the collision time. In other words the bubble ruptures when time of the film drainage (t_{drain}), determined by the film radius, are shorter than the time of the bubble-interface contact ($t_{collision}$). Otherwise, the bubble bounces backward. The results of experiments with vibrated liquid/gas interface are a strong evidence confirming correctness of this hypothesis. It was found that when the dissipated kinetic energy of the colliding bubble was re-supplied from the external source (by the surface waves induced), the bubble "lifetime" at the liquid/gas interface was spectacularly elongated, from a few milliseconds up to many minutes. Analysis of the results obtained allowed us to propose a general mechanism describing the conditions determining outcome of the bubble collisions (bubble rupture or bouncing) with liquid/gas interfaces (see Fig. 1).

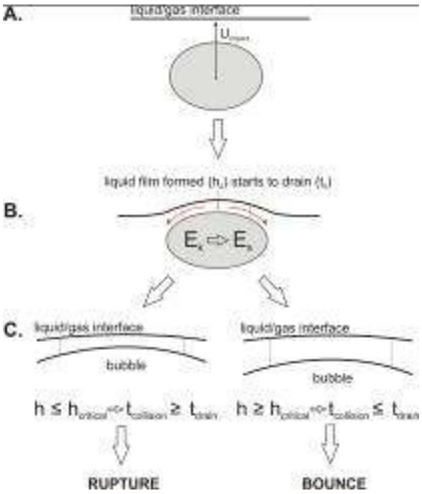


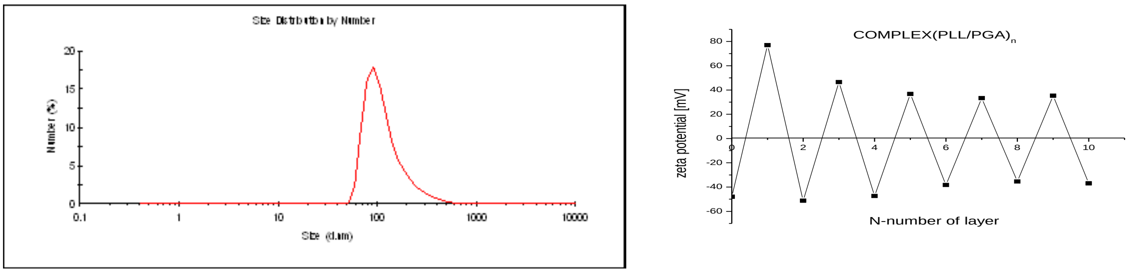
Fig. 1. The mechanism presenting the conditions determining the outcome of the bubble collision with liquid/gas interface (rupture or bounce)

Application of Nanoparticles/Nanocapsules for Targeted Delivery of Therapeutic Agents

Iuventus Plus research project [2010-2011]
(project leader: Krzysztof Szczepanowicz PhD)

The aim of this project was to develop scientific background of the technique of incorporation of therapeutic agents (e.g. drugs, RNA, DNA) inside nanocapsules and modification of capsules surface in order to eliminate nonspecific interaction with proteins. Such approach should eliminate side effects of applied therapeutics due to reduction of their toxic effects in the whole body. The main advantages of drug targeting (passive targeting) are as following: the drug quantity required for successful therapy can be reduced (resulting also in the cost reduction), drug targeting makes it possible to increase noticeably the local drug concentration in the target area (i.e., drug efficacy) without harmful side-effects on healthy organs or/and systemic side-effects. Nanocarriers are very effective in anticancer therapy, e.g. objects smaller than 10 nm are rapidly removed from the body by kidneys, the objects larger than 100nm are too big for penetration of the tumor. Carriers in the range 10-100nm does not migrate through the walls of blood vessels of most normal tissues but in case of cancer blood vessels, which are more porous, such carriers can easily pass into the surrounding tissue and accumulate in the tumor without affecting other healthy parts of the body. It allows to minimize one of the biggest weaknesses of pharmacological formulations time and space non-specificity, thus, it can eliminate the serious side effects applied therapeutics due to their toxic effects throughout the body.

In this project we focused on development of two methods of preparation of nanocarriers containing active substance. First method was based on encapsulation of emulsion droplets containing active substance in polyelectrolyte multilayer shell. The size of obtained emulsion droplets was in the range 100nm, such emulsion droplets were encapsulated in polyelectrolyte multilayer shell using layer by layer method. Second method was based on formation of macromolecular complexes containing active specious (polycation/polyanion) and such prepared complexes were encapsulated in polyelectrolyte multilayer shell using layer by layer method. The Figure 1 present a) Size distribution of the polyelectrolytes complex PLL/PGA b) variation of Zeta-potential of negatively charged PLL/PGA complex as a function of number of deposited polyelectrolyte layers.



a) b)

Fig. 1a) Size distribution of the polyelectrolytes complex PLL/PGA, b) variation of Zeta-potential of negatively charged PLL/PGA complex as a function of number of deposited polyelectrolyte layers.

All prepared nanocarriers were modified by creating PEG corona in order to eliminate nonspecific adsorption of proteins.

Influence of the Type of Active Center and Structure of Macrocyclic Ligand on Catalytic Activity of Metalocomplexes in Liquid Phase Phenol Oxidation

Iuventus Plus research project IP2010 016970 [2010-2011]
(project leader: Robert Karcz MSc)

Phenol oxidation is interesting process both in the field of environmental and fine chemistry. In environmental science phenols and its derivatives are known to be common pollutants. In fine chemistry phenol derivatives - quinones are valuable substrate for production of pharmaceuticals, dyes and substrates for organic synthesis. Biomimetic oxidation of phenol is a method of phenol conversion which can be used in both fields.

The aim of this work was to prepare cationic and anionic porphyrins and phthalocyanines, containing iron, manganese or cobalt in their structure. Such complexes bearing ionic substituents are soluble in water. Prepared complexes were characterized using UV-Vis spectroscopy and applied as catalyst for phenol oxidation with hydrogen peroxide. In studied reaction phenol is converted to catechol and hydroquinone (Fig. 1). Reaction was performed at 80°C using thermostated glass reactor, and stoichiometric amount of oxygen donor.

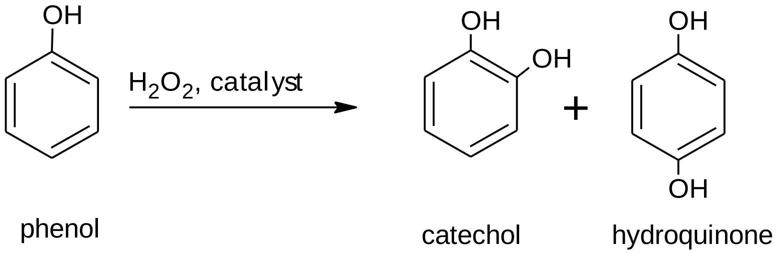


Fig. 1. Reaction scheme

All of the prepared metallocomplexes were active in the studied reaction. Complexes containing sulphonated phthalocyanine ligand (PcS) can arranged in the following order of activity:

FePcS > MnPcS > CoPcS

Further research was performed using iron containing complexes of anionic and cationic porphyrins. Basing on the results following order of catalytic activity may be formed:

FeTSPP > FePcS > FeTCPP > FeTMPyP

The obtained results allowed us to verify that both the structure of the macrocyclic ligand and nature of the metal center have influence on the catalytic activity. All of the water soluble compounds showed good catalytic activity. Porphyrin complexes bearing sulphonate groups are more active than their sulphonated phtalocyanine counterparts. Moreover all of the complexes with anionic character (TSPP, PcS, TCPP) were more active than cationic complex (TMPyP). The highest selectivity towards catechol was attained with FeTCPP catalyst.

New Protein Layered Systems

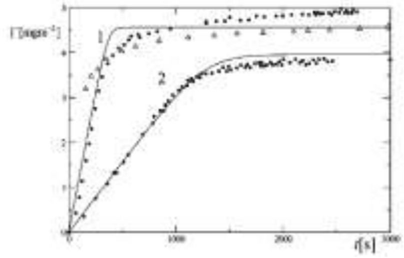
Iuventus Plus research project [2010-2011]
(project leader: Jakub Barbasz PhD)

The project was implemented according to schedule. Computer simulations have been carried out protein film formation, the methods used in molecular dynamics and simulations based on the RSA algorithm.

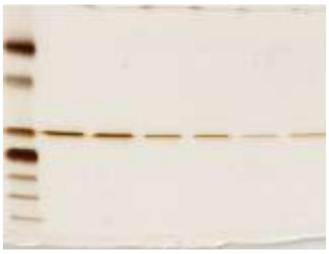
Reported in the literature, large differences in maximum covering fibrinogen $(2.27\cdot 10^{-}6.13\cdot 10^{3}\ \mathrm{N}/\mu\mathrm{m}^{-2})$ were explained on the basis of a mathematical model.

The mathematical model was developed describing the kinetics of protein adsorption, depending on process conditions (see below).

Measurements were performed for the protein film formed of two proteins with different structure (globular and linear) sequentially deposited on the surface.



Kinetics of fibrinogen adsorption expressed as the dependence of the coverage Γ [mg m^{-2}] on the time t [seconds]. The solid points denote experimental results derived by the TIRF method for cb = 100 ppm (curve 1) and cb = 25 ppm (curve 2), and the hollow points show the experimental results obtained by ellipsometry



Electrophoresis gel - high purity fibrynogen

Reaction Mechanism of Nitrogen Oxides Reduction with Hydrocarbons, Catalyzed by Pd-Exchanged Mordenite. Quantum-chemical Simulations

Iuventus Plus research project [2010-2011]
(project leader: Robert Gryboś PhD)

Establishing a reaction mechanism, especially such a complicated one as the catalytic reduction of nitrogen oxides, is a great challenge to theoretical methods. On the other hand, intrinsic limitations of experimental *in situ* methods make theory the only tool that can be universally used.

Removal of nitrogen oxides from exhaust gases of internal combustion engines is very important from practical point of view. Increasingly stringent norms adopted in European Union require use of more and more advanced deNOx catalysts, like zeolites exchanged with noble metals. One of the most promising systems is Pd-exchanged mordenite - showing high activity and at the same time being rather resistant to hot water vapor.

Traditional NO-SCR process, employed in stationary NO sources (e.g. furnaces), is based on NO reduction by ammonia. For practical reasons, this system is not used in vehicles, apart from few Diesel engines from Mercedes, where ammonia is produced from urea (the AdBlue technology). In other catalysts, ammonia is produced during the reaction from hydrocarbons - engine fuel that is dosed through a by-pass. In model systems methane is most commonly used.

Mechanism based on experimental data was proposed by Shimizu and Okada, but it is rather general and, in some parts, definitely unclear. By using methods of quantum chemistry (periodic DFT) I simulated a number of reaction steps, like adsorption of NO, CO, CO_2, O_2, CH_4, CH_3, CH_5^+, NH_3, NH_4^+, H_2O, HNO on isolated palladium centres; methane activations; CN hydrolysis; reaction of NO with ammonium cation. The mechanism of methane activation could not be established. The CH_4 molecule does not interact with acidic centres, which could, otherwise, lead to formation of CH_5^+ cation as a precursor for C-H bond cleavage. Adsorption of small molecules on palladium centre causes considerable weakening of bonds between the metal and the zeolite framework, what leads to increased mobility, and eventually, to sintering of isolated palladium into clusters, what is observed experimentally. Protons show larger affinity to palladium, than to framework oxygen atoms and creation of Brønsted acid sites.

Using 16 different locations of Pd cation in the mordenite cell showed that properties of palladium centres strongly depend on the surroundings of the anchoring site. A spectacular example is observation of spontaneous (no barrier) O—O bond cleavage in oxygen molecule when adsorbed at a Pd centre anchored at one specific site.

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SURUZ Surfactants and Dispersed Systems in Theory and Practice

(project coordinator: Professor Piotr Warszyński DSc)

The main aim of the Scientific Network SURUZ is the development of scientific cooperation and taking advantage of apparatus backup present in different research centres in Poland, which carry on studies on the surface active agents (surfactants) and colloidal systems. The teams of Scientific Network work on both basic and applicable researches on the new surfactants and technologies employing dispersed systems, thin films, adsorptive layers and so forth. The SURUZ project is accomplished by the teams from 11 research centres in Poland and the coordinator of the Network is Professor. P. Warszyński (IKiFP PAN).

The tasks planned to carry on within the activity of the Network can be divided as following:

- The implementation of mutual research topics, supplemental or complementary to the tasks pursued within the basic, statutory activity of the units creating Scientific Network. The aim of these research is presented below.
- The exchange of scientific personnel as well as PhD students for optimalization of using the research infrastructure accesible for several participants of the Network. The extend of the possibility of using complementary research methods aiming at the solution of scientific problems.
- The organization of workshops intended mainly for young scientists, which will give them an opportunity to discuss about their research results and to solve emerging problems with more experienced scientists.
- The organization of meetings of the teams participating in the project for the presentation of main achievements, as well as for the discussions.
- The extend of the research area which aims at the preparation of mutual scientific projects, both national and international, especially within the 7th Framework Programme of the European Union.
- The establishing, controlling and coordinating of the researches performed within the Network; planning expenses for several tasks and controlling if the granted funds are utilized in a correct way.

The research proposed within the Scientific Network SURUZ includes three priority scientific topics:

I. Surfactants and dispersed systems – synthesis and physicochemical characteristic.
II. Dispersed systems of importance for biomedicine.
III. Dispersed systems of importance for technology.

PV-TECH Development of New Technologies and Research Techniques in Area of Photovoltaic Cells

(subject leader: Robert Socha PhD)

The increase of industrial and household demand on electricity and the necessity to fulfill the CO_2 regulations result with growing importance of the ‘pure’ energy obtained from photovoltaic cell. In this aspect, an application of the nanotechnology for, so called, solar cells of third generation seems to be important. Additionally, the silicon shortage in the global market, followed by increasing the silicon price, results in the need to utilize silicon waste from the electronic industry that leads to ‘multicrystalline silicon ribbon’ production, which can be applied in photovoltaic. PV-Tech network should help solution of above mentioned problems. Therefore, the project has following tasks:

a) development of new technologies in photovoltaic cell production i.e. dedicated mainly to multicrystalline silicon ribbon cells,
b) development of the research techniques dedicated to production and to analysis of the final product.

In the frame of the project, ICSC PAS was delivering the test samples of the compounds that can be applied as catalysts for silicon etching process or as the materials that increase the internal reflection of light in the photovoltaic cell body. Additionally, the systems containing silver nanoparticles and nanowires embedded in dielectric TiO_x matrix were tested. The preliminary tests of the photoelectric effect on the studied surfaces showed high enhancement of the photocurrent in case of silver nanoparticles application.

BIONAN Molecular Mechanisms of Interactions in Biological Nanosystems and in Biologically Active Systems modified with Nanoparticles

(subjects leaders: Professor Piotr Warszyński DSc, Professor Józef Korecki DSc)

Understanding of molecular mechanisms responsible for alterations in the liquidity of biological membranes is of primary importance for both biologists and physicians, pharmacists as well as for physicists and chemists working on catalytic processes. It is known that destructive processes due to oxidative stress take place in living organisms. As a result singlet oxygen or free oxygen radicals are produced, causing the destruction of lipid and protein structures. Thus, the recognition of molecular mechanism which enables controlling these processes is crucial for designing of new generation drugs. These medicines exploit the encapsulation of pharmaceutically active substances. Such created capsules should be specifically delivered to the target in the organism. Moreover, the dosage of drug released should also be controlled. Therefore, a non-invasive method of controlling the transport and the permeability of the capsules is required. The implementation of nanosensors/nanomarkers based on modified carbon nanofibers, whose minor toxicity for living organisms has been proved, might significantly improve the selectivity and effectiveness of encapsulateded drugs.

The researches proposed within BIONAN project are meant for studying of the activity of biologically active systems depending on their interaction with the surfaces with well defined physicochemical properties or with the nanoparticles in solution. Understanding of adhesive mechanisms at molecular level (interactions at membrane - nanolayer interface) will contribute to the conscious modeling of systems of required molecular dynamic and its affinity to specified structures.

The aim of research carried on within BIONAN project is:

I. A built-in actions of physicians, chemists and biologists in the study of natural photosynthetic membranes and their artificial model equivalents suspended in solutions or moved onto defined solid surfaces.
II. The study of physicochemical properties of natural and artificial systems under the influence of controlled, variable exterior factors.
III. The establishment of optimal environment conditions and properties of the surfaces for obtaining the highest possible activity of examined, biologically active systems, or for obtaining the biochemical activity in model systems.
IV. The development of manufacturing methods of biologically active systems with specific surface properties.
V. The evaluation of biological nanosystems (components of photosynthetic membranes) as a platform for the construction of nanosystems that converts light energy into chemical energy.

The BIONAN network is coordinated by the Institute of Physics and Applied Informatics of AGH University of Technology.

Commissioned research projects of the Ministry of Science and Higher Education

Technology and Equipment for Neutralization of Chemical Warfare Agents with Aid of Nanosorbents

Development project 0R00003605 [2008-2011]
(project leader: Professor Ewa Serwicka-Bahranowska DSc)

Project aims at implementation of the results achieved previously within research grant 0 T00C 01827 and development project 0R00003605, devoted to the preparation of a nanostructural sorbent/decontaminator capable of sorption and destruction of chemical warfare agents and design of a prototype decontaminating equipment. The project is realised by a consortium consisting of Military Institute of Chemistry and Radiochemistry, IKiFP PAN, and two companies: "Ravimed" and "ADAL". The formula of the decontaminating powder has been developed in IKiFP PAN. The work carried out in 2011 encompassed:

- research into the possibility of further improvement of nanosrbent properties
- upscaling of the nanosorbent manufacturing

"Homing Plus" programme projects of the Polish Foundation for Science

Structure and Electric Properties of the Composite Films Containing Conductive Nanoparticles

Homing Plus programme project 2010-1/8 [2010-2012]
(project leader: Marta Kolasińska-Sojka PhD)

The influence of the underlying PEI layer on the adsorption of Prussian Blue (PB) nanoparticles was considered. As PEI is a weak electrolyte, its dissociation degree depends on the pH value of the solution. Two cases were studied: fully charged PEI (pH=7) and partially charged PEI in its natural conditions: pH=10.5. It turned out, that amount of PB adsorbed on the layer of PEI deposited from the solution of pH=7 was two times smaller comparing to PEI layer deposited from pH=10.5. Both types of nanocomposites were imaged with atomic force microscopy. AFM measurements proved the irreversible adsorption of PB nanoparticles on the layer of PEI. Moreover, analysis of the AFM images revealed, that nanoparticles deposited on the PEI adsorbed from the solution of pH=7 kept their size (c.a. 10 nm) comparing to one measured directly in the suspension of nanoparticles. In opposition, an average diameter of nanoparticles deposited on PEI pH=10.5 was more than 3 times bigger, although deposition took place from the suspension of PB of 10 nm in diameter. In the second case, aggregation of the nanoparticles on the surface of PEI occurred. Voltammetry confirmed the significant influence of the anchoring layer of PEI on the electrochemical activity of the studied films. In the case of films, where PB layer was deposited on PEI layer, adsorbed on a gold electrode from a solution of pH=10.5, both oxidation and reduction currents, were twice smaller than for the case of PB adsorbed on the PEI deposited from a solution of pH=7 (Fig. 1), although the amount of PB deposited was approximately twice as large as for the case of pH=7. Probably due to the fact that Prussian Blue formed aggregates on the surface of PEI of pH=10.5, its surface active area was lower, which decreased the electrochemical activity of PB of about 50%. The fact that the electrochemical activity came exclusively from the present Prussian blue was proved by measurements of films without the addition of Prussian blue (black curve in Fig. 1 showed no reduction/oxidation currents).

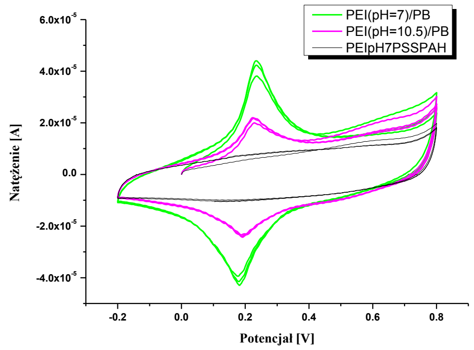


Fig. 1. Voltammetric curves of gold electrode modified with bilayers of PEI/PB, the PEI adsorbed from solution of pH=7 (green curve) or pH=10.5 (pink curve), in addition – three-layer polyelectrolyte film (black curve)

In order to explain the reason of differences in nanoparticle deposition on both types of PEI, thickness and optical properties of PEI monolayers deposited from solutions of both pH values were measured. Thicknesses of both types of monolayers were similar (ca.1.4 nm). Some differences were observed in the refractive index spectra, which may be due to the difference of monolayers' density.

"Pomost" programme projects of the Polish Foundation for Science

Selective Hydrogenolysis of Glycerol to Glycols via Acetol on Heterogeneous Metal/Metal Oxides Baased Catalysts

Pomost programme project 2011-3/7 [2011-2014]
(participant: Katarzyna Samson PhD)

The contract for supporting this project by Foundation for Polish Science was signed on November 11th, 2011.

During first two months of project realization the following tasks have been accomplished:

a) the necessary administrative and cleric works, required for formal realization of this project (for instance description and marking of invoices by UE and Foundation for Polish Science logos) were performed,
b) one item of planned laboratory equipment was on order and bought (WTW pH-meter),
c) the reagents crucial for synthesis of the catalysts were on bought,
d) the detailed literature review was started, focused particularly on the methods of preparation of the catalysts for studied reaction and required conditions of laboratory set – up for hydrogenolysis of glycerol reaction.

EU 6th Framework Programme projects

PARFUN Nanoscale Surface Treatments to Functionalise Polymer Particles for Electronic Applications

Controlled attachment of polystyrene particles at PEI modified surfaces

PARFUN [2007-2011] in frameworks of ERA-NET MNT project
(project leader: Professor Piotr Warszyński DSc)

The main objective of the project is to develop a new generation of spacer particles for LCD based on new concepts for surface treatment of polymer particles, and thereby also greatly improve the manufacturing process of LCD screens. There is a strong need for spacers with a careful control of the particle size and size distribution together with suitable surface properties. The introduction of flexible displays that can be bend and twisted during their use will need better adhesion between the spacers and the inner surface of the display. Also new and improved techniques for distribution of the spacers in the display is needed.

The aim of our activities in the project was to develop methods for surface modification of glass and/or plastic plates (polyimid - PI) in order to obtain better adhesion of micron size polystyrene particles in well controlled patterns. For surface modification cationic polyelectrolyte polyethyleneimine (PEI) was used. PEI of molecular weight 700 kD was adsorbed from 500 ppm aqueous, ethanol, and isopropanol solutions by microcontact printing. The adhesion of latex particles, provided by project partners was examined from water, ethanol and isopropanol suspension. We found high selectivity of particle adhesion at the surfaces covered with PEI film. For example the ratios of CONPART particles deposited from isopropanol suspension at covered surface to the uncovered one were: 10:1 for polyimide plates and 300:1 for glass plates.

In 2011 we optimized the rheological and surface properties of PEI solutions and we developed (together with project partners from LCD Centre) the method of deposition of PEI on polyimide and glass surfaces by INK JET Printing. For the deposition the XAAR XJ126/50 head with 126 nozzles was used. Typical droplet volume was 50 pl. We used solutions: isopropanol containing 15% ethanol and ethylene glycol containing 15% ethanol containing 500 ppm of PEI with the molecular weight 70 kD or 750 kD. There was no dependence of the droplet size and shape on presence of PEI. Figure 1a illustrates the snapshot of Eth+Get+PEI droplets at glass surface. At so prepared surfaces the AA028 latex particles (CONPART) were deposited by dipping in the isopropanol suspension with various concentrations. We observed deposition on the areas coated with PEI only. Surface coverage was dependent on the particle concentration in the dipping solution.

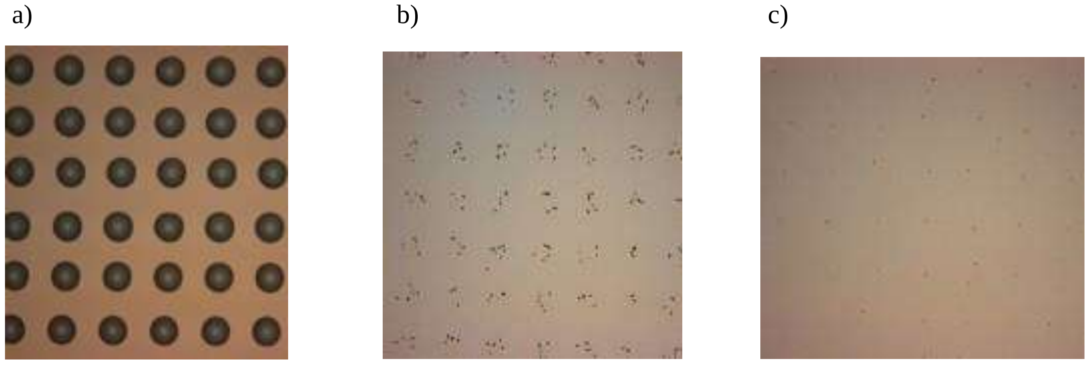


Fig. 1. a. Snapshot of the of Eth+Get+PEI droplets at glass surface deposited by the INK JET method. b. and c. AA028 latex particles (CONPART) deposited by dipping the patterned surface in the isopropanol suspension with various particle concentrations

NANOREP II Multifunctional Surface Coatings and Highly Scratch Resistant Plastic Parts

Surface Modification of Nano- and Micron Size Plastic Modifiers

NANOREP II [2007-2011] in frameworks of ERA-NET MNT project
(project leader: Professor Piotr Warszyński DSc)

The main objective of the NANOREP II project is the development of technology that will allow application of nanosized particles and nanostructured coating materials with multifunctional properties for (near)future high quality polymer products. The project is aiming to create a strong transnational network of research activities in the field of nanoparticle materials and bring the partners a step forward into implementation of nanotechnology in their products and applications.

The aim of our investigation in 2011 was to select silanes for surface modification of glass beads and silica nanoparticles to increase their compatibility with polymer coatings or thermoplastic. On the other hand to increase scratch resistance of plastic parts the micro- or nanoparticles should be build-in the stryсture of polymer. Therefore, the silanes should contain chemical groups, which could form bonds with polymer during polymerization or curing stage. The proposed silanes for acrylic, polyurea-acrylic, epoxy coatings and polyamide 6 are listed in the table below.

No.	SILANE	Symbol	Density	Molecular weight
ACRYLIC	**SIA0200.0 (3-ACRYLOXYPROPYL)TRIMETHOXYSILANE**	**ACS**	**1.06**	**234.32**
PU-ACRYLIC	**SII6455.0 3-ISOCYANATOPROPYLTRIETHOXYSILANE**	**CYS**	**0.99**	**247.32**
EPOXY	**SIA0610.0 3-AMINOPROPYLTRIETHOXYSILANE**	**AMS**	**0.95**	**221.37**
EPOXY	**SIG5840.0 (3-GLYCIDOXYPROPYL)TRIMETHOXYSILANE**	**GPS**	**1.07**	**236.34**
PA6	**SIA0591.0 N-(2-AMINOETHYL)-3-AMINOPROPYLTRIMETHOXYSILANE**	**AES**	**1.01**	**226.36**
PA6	**N-[5-(TRIMETHOXYSILYL)-2-AZA-1-OXOPENTYL]CAPROLACTAM, 95%**	**CAS**	**1.14**	**318.4**

The compatibility of modified glass beads was verified by monitoring the changes of their wettability and analysed by SEM. Figure 1 shows the diference of the SEM images in acrylic coating of unmodified glass spheres and ones modified with ACS.

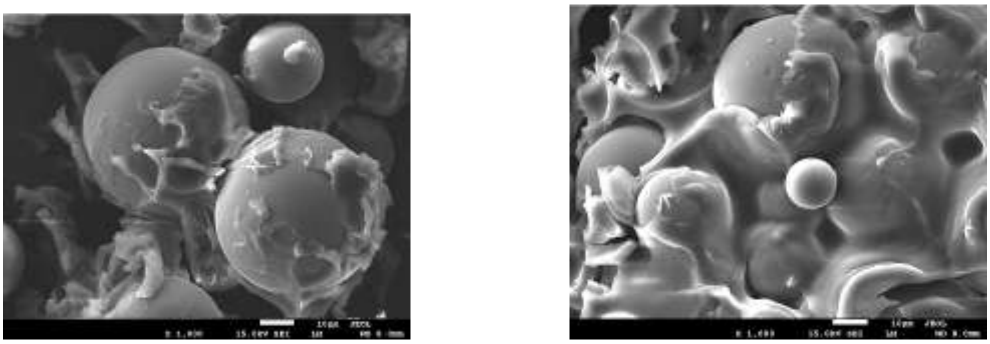


Fig. 1. SEM image of glass beads in the acrylic coating.
Left unmodified beads, right – beads surface modified with ACS

EU 7th Framework Pprogramme projects

InGAS Integrated Gas Powertrain – Low Emission, CO_2 Optimised and Efficient CNG Engines for Passenger Cars and Light Duty Vehicles

EU 7th FP InGAS Collaborative Project [2008-2011]
(project leader: Professor Ewa Serwicka-Bahranowska DSc,
principal investigator: Tadeusz Machej, PhD)

InGAS is a large-scale international collaborative research project launched within 7th EU Framework Programme for Research and Technical Development. The project integrates 28 partners from 11 European Countries: Austria, Czech Republic, Denmark, Finland, France, Luxemburg, Germany, Poland, Sweden, Switzerland and Italy. The Consortium is coordinated by Centro Ricerche Fiat SCpA. Starting date of the project is 1st October 2008.

Main objective of the InGAS project is to deploy custom designed CNG engine integrated with specific aftertreatment systems applied to passenger cars and light duty vehicles able to achieve 10% higher fuel conversion efficiency than that of a corresponding 2006 Diesel vehicle and complying with an emission level lower that Euro 6.

ICSC PAS is involved in Sub-project B2 "Aftertreatment for passengers cars CNG engines", Workpackage B2.2 "Advanced Catalysts Development". Research aims at design, synthesis, characterization and catalytic testing of new catalyst formulations for methane oxidation in CNG fueled engine exhausts, based on mixed transition metal oxides.

In 2011 the activities of ICSC PAS encompassed preparation of the 2nd Generation mixed oxide catalyst and further catalyst optimization. The preparation of 2nd Generation mixed oxide catalyst was based on previously obtained results, which indicated that addition of a small amount of palladium at the stage of the hydrotalcite precursor synthesis resulted in a synergetic effect and increased the activity of both the mixed oxide and the palladium component. Further catalyst optimization focused on a) modification of the support, b) optimization of the synthetic procedure of hydrotalcite-derived CuMn-based catalyst, and c) modification of the synthetic procedure of thermally stable low surface area oxidic phases. It turned out that modification of the synthetic procedure of hydrotalcite-derived CuMn-based catalyst at the stage of support impregnation proved beneficial. Catalyst obtained in such a way was more active than the Pd-containing 2nd Generation sample.

NEXT-GTL Innovative Catalytic Technologies & Materials for Next Gas to Liquid Processes

EU 7th FP NEXT-GTL Large-scale Integrating Project [2008-2011]
(project leader: Professor Małgorzata Witko DSc)

Synthesis and characterization of physicochemical properties of HPA

The synthetic approach was based on the concept of preparation of bifunctional solids, with both the acidic and the redox properties, whose relative contributions could be controlled by an appropriate design of a heteropolycompound formula. 12-tungstophosphoric acid, known for its strong acidic properties, and 12-molybdophosphoric acid possessing stronger redox properties have been chosen as the basis for further modifications. A new heteropolycompound, $H_4[PW_{11}VO_{40}]$, containing V as an element responsible for the enhancement of the redox function, has been synthesized and characterized. All materials synthesized over the project duration, have been characterized by XRF, XRD, BET, FTIR, TPR.

Electronic structure of heteropolyacids

The activity in theoretical analysis/modeling of the activation of C-H bond and its further oxidation was focused on description of oxidative properties of HPA. Catalytic properties of HPA as oxidative catalysts depend strongly on their ability to provide oxygen as a reactant. Therefore, the studies on vacancy formation as a function of their location in Keggin anion as well as chemical character of neighbors were considered. The preliminary studies on the removal of neutral oxygen atom and oxygen ions (O^- and O^{2-}) show that O^- removal leads to the most stable local defects in heteropolyacids system. High and positive values of energies of the defect formation indicate that the creations of oxygen vacancies are strongly endoenergetic processes in the Keggin structure. The results of calculations show that the energy of vacancy formation is a function of defect location. Lower values are obtained for the bridging oxygen atoms (coordinated to two addenda atoms) than for terminal oxygen atoms (bound with only one addenda atom). The effect of addenda ions on the energy of vacancy formation was tested for various metals (W, Mo, V, Cu). The results of theoretical modeling show that the greatest changes in energy are observed for copper ions.

Electronic structure of MoOxCy system

Research activities focused on the theoretical modeling of activation of methane and its further transformations to yield C_2H_4 on MoO_3/ZSM-5 catalyst. The theoretical model of the possible reactions was based on the microkinetic model developed by University of Ghent partner. Up to date not all of the intermediate states are identified, but most of stationary points on the reaction pathways are characterized. It is found that the first step of the reaction consists of the methane physisorption on the catalyst. Next, the C-H bond is activated and broken. The process seems to be easier on the reduced form of the catalyst. In that case, the resulting CH_3 and H radicals are bound to the reduced molybdenum center. Next, the second hydrogen atom from CH_3 group is abstracted, the resulting H_2 molecule desorbs from the catalyst leaving CH_2 species double bound to Mo ion. Ethylene might be then formed as a result of recombination of two CH_2 groups present on the adjacent molybdenum centers. The barrier of such a process is ca. 24 kcal/mol. Ethylene desorption needs ca. 44 kcal/mol and requires change in the system multiplicity. No barrier for ethylene desorption is found, but more detailed studies are in progress.

MUST Multi-level Protection of Materials for Vehicles by "Smart" Nanocontainers

EU 7th FP MUST Collaborative Project [2008-2011]
(project leader: Professor Piotr Warszyński DSc)

The destructive effect of environment and the corrosion induced degradation are the important problems which determine the service life of vehicles and their components. The application of organic coatings is the most common and cost effective method of improving protection and durability of metallic and plastic structures. The object of the MUST project is the development of new active multi-level protective systems for future vehicle materials based on "smart" release nanocontainers containing anticorrosive agents incorporated in the polymer matrix or particles showing barrier properties for the diffusion of water and other corrosive media. Main objects of the investigations at the ICSC PAS in 2011 year was the development of the mathematical model for the diffusion of water and other corrosive media through the polymer coatings and its experimental verification.

A package of computer programs for simulation of diffusion in polymer coatings containing dispersed particles which can bind the diffusing substance, based on finite-difference method was developed. Simultaneously a package of programs enabling the calculation of the effective diffusion coefficients from the results of the measurements was also developed.

The mathematical model was verified experimentally for the case of water diffusion through the polymer coatings containing water-trapping particles (water traps). Spherical (0.55 μm diameter) water microtraps developed by one of the MUST project partners, prepared via a two steps process, which comprises the preparation of cross-linked poly(methacrylic acid) spheres by distillation-precipitation polymerization and the subsequent conversion of carboxylic groups to the corresponding sodium salts by treatment with aqueous sodium hydroxide solution were used. Composite coatings were prepared by mixing water traps with model water-based epoxy resin supplied by one of the MUST project partners. Diffusion of water in coatings made of composite medium was investigated by IR ATR spectroscopy and microbalance measurements.

According to the predictions of developed mathematical model, to show the good barrier properties water traps should show high sorption capacity and low diffusion coefficient. The water traps used were able to absorb water in the amount of 180% of its weight and had diffusion coefficient of water 5 orders of magnitude lower than the resin used. The results of the experiments fully confirmed the theoretical predictions – coatings containing only 5% of traps by weight showed the effective diffusion coefficient of water three times lower than coatings made from the pure epoxy resin.

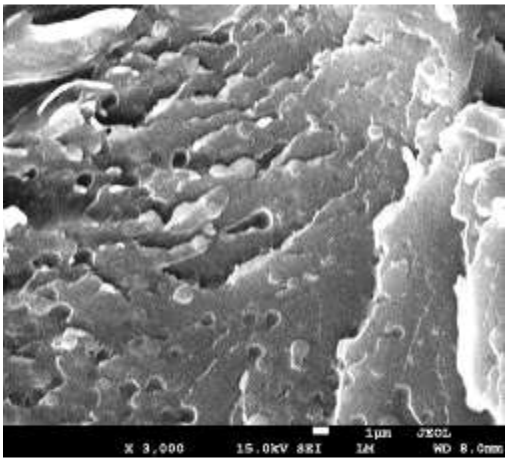


Fig. 1. SEM picture of the cross-section of the epoxy resin containing the water-traps

Smart Monitoring of Historic Structures

EU 7th FP SMOOHS Collaborative Project [2008-2011]
(project leader: Michał Łukomski PhD)

The main aim of the project is to develop a wireless monitoring system of historic structures which will be used by conservation practitioners in the field. The system has a modular structure so that one can select monitoring modules and combinations of sensors to answer specific questions arising at an object. During the third year of the project the emphasis was placed on testing the developed monitoring systems and dissemination of the project results.

Acoustic emission methods were utilized in cooperation with partners from Bologna University for monitoring micro-fracturing of wooden construction elements. In most crystalline materials (especially metals), acoustic emission is not observed during the reloading of a material until the stress exceeds its previous value. This ability to memorize the highest stress level experienced in the past is called the Kaiser effect. Investigation of the Kaiser effect in organic materials, such as wood, is very complex due to pronounced viscoelasticity, which leads to erasing stress memory in this material with time. The recovery of 150-year old timber beams from the roof of a historic building made possible a study of the Kaiser effect in old wood by monitoring AE from the specimens subjected to cyclic loading. The results obtained clearly showed the existence of short-term Kaiser effect. Additionally, the measurements repeated after one year revealed a long-term persistence of the Kaiser effect. An experimental verification of the Kaiser effect in old wood has opened a new perspective for determination of load histories of wooden works of art and constructions, which is essential for assessing the risk of their mechanical damage.

The most important means of dissemination developed during the third year of the project were freely-available, web-based Toolbox and Smart Monitoring Guidelines elaborated within the frame of Work Package 7, led by the Institute. The web-based toolbox of the SMooHs project provides information on smart monitoring systems which are non-destructive, minimal-invasive and capable of operating in the real-world conditions. The smart diagnostic techniques and sensors contained in the Toolbox assess structural integrity, warn of danger, safeguard against catastrophic failures, help to understand the connection between damage development and the agents of destruction in the environment, and therefore can enhance the preservation of a wide range of historic structures.

The Guidelines are the product of three years of research and implementation work. These Guidelines contain information about competitive and simple-to-use wireless monitoring technologies, minimally invasive mounting and installation procedures, long-term behaviour, multi-sensor platforms open for different sensor technologies, and integrated data analysis and interpretation methodologies. The aim of the Guidelines is to provide comprehensive and useful information to all interested in diagnosing and preservation of the architectural heritage.

All achievements of the SMooHS project were summarised during the final international conference held on September 26-27, 2011 in Berlin, hosted by the Rathgen Research Laboratory, with the Staatliche Museen zu Berlin.

ROCARE ROman Cements for Architectural REstoration to New High Standards

EU 7th FP 226898 ROCARE Collaborative Project [2008-2011]
(project leader: Professor Roman Kozłowski DSc)

Highly hydraulic binders, known as natural or Roman cements, were key materials to decorate - on a massive scale - façades of buildings during the nineteenth and early twentieth centuries, a period of rapid urban growth in Europe. The former EU project ROCEM (2003-2006, coordinated by the Institute) has re-established manufacturing of Roman cements at a pilot scale and initiated their use in conservation practice. The main steps of the new ROCARE project are scaling up of the production, laboratory studies to fully understand optimum conditions of mortar processing and handling, and broad dissemination measures.

A further step in elucidating the mechanism of shrinkage cracking of Roman cement pastes and mortars, which is the key research task of the institute, was accomplished in the reporting period. Acoustic Emission (AE) analysis was used to trace directly the progress of cracking caused by the non-uniform drying. The results correlated well with variations in the drying shrinkage and tensile properties associated with different pore structures developed at various curing times. Only few low-energetic AE events were recorded for young materials, of shorter curing times and a broad-pore structure, showing low drying shrinkage. In contrast, large number of intense events were recorded for matured materials, of longer curing times and a denser microstructure. The kinetics of cracking was precisely determined by the AE measurements which showed that the most intense damage occurs during the abrupt shrinkage after 6 to 9 days of drying.

The mechanism of shrinkage cracking established in the laboratory was used in implementing an extensive programme of practical applications of the mortars outdoors on a test brick wall in collaboration with project partners engaged in practical restoration. The mortar formulations were those covering the range of casting and render applications. The practical tests allowed optimising practical processing and handling of the mortars, elucidating the impact of the real-world conditions of curing which involve strong variations of temperature and relative humidity and suction of water into the brick masonry, as well as determining how the drying shrinkage of the mortar affects its adhesion to the substrate. The trials confirmed that the risk of physical damage in mortars in the realistic conditions encountered during the restoration of buildings can be minimized by ensuring adequate volume of aggregate in the mortar mix and a moderate curing time. The outcome of the practical trials will be included in the manual on best practice in the application of Roman cements, a key publication of the project to approach the market.

The institute participated also in generating a database of properties so that a comparison can be made between ROCARE mortars and mortars based on existing binder formulations which conservators had been using so far in the building restoration. The institute provided data on the pore structure of a wide range of mortar formulations at various curing times.

The Institute leads Workpackage 3 "Dissemination and marketing". During the reporting period the mid-term project meeting was organised in Krakow and the mid-term report was prepared and approved by the European Commission. The training and information activities within this Workpackage comprised workshops and brochures on conservation projects using Roman cement technology.

F3 Factory Flexible, Fast and Future Factory – European Chemistry Consortium Begins the Journey into the Future of Production

EC 7th FP CP-IP 228867-2 F3 Large-scale Integrating Project [2009-2013]
(project leader: Professor Piotr Warszyński DSc)

The F^3 Factory consortium believes that the EU chemical industry's competitive position would be significantly enhanced if it could operate modular continuous plant (F^3 Factory plant) for low to medium scale production rates. As such, the F^3 Factory project has united a wide variety of stakeholders from across EU member states around this common vision, mobilizing a critical mass of research and innovation effort necessary to realize the project's objectives. The F^3 Factory premise is that the operation of a modular, continuous F^3 plant will be more economical and more sustainable than either the: operation of continuous processes at world scale, or operation of batch processes at low to medium scale. The table below shows the current situation and the modern F3 concept

Current situation	Future concept
World scale continuous facilities fore large volume chemical, polymers products: Efficient but inflexible	Introduce efficiency to Multi-purpose, Multi-product batch manufacturing facilities
Multi-purpose, Multi-product batch facilities for actives, formulations and specialties: Flexible but inefficient	Add flexibility to the efficiency of world-class continuous facilities
Both concepts require significant upfront investments: High business risk	Reduce risk in large scale investments

The F^3 Factory project has two key aims:

- to deliver radically new 'plug and play' modular chemical production technology, capable of widespread implementation throughout the chemical industry
- to deliver holistic process design methodology applying process intensification concepts and innovative decision tools

The F^3 Factory mode of production therefore combines the best of these two conventional production modes.

Our aim in this project is validation of the F^3 technology. Studies performed in our institute in last year concern the evaluation of adsorption properties of poly(acrylic acid) PAA synthesized in a new production process, from acrylic acid monomer derived from bio-resources, resulting. The adsorption properties of PAA polymer were studied with a quartz crystal microbalance QCM (adsorption on gold surface) and on colloidal particles (eg. $CaCO_3$). We demonstrated that the new polymer synthesized from monomer produced in the new production process (bio-source concept F^3) has similar adsorption properties as the polymer synthesized by the old method. We also shown that impurities arising from the new process did not affect the final adsorption properties of the PAA polymer.

EU COST Actions projects

Molecular Structure-Performance Relationships at the Surface of Functional Materials

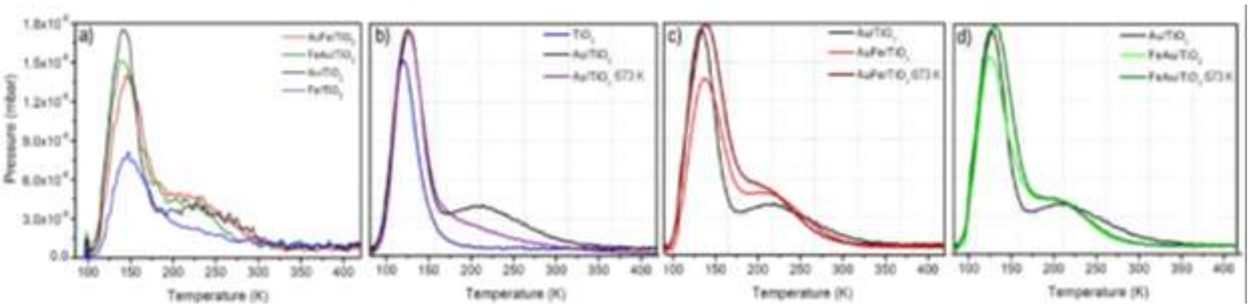
Interfacial functionalization of (bi)-metallic nanoparticles to prepare highly active and selective catalysts: understanding synergy and/or promotion effect

EC COST Action D36 research project [2006-2011]
(Polish representative: Professor Józef Korecki DSc)

In catalytic processes, sintering of the active clusters can lead to the loss of activity. To avoid this, the Au clusters morphology and their electronic properties can be changed by adding a second metal, e.g. iron. Bimetallic Au-Fe nanoclusters were deposited under ultrahigh vacuum (UHV) on a rutile-TiO_2(110) and characterized by STM and XPS in a wide coverage range. The influence of the deposition sequence (Au, Fe or Fe, Au) on adsorption of CO on the bimetallic clusters was studied *in situ* by temperature programmed desorption (TPD) as a function of annealing. In the TPD measurements, the adsorption of CO (1 Langmuir at $1.3 \cdot 10^{-8}$ mbar) was performed at 95 K and the desorption signal was acquired using a quadrupole mass spectrometer (SRS 200, Stanford Research) up to 400 K with temperature ramped at $1.5\ K \cdot s^{-1}$.

For the TPD measurements, the Au-Fe clusters were formed by room temperature (RT) deposition of 0.1 monolayer (ML) of Au and 0.1 ML of Fe. TPD spectra (mass 28) obtained for CO desorption from single-metal (Fe or Au) and bi-metallic clusters deposited in the different sequence (AuFe or FeAu) showed a large peak at 150 K that was assigned to desorption from the titania substrate (Fig. b, blue curve). Deposition of gold only has no impact on CO desorption from the substrate, however it results in an additional broad peak extending to RT, with a maximum at 230 K (Figs a,b,c,d, black curves). On the contrary, deposition of Fe resulted in a significant decrease of the CO adsorption on the titania surface and produced only a tail at higher temperatures, between 180 K and 250 K. In both bimetallic systems, the overall TPD spectra characters were similar (broad maximum at 235 K) although the spectra differ in some details characteristic for desorption from single-metal clusters. Fe deposited as the second metal limited CO desorption above 250 K. Additionally, when Au deposition follows Fe deposition, desorption at higher temperatures was similar to that for the Au/TiO_2(110) system.

For Au/TiO_2, the 0.5h annealing at 673 K induces a significant decrease of the CO adsorption and a disappearance of desorption peak at 230 K. In all cases, the presence of iron prevents reduction of the high temperature peak intensity, suggesting stabilization of the small Au clusters by iron. A limited influence of the annealing temperature on the cluster number was observed previously by STM measurements.



Colloid and Interface Chemistry for Nanotechnology

EU COST Action D43 research project [2006-2011]
(Polish representative: Professor Zbigniew Adamczyk DSc)

Research works carried out within the framework of the project were aimed at determination of mono- and multilayer adsorption mechanisms of polyelectrolytes and proteins at various solid substrates. This has essential practical significance for example by devising new systems of controlled drug delivery, especially microcapsules. One of the most reliable methods of monitoring mono- and mulilayer formation at solid substrates represent the streaming potential measurements enabling direct, *in situ* measurements. However, a proper interpretation of these results obtained for polyelectrolytes requires calibrating measurements for model colloid systems. Therefore, one of the major aspects of this work was performing such measurements for monodisperse polystyrene latexes of well-defined surface properties and other physicochemical parameters. In Fig. 1 results obtained using the streaming potential method for the bilayer of two latexes: A500 (exhibiting a positive surface charge) and L800 (exhibiting a negative surface charge) are shown. The dependence of the zeta potential of the bilayer ζ was determined for various coverage of the first (precursor) layer. The zeta potential is the most relevant parameter characterizing the stability of microcapsule systems. En essential conclusion which can be drawn from these measurements is that the zeta potential of the bilayer becomes practically independent of the first layer coverage as low as 5%. It is also worthwhile mentioning that the results shown in Fig. 1 have significance for the interpretation of protein bilayer formation, especially for the antigen/antibody systems.

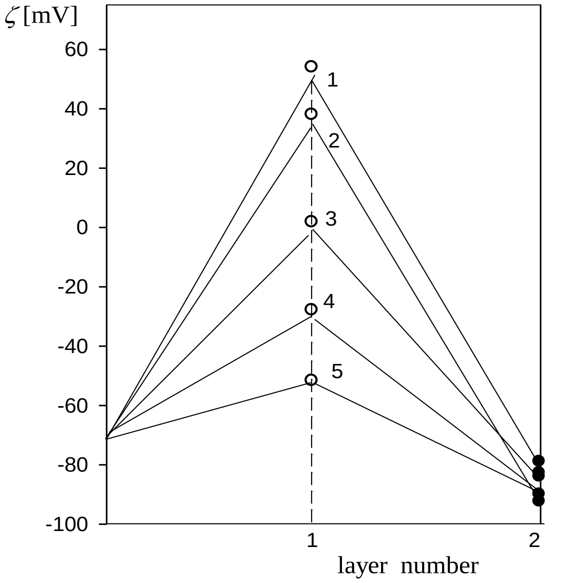


Fig.1. Formation of bilayers of the A500/L800 latex on mica shown as the dependence of the zeta potential ζ on the layer number (pH = 5.5, I=10^{-2} M, T = 293 K).
1. $\Theta_s = 0.50$, $\Theta_p = 0.5$ (complete bilayer), 2. $\Theta_s = 0.20$, $\Theta_p = 0.5$ (incomplete bilayer),
3. $\Theta_s = 0.10$, $\Theta_p = 0.45$ (incomplete bilayer), 4. $\Theta_s = 0.05$, $\Theta_p = 0.25$ (incomplete bilayer),
5. $\Theta_s = 0.02$, $\Theta_p = 0.15$ (incomplete bilayer),
The points denote experimental results obtained by the streaming potential measurements. [M.Zaucha, Z.Adamczyk, J.Barbasz; J. Colloid Interface Sci., 360, 2011, 195]

Wood Science for Conservation of Cultural Heritage

Management of the museum collection based on computer modeling of the impact of the microclimatic fluctuations on historic objects

EU COST Action IE0601 research project [2006-2011]
(Polish representative: Professor Roman Kozłowski DSc)

The project concerns development of management strategies for the microclimatic control for museum collections consisting of wooden objects. Partners of the project - the National Museums in Krakow and Warsaw are particularly interested in the optimum microclimatic control in their galleries and storage rooms as they own the most important collections of medieval and modern art consisting of wooden objects in Poland. The main aim of the project is to develop management strategies for the microclimate control, which will on the one hand reduce the costs and on the other ensure the effective protection of art objects.

The key task of the institute in the project was to develop finite element analysis (FEA), supported by measurements of the physical properties of materials, to model the water vapour movement, strains, and stresses, in panel paintings and polychrome wooden sculpture, in response to changing climate conditions. This research tool enabled a scientific assessment of the impact of microclimatic parameter fluctuations on the process of destruction of historic objects.

In the reporting period, the method developed was used to establish the allowable amplitude of cyclic sinusoidal relative humidity (RH) fluctuations for an unrestrained, single wood panel coated with a layer of gesso, that is the amplitude which the gesso layer endures without physical damage over a selected time of exposure. The parameter was derived as a function of cycle duration, panel thickness and diffusion configuration. The dimensional response of thin painted panels becomes subject to restraint by the applied layer of gesso, the restraint being dependent on the gesso's modulus of elasticity and thickness. The panels do not respond significantly to diurnal fluctuations or shorter irrespectively of the panel thickness. The panels respond more and more significantly when the duration of the fluctuations increases until a certain critical period at which the panel fully responds to each cycle. The worst-case represents a panel 10 mm thick with two faces permeable to water vapour which is subjected to the fluctuation cycles lasting 14 days. The corresponding lowest allowable amplitude of fluctuations determined in this study is ±14% RH. Hence, by taking into account the response of a composite object as well as the dependence of the strain causing damage in the gesso on the number of strain cycles, the allowable amplitude for the worst case RH cycles was increased from mere ±6% RH derived for the simplified criterion of single-cycle yield strain and without considering the restraint of the applied gesso layer on the free movement of the wood support.

Numerical modelling of the moisture movement and strain in a system of wood coated with a layer of gesso in conditions of high yearly average RH and low winter temperatures was advanced. Such environments are important to the protection of vulnerable heritage objects in unheated churches or historic houses in northern climates. The allowable amplitude of RH fluctuations was found to increase significantly if the temperature at which the panel painting is displayed is lowered. The effect is caused by a decrease in the water vapour diffusion coefficients in wood and hence an increase of the time of panel's response.

Projects of EU structural funds programmes

MPD Krakow Interdisciplinary PhD Projects in Nanoscience and Advanced Nanostructures

PO IG 1.1.2. MPD [2008-2012]
(project leader: Professor Józef Korecki DSc)

Project "MPD Krakow Interdisciplinary PhD-Projects in Nanoscience and Advanced Nanostructures" is implemented within the Innovative Economy Operational Programme, Priority 1. Research and development of new technologies, Measure 1.2 - Strengthening the human potential of science, The Project Coordinator is Prof. Bartłomiej Szafran affiliated at Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, who is the partner in the Project. The project is also carried out in cooperation with the following foreign partners: Universiteit Antwerpen (Belgium), University of Leeds (The United Kingdom), National Research Centre INFM-CNR (Italy), University of Stockholm (Sweden), Max Plank Institute für Molekulare Pflanzenphysiologie (Germany), Max Plank Instytut für Kolloid und Grenzflächenforschung (Germany), Basque Country University (Spain), SINTEF Material and Chemistry (Norway), VŠB-Technical University of Ostrava, (Czech Republic), Institute of Physical Chemistry , Bulgarian Academy of Sciences, Sofia (Bulgaria).

The five-year Project started on 1st November 2008 aims to accomplish twelve PhD thesis within twelve individually defined PhD projects. Recruitment procedure of the PhD students was in the form of the open calls. In 2009 the recruitment procedure was completed and since that time in the ICSC the following five individual PhD project are being implemented:

1. supervisor: Professor Ewa Brocławik DSc, PhD student: Anna Wójcik MSc
   Project title: Computer modeling of biological nanostructures. The student has been accomplishing her research program at the University of Stockholm since May 2011.
2. supervisor: Professor Piotr Warszyńsk DSc, PhD student: Małgorzata Adamczak MScEng. Project title: Surfactants, polyelectrolytes and nanoparticles as building blocks for surface nanostructures. The student is has been accomplishing her research program at SINTEF Material and Chemistry since November 2010.
3. supervisor: Professor Kazimierz Małysa DSc, PhD student: Dominik Kosior MScEng
   Project title: Nanostructures and stability of thin liquid layers. In 2011, the student accomplished his 6-months research program at the Bulgarian Academy of Sciences.
4. supervisor: Professor Wiesław Łasocha DSc, PhD student: Katarzyna Luberda-Durnaś MScEng. Project title: Hybrid organic-inorganic layered materials - precursors of semiconducting nanostructures. In 2011, the student accomplished her 6-months research program at the VŠB-Technical University of Ostrava.
5. supervisor: Professor Józef Korecki DSc, PhD student: Ewa Młyńczak MScEng.
   Project title: Surface and interface properties of metal-oxide magnetic nanostructures. In 2011, the student accomplished her 6-months research program at National Research Centre INFM-CNR Modena.

The PhD programs are realized according to schedules.

ISD Advanced Materials for the New Technologies and Energy of the Future

PO KL 4.1.1 ISD [2008-2012]

(project leader: Assoc. Professor Renata Tokarz-Sobieraj DSc)

The Interdisciplinary PhD Project is implemented within the Human Capital Operative Programme funded form the European Union Structural Funds and the national budget sources. The project is coordinated by the Faculty of Physics & Applied Computer Science AGH University of Science and Technology and carried out in the partnership with the Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences and the Institute of the Nuclear Physics of the Polish Academy of Sciences. The aim of the Project is to educate high level specialist with the PhD diploma in the disciplines considered as strategic in the European and national research policy, i.e. Info, Bio, Nano, Techno.

Research and education within the project involve physical, chemical and technological aspects of material science and modern energy science. The project is being implemented since 2009. At the moment, 60 PhD students are studying in all partner institutions (1 year - 14 students, 2 year - 24 students, 3 year - 22 students). The following 17 individual PhD projects are running:

1st year

- K. Kubiak MSc (supervisor: Professor Z. Adamczyk DSc) The synthesis of new layered materials based on silver nanoparticles, active in the processes of selective binding of proteins
- Ł. Kuterasiński MSc (supervisor: Assoc. Professor M. Derewiński DSc) Hierarchic porous materials as the basis of the modern refinery processes2nd year
- P. Batys MSc (supervisor: Assoc. Professor P. Weroński DSc) Multi-scale modeling of irreversible adsorption of nanoparticles at the solid/liquid interface
- Dziedzicka MSc (supervisor: Professor B. Sulikowski DSc) Physicochemical properties of hierarchic molecular sieves
- M. Grzesiak MSc (supervisor: Professor W. Łasocham DSc) Metal-organic structures: materials for catalysis, crystal engineering and "gas sorbents"
- Ż. Kalemba MSc (supervisor: Assoc. Professor A. Drelinkiewicz DSc) Research for the selection of catalysts for the reaction of glycerol etherification
- Miłaczewska MSc (supervisor: Assoc. Professor T. Borowski DSc) Molecular modeling of the structure and catalytic activity of biological materials;
- D. Szepietowska MSc (supervisor: Professor B. Sulikowski DSc) Physicochemical properties of zeolites/heteropolyacids hybrid types catalysts
- Szymańska MSc (supervisor: Professor W. Łasocha DSc) New polymetalates and peroxocomplexes as materials for applications in catalysis, medicine and industry
- M. Tatko MSc(supervisor: Assoc. Professor P. Nowak DSc) Highly conductive ionic conductors based on lantanide metal oxides for high-temperature solid oxide fuel cell
- P. Niemiec MSc(supervisor: Assoc. Professor R. Tokarz-Sobieraj DSc) Theoretical modeling of the physicochemical properties of heteropolyacids

3rd year

- J. Dziedzic MSc (supervisor: Professor P. Warszyński DSc) Photocatalytic decomposition of organic compounds in water enhanced by encapsulated oxidants
- M. Krzak MSc (supervisor: Assoc. Professor P. Nowak DSc) High-performance anticorosive coatings prepared from composite meterial based on organic polymers
- M. Nosek MSc (supervisor: Assoc. Professor P. Weroński DSc) Analysis of multilayer porous colloidal materials with controlled architecture
- M. Oćwieja MSc (supervisor Professor Z. Adamczyk DSc) Kinetics of silver particle adsorption on heterogeneous surfaces and morphology of silver monolayers
- K. Onik MSc (supervisor Assoc. Professor M. Derewiński DSc) Hierarchic materials based on zeolites precursor as the basis of the modern catalytic systems
- Pajor MSc (supervisor: Professor P. Warszyński DSc) Electroactive polyelectrolyte multilayer films with embedded nanoparticles

SPINLAB National Centre of Nanostructures for Spintronic Applications

PO IG 2.2. SPINLAB [2009-2011]
(project leader: Professor Józef Korecki DSc)

Commissioning of the PEEM and LEEM microscope at laboratory conditions

Two electron microscopes for surface imaging were purchased from ELMITEC company in the frame of SPINLAB project:

- LEEM III – the microscope imaging with low energy electrons (LEEM) and with photoemitted electrons (PEEM), intended for installation at the Laboratory of Surface and Nanostructures (ICSC PAS).
- SPE-PEEM III - photoemission electron microscope with band-pass energy filter meant for implementation at first Polish synchrotron „SOLARIS" (~2014)

Both microscopes were installed and configured at the Laboratory of Surface and Nanostructures. The parameters of the microscopes working under laboratory conditions were verified. Following tests within accessible modes of operation were carried out: bright field LEEM, dark field LEEM, low energy electron diffraction (LEED), diffraction from microareas (μ-LEED), PEEM with Hg lamp excitation, mirror electron microscopy (MEM) and thermoemission electron microscopy (TEM). The best resolution (criterion 84% - 16%) achieved during tests are 3nm in LEEM mode for the Si(100) surface (Fig. 1) and 10nm in PEEM mode for the Pb nanoparticles on the Mo(100) surface (Fig. 2).

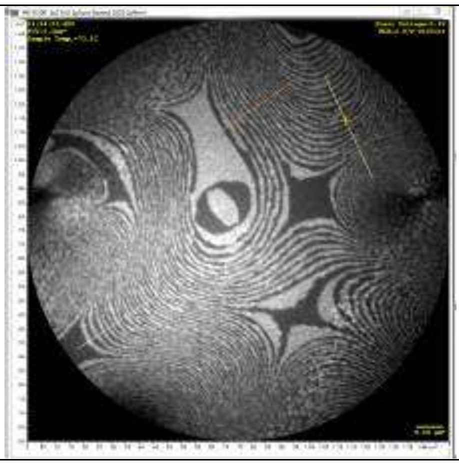
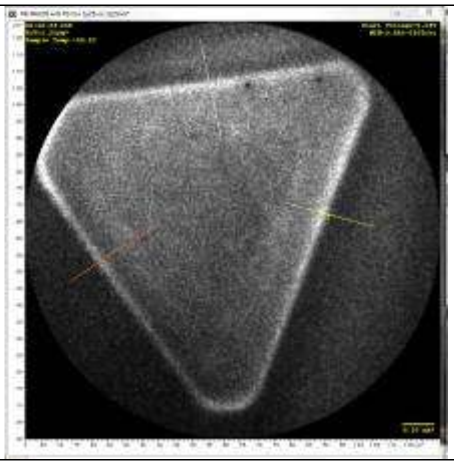
	

Fig.1. Dark field image taken with half order spot on the reconstructed Si(100) surface with LEEM III. Field of view: 1.5um, resolution measured at three different positions: 2.9nm, 3.7nm and 3.8nm	Fig.2. PEEM image of a Pb island on Mo(100), taken with the spectroscopic Elmitec instrument. Field of view: 1.25um, resolution measured at three different positions:14.8nm, 13.9nm and 12.5nm

The LEEM microscope was equipped with preparation chamber with facilities indispensable for sample preparation. At present, accommodation of PEEM microscope for working with synchrotron radiation and equipping it with UHV components for in situ sample preparation are in progress.

BIOTRANSFORMACJE Biotransformations Useful in Pharmaceutical and Cosmetics Industry

Task 6. Biocatalytic Methods for Synthesis of Chiral Alcohols

POIG 1.3.1 BIOTRASFORMACJE [2009-2014]
(project leader: Maciej Szaleniec PhD)

The research conducted within task 6 of Biotransformation project focused on two enzymatic systems catalyzing synthesis of chiral alkilaromatic alcohols: ethylbenzene dehydrogenase (EBDH) and phenylethanol dehydrogenase (PEDH).

In the first quarter of the year inactivation of catalytic properties of PEDH and EBDH was examined. For this purpose temperature-activity profiles, effects of pH, influence of organic solvents and substances common used to terminate reaction (e.g. organic and mineral acids, chemicals) were evaluated. Thermal inactivation of both enzymes was observed in the higher temperature (45-55^{o}C). For EBDH no loss of activity in electrochemical reactor was noticed. Spectrophotometric temperature-dependent enzyme assay for several substrates of PEDH showed that it is possible to build quantum structure-activity relationship based on energy activation measurements. Our investigations indicate that electron-acceptor substituents increase reverse reaction rate (reduction) as in case of substrate with such substituents the lower activation energy was observed. Investigation of the pH effect showed that the optimum pH for the reduction of alkylaromatic ketones catalyzed by PEDH is 5.5. Due to the limitations of test activity we did not find appropriate chemical factor which can terminate a reaction. As a result, a reaction was stopped by protein precipitation and centrifugation. Influence of typical organic solvents on the enzyme activity was checked by adding 5% (v/v) of particular solvent. No loss of activity was detected. Moreover an increase of activity was observed up to 15% of acetonitrile and ethanol or 40% of methanol in the assay reaction mixture.

The optimal test conditions were used in the studies of catalytic activity of several new substrates. For many of them we confirmed the presence of only one enantiomer of the alcohol in the reaction mixture with PEDH.

The tasks planned for the second and third quarter of the year focused on the optimization of processing conditions for purified enzyme in a batch reactor with NADH cofactor recycling. First, an optimal concentration of isopropanol in reaction mixture was determined. As a result, it was decided to use 60% v/v of that solvent. Isopropanol appears not to affect PEDH stereoselectivity even in such a high concentration. For several ketones conversion rate to alcohol product were investigated. Alcohol product concentrations were studied with RP-HPLC. In every case a reaction yield was higher than 40%. During the research a gradual up-scaling of a substrate concentration was performed. For this purpose acetophenone concentration was increased from 0.5 mM to 50 mM.. In further studies, pure enzyme was replaced by whole *E. coli* cells, the bacteria used as a source of PEDH. This improved reaction control as a simple way of reaction termination with centrifugation of bacteria cells was possible. The recovered catalyst was reused in fresh medium, confirming the high conversion in two cycles (95% after 31 h).

The task for the last quarter of 2011 was to develop quantum-mechanical descriptors for EBDH and PEDH substrates. As in the currently accepted reaction mechanism of short-chain alcohol dehydrogenases the presence of alkoxy anion in transition state is postulated free enthalpies of alkoxy anions formation were calculated. ΔG values were then related to model substrate (acetophenone). Calculations indicate existence of the relationship between the nature of the substituents and ΔG: electron withdrawing substituents seem to accelerate a reaction rate.

FUNANO Functional Nano- and Microparticles, Synthesis and Applications in Innovative Materials and Technologies

POIG 2.1.1 FUNANO [2009-2014]
(project leader: Professor Zbigniew Adamczyk DSc)

Syntheses of monodisperse silver nanoparticles were performed under various conditions according to the method of Creighton et al. by reduction of $AgNO_3$ solutions with $NaBH_4$ in the presence of citrates. Extensive physicochemical characteristics of silver sols were performed including the electrophoretic mobility. It was shown that these suspensions were stable within a prolonged storage time reaching one year. These silver suspensions were used in subsequent measurements of deposition kinetics on mica modified by adsorption of various cationic polyelectrolytes (Fig. 1). The surface coverage of particles was determined directly by counting the number of particles over various surface areas using the atomic force microscopy and the scanning microscopy. The maximum surface coverage obtained in in these kinetic measurements exceeded 40%, which is the highest value reported in the literature. It is also interesting to mention that both the kinetic runs and the maximum coverage determined in experiments were in a good agreement with theoretical predictions derived from the random sequential adsorption (RSA) model. Our investigations confirmed that it is feasible to produce uniform silver nanoparticle monolayers on solid substrates, characterized by controlled density and structure using the colloid self-assembly from aqueous sols.

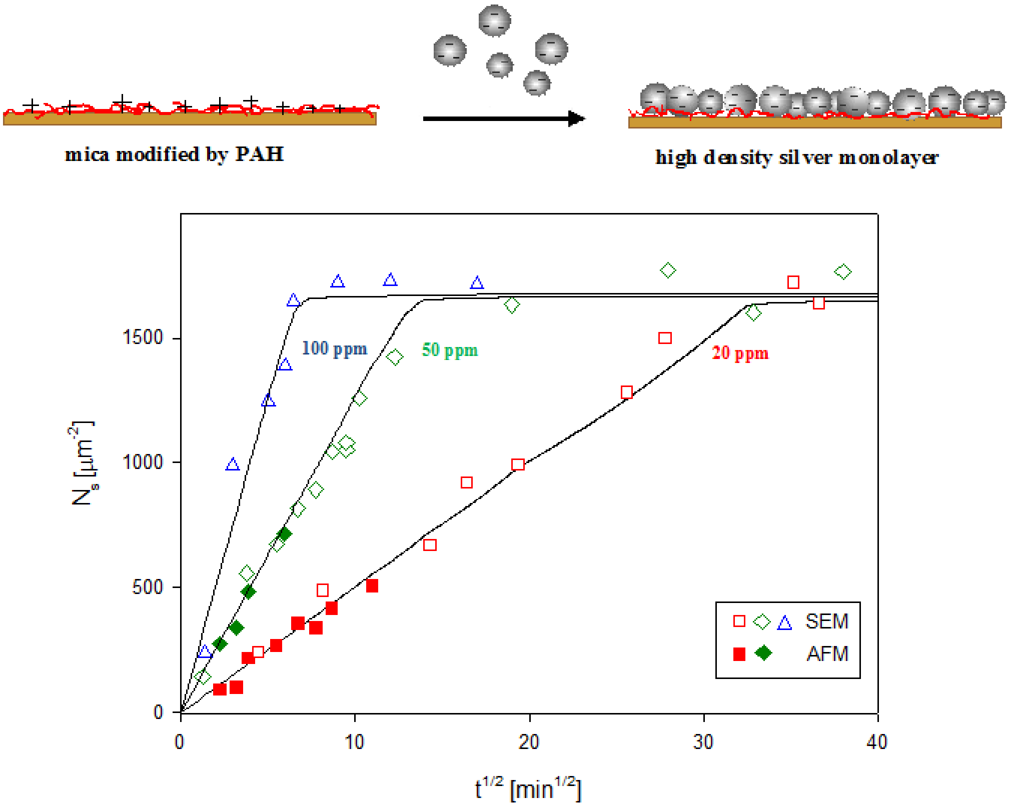


Fig. 1. Kinetics of silver particle (average diameter 16 nm) deposition on mica modified by the cationic polyelectrolyte (PAH) pre-adsorption. Particle deposition was carried out under diffusion-controlled transport for the bulk concentration c_b=100, 50 and 20 ppm, t=11 h, pH=5,5, I=10^{-2} M NaCl. The points denote experimental data and the solid lines represent theoretical predictions derived from the RSA model elaborated in this work.

VOX Development of Technology for Synthesis of Nanostructured Oxide Catalysts for Purification of Air from Toxic Volatile Organic Compounds

PO IG 2.1.1. VOX [2009-2013]
(project leader: Professor Ewa Serwicka-Bahranowska DSc,
principal investigator: Tadeusz Machej PhD)

Project aims at development of technology of manufacturing efficient and cheap mixed oxide catalysts for purification of industrial flue gases from toxic volatile organic compounds. The basis for catalytic design are synthetic layered minerals isomorphous with hydrotalcite, of general formula $[(M^{2+})_{1-x}(M^{3+})_x(OH)_2](A^{n-})_{x/n}\cdot mH_2O$, whose specific structure allows for uniform mixing of catalytically active elements at atomic level.

In the reported period the work concentrated on further adjustment of the catalyst active phase composition and optimisation of the synthesis conditions. Next to the main components of the brucite layer, i.e. Mn, Cu and Al, other metallic elements, e.g. Co, Ce, Zr and La were added. Beside conventional interlayer anions such as carbonate or nitrate, permanganate was used as species compensating the layer charge. The possibility of hydrotalcite synthesis by means of inverse microemulsion procedure has been expolored using a model Mg-Al system. Hydrotalcite precursors were subjected to thermal decomposition in order to obtain mixed oxide cataysts. Both the precursors and the products of their thermal decomposition were characterized by means of ICP OES, XRD, XPS, TPR, TG/DTG/DTA, BET, SEM, TEM. Mixed oxides were used as catalysts in the reaction of complete oxidation of toluene. The most active mixed oxide solids were selected for the preparation, at laboratory scale, of monolith supported catalyst. An important part of this stage of research was the choice of appropriate conditions for the preparation of washcoat, in particular optimization of its grain size.

ISD MOLMED Molecular Sciences for Medicine

PO KL 4.1.1. ISD MOLMED [2010-2015]
(project leader: Professor Małgorzata Witko DSc)

The Interdisciplinary PhD project entitled "Molecular Sciences for Medicine" is implemented within the Operational Programme Human Capital, Priority IV Higher Education and Science, sub-measure 4.1.1 Strengthening and development of didactic potential of universities. This project is co-financed by the European Social Fund (ESF).

ISD MOL-MED is coordinated by Professor M. Witko from Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences (the project leader), and involves the following participants: Jagiellonian University Faculty of Chemistry, Jagiellonian University Medical College, and Institute of Pharmacology Polish Academy of Sciences.

The five-year project has been running since October 1, 2010. Its goal is to improve the quality of interdisciplinary education at doctoral level in the fields of: chemistry, advanced materials, nanotechnology, (bio)catalysis, medicinal chemistry, pharmacology and medicine by opening and implementation of PhD studies. Simultaneously, a parallel goal of the project is to increase the didactic potential of university by broadening and enriching the training at tertiary education level and to improve teaching competence of academic staff.

In the course of this project the following tasks were completed in the year 2011:

- in the first quarter of the year the recruitment process was conducted as a result of which 17 PhD students were admitted;
- in the second quarter of the year the competition for the selection of doctoral dissertation themes was organized. A total of 23 themes were selected for the implementation;
- in the fourth quarter of the year additional 23 students were accepted for doctoral studies.

As a result of recruitment process, a total of 40 PhD students were accepted who started taking classes as well as the lab research was undertaken in all four partnership unit. The PhD students receive their fellowships monthly and they make purchases of materials and equipment necessary for their work. The progress of the project is supervised by the Programme Board consisting of 8 members two representatives from each partnership unit.

Other international projects

Adsorbates on Fe Monolayer on W (110)

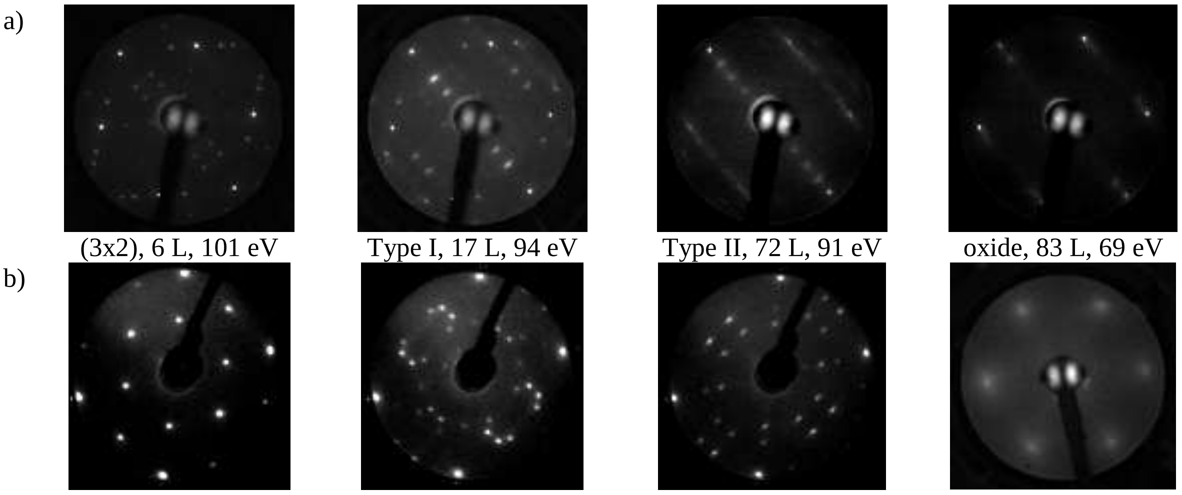
Intergovernmental Polish-Austrian project [2009-2011]
(project leader: Professor Józef Korecki DSc)

Growth and magnetism of ultrathin iron films on W(110)

Iron nanostructures on W(110) show puzzling magnetic effects related to their structural properties. Using the nuclear resonant scattering of synchrotron radiation we were able to reveal evolution of a complex magnetic structure for the films with thickness between one and five monolayers. During the film growth, the local magnetization probed by hyperfine magnetic field changes from a non-collinear configuration with a considerable out-of-plane magnetic component to the homogenously magnetized state with the in-plane [1-10] easy direction. The non-collinear states appear in mono-, bi- and tri-layers areas that coexist as a result of deviation perfect layer-by-layer growth. Significantly, we observed perpendicular magnetization in small double-layer patches surrounded by the non-magnetic monolayer sea. This observation sheds some light on interpretation of previous magnetization measurements for this system which did not indicate magnetic order because of superparamagnetic relaxation of magnetic moments in double-layer islands. The NRS method with distinctly shorter characteristic measurement and acquisition time revealed the magnetic structure showing its applicability in the studies of nanomagnetism.

Oxygen adsorption on iron surface (110)

Our earlier studies of oxygen adsorption on Fe/W(110) indicated significant diversification of the adsorption structure depending on the Fe surface type ranging from pseudomorphic monolayers (denoted as M) to surfaces of epitaxial Fe(110) films with a thickness of approximately 5 nm (denoted as B), well simulating behavior of the bulk Fe surface. For the two limiting surfaces, M and B, we were able to classify distinct surface structure resulting from the adsorption of molecular oxygen at room temperature in the exposure range 0 to 200 L. The adsorption process undergoes through several discrete structures leading to the onset of oxidation at the highest exposure. The structure whose symmetry were interpreted based on simple geometrical models are shown in Fig. 1.


a)
(3x2), 6 L, 101 eV
Type I, 17 L, 94 eV
Type II, 72 L, 91 eV
oxide, 83 L, 69 eV

b)
(2x2), 0.6 L, 55 eV
Type III, 5 L, 55 eV
(3x2) 13 L, 55 eV
oxide, 280 L, 65 eV

Fig. 1. LEED patterns for oxygen adorbates on the surfaces M (a) i B (b). Structure III corresponds to better defined so called „3x1"; I and II are new, complicated structures being superposition of several primitive ones. For example structure I is superposition of (5x1), (3x1) and one more unidenfied.

Metal and Oxide Epitaxial Nanostructures as Seen by Nuclear Resonance Scattering of Synchrotron Radiation

Intergovernmental Polish-French POLONIUM Project [2010-2011]
(project leader: Professor Józef Korecki DSc)

In bulk FeO (wüstite), oxygen and iron form the (111) planes of ideal two-dimensional hexagonal lattices. The iron planes are antiferro-magnetically coupled between each other. The FeO(111) layers are polar, which may strongly influence properties of epitaxial films with this orientation. FeO(111) ultrathin films could be stabilized in past on the single crystal Pt(111) substrate up to 2-2.5 ML, showing complex structural properties, however so far their magnetic properties were not verified experimentally. Recently, we applied a growth protocol that allowed to stabilize several nanometer thick FeO-like films on Pt(111). The conversion electron Mössbauer spectroscopy measurements showed a drastic change of the magnetic properties as a function of the film thickness. In particular, we observed a long-range magnetic order for in the 3 to 7 ML thickness range. To explain this unusual behavior we have performed measurements of the nuclear resonance scattering (NRS) of synchrotron radiation in the ultrahigh vacuum (UHV) system at the ID18 beamline at ESRF Grenoble. The new instrument allowed systematic investigation of the thermo-elastic properties of the ^{57}Fe containing nano-systems by measuring the density of phonon states (DOS) *in situ.*

The LEED-characterized FeO films with thickness between 1 and 16 ML were UHV transferred to the NRS chamber, where the grazing incidence NRS time spectra and the energy dependence of the nuclear inelastic scattering (NIS) were measured. The analysis of the NIS data shows a structural transition between 4th and 11th monolayer (increasing of the lattice stiffness), which correlates with a magnetic transition documented in parallel by the time spectra. Remarkably, for the thickest investigated film, the phonon-DOS deviates strongly from that of bulk FeO, similarly as the Mössbauer hyperfine parameters do. To account for this phenomenon we suggest formation of a meta-stable FeO structural phase. Such a new phase (e.g. wurtzite or NiAs-type) could compensate the polarity of the (111) surface.

Other activities

Centre for Environmental Pollution Analyses "CezaŚ"

(Janusz Janas MSc, Joanna Kryściak-Czerwenka PhD,
Joanna Opalińska-Piskorz MSc)

In 2011 CezaŚ Laboratory carried out the measurements using 4 accredited methods as well as internal (for Institute's research group) measurements using different experimental techniques.

In March, the CezaŚ Laboratory was subjected to the "surveillance visit", to make sure that management system is still effective and laboratory still meets PCA (Polish Centre for Accreditation) requirements. Two of accredited methods were temporary suspended because of want of orders from industrial companies.

In the course of evaluation 3 minor nonconformities with the demands was found. The sources of these nonconformities were then identified and the proper correction procedures have been initiated and finally completed. These attempts were positively appreciated by the PCA.

In the said reporting period the activity of the CezaŚ Laboratory comprised the following works:

1. Realization of 4 external orders amounted on 13272 PLN (gross).
   The scope of all orders comprised the measurements of:
   - VOC conversion in various industrial plants,
   - chemical composition and concentration of organic and inorganic atmospheric contaminants,
   - adsorption-desorption process characteristics,
   - emission of gaseous organic contaminants and efficiency of RCO (regenerative catalytic oxidizer) units.
2. Realization of 14 internal orders in the ICSC PAS comprising 17 different measuring series using the following experimental techniques:
   - GCMS (gas chromatography with mass detection),
   - FT-IR based on DRIFT, transmission and ATR equipment,
   - HPLC (liquid chromatography with mass detection).

In the aim to find new external clients the CezaŚ Laboratory was sent 188 enquiries offering their services.

Preliminary Evaluation of Application of Molecular Simulation for Evaluation of Polymer Adhesion

Commissioned research for ABB [2011]
(Professor Piotr Warszyński DSc)

The aim of this work was the preliminary evaluation of applicability of molecular simulations for evaluation of adhesion force of polymers to various surfaces. The main area of research was selection of the simulation methods and determination of their ability for identification of the main factors affecting adhesion in the systems: PPA glass (SiO_2), PPA metal (Al), PPA epoxy, epoxy-steel (Fe), epoxy DLC(sp2), epoxy DLC(sp3). For the purpose of preliminary analysis first three systems were selected. The representative model molecules and surfaces were proposed. The three different levels of simulations were proposed for the systems PPA SiO_2 and PPA Al:

- single molecules level – quantum mechanical computations with DFT method;
- level of single molecule – surface – molecular mechanics computations;
- level of cluster of molecules – surface - molecular mechanics computations.

Modeling at the level single molecule-surface was performed by molecular dynamics using AMBER99 force field implemented in the Hyperchem 8 modeling package. First model molecule representing polymer (PPA) was generated, the ESP charges, primarily computed by the DFT method were assigned and the molecule was optimized. Next the model surface was generated as the surface of crystal with the size (length and width) equal to at least three times linear size of PPA molecule and thickness corresponding to one or two elementary cells. ESP charges were assigned to crystal atoms. Then PPA molecule was placed in the central location at the surface and the energy was minimized keeping positions of the crystal atoms frozen. The example of conformation of PPA molecule at the plane (001) of α-quartz is illustrated in Figure 1. Finally, the dependence of the potential energy on the separation distance between center of mass of PPA molecule and the crystal surface was determined.

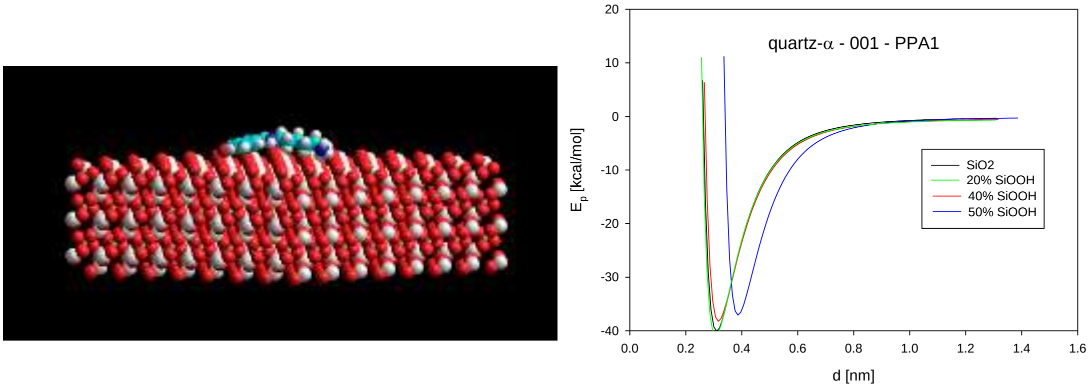


Fig. 1. Left - the example of conformation of PPA molecule at the plane (001) of α-quartz. Right - the dependence of the potential energy on the separation distance between center of mass of PPA molecule and the crystal surface, for various levels of SiO_2 hydroxylation.

Experimental Study on the Deposition of Rhenium and Its Alloys, Especially Alloys of the Composition Close to 'so called' Superalloys, on the Metallic Substrate by Electrolysis

Commissioned research for KGHM ECOREN S.A.[2010-2011]
(Assoc. Professor Paweł Nowak DSc, Grzegorz Mordarski PhD, Elżbieta Bielańska PhD, Robert Socha PhD, Dariusz Mucha PhD, Roman Dula, PhD, Daria Napruszewska, Eng, Dawid Wodk, MSc, Maciej Tatko,MScEng)

The aim of the investigations was the development of the technology of the deposition of thin layers of Rhenium and its alloys, especially alloys with Nickel as well as triple alloys containing Rhenium Nickel and third metal, on the metallic substrate by electrolysis. The development of the technology was preceded by the investigations of the electrocrystallization of Rhenium and its alloys. Many analytical methods and the physicochemical methods of surface analysis were applied in the investigations: X-ray diffraction (XRD) with the use of low-angle attachment, photoelectron spectroscopy (XPS), scanning electron microscopy (SEM + EDS), X-ray fluorescence (XRF) and electrochemical methods like cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).
The results of the investigations cannot be revealed due to the requirements of the intellectual property protection.

Spectroscopic Ellipsometry Measurements of Polymeric Layer Thickness and the Analysis of Structure of Thermoactive Polymeric Layers for Cell Culture

Commisioned research for the Centre of Carbon and Polymer Materials PAS [2011]
(Lilianna Szyk-Warszyńska PhD)

Silicon and glass plates covered by thermoresponsive polymer films delivered by Centre of Polymer and Carbon Materials PAS were investigated by ellipsometry to determine the thickness of the layer in dependence of temperature. The composition of the layers was as follows: a) copolymer of ethylene and anhydride maleine (Et-MA) and b) layer of Et-MA and thermoresponsive layer of derivative of polyglicidol. Silicon and glass plates were also hydroxylated (DSP) and functionalized with amino groups (DSA). Then the amino groups were reacted with bromine compounds forming layer labeled as DSB. Finally the DSB layer was polymerized with methacrylate monomer forming the DSM layer.

The silicon plates were placed in the ellipsometric liquid cell and the measurements were performed in water, changing temperature from 20^{o}C to 60^{o}C. Thickness of polymer film was measured by Angle Of Incidence (AOI) and Lambda Variation methods. The AOI method was performed with wavelength (λ) set to 510.3 nm and angle of incident varied between 50 and 80 degrees. The Lambda Variation method was performed using settings: AOI=75 degree, and lambda varied between 350 nm and 1100 nm. The analysis of measured data was done by Cauchy method and n,k-fix method.

The results obtained show that the thickness of thermoresponsive polymers of the derivative of polyglicidol increases with increase of temperature. The DSM layers, which were polymerized on the silicon plates, displayed the opposite behavior - the increase of temperature caused decrease of layer thickness, which was expected for grafted thermoresponsive polymers.