JERZY HABER INSTITUTEOF CATALYSIS
AND SURFACE CHEMISTRY
POLISH ACADEMY OF SCIENCES

KNOW | Leading National Research Centers

DETAILED RESEARCH REPORT

year 2012

Leading National Research Centre

Marian Smoluchowski Krakow Research Consortium "Matter-Energy-Future"

Leading National Research Centre [2012-2017]
(coordinator: Professor Małgorzata Witko)

In July 2012, the Institute was granted status of the National Leading Research Centre KNOW in physical sciences for 2012 – 2017 in the framework of the Marian Smoluchowski Krakow Research Consortium „Matter – energy – future". The Consortium is formed by Faculty of Chemistry, Jagiellonian University; Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University; Faculty of Physics and Applied Computer Science, AGH University of Science and Technology; the Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences and the Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences.

The activities of the Consortium aim at creating a unique centre of interdisciplinary studies in key areas of contemporary physics and chemistry, exploring ambitious research challenges and undertaking innovative R&D ventures of high scientific potential and knowledge transfer to industrial and public sectors. Owing to the consolidation of the vast research potential based on highly-qualified staff from leading academic institutions in Krakow, and the excellent research infrastructure, the Consortium seeks to play the role of an organization well recognized in the global research community, creating attractive opportunities for employment and education for talented Polish and foreign researchers.

The Consortium undertakes actions in two principal directions: intensification of the research activity of the partners in the area of joint research themes and organization of joint actions. The latter comprise organization of joint International Laboratory employing, in rotation, leading national or foreign specialists, as well as launching International Doctoral Programmes (the Smoluchowski Doctoral School) concentrated in the areas of medical physics and chemistry, nuclear physics and nuclear energy, advanced materials, catalysis and nanotechnology, photonics, spectroscopy and quantum informatics, conservation science, and diagnostics of cultural heritage objects. Organization of the Krakow Seminar in which lectures and panel discussions are held by invited specialists from leading research organizations in the country and from abroad, as well as co-financing international conferences organized under the Consortium's auspices are other joint activities .

The Consortium supports joint research in four existing centres which are flagships of the Krakow research community: Academic Centre of Materials and Nanotechnology ACMIN, Centre of Atomic Scale Science ATOMIN, National Centre of Hadron Radiotherapy: Bronowice Cyclotron Centre CCB, National Centre of Synchrotron Radiation SOLARIS. The consolidation of research on cultural heritage protection, dispersed so far, is planned by launching the HEREDITAS centre.

The Consortium also undertakes manifold activities to disseminate the research results obtained to inform society on the importance of sciences for innovation, economic and technical progress and for the sustainable development of civilization and society.

Statutory Research

Catalytic Materials and Processes for Sustainable Development

Nanomaterials based on layered minerals

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

Work concentrated on detailed characterization of aluminium distribution in porous clay heterostructures (PCH) derived from the synthetic layered mineral Laponite (referred to as PCH-L). Alumination was carried out by post-synthesis impregnation of PCH-L with aluminium nitrate (n) or isoprpoxide (i), to obtain Si/Al=30 or 10. The materials were characterized with XRD, ICP-OES, XRF, SEM, TG/DTG/DSC, FTIR, MAS NMR. It has been shown that reliable information on the distribution of Al within the PCH solid can be obtained by completing the ^{27}Al and ^{29}Si MAS NMR data with FTIR analysis in MIR (mid-infrared) and NIR (near-infrared) ranges. In MIR the Si-O vibrations characteristic of the layered silicate and of the amorphous silica could be distinguished (Fig. 1). On the other hand NIR showed well resolved overtones of hydroxyl groups present in the layered silicate and silanol groups present at the surface of the mesoporous silica (Fig. 1, insert). Change of the relative intensities of bands visible in MIR and NIR occurring upon Al doping, combined with changes observed in the spectra of ^{29}Si MAS NMR, allowed for a univocal conclusion as to the localization of Al and its distribution between the components of the PCH composite. In particular, it has been shown that incorporation of aluminium occurs preferentially within the network of amorphous silica developed during PCH synthesis. No Al substitution into the Si-based tetrahedral sheets of clay layers has been observed.

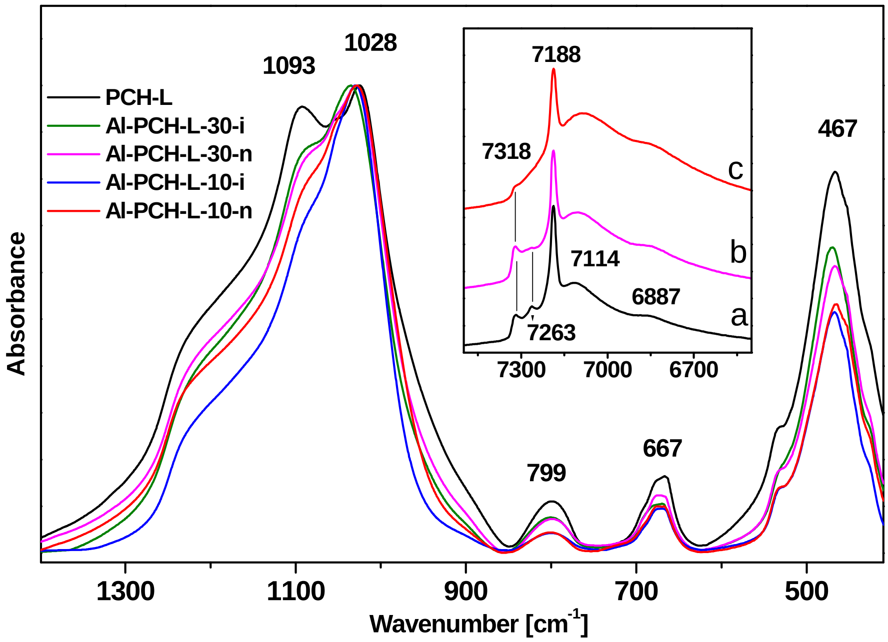


Figure 1. FTIR spectra in MIR and NIR region of PCH-L (“a” in insert), Al-PCH-L-30-n (“b” in insert), Al-PCH-L-10-n (“c” in insert), Al-PCH-L-30-i, and Al-PCH-L-10-i.

New peroxo-compounds of Mo(VI), W(VI) i V(V). Synthesis, structural studies and applications in processes of oxidation

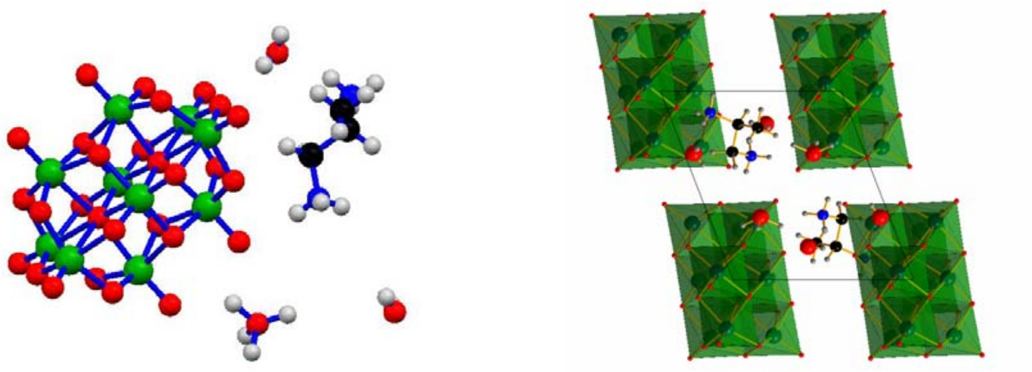
(Professor Wiesław Łasocha, Dariusz Mucha PhD, Anna Szymańska MSc,
Katarzyna Luberda-Durnaś MSc, Marta Grzesiak MSc)

Conducted research related to the synthesis and structural studies of new peroxo compounds of Mo, W, V and new polymolybdates of amines. Part of obtained compounds were tested as catalyst in reaction of oxidation of cycloalkanes.

Research conducted in the last period of time, can be summarized as:

1) Structural studies were performed of new vanadate obtained by the reaction of V_2O_5 with aliphatic amines: 1-aminopropane (1-AP), 1,3-diaminopropane (1,3-DIAP), 1,2-diaminopropane (1,2-DIAP). Syntheses were carried out in a moderately acid medium (pH ~3-5) with 30% solution of H_2O_2, the reaction temperature ~0°C and crystallization at 5-10° C.
2) A number of attempts to synthesize new peroxovanadates of Rb and Cs were undertaken. In the case of Rb orange-yellow crystals were obtained, which have became the subject of structural studies (X-ray single crystal diffraction), analogous cesium compound has been tested by methods of XRPD (powder diffraction).
3) Peroxocompounds with nicotinic acid have been tested in reactions of catalytic oxidation of cyclooctane using oxygen from the air. Tests were carried in cooperation with dr J.Połtowicz and dr K.Pamin.
4) For selected polimolibdenianów amines (received and reported in previous years) similar catalytic tests were performed.

Figure below shows the refined asymmetric unit (a), and the projection of the structure (b) of triclinic 1,2-diammoniumpropane dekavanadate tetrahydrate. Balls of colors: green, red, blue and black represent vanadium, oxygen, nitrogen and carbon.



a) **b**)

In conclusion, we can state that, in our research:

a) We have determined the crystal structures of 3 new decavanadates with ali[hatic amines and new decavanadates of rubidium and cesium.
b) Complexes of nicotinic acid with peroxomolybdates were found to be highly active in the reactions of catalytic oxidation of cyclic hydrocarbons.
c) We have found a high activity in the oxidation process using oxygen from the air in case of layered or polymeric isopolymolybdates. Their catalytic activity is based on reactions involving free radicals. The most active catalysts are able to oxidize cyclooctane to ketone, alcohol and octanedicarboxylic acid (suberic acid).
d) The activity obtained by us new compounds were comparable, or higher, than the activity of catalysts used in commercial systems in industry.

Ceramic foam catalysts for total oxidation of volatile organic compounds

(Tadeusz Machej PhD, Łukasz Mokrzycki PhD, Wojciech Rojek MSc)

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 3) washcoat preparation procedure and 4) preparation for ceramic foam based catalyst.

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 (PU) is used as a skeleton/template (green body) which is being removed in a heating process. The PU foams with 10 and 20 cells per square inch were chosen for this synthesis procedure.

Different inorganic substrates have been used in the synthesis procedure, i.e: PURALOX (activated γ-Al_2O_3), silica (SiO2, POCh), kaolin clay (Aldrich), Disperal S, phosphoric acid (POCh), water glass (POCh) and distilled water. Several samples with varied 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 50°C e) burning out the organics at 600 °C and sintering at the temperature of 1150 °C- figure 1.

Figure 1. Polyurethane foam, sintered ceramic foam and ceramic foam catalyst (from left to right)

The next elements of the research task were preparation of a catalyst active phase and a ceramic foam coating mixture (washcoat). Mixed oxide active phase containing Mn, Cu, Ce by different synthesis routes: i) microemulsion method, ii) citric acid method and iii) solid state reaction. Washcoat aqueous slurry with 15 wt% of solid content (Puralox, Disperal S, active phase, acetic acid) was obtained after 48 hrs ball milling. The physicochemical characterization of active phase, ceramic foam and ceramic foam based catalyst 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 ceria improved catalytic activity of samples investigated.

Photocatalytic degradation processes of organic pollutants in water with the simultaneous action of oxidant - synergistic effects

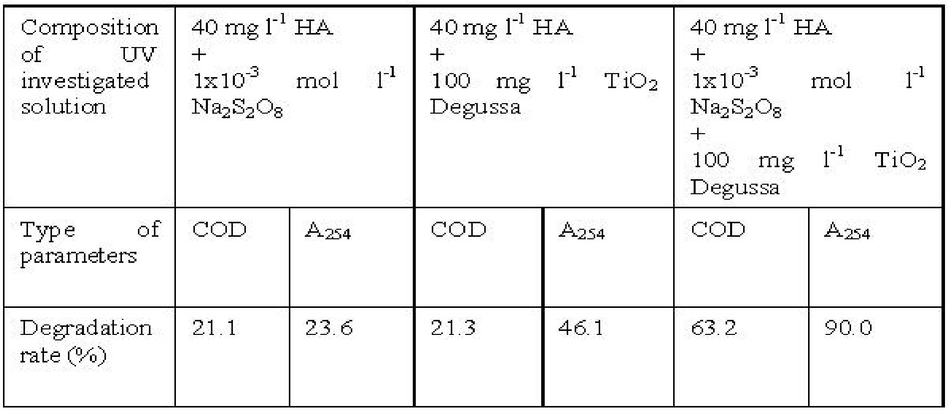
(Professor Piotr Warszyński, Assoc. Professor Paweł Nowak)

In view of increasing restrictive requirements regarding the quality of drinking water is necessary to elaborate innovative methods of water purification. In this project, the main focus was to investigate the synergistic effect of the setting by a combination of several methods, including photocatalytic oxidation process on the semiconductor surface and the chemical oxidation with active substances, which in turn will enhance the efficiency of the removal of natural organic matter (NOM) from water greatly in excess of the performance achieved by conventional methods used so far (filtration, coagulation).

The degradation of model organic compounds (humic acids, methylene blue, rhodamine B) in the system, which is based on the compilation of the UV-activated catalyst and a strong oxidizing agent, which was introduced into the photocatalytic system in two ways: continuous dosing and application of inorganic carriers with oxidizing agent. Among several capsules with oxidants synthesized and examined to take into account the release of the active agent (permeability of layers), stability and activity were selected the best, taking also into account the criterion of simple synthesis and aquatic inert of matrix. Wax and polydimethylsiloxane (PDMS) showed the best properties as materials for encapsulating of the active agent. Detection of organic matter decomposition was carried out using spectrophotometry in the UV – VIS region with a suitable analysis wavelength for each substance and comparison with the parameter COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon). Spectrofluorimetric measurements were also performed.

As a result of the simultaneous action of the catalyst (TiO_2) and an oxidizing agent - sodium persulphate was observed a high conversion of the organic compounds, substantially higher than when catalyst or oxidant were used alone in the same conditions. Synergies have been identified in the case of simultaneous application of TiO_2 and $Na_2S_2O_8$, which is confirmed by both the spectrophotometric measurements and COD parameter (example results for humic acids are summarized in Table 1). However, the preliminary TOC results suggest that the complete mineralization of HA was not achieved.

Table 1. Results of synergistic effect of TiO_2 and sodium persulphate in the degradation process of humic acids. COD – Chemical Oxygen Demand, A_{254} - absorbance of humic acids with the analytical wavelength of 254 nm.



Composition of UV investigated solution	40 mg l^{-1} HA + $1x10^{-3}$ mol l^{-1} $Na_2S_2O_8$		40 mg l^{-1} HA + 100 mg l^{-1} TiO_2 Degussa		40 mg l^{-1} HA + $1x10^{-3}$ mol l^{-1} $Na_2S_2O_8$ + 100 mg l^{-1} TiO_2 Degussa	
Type of parameters	COD	A_{254}	COD	A_{254}	COD	A_{254}
Degradation rate (%)	21.1	23.6	21.3	46.1	63.2	90.0

Physicochemistry of heteropolyacid – MOF systems

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

The aim of this research was the examination of metal-organic frameworks (called MOF) materials and heteropolyacid systems as the catalysts and sorbents. Mesoporous materials with large channels and regular cages have many applications including catalysis, purification, biotechnology, and gas storage. The incorporation of heteropolyacids' Keggin anions into various nanoporous materials like silica, zeolites, MCM and SBA types, improved the catalytic properties of the supports by modification of their surface area. In our research we have chosen a combination of dodecatungsto-phosphoric acid $H_3PW_{12}O_{40}$ (HPW) and MOF material, namely Fe(BTC) where BTC is organic linker from trimesic acid. HPW used here belongs to the strongest heteropolyacid. The new solid acid catalyst HPW/Fe(BTC) seem to be a potential candidate for application in ethanol conversion where the presence of strong acid centers is necessary and the high surface area MOF materials is beneficial.

The catalysts containing heteropolyacid introduced into the metal–organic framework (MOF) material were prepared using purchased Basolite™ F 300 Sigma-Aldrich, of the nominal formula $C_9H_3FeO_6$ and Keggin type heteropolyacid $H_3PW_{12}O_{40}\cdot nH_2O$ (Aldrich p.a.). The volume of used heteropolyacid corresponded to 15 and 80 % pore volume of MOF. FTIR spectra of particular catalysts were compared with the spectra of Fe(BTC) and pure $H_3PW_{12}O_{40}$. Practically for heteropolyacid supported on MOF no changes in this frequency range were observed. This indicates that Keggin heteropolyacid was incorporated into the structure of chosen MOF in non-altered form. Accordingly, also the characteristic maxima of MOF's organic linkers were not changed after acid incorporation. A constant flow differential microreactor was used for catalytic experiments. Before the catalytic experiments hydrated catalysts were preheated in situ in a catalytic reactor at 200^oC for 20 minutes to obtain the anhydrous catalysts. The weight of the catalysts sample was adjusted in such way that always 0.025 g of anhydrous HPW was tested. Catalytic conversion of ethanol was chosen as the testing reaction. The catalytic tests were taken on the catalysts HPW(n)F300 (where n % of MOF pore volume filled by HPW) and also on pure MOF and HPW within the temperature range 90 to 200 ^oC. There were two products of catalytic ethanol dehydration: diethyl ether (DEE) and ethylene (C_2H_4). The unsupported MOF material was not active in opposition to supported MOF. Below 90 ^oC ethanol conversion did not proceed. In the case of supported MOF those two products began to form in parallel at 110 ^oC.

Summarizing, microgravimetric studies combined with IR experiments allowed to determine that the presence of the MOF material increased the sorption capacity for ethanol of hybrid materials in comparison to the pure heteropolyacid. Some portion of the ethanol is retained in the structure of hybrid materials, mainly in the form of ethoxy ions and physisorbed ethanol. Catalytic behavior of heteropolyacid supported on mesoporous MOF material allowed determination of the influence of internal versus external location of the heteropolyacid in hybrid catalysts on selectivity in ethanol conversion. The location of the heteropolyacid on the external or internal surfaces of the F300 may be responsible for the presence of two temperature maxima in diethyl ether yield. Heteropolyacid located mainly inside the MOF structure (low HPW loading) resulted in the higher temperature required for a significant yield of ether. For higher HPW loading, heteropolyacid is located at the external surfaces and the ethanol reaction proceeds similarly as for pure HPW – giving the low-temperature maximum of diethyl ether formation.

The new samples synthesized in our laboratory: heteropolyacid encapsulated into the MOF materials can be used as adsorbents, molecular sieves or as acidic catalysts.

Assembling nanoparticles of zeolite MFI into hierarchical porous materials

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

Molecular sieves (zeolites) are widely used as acid-base catalysts and active supports for bifunctional catalysts. However, small diameter of the channels present in the zeolite crystals can cause a steric hindrance for the transport of substrates/products molecules and/or formation of the intermediate active complexes. It can limit use of the zeolites as catalysts, especially for the reaction carried out in a liquid phase. One of the ways to decrease such limitations is use of very small zeolite nanoparticles, i.e. below 10 nm in size (also named *zeolite precursors* or *protozeolitic species*) as an active phase dispersed in porous structures.

The aim of the study was to design, prepare and characterize novel solid-state systems, composed of zeolitic nanoparticles assembled into highly porous, layered materials.

Synthesis parameters necessary for the formation of the new micro-/mesoporous materials (denoted as *meso (Sl/Al= x)*) have been determined. Assembling of the colloidal suspensions containing both ultra small protozeolitic clusters (5-6 nm in size) as well as silica mono-/oligomers was carried out in the presence of heksadecylamine (HDA) as a surfactant. The lamellar mesoporous structure of new materials – proved with SEM and TEM measurements - consisted of thin silica layers (approx. 40 nm in thickness) containing dispersed the MFI type nanoparticles. Calcinations conditions necessary for elimination of the occluded template and surfactant molecules and enabling generation of the protonic active sites were found. The tetrahedral coordination of the Al atoms present in the structure of new materials was proved with ^{27}Al MAS NMR analysis and pyridine sorption monitored with FTIR spectroscopy has been effectively used to determine the nature, number and strength of the acid sites. The obtained hierarchical materials were successfully used as catalysts for isomerisation of α- pinene to highly demanded isomers, i.e. camphene and limonene. The reaction was carried out in a liquid phase, at the temperature below 100^{o}C. The performed tests confirmed a high activity of the new hierarchical porous materials, considerably higher that that observed for standard MFI type zeolite, amorphous aluminosilicates and mesoporous materials of the SBA-15 type (Fig. 1). The main products were camphene (50-45%) and limonene (40-35%) (Fig. 2).

The new layered materials might become in future the basis for implementation a new class of environmentally friendly catalysts for the liquid-phase processes.

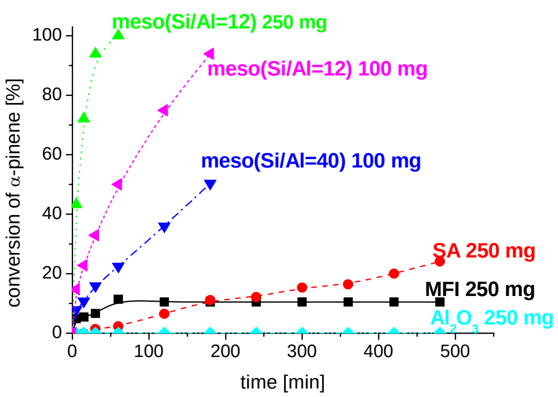


Figure 1. α-pinene conversion: *mezo (Si/Al=x)* – new hierarchical structures, *SA* – amorphous alumino- silicate (Si/Al=7), *MFI* – standard zeolit (Si/Al=40). Reaction temp. 75^{o}C, 5 ml of α-pinene, m$_{calat}$= 250 mg

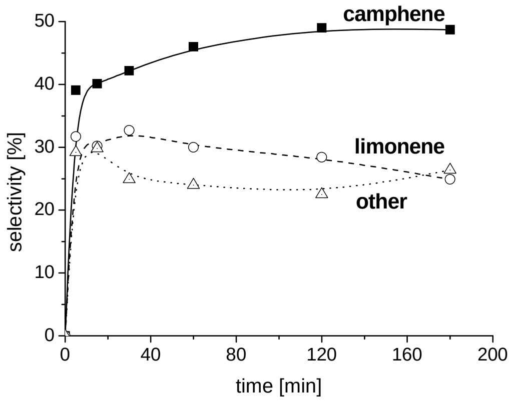


Figure 2. Selectivity of α-pinene isomerisation. Reaction carried out in the presence of *mezo (Si/Al=40)* as catalyst. Reaction temp. 75^{o}C, 5 ml of α-pinene, m$_{calat}$= 100 mg

Nanostuctured composites containing carbon and metal oxides as the catalysts for the reaction of electrochemical reduction and oxidation of hydrogen peroxide

(Assoc. Professor Paweł Nowak; Aleksandra Pacuła PhD)

Many different substances, starting from hydrogen to solid carbon materials may be used as a fuel (substrate of the anodic process) in the fuel cell. However in the case of the cathodic reaction practically the only available substrate is the atmospheric oxygen. The oxygen reduction reaction (ORR) may proceeds either as the four electron process, leading to water as the product of the reaction or as the two electron reaction with hydrogen peroxide as the product of the reaction. In the latter case not only the amount of electrical energy that may be produced by the cell is lower but also hydrogen peroxide is accumulated in the cell which may exert negative influence on the performance of the cell. So, the catalyst of the cathodic reaction in a fuel cell must be not only a good catalyst of ORR but also a good catalyst of the reaction of hydrogen peroxide reduction.

Since several years the investigations on the synthesis of nanostructured composite materials composed of carbon and metal oxides have been conducted in the Institute. Such materials might be applied also as catalysts of the ORR in fuel cells. High activity of those composites in the ORR was documented, but no information on their activity in the reaction of hydrogen peroxide reduction is available.

Composites composed of carbon nanotubes, metallic cobalt and the oxides of cobalt and aluminum, prepared at the temperatures of 600, 700 and 800 ^{o}C by thermal decomposition of acetonitrile and hydrotalcite-type materials were selected for the investigations. Aluminum-cobalt hydrotalcite-type materials of the Co/Al atomic ratio 2 and 3 were used. The excess of the oxide material was removed from the sample by washing with the solution of hydrochloric acid.

Cyclic voltammetry with the sweep rate of 100, 50, 20, 10 and 5 mV/s in both alkaline and acidic solutions was used to investigate the catalytic activity of the prepared materials. Measurements were performed in oxygen-saturated solutions and in the solutions containing hydrogen peroxide of the same concentration as the concentration of oxygen in its saturated solution. The working electrode was the glass carbon (GC) electrode with the layer of investigated material deposited on the surface.

In the alkaline solutions the reduction of hydrogen peroxide occurred at the potentials much more positive than the reduction of oxygen, by 60 – 90 mV, depending on the temperature of the preparation of the composite and the Co/Al ratio (see the figure below). It means that at the potential of oxygen reduction hydrogen peroxide should be reduced completely and the prepared catalysts may be used in the fuel cell working with the alkaline electrolyte. However in the acidic environment the reduction of hydrogen peroxide occurred at almost the same potential as ORR. It means that the prepared composites may not be used in the fuel cells working with acidic electrolyte because the oxygen peroxide would accumulate in the electrolyte.

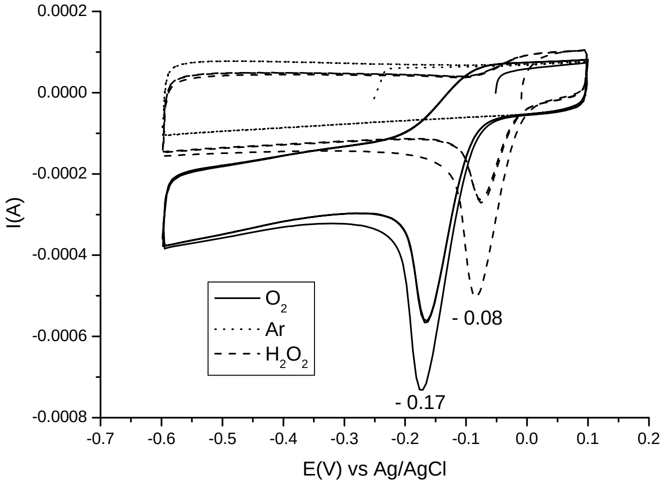


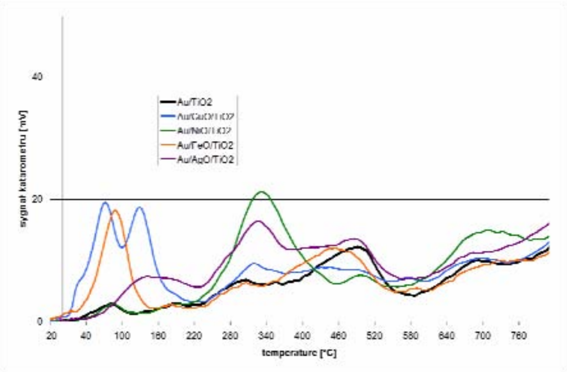
Figure 1. Cyclic voltammograms recorded in 0.1 mol dm^{-3} KOH solution at the sweep rate of 10 mV/s on the GC electrode covered with the composite of the Co/Al ratio = 2, prepared at the temperature 600 ^{o}C, in the solution purified from oxygen by bubbling with argon, in the solution saturated with oxygen and in the solution containing hydrogen peroxide of the same concentration as the concentration of oxygen in its saturated solution.

Examination of the reduction and catalytic properties of Au-MeOx/TiO_2 systems in oxidation of CO

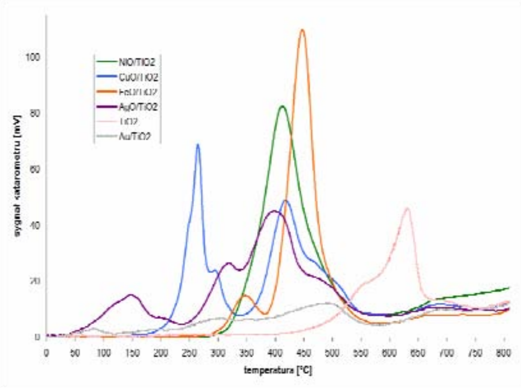
(Jan Mizera MSc, Katarzyna Samson PhD, Małgorzata Ruggiero-Mikołajczyk PhD,
Michał Śliwa PhD, Assoc. Professor Ryszard Grabowski)

The aim of the studies was to determine the reduction and catalytic properties of Au-MeO/TiO_2 systems in CO oxidation. The research carried out in the recent years have shown that the catalyst carrier in a Au/metal oxide which the specific properties and reducibility in particular, can affect the properties of the gold nanoparticles, such as their size or the electron state . Easily reducible supports can also generate more oxygen vacancies on the border of Au nanoparticle - oxide support, which is considered the center of the activation of oxygen in oxidation reactions. It also shows that the abundance of surface carrier mobility in the oxide oxygen has an important effect on the catalytic activity.

H_2-TPR studies of Au/MO_X/TiO_2 catalysts and doped carriers MO_X/TiO_2 showed that the introduction of oxides leads to the changes in TPR profiles and modifies their catalytic properties. At the same time, it was found that the amount of hydrogen consumed in the reduction process of the studied catalyst is more than 40% lower than the supports. In order to explain the difference in the consumption of hydrogen for supports and catalysts a series of experiments was performed having to show which of factors appearing in the deposition of gold nanoparticles causes the reduction of hydrogen amount consumption.



TPR profiles of Au/MO_X/TiO_2 catalysts



TPR profiles MO_X/TiO_2 supports

Catalytic activity of the fresh catalysts, obtained by sequential deposition, measured at 35°C, have similar values (within the CO conversion of 80%). Their activity decreases in the series:

Au/NiO/TiO_2 (1) > Au / TiO_2 > Au/FeOX/TiO_2 > Au/CuO/TiO_2 (1) > Au/NiO/TiO_2 (2)

Activity at all reaction temperatures after hydrogen treatment is changing like it is shown in the following series:

Au/TiO_2 > Au/CuO/TiO_2 (1) > Au/FeOX/TiO_2 > Au/NiO/TiO_2 (2)> Au/NiO/TiO_2 (1)

Reoxidation does not restore of the catalysts the initial activity, but in each case the activity after is higher than after hydrogen treatment which may indicate that the reduction may irreversible change change of the catalyst surface. A number of the process illustrating reutlenienia activity is as follows:

Au/CuO/TiO_2 (1) > Au/NiO/TiO_2 (2)> Au/FeO_X/TiO_2 > Au/NiO/TiO_2 (1)

The obtained results allowed to determine the effect of the various additives on the catalytic activity of the mixed oxide catalysts Au-MOx/TiO_2 in oxidation reactions and present the role of the additional oxide (MO_X).

Synthesis of salen metallocomplexes with electron-acceptor substituents – investigation of the influence of the catalyst structure on their catalytic properties in reaction of phenol oxidation

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

Phenols - allochtonic compounds are pollutants most frequently present in natural environment. These compounds are highly toxic, persistent and regarded as priority pollutants for which chemical treatment processes are needed. The removal of phenols can be accomplished on the way of catalytic oxidation. The macrocyclic compounds are often used as catalysts of these reactions. Synthetic metallosalen complexes are well known as efficient catalysts for selective oxidation of organic compounds.

Herein, we report the results of the catalytic oxidation of phenol with hydrogen peroxide as oxygen donor and cobalt salen complexes with electron-withdrawing substituents as catalysts. Two series of catalysts were tested. The first group was complexes with Co(II) as active centre: Co(II)salen, Co(II)salenCl_2, Co(II)salenBr_2, Co(II)salen$(NO_2)_2$ and Co(II)salen(eda)$(NO_2)_2$. The complexes with Co(III) and axial ligand: OAcCo(III)salen, OAcCo(III)salen-Cl_2, OAcCo(III)salenBr_2 and OAcCo(III)salen$(NO_2)_2$ and OAcCo(III)salen(eda)$(NO_2)_2$ were the second group.

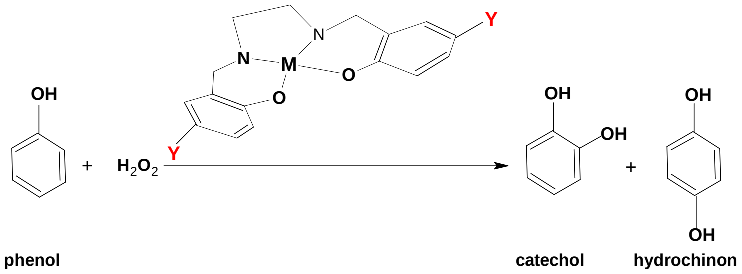


Figure 1. Oxidation of phenol with hydrogen peroxide

All the tested metallosalen complexes were active catalysts in the reaction of phenol oxidation with hydrogen peroxide.The hydroxylation of phenol yielded catechol and hydroquinone as the major products. All investigated catalysts showed good selectivity for diphenol products. It was shown that the activity of macrocyclic complexes depends on the ligand structure and electronegativity of the substituents. In the case of Co(II) complexes their activity increases with the electronegativity of the substituents. The most active were the complexes with nitro group which are the most electron-withdrawing substituent. Introduction of the electron-acceptor substituents enhances the phenol conversion and selectivity to catechol. The results showed that catalytic activity of the Co(II)complexes varies in the following order:

Co(II)salen$(NO_2)_2$ $\geq$ Co(II)salen(eda)$(NO_2)_2$ > Co(II)salenBr_2 > Co(II)salenCl_2 > Co(II)salen

For Co(III) salen complexes the following order was obtain:

Co(III)salen > Co(III)salenCl_2 > Co(III)salenBr_2 > Co(III)salen$(NO_2)_2$ $\geq$ Co(III)salen(eda)$(NO_2)_2$

In this case, introduction of the electron-acceptor substituents decreases the phenol conversion and enhances selectivity to hydrochinon. Our results show that both Co(II)salen complexes and Co(III)salen complexes with axial ligand are active as catalysts in the hydroxylation of phenol with hydrogen peroxide and their catalytic activity depends on the electron-withdrawing properties of the substituents.

Transformations of terpene hydrocarbons on hierarchical zeolite catalysts: catalysis and physicochemical properties of the catalysts studied by NMR

(Professor Bogdan Sulikowski, Ewa Włoch PhD)

In the last decades or so there is a marked tendency to use in organic technology more and more efficient catalytic properties. Another trend observed is implementation of processes carried out in the liquid, rather than gas, phase. α-Pinene is the most important natural raw material in the chemistry of terpenes. This member of the monoterpene hydrocarbons can be transformed to numerous important raw products for pharmaceutical and cosmetic industries, like camphene, limonene and *p*-cymene. Classically, the impregnated TiO_2 is used as an industrial catalyst for the catalytic isomerization of α-pinene. However, due to the low rate of the reaction and other disadvantages, there is still a great interest in developing novel, viable catalysts for the process. Thus, some years ago we commenced studies aimed at preparation of more efficient contacts on the basis of micro- and mesoporous materials.

Synthetic zeolites, due to the presence of Brønsted and Lewis acid sites, are the excellent materials for preparation of new catalysts for terpene transformations. Zeolite Y was chosen as a parent material, which was modified further by chelating agents, using *inter alia* organic acids H_4EDTA, $(COOH)_2$ and other. Under the carefully chosen experiment conditions some of the framework aluminium was removed, yielding hierarchical solids with bimodal pore distribution. The samples prepared from Y type zeolite were standardized, and then characterized by XRD, nitrogen sorption, and FT IR in the framework vibration region. For the selected materials silicon and aluminium spectra were acquired on a Bruker 500 MHz, Avance III spectrometer working at 11.7 T. As was shown by the earlier studies, the activity and selectivity of the zeolite contacts in the transformation of α-pinene depend not only on the *framework* aluminium, but the presence of aluminium species in the *extraframework* positions. Consequently, deconvolution of the NMR spectra led to estimation both the framework composition (i.e., the Si/Al ratio) and distribution of aluminium between the *framework* and *nonframework* positions. Analysis of the catalytic data obtained on these zeolites, coupled with the data acquired on aluminosilicates with different framework architecture, will allow us to arrive at relationships between the zeolite composition, framework Si/Al ratio, aluminium distribution, the presence of acid sites and the course of α-pinene isomerization process in the liquid phase.

Additionally, during the reporting period structural studies of the new materials exhibiting interesting catalytic properties, the so-called *mesoporous cellular foams*, were carried out using solid-state NMR.

The results of our studies might be used in the future to come for selection, modification and manufacturing of the industrial catalysts for the terpene hydrocarbons transformations proceeding in the liquid phase.

Electrocatalytic properties of alloys containing transition metals or rare earth metals – hydrogen ionization and hydrogen evolution reaction

(Assoc. Professor Paweł Nowak, Grzegorz Mordarski PhD)

Hydrogen evolution from water by electrolysis is one of the most important electrochemical reactions. Platinum is an excellent cathodic material for that reaction, showing very high catalytic activity. Also some noble metals (palladium for example) show high catalytic activity in hydrogen evolution reaction (HER). Nowadays platinum (and other noble metals) are expensive and their availability is very limited. So, the investigations to find the replacements for platinum are being conducted all over the world.

In our investigations to find such materials we paid attention to rhenium. Information of the high activity of rhenium in HER may be found in the literature. Poland is one of the biggest producer of rhenium in the world and Polish industry is interested in finding new applications for rhenium. In our former investigations we confirmed high catalytic activity of the alloys of rhenium and cobalt in HER. In 2012 year we have investigated alloys and composite materials containing, besides rhenium, nickel, titanium and titanium dioxide.

Alloys of nickel and rhenium were prepared by electrolysis of the aqueous solutions of the salts of both metals. By electrolysis of the suspensions of fine titanium or titanium dioxide grains in those solutions the composites containing grains of mentioned substances dispersed in the matrix of Ni-Re alloy were obtained. The prepared alloys and composites were subjected to the thermal treatment in the gas atmosphere of different composition. Phase composition of the alloys and composite materials was investigated by X-ray diffraction method whereas their chemical composition was investigated by X-ray fluorescence and optical emission spectroscopy with inductively coupled plasma (after dissolution). Kinetics of HER was investigated by tracing the polarization curves as well as by electrochemical impedance spectroscopy.

Catalytic activity of a material depends mainly on two factors: specific activity and the specific surface area. The aim of the work was to establish if the addition of rhenium to nickel and composites containing nickel would cause the increase their catalytic activity in HER. For that reason electrodes of low and repeatable roughness factor were prepared and investigated, which allowed the comparison of their specific catalytic activity.

It was established that all investigated materials containing rhenium show high catalytic activity in HER. Impedance spectra registered during HER in 6 mol dm^{-3} KOH solution (such solution is used in the industry) on nickel and rhenium-nickel alloy containing 2 atomic percent of rhenium are showed in the figure below. It may be seen that even such small addition of rhenium (2 at%) to nickel causes very significant decrease in the polarization resistance which is equivalent to the increase in the rate of HER.

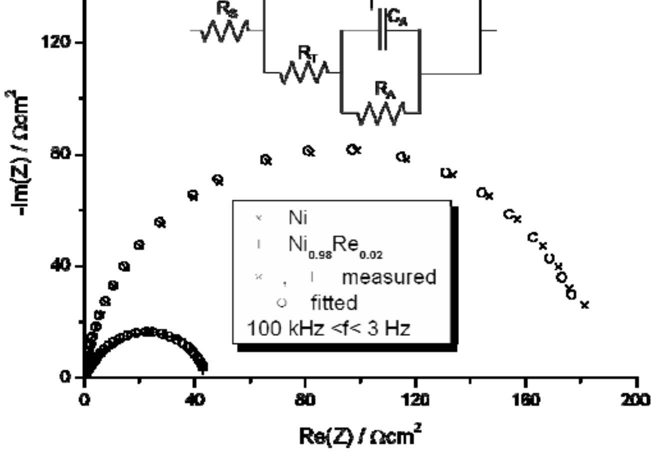


Figure 1. Impedance spectra registered during HER in 6 mol dm^{-3} KOH solution on nickel and rhenium-nickel alloy at the potential -1,2 V vs Hg/HgO/NaOH 1 mol dm^{-3} electrode. The equivalent electrical circuit used in the interpretation of impedance data is showed also in the figure.

Transesterification of triglycerides with methanol in the presence of polymeric catalysts

(Assoc. Professor Alicja Drelinkiewicz, Żaneta Kalemba-Jaje MSc, Erwin Lalik PhD)

Transesterification of triglycerides with methanol is reaction producing bio-esters, Biodiesel. Owing to environmental, technological and economic reasons, the substitution of homogeneous catalysts by heterogeneous ones is a desirable goal. The advantage of solid catalysts consists of the ease of product separation and recycling of the catalyst.

Recent studies concentrated mostly on solid acid catalysts as they are able to catalyse both transesterification of triglycerides and esterification of free fatty acids present in oil feedstock. In the present work polyaniline-sulfate deposited on three different carriers was studied for transesterification of triacetin and castor oil with methanol at mild reaction conditions (temperature of 55 ^{0}C). The catalysts were also tested in esterification of ricinoleic acid with methanol.

Multi-wall carbon nanotubes (CNT), carbon and silica were coated with polyaniline sulfate (ca. 10-20 wt %) during polymerization of aniline. The textural and acid properties of catalysts were evaluated by FT-IR, XRD, ammonia sorption and electron microscopy techniques. Because of different textural and hydrophobic properties of the carriers, the polymer coatings of various morphologies were formed. A uniform coating of CNT with polymer (Fig. 1) resulted in the most extended polymer structure. On the other hand, nanorods of polymer forming branched dendritic structures appeared in the other two carbon and silica supported catalysts. The acid capacity and the strength of acid sites were similar in all studied catalysts.

All the samples were found to be active solid acid catalysts in all studied reactions. Among all tested catalysts, the CNT-coated polyaniline sulfate exhibited the highest activity. The course of reaction during methanolysis of triacetin on CNT-containing catalyst was similar to that in the presence of soluble sulfuric acid and the maximum yield of methyl esters ca. 95 % was attained. The properties of CNT-PANI-S catalyst can be attributed to a combination of mesoporous structure together with well extended polymer coating. This gives easily accessible active sites for the reactants and does not hinder the migration of reagents from the catalyst. On the other hand, a partial blockage of active sites was observed during methanolysis carried out on carbon and silica coated with polymer. This was attributed to the aggregated morphology of polymer coating resulting in a locally high density of acid sites. Microporous structure of catalysts as in the carbon-supported sample facilitated also products accumulation effect. These results demonstrated that too high density of active sites and especially inside the pore structure of catalyst could facilitate interaction with polyol, such as glycerol, which might lead to the accumulation of reagents with consequent blockage of active sites.

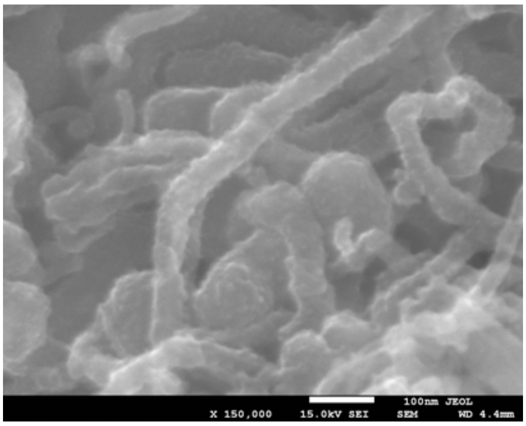


Figure 1. CNT-carrier coated with polyaniline sulfate

Selective hydrogenation processes in the presence of ruthenium catalysts

(Dorota Duraczyńska PhD, Professor Ewa Serwicka-Bahranowska,
Assoc. Professor Alicja Drelinkiewicz)

Work aimed at investigation of catalytic properties of ruthenium nanoparticles immobilized on supports, in reactions of hydrogenation of prochiral ketones to secondary alcohols. Products of such reactions are frequently employed as precursors of drugs or biologically active compounds. Hydrogenation of acetol to 1,2-propanodiol has been chosen as a test reaction. This process is one of the key stages in the synthesis of Levofloxacin, a drug with antimicrobial activity. Ruthenium catalyst was immobilized on polymeric supports possessing finctional groups capable of interacting with ruthenium centers. In particular, glycidyl methacrylate-based co-polymer, functionalized with two types of amines - achiral and chiral, was used as a support. The synthesized catalysts were characterized with FT-IR, XRD, SEM, EDS, STEM, XPS and DSC methods. Tests aiming at determination of the reaction conditions were carried out with the use of Ru catalyst immobilized on the polymer functionalized with an achiral amine. As a result of optimization procedure hydrogenation has been carried out in a batch reactor, in mild conditions: hydrogen pressure 1 atm and temperature 40^{o}C. Reaction was conducted in the presence of ca. 0.2 g catalyst (2 wt.% Ru), wetted with water. Acetol was introduced as a solution in isooctane. Under these conditions, a complete conversion of acetol with 100% selectivity to secondary alcohol was observed. After separation of optical isomers of the reaction product it has been found that the alcohol obtained as a result of the reaction over Ru catalyst supported on the carrier functionalized with an achiral amine is a racemic mixture of isomers R and S.

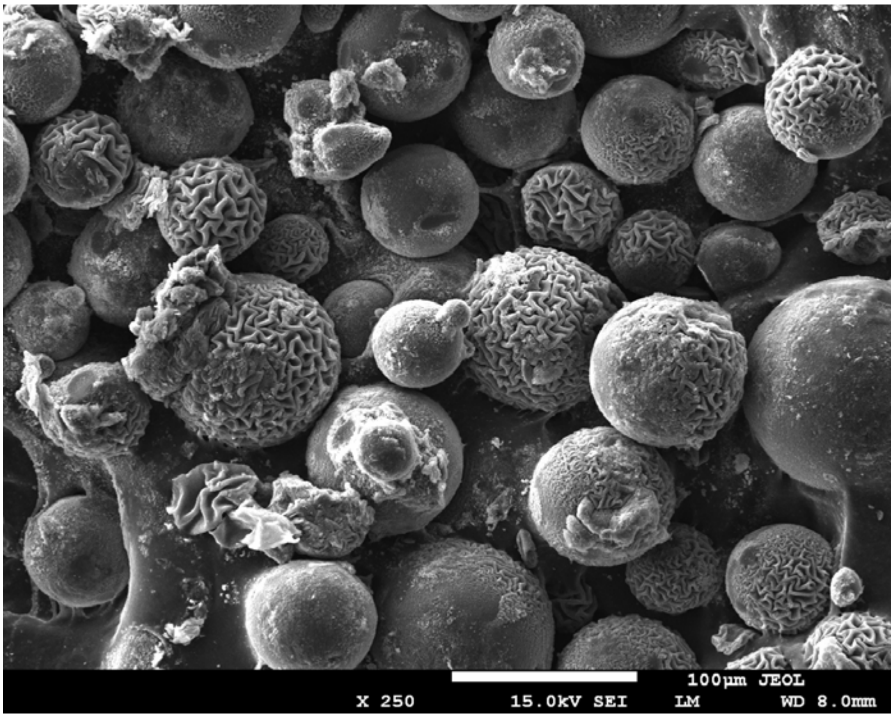


Figure 1. Ru catalyst (2 wt.%) on a polymeric support

Statutory Research

Physics and Chemistry of Surfaces and Nanostructures – Experiment and Theory

Structural properties and dynamics in epitaxial oxide and metal nanostructures studied with microscopic and spectroscopic techniques radiation

(Professor Józef Korecki, Nika Spiridis PhD, Jacek Gurgul PhD, Robert Socha PhD,
Dorota Wilgocka-Ślęzak PhD, Ewa Madej (Zackiewicz) PhD, Barbara Figarska MSc,
Kinga Freindl MSc, Tomasz Giela MSc, Ewa Młyńczak MSc, in cooperation with WFiIS AGH)

Exchange bias in the metal-oxide systems

In the latest years the substantial increase of the thin epitaxial magnetic film research has been observed due to their technological significance, for example in the microelectronics. Metal-oxide bi-layers, multilayers and superlattices attract a lot of interest because of the possibility of tailoring their magnetic properties (such as anisotropy or magnetostriction) by playing with the metal and oxide sublayer thickness, by optimizing the layers growth mode or selecting a proper substrate. The aim of these studies was to analyze the influence of the preparation and structure on the magnetic and electric properties of the interface in ultrathin metal-oxide layers. The studied systems were Fe-CoO and Fe-NiO (ferromagnetic/antiferromagnetic) bi-layers of different layers sequence in which the characteristic exchange-bias interaction was observed in the low temperature range. The spin structure of the systems was imaged by means of the photoemission electron microscopy (PEEM) using synchrotron radiation. The dependence of the magnetic domains structure of the sublayers on temperature and the external magnetic field was analysed. The results of the investigations will be invaluable during commissioning of the Polish synchrotron, they have been used in the application for NCN project Harmonia and will be included in a PhD thesis and publications.

Model metal-oxide catalysts

The aim of this task was the analysis of the correlation between the composition and structure of the bi-metallic phase and potential catalytic properties for the system containing Au and Fe clusters dispersed on the TiO_2(110) surface. The influence of the promoter on the physicochemical properties of the model catalysts prepared under the ultra high vacuum conditions was characterized by scanning tunnelling microscopy and by X-ray photoelectron spectroscopy. The temperature programmed desorption (TPD) experiments allowed to determine the potential catalytic properties of studied systems.

For a comparison, the analysis of the bi-metallic structures was preceded by the studies of nucleation and growth of gold and iron on the rutile substrate. The experiments proved that gold preferentially nucleates on step edges and point defects on terraces, while the iron nanoparticles homogenously cover the whole TiO_2 surface. Due to the different nucleation the growth mode of both the metals, the Fe clusters formed at the room temperature are 1.5 to 2 time bigger than the Au ones. The important aspect of the studies was investigation of the influence of pre-adsorbed iron on the gold adsorption and the thermal stability of the bi-metallic clusters. It was shown that iron stabilizes clusters and increases their density. For such model catalyst, the adsorption of CO was studied usin TPD.

In summary, the study shows that the use of iron as the precursor for deposition of gold may have a positive effect on the performance of real catalysts. It is expected that the higher activity can be achieved by better distribution of the bimetallic clusters, which remain stable at higher temperatures.

Analysis of the element electronic states on the surfaces of materials active in heterogeneous reactions

(Professor Józef Korecki, Jacek Gurgul PhD, Robert Socha PhD)

The presented research performed in the Laboratory of Surfaces and Nanostructures were focused on determination of the electronic states of elements on the surfaces of different materials active in heterogeneous catalytic reactions. More than 50% of the Laboratory work time was dedicated to accomplish all the tasks that are collected in Table below.

No.	Head of the group	Subject	No. samples
1	P. Warszyński	Graphene oxides Ca adsorption on polylayered structures	25 18
2	P. Nowak	Adsorption of organic compounds on minerals Cobaltium-Palladium alloys Fuel cells electrodes Carbon nanotubes	3 2 10 2
3	Z. Adamczyk	Ag nanoparticles on Si HSA/mica Polylayers	6 8 43
4	T. Machej	Heteropolyacid salts of Keggin structure	9
5	A. Drelinkiewicz	Pd nanoparticles at different substrates Polypiroles	14 14
6	E. Serwicka	Cu:Mn:Al layered minerals Cyclooctane oxidation (Mo)	4 1
7	J. Korecki	FeSiBEA zeolites Nanowires on heteropolyacid salts Electrode materials	12 12 3
8	A. Bielański	Heteropolyacid of Dawson structure	1

The exemplary results concern the selected catalyst materials working in gas/solid (zeolite BEA) or liquid/solid (graphene and graphene oxide) systems. In the studies of SiBEA zeolite, two stage synthesis was applied for controlled introduction of Fe into BEA zeolite. The electronic states of the elements in the studied samples were then analyzed by X-ray photoelectron spectroscopy (XPS). The detailed analysis of the electronic states of iron was supported by Mössbauer spectroscopy for ^{57}Fe nuclei. The studies showed that, in the Fe-SiBEA system containing 3.8 at% of iron at maximum, the Fe^{3+} ions are incorporated in the tetrahedral positions. In case of higher Fe(III) content, the formation of oligomeric oxide systems was observed.

The task concerning the graphene oxide (GO) investigation was focused on determination of the reaction conditions for GO reduction to the pure graphene layers. The XPS analysis allowed to correlate the applied methodology with the resulting composition. The GO reduction was performed with chemical (reaction with hydrazine in aqueous solution) or physical (annealing in vacuum or UV illumination) methods. It was found that chemical reduction and annealing led to reduction over 80 at.% of GO, whereas UV illumination to only of about 50 at.%.

The obtained results lead to the development of the synthesis methodology of selective Fe-SiBEA catalysts and to the synthesis of graphene layers optimized for applications in functional materials.

Structural and electronic factors in catalytic activity of metal sites in nanoporous materials: quantum chemical investigations

(Professor Ewa Brocławik)

Our research in 2012 was aimed at detailed analysis and characterization of electron density flow between the Cu(I) site in a zeolite in the act of the adsorption of NO ligand. The interpretation of the independent, spin- and orbital-resolved electron transfer channels and their roles in the mechanism of the activation of NO molecule brought about new insights into catalytic de-Nox processes and other vital NO transformations. On the other hand, the influence of zeolitic environment on the catalytic ability of embedded copper cations was further clarified.

The analyzes of the global reconstruction of electron density upon adsorption of NO on the active site (deformation density) were done with the use of theoretical NOCV (Natural Orbital for Chemical Valence) method that decomposes deformation density into independent charge density transfer channels between the predefined fragments. NOCV analysis within spin resolution (indispensable due to radical character of NO) was executed with the in-home software (http://www.chemia.uj.edu.pl/~mradon). Three models for the adsorption of NO on copper site have been considered: NO ligand interacting with isolated Cu^+ cation (a: $CuNO^+$), with Cu^+ cation coordinated by $[Al(OH)_4]^-$ (b: (T1)CuNO) and by extended fragment of a zaolite (c: (M7)CuNO). Table 1 lists the measures for the number of electrons transferred between NO and appropriately coordinated copper via dominating electron transfer channel, resolved with respect to α or β spin polarization. Our results confirmed that the channel dominating total electron transfer between NO ligand and Cu(I) site is the π*-backdonation one (enhancing NO activation) whereas for the isolated Cu^+ cation the donation of unpaired electron (diminishing NO activation) dominates electron density transfer; it is effective solely within the α spin polarization. The analysis performed for the alternative fragmentation pattern ([Cu^+-NO] and [T1] or [M7]) illustrates the influence of the electron flow between the framework and the copper with bound NO ligand; it explains the influence of the zeolitic environment on the donation and backdonation processes which clarifies why the Cu(I) site in ZSM-5 zeolite shows high activity in catalytic decomposition of NO, in variance to the isolated cation.

		v_i, measure for transferred of electrons		
		$[CuNO]^+$	(T1)CuNO	(M7)CuNO
donation of unpaired electron	α	0.46	<0.1	<0.1
(diminishes NO activation)	β	-	-	-
π*-backdonation	α	0.23	0.39	0.38
(enhances NO activation)	β	0.21	0.33	0.32

The novelty of our results lies in the application of spin resolution to the analysis of electron transfer between the adsorbed NO and Cu(I) site which identified the role of spin polarization. Some of individual electron transfer channel are effective exclusively for a selected spin polarization which may be very important in the recently developing area of *spin catalysis*.

Theoretical studies on the reaction mechanism of intradiol dioxygenases

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

The purpose of this research project is elucidation of the mechanism of the catalytic reaction of intradiol dioxygenases – Fe(III) dependent metalloenzymes encountered in several strains of soil bacteria that are involved in biodegradation of aromatic compounds. The research work involved computer simulations with molecular dynamics methods, DFT and QM/MM investigations. Energy profiles along reaction coordinates were obtained for three plausible mechanisms for oxidative cleavage of the aromatic ring. Changes of the electronic structure along the critical steps were also analysed. The outcome of this research was identification of several structure/electronic factors responsible for the reaction specificity of the studied group of enzymes.

Catalytic properties of non-stoichiometric surfaces of V_2O_5 – theoretical modelling

(Professor Małgorzata Witko, Robert Gryboś PhD)

Objective of present research was to describe catalytic properties of non-stoichiometric surfaces of V_2O_5 with quantum-chemical methods. In our previous works a comparison of stability of two low-index surfaces: (100) and (001) with the most stable (010) surface was made. A tendency of a surface to reconstruct after creation of oxygen vacancy was observed. Relaxation considerably lowered the energy required to create the vacancy, what suggested that surfaces other than (010) can be rather active in reactions of total combustion. Additionally, chains of tetrahedral vanadium atoms where found after relaxation, analogous to the structure of amorphous vanadium oxide. Finding a mechanism of formation of such surfaces would greatly help in understanding the mode of operation of catalysts based on vanadium pentoxide.

Several calculations were performed for (100) surface using cells of varying size. Also molecular dynamics simulations were run for 10, 100 and 1000K. In all cases, there was no surface reconstruction prior to vacancy creation. Only after explicit creation of V-O-V bridges between neighboring rows of vanadium atoms a reconstruction without vacancy was achieved. For this new, reconstructed surface catalytically-important parameters were calculated: (i) ability to oxidize CO to CO_2 with oxygen vacancy creation, which shows the surface activity in oxygen insertion into an adsorbed molecule; (ii) stability of surface OH groups against attack of HS radical (which captures the hydrogen atom and transforms into H_2S) which shows surface activity in the extraction of hydrogen atoms from adsorbed molecules. Both parameters are expressed as the thermodynamic effect of appropriate reactions.

The new, reconstructed (100) surface is more stable the the initial surface. Amount of stabilization depends on the assumed depth to which the deformation can penetrate below the surface and varies between 0.03 J/m^2 if only the surface layer is reconstructed, up to 0.11 J/m^2 if the reconstruction reaches three vanadium layers (ca. 7 Å) into the bulk. Upon reconstruction the types of oxygen centers on the surface were changed. Initially only two centers are present – O1 and O2. After reconstruction four centers can be distinguished: singly coordinated O1, and three types of doubly coordinated: O2, O2' and O2". It is interesting to compare catalytic parameters for the (010) surface and the unreconstructed and reconstructed (100) surfaces. On the stable (010) surface the highest activity towards CO oxidation is exhibited by O1 center, giving the reaction energy of -1.61 eV. Unreconstructed surface shows considerably higher activity, -1.99 eV, which is lowered after reconstruction to -1.75, what shows that the activity of the (100) surface in total combustion might be overestimated in first calculations. Influence of reconstruction on the stability of OH groups is similar. Relatively stable OH groups (-0.34 eV) on the unreconstructed surface are less stable (-1.03 eV) after reconstruction. For comparison, stability of OH groups on (010) surface is even lower and equals -1.25 eV.

A new, reconstructed (100) V_2O_5 surface was found and its basic catalytic parameters were calculated. Further study concentrates on finding a similar reconstruction for (001) surface and performing a more detailed research and comparison of both surfaces.

Adsorption centers of colloid nanoparticles on surfaces of carbon nanotubes

(Assoc. Professor Tomasz Pańczyk)

Interaction of colloid nanoparticles with surfaces of carbon nanotubes leads to creation of hybrid materials with interesting properties. In that way fibriral materials with controlled electrical, magnetic, biologic and catalytic properties can be fabricated. An important aspect in designing and studies of such materials is possibility of their studies at microscopic level using molecular modelling. However, due to large sizes of such systems and normally impossible to apply a slab geometry the direct application of standard methods of molecular modelling is not effective. The aim of the studies was development of an implicit solvent model and force field which allows for efficient simulation of systems composed of colloid nanoparticles with diameters of the order 100Å and multiwalled carbon nanotubes with sizes of the order 200 x 80 Å.

The most important components of the force field was the Hamaker potential for description of colloid-colloid and colloid-atom interactions and the semi-empirical ai-REBO potential (Brenner) for description of the nanotube structure. The implicit solvent model has been derived from the analysis of the Hamaker constants for the colloid-atom interactions across solvent. By comparing values of the works of adhesion in a reference system (with explicit water molecules) and in the system where solvent was treated as an implicit medium, general relationships have been derived, which allow for 'tuning' the implicit solvent model so that it correctly recovers the works of adhesion in the reference system.

The developed model and the force field have been used for determination of preferred locations of colloid nanoparticles, having various physiochemical properties, on surfaces of multiwalled carbon nanotubes. The studies were carried out using molecular dynamics simulations and by applying the ai-REBO potential in the case of flexible carbon nanotubes or by assuming the rigid model for carbon nanotubes. Figures 1 and 2 show some selected results obtained in this project; Fig. 1 defines various locations of colloid nanoparticles on the surface of nanotube, whereas Fig. 2 shows how the adsorption energy changes as a function of the localization.

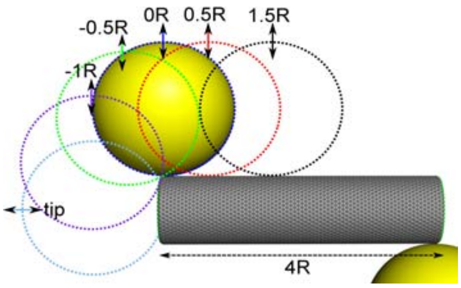


Figure 1 Studied localizations of nanoparticle on the surface of nanotube

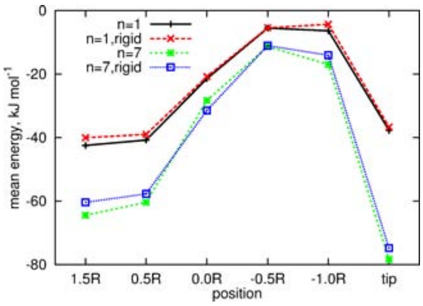


Figure 2 Adsorption energy as a function of localization for flexible and rigid carbon nanotubes

The most important outcomes of the studies can be summarized as follows: (i) the strongest interaction exists on the nanotube tips (for multiwalled nanotubes) or on the sidewalls (for single-walled), in any case there exists an activation barrier at the edges of nanotubes , (ii) deformation of the the nanotube structure occurs when the colloid nanoparticles have large Hamaker constants (eg. metals), typical metal oxides have moderate values of the Hamaker constant and in such cases deformation of nanotubes do not occur upon adsorption of the nanoparticles.

Dynamics of the calcium alginate formation: computer simulations

(Professor Władysław Rudziński, Wojciech Płaziński PhD)

There are no experimental nor theoretical results regarding the dynamics of the calcium-induced chain–chain association of polyguluronates. The main aim of the study was to fill this gap by applying the appropriate molecular modeling techniques. Our attempts were aimed at identifying the possible transition paths connecting the two states, which can be described as 'disconnected chains' and 'connected chains'.

The method of choice was the standard molecular dynamics (MD) combined, when necessary, with the transition path sampling (TPS) algorithms. Such combination allowed for harvesting the 'reactive' MD trajectories (>1000) and their subsequent analysis.

The calcium-induced joining of polyuronates chains can be described by the following consecutive steps: (i) Approaching of chains to each other (the average distance: ~1.4 nm); this is usually combined with the formation of the interchain-type hydrogen bonds, not necessarily corresponding to the hydrogen bond network present in the final (equilibrium) state. (ii) Tight binding of calcium ion by the carboxylic groups belonging to two distinct chains; numerous intermediate structures may exist, corresponding to different local minima of free energy. Most of them can be associated with the case in which water molecules play a role of the "bridge" linking carboxyl group with the calcium ion (loose calcium binding). (iii) Developing the full hydrogen bond network between the chains (after the calcium ion is fully bound). In some cases, the equilibrium-like HB between the residues being in the vicinity of the bound calcium ion is created, before the ion is fully bound. In parallel to these processes, tight binding of calcium ions by single chains (involving one carboxyl moiety at most) may occur. The crossing of the highest free energy barriers is associated with the significant perturbation of the water molecules arrangement within the first coordination sphere of the calcium ion.

The results explain the mechanism of the calcium binding by two chains of α-L-guluronate (treated as a model system) but may also be used to describe the gelling behaviour of other polyuronates.

Studies on possibility of selective modification of vitamin B_{12} – potential drug carrier

(Dorota Rutkowska-Żbik PhD, Professor Małgorzata Witko)

The aim of theoretical studies was to assess the possibility of a selective modification of cobalamin (vitamin B_{12}) structure as potential drug carrier. The motivation for undertaking the present studies was the observed higher intake of vitamin B_{12} by anomalous cells. The cobalamin structure was examined with the stress put on the modification of corrin ring peripheral substituents. In particular two ways of functionalization were considered: a) the possibility of a selective binding of bio-metal ions through coordination to peripheral corrin groups – for which their nucleophilicity would be a decisive factor; b) steering of their physico-chemical properties (especially hydro-philo/phobi-city) in order to tune their solubility.

The present studies were done within quantum-chemical method based on Density Functional Theory (DFT) with the non-local gradient-corrected Becke-Perdew functional, with Ri approximation. All electrons are described with def2-TZVP basis sets. Native structure of vitamin B_{12} and its derivative – dicyanocobinamide, both easily available for a purpose of organic synthesis, were considered. The systems are characterized by geometry (bond lengths, valence angles) and electronic (Mayer bond orders, ESP charges, electrostatic potential) parameters. The possibility of the formation of the possible isomers was further examined based on the computed Gibbs free energies of formation.

As the first step, electronic parameters of amide groups (functional groups of the native vit. B_{12} in literature referred to as *a*-*g*), were computed. It is found that all nitrogen atoms from –$CONH_2$ groups are characterized by negative charges, which fall into -0.89 ÷ -1.02 range. These values are not considerably differentiated, what would be manifested in the non-selective metal ion binding.

Next, dicyanocobinamide species, functionalized by exchange of amide to ester groups, was investigated. In this way the change of physicochemical properties of peripheral substituents may be achieved by using different ester building blocks. Nucleophilic sites in dicyanocobinamide moiety were identified. These are cobalt axial ligands and immediate neighborhood of ester functionalities.

The *a* chain is characterized by the lowest nucleophilicity (the smallest negative charge on O atom), while the rest have comparable properties (their charge ranges from -0.26 to -0.32). The present peripheral substituents were classified according their increasing electrophilicity: $b \approx e < c \approx d \approx f < a \approx g$. The computed changes of free Gibbs enthalpy formation indicate that the amide functionalization would occur on *d* side chain. This suggest that it would be possible to obtain adducts with bio-metals coordinating this fragment of the carrier.

Electrostatic potential of dicyanocobinamide was plotted. It is seen that the investigated molecule is not symmetric: there is a considerable opening of the site of the species in the vicinity of *c* and *d* groups, enabling for its interaction with e.g. surface, a property which would be interesting when immobilization is considered.

The performed calculations facilitated the assessment of the possibility of selective modification of corrole functional groups in view of their possible application as drug carrier. They help to rationalize organic syntheses results aiming at cobalamin derivatives. The obtained results were then transferred to experimental group, which works on synthesis of vitamin B_{12} derivatives.

DFT description of catalytic properties of heteropolyacids with Keggin and Well-Dawson structure

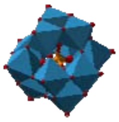
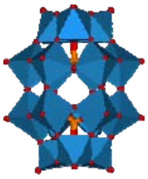
(Assoc. Professor Renata Tokarz-Sobiera))

The goal of the presented project was to determine similarities and differences in the properties of active centers present in the heteropolyacids with Keggin and Well Dawson structures. The central position of Keggin's anion, $PW(Mo)_{12}O_{40}^{3-}$, is occupied by the four-coordinated central ion (X), which creates internal tetrahedron XO_4^{n-} with four oxygen atoms. The tetrahedron is surrounded by twelve edge- and corner-sharing metal-oxygen octahedra MO_6. The octahedra are arranged in four Me_3O_{13} groups. The Dawson type HPA, $P_2W(Mo)_{18}O_{62}^{6-}$, is built of two trivacant Keggin anions connected by six edges. Similar to the Keggin system, in the Dawson type HPA, the central anion forms a tetrahedron and three edge-connected octahedra are building units.

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.

The results of Mulliken population analysis show that in the Dawson type structure the variation of charges at active sites (the charges of atoms that are located closer to the center) are higher than those located on corners. The charges at oxygen atoms Op (that are connected to two different trivacant Keggin anions) are similar to the charges at Ob bridging oxygen sites (that are linked to two addenda atoms from different M_3O_{13} groups).

Table 1. Mulliken population analysis and energy of frontier orbitals for HPW (Keggin and Dawson) systems

	W	P	Oa	Ob	Oc	Od	Op	HOMO LUMO
Keggin 	1.68	1.14	-0.70	-0.69	-0.63	-0.48	-	-7.03 -4.47
Dawson 	1.71 1.66	1.11	-0.73 -0.63	-0.69 -0.65	-0.64	-0.55 -0.50	-0.67	-6.48 -4.35

The results of calculations for solvated HPA system (in H_2O) indicate higher values of HOMO, LUMO energies in the Dawson type HPA. Earlier calculations have shown a linear correlation between LUMO energy values and experimental values of redox potentials.

The differences in two studied systems are shown also by detailed analysis of character of frontier orbitals. In the Keggin type systems, the HOMO orbital is composed of 2p orbitals from bridging oxygen atoms Ob, Oc (the corresponding percentage is 47% and 51%). Orbital LUMO is composed mainly of 5d tungsten orbitals (75%) and mixed with 2p orbitals from bridging oxygen atoms Ob, Oc (12%, 13%). In the Dawson type HPA, HOMO orbital consists mainly (78%) of the 2p orbitals of oxygen Oa (not available to the reactants, which are part of the internal tetrahedron). The LUMO orbital, similar to the Keggin structure, is dominated by orbitals from addenda atoms (71%) with small admixture of orbitals of bridging oxygen Oc (which links two tungsten atoms in the same M_3O_{13} group) (27%).

Preferred site for hydrogen adsorption are both bridging oxygen atoms Ob, Oc in the Keggin system, whereas in the Dawson type HPA only oxygen atoms Ob.

Statutory Research

Nanostructures of Soft Matter

Physicochemical background of the colloid enhancement method for protein monolayer detection at solid/electrolyte interfaces

(Professor Zbigniew Adamczyk, Jakub Barbasz PhD, Małgorzata Nattich-Rak PhD,
Marta Sadowska MSc)

An efficient experimental method aimed at detecting protein monolayers at solid interfaces was elaborated. The method is based on non-specific (driven by electrostatic interactions) deposition of colloid micro-particles on protein layers. The number and distribution of colloid particles is determined in a convenient way by optical and AFM microscopy. The method, referred to as the colloid enhancement (CE), can be used for a quantitative determination of the surface coverage of adsorbed protein. The CE method can also be to determine the zeta potential and electrokinetic charge of adsorbed protein layers 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 micro-electrophoretic methods. Knowing the surface coverage of proteins one can sensitively determine the protein bulk concentration at a level as low as 0.01 ppm (10 ppb). 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 from solutions of various pH and ionic strength. Afterwards, negatively charged latex particles (800 nm in diameter) were deposited and their coverage was determined as a function of the fibrinogen monolayer density using optical and AFM microscopy. In Fig .1 results of experiments performed for various pH are shown in the form of the dependence of the normalized latex coverage Θ_L / Θ_{max} on the fibrinogen coverage Θ_f (ionic strength 10^{-2} M). As can be seen, in the results can be well accounted for by the fluctuation theory (solid lines in Fig. 1). It was determined that an efficient latex particle immobilization at pH 3.5 occurred on sites formed by two fibrinogen molecules and for pH 7.4-9.7 by three fibrinogen molecules. On the other hand, for pH = 11 there was practically no deposition of latex on fibrinogen covered mica. This behavior unequivocally confirms that latex deposition is governed by electrostatic interactions induced by a heterogeneous charge distribution on fibrinogen molecules.

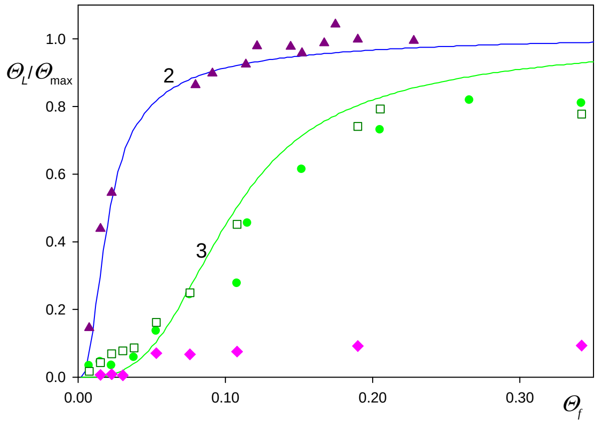


Figure 1. The dependence of the normalized coverage of latex particles, Θ_L / Θ_{max} on the fibrinogen coverage Θ_f. The points denote experimental results obtained for ionic strength of 10^{-2} M and various pH: (▲), pH = 3.5 (●), pH = 7.4, (□), pH = 9.7, (♦), pH = 11. The solid line denotes theoretical prediction derived from the fluctuation theory, for the adsorption site composed of two (curve 2) and three (curve 3) fibrinogen molecules.

Modeling the adsorption of nanoparticles - multiscale theoretical description of the adsorption kinetics of spherical particles on the homogenous surface

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

A common experimental method for nanoparticle multilayer adsorption is the layer by layer technique. It is based on the consecutive adsorption of oppositely charged layers by immersing the substrate alternately in suspensions of colloidal particles with positive and negative surface charge. The structure of multilayer obtained in this way depends strongly on the number of adsorption cycles, amount of particles adsorbed in each cycle, and interactions in the system. Unfortunately, in case of multilayers of the thickness of the order of 1 micron there has been neither satisfactory mathematical model nor experimental methods for the precise determination of synthesized multilayer key parameters, such as the thickness or porosity.

The aim of the research conducted at the ICSC PAS in 2012 was the quantitative theoretical description of the relationship between the limiting diffusion current, as measured in the system of rotating disc electrode with an adsorbed multilayer of monodisperse colloidal particles, and other parameters of the system, such as the mass of adsorbed multilayer, its porosity or thickness, and the electrode surface or rotation frequency.

We have extended the earlier developed theoretical model, describing monolayers of monodisperse particles, for systems of multilayers of such particles. We have derived equations for the determination of mass of the second particle layer by the measurement of total mass of the two-layer and the measurement of limiting diffusion current at the rotating disc electrode covered with a one- and two-layer. We have also developed equations describing the relationship between the adsorbed multilayer porosity and thickness on one hand, and the multilayer mass, particle radius, and limiting diffusion current on the other, valid for multilayers of the porosity $\varepsilon < 0.9$. The theoretical results have been experimentally verified by the measurements of mass of multilayers produced from micron-sized particles on a gold rotating disc electrode, using an ultra microbalance, as well as by measurements of limiting diffusion current at the electrode covered with the multilayers, using the method of cyclic voltammetry. We have found a good agreement between the theoretical and experimental results.

The results of our research can be used in two main areas: fabrication of layer-based devices, such as microcapsules or membranes, and production of volume systems controlling interactions with the environment. Examples of the latter are anti-corrosion, anti-reflective, and anti-bacterial coatings, as well as biocompatible materials. Also, by depositing a porous layer on a surface we can change the shear forces acting on it to, e.g., regularize the flow and reduce the vortex induced vibration or drag coefficient.

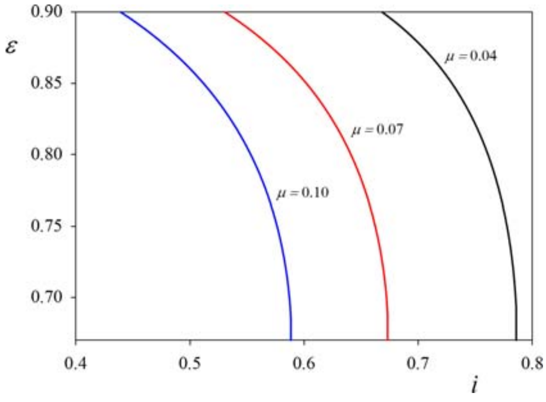


Figure 1. Relationship between porosity ε of colloidal particle multilayer and dimensionless limiting diffusion current $i = I / I_L$, calculated for different values of dimensionless mass of multilayer $\mu = m / (\rho\ S\ \delta_L)$, where I, I_L, m, ρ, S i δ_L denote respectively limiting diffusion current at electrode covered with multilayer, Levich current at bare rotating disc electrode, mass of adsorbed particle multilayer, particle density, disc electrode surface area, and thickness of diffusion boundary layer.

Influence of electrical charge on kinetics of the three phase contact formation at surfaces of low hydrophobicity

(Professor Kazimierz Małysa, Marcel Krzan PhD, Jan Zawała PhD)

The study aims at determination an influence of modification of the interface electrical state on kinetics of the three phase contact formation during the bubble collisions with solid surface of low hydrophobicity. During the time of the bubble collision with the solid surface the three phase contact can be formed if the liquid film separating the solid and bubble surfaces is ruptured. According to the DLVO theory the electrostatic interaction between double layers of the interacting interfaces and van der Waals forces are the main factors determining stability of the thin liquid films. Thus, modification of a magnitude and especially a sign reversal of the electrical charge at the interface should diminish stability of the thin liquid film and lead to formation of the three phase contact gas/solution/solid.

Influence of a preferential adsorption of cationic surfactants (n-alkyl-trimethyloamonium bromides) at liquid/gas interface on kinetics of the three phase contact formation on hydrophilic mica surface was determined. The experiments were carried out for two different locations (L=3mm and L=100mm) of the mica plate in respect to the capillary orifice. Series of the experiments, for these two different solid surface locations, were carried out to evaluate influence of the motion induced dynamic architecture of the adsorption layer (DAL) over surface of the colliding bubble on kinetics of the three phase contact (TPC) formation at mica surface. The DAL formation means that amount of the adsorbed surfactant molecule at the upstream bubble pole is much lower than the equilibrium one and is higher at the bubble bottom pole. Phenomena occurring during the collisions were monitored with a high speed camera of frequency 1040Hz.

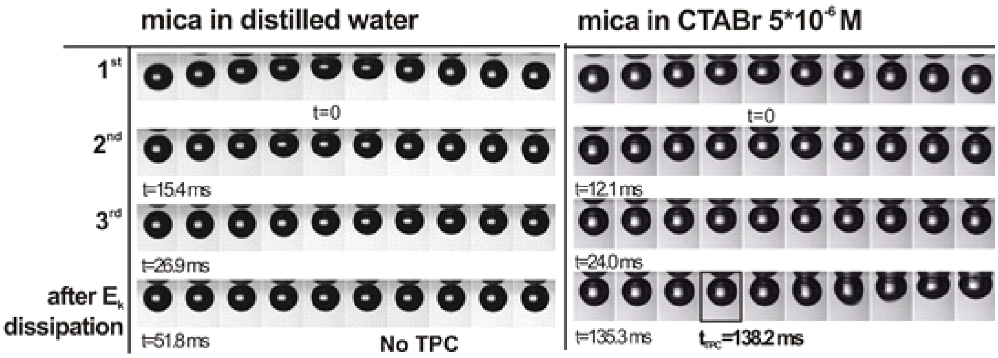


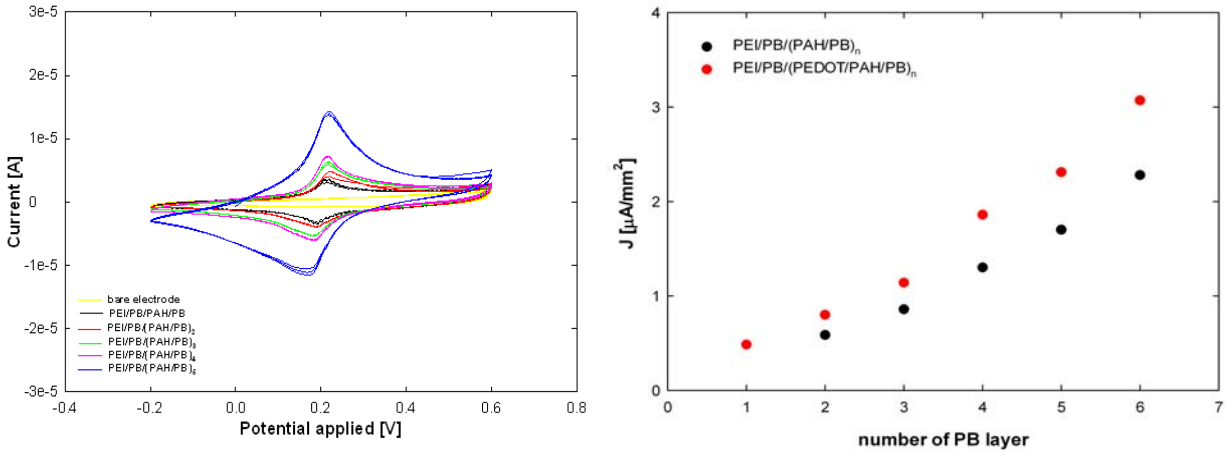
Figure presents sequences of the photos showing the bubble collisions with mica surface in distilled water and in $5*10^{-6}$ M CTABr solution. As can be observed, adsorption of the cationic surfactant over the bubble surface caused the TPC formation, due to the wetting film destabilization (electrical charge reversal at the gas/solution interface). It was found also that the time of the TPC formation (t_{TPC}) was shorter when the mica plate was mounted at the location "close" (L=3mm). These differences in the t_{TPC} values indicate that at the location "far" (L=100mm) the DAL was established over surface of the rising bubble – time of the TPC formation was longer because additional time was needed (diffusion) to re-establish at the bubble top pole, the adsorption coverage's of the cationic surfactant high enough, to have the positive surface charge there. At the location "close" the DAL was not established and therefore the time of the TPC formation due to electrostatic interactions between negatively charged mica surface and positively charged bubble surface was shorter.

Functional polyelectrolyte multilayers films

(Professor Piotr Warszyński + his team)

Functional polyelectrolyte multilayers formed on macroscopic surfaces or nano- and microsize particles or droplets are new materials with potential brad applicability. They are produced by sequential deposition of polyelectrolytes and/or nanoparticles, surfactant micelles, proteins, etc. The properties of the films and their function depend on the components used and on the conditions of their formation.

The aim of our work in 2012 was to determine the optimal conditions of formation of multilayer films containing Prussian blue nanoparticles (PBN) in polyelectrolyte (PE) multilayers and to study sensing ability of such hybrid films deposited on metal electrodes towards hydrogen peroxide electrochemical detection. Multilayer films containing various number of layers with Prussian blue nanoparticles were formed using the Layer-by-Layer adsorption method. The build up process of PE/PB multilayer films was monitored by Quartz Crystal Microbalance (QCM). The electroactive properties of these films deposited on gold electrodes were studied by cyclic voltammetry (CV). We determined the dependence of PB redox current on the number of layers as well as the effect of selected conductive polymers: PDOT:PSS, polypyrrol and polianiline embedded in the film structure. The example of experimental results is illustrated in Fig. 1.



Firure 1. Left – the ex ample of voltamperometric curves for the gold electrode covered with multilayer films with various number of layers with Prussian blue nanoparticles. Right – the comparison of the dependence of PB reduction current on the number of layers without and with conductive polymer PDOT:PSS.

We found the linear dependence between the PB redox current and the number of PBN layers in the film. That current was enhanced when the conductive polyelectrolytes were present in the film structure. The enhancement was the most pronounced for polyaniline. The gold electrodes with multilayer films were used for the electrochemical detection of hydrogen peroxide in the solution. We demonstrated a linear relationship between H_2O_2 redox current and the number of layers with PBN. For the electrode of the given structure the linear dependence between the concentration of hydrogen peroxide and redox current was observed. There was the positive effect of conductive polymers in the film structure as the sensitivity of the gold electrode covered with multilayer PBN film was increase by c.a. 20%.

First attempts for the construction of PE/PBM multilayers films with the reduced graphene oxide sheets were made.

Statutory Research

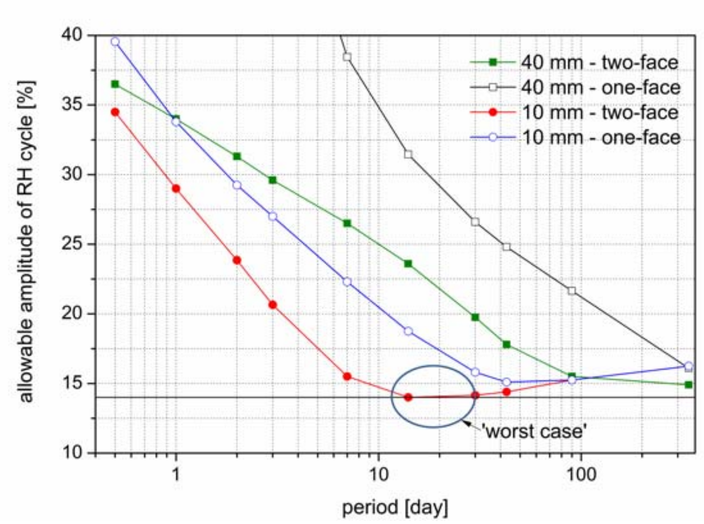
Physics and Chemistry in Cultural Heritage Protection

Modeling of the response of historic polychrome wooden objects to changes of the ambient environmental conditions

(Prpfessor Roman Kozłowski, Łukasz Bratasz PhD, Michał Łukomski PhD, Bartosz Rachwał PhD)

The task consisted in a further refinement of the finite element analysis to model the water vapour diffusion and strains in the multilayer structure of decorated wood in response to changing climate conditions. The aim was to expand the understanding of decorated wood response to cyclic RH variations represented in the calculations by a simple sine function.

Each sinusoidal RH cycle of a given amplitude and duration causes a certain strain in a freely responding panel which impacts on the decorative layer. The strain magnitude depends on the panel thickness and the configuration of diffusion that is if the moisture is exchanged through both faces of the panel or through one of the two faces only to simulate the extreme effect of a pictorial layer completely impermeable to the moisture flow. The allowable amplitude of an RH cycle for a given panel was expressed as a value reaching cyclically the critical mismatch between the moisture-related responses of the wood substrate and the paint layer, respectively, without occurrence of fracture in 100 years; the critical mismatch values was determined experimentally in the fatigue testing of specimens imitating painted wood.



The figure shows the allowable amplitude of the sinusoidal RH cycles (as defined above) at 20 ^{o}C as a function of the cycle duration for two panel thicknesses of 10 and 40 mm and the moisture flow through one or both faces of a panel. The most responsive tangential direction in wood was considered

The 10 mm panel with two faces permeable to the water vapour flux subjected to fluctuation cycles lasting long enough to bring about the full response of the panel represents the worst case of the study performed (marked with a circle in the figure) and the allowable amplitude of an RH cycle for this case is only ±14%.

The modelling performed indicated that moderate variations within the approximate range 50 ± 15% were safe. As such, the range provides a cautious ‘baseline’ for the environmental standards for safe display of painted wood. This baseline can be re-defined when the understanding of critical strain levels is refined with advances in experimental research on physical fracture in painted wood.

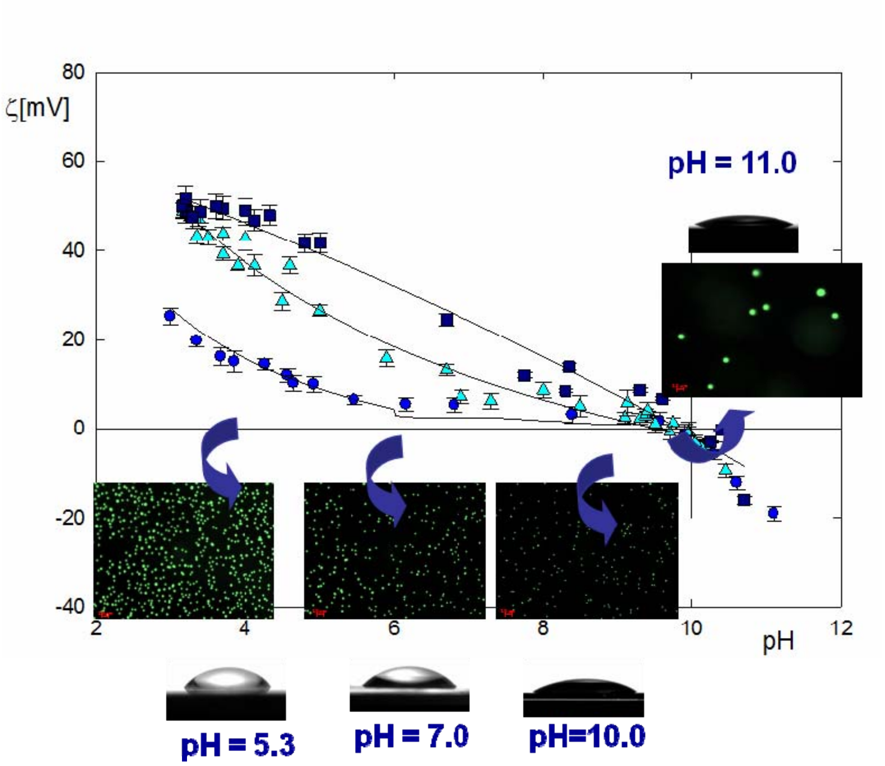
Research projects
of the Ministry of Science and Higher Education

Formation of biologically active multilayer films of polyelectrolytes, proteins and dendrimers

Research project N N204 02536 [2009-2012]
(project leader: Barbara Jachimska DSc)

Adsorption of protein at the surface play an important role in different areas of natural sciences, including materials science, colloidal science and biophysics. A controlled formation of bio-film requires a throughout knowledge of the structure of the protein molecules in relation to its molecular weight, ionic strength and pH of the solutions. The conformation of the protein on the surface and the conformation of the proteins in solution will also affect protein adsorption.

Combine different physicochemical methods gives the possibility to obtained conformations and structure in the bulk and a very promising tools for controlling 3D structure at the surface, especially at higher coverage’s when the flat orientation of anisotropic molecules is prohibited due to steric interaction. The goal of the project was to extend the mechanisms of protein coating formation and providing the necessary physicochemical characteristics of these processes. Additionally these studies can lead to the founding of a new technology of preparation of bioactive surface with controlled architecture.



New nanostructured carbon materials, oxide materials and their composites as components of capacitors

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

The project objectives such as the preparation of three types of electrode materials, i.e. carbon materials, oxide materials and their composites and characterization of their physicochemical and electrochemical properties (in alkaline medium) were accomplished. The influence of composition, morphology, crystallization degree, graphitization extent and porosity of newly prepared materials on their capacitance was described.

During electrochemical experiments no reduction/oxidation reaction involving the change of oxidation state of transition metals was observed. Therefore, the capacitance of the electrode materials was calculated using only the current associated with charging/discharging the electrical double layer. Among examined materials, the carbon materials had the highest capacitance (ca. 10-30 F/g), the composites had a moderate capacitance (ca. 5-15 F/g) and the oxide materials had the lowest capacitance (< 1 F/g).

The carbon materials had the best ability to store the charge, as they were mostly composed of porous carbon component (graphitic carbon in form of carbon nanotubes and amorphous carbon). Nitrogen sorption measurements revealed that the carbon materials were much more porous than other electrode materials. It seemed that graphitic carbon acted as an electrically conductive and porous matrix offering the charge and electrolyte transport. The composites had much more lower porosity than the carbon materials as they were mostly composed of oxide component, which consisted of non-conductive and non-porous grains.

The type and proportion of divalent and trivalent cations in LDHs (layered double hydroxides) used as metal/metal oxide precursor for the preparation of the electrode materials, had no distinct impact on the capacitive properties of the tested materials. Synthesis temperature strongly affected crystallization degree of oxide constituent and graphitization extent of carbon constituent. It seemed that the samples prepared at the lowest temperature (600 ^{o}C) might have the largest electrolyte/electrode interfacial area and they showed the highest capacitance.

Newly prepared electrode materials cannot serve as charge storage materials (as electrode materials in capacitors) as they had rather low capacitance. However, they may be tested as electrocatalysts for oxygen reduction reaction or methanol oxidation reaction (as electrode materials in fuel cells) as they contained transition metal (Co and/or Ni) compounds.

Theoretical and experimental analysis of porosity of multilayer of spherical colloidal particles

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

In the frame of this research project we accomplished a series of tasks. We developed methods of polishing of gold rotating disk electrode, which let us achieve a smooth and clean surface, necessary for reproducible results. We determined physicochemical properties of the electrode by means of AFM, electrochemical impedance spectroscopy, and measurements of its surface potential as a function of pH and ionic strength of electrolyte solution. We determined the isoelectric point of the surface using the method of adsorption kinetics of colloid particle at various electrolyte pH values.

We used the dynamic light scattering and optical diffractometry to determine the diffusion coefficient, electrophoretic mobility, diameter, and surface potential of various colloidal particles, to be exploited in adsorption, as functions of electrolyte concentration and pH.

We developed the method and found the optimal parameters for adsorption of monolayer of colloidal particles on the surface of gold rotating disk electrode. We adsorbed several monolayers at various surface coverages under various physicochemical conditions. Then, we used optical microscopy to characterize the monolayers.

We conducted extensive electrochemical research. We used cyclic voltammetry and electrochemical impedance spectroscopy with the rotating disk electrode technique to determine the diameter of adsorbed particles and the electrode surface coverage. We derived equations determining the relationship between the limiting diffusion current at the rotating disk electrode with a layer of particles and the electrode surface coverage or particle size. We compared the theoretical predictions with our experimental results and found a good agreement between them.

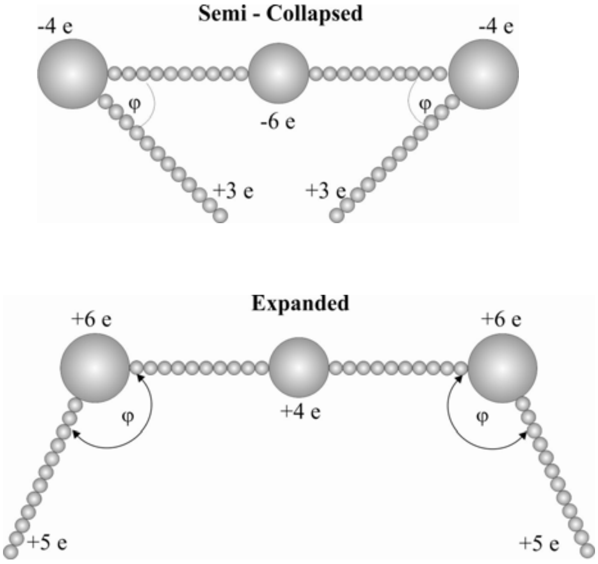
We then employed the electrochemical methods to experimentally determine parameters of colloidal particle multilayers. We found them especially useful for the measurements of porosity and thickness of colloidal particle multilayers, as well as for ion path tortuosity within the layers. We compared the experimental results obtained in the electrochemical measurements of spherical particle multilayers with the results derived from measurements of mass of adsorbed particles, conducted with an ultra-microbalance. We found a good agreement between the results obtained with the two methods.

We also developed a theoretical model of multilayer adsorption of spherical particles and conducted computer simulation of the process under conditions analogous to those applied in the experiments. We characterized quantitatively the virtual multilayers in terms of various distribution functions and average parameters. We found a series of important conclusions on properties of multilayers synthesized with the „layer by layer” method. The theoretical results confirmed a strong dependence of the multilayer structure on the experimental conditions at its formation. A comparison of theoretical and experimental results revealed they were in a good agreement, which confirmed our theoretical model.

New method of evaluating colloid particle and protein interactions with interfaces based on streaming potential measurements

Research project MNiSW N N204 026438 [2009-2013]
(project leader: Professor Zbigniew Adamczyk)

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 an efficient hydrodynamic bead model of fibrinogen. According to this model, the real shape of the molecule is replaced by a constellation of touching beads of various size (see Fig. 1). Using this model, extensive calculations were carried out, in which the hydrodynamic resistance matrix, the diffusion tensor and the intrinsic viscosity of fibrinogen were calculated. These 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. 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 diameter and the intrinsic viscosity were calculated as a function of the number of beads in the side arms forming an arbitrary angle φ with the main body of the molecule (see Fig. 1). It was shown that these theoretical calculations adequately describe experimental data obtained by the DLS and dynamic viscosity measurements of fibrinogen solutions. This allowed one to unequivocally determine conformations of this protein in electrolyte solutions and charge distribution for various pH (see Fig. 1).



pH 7.4 $\langle R_H \rangle = 10$ nm, $\langle [\eta] \rangle = 35$, $\varphi = 56^{\circ}$

pH < 4or pH >10, $\langle R_H \rangle = 10.7$ nm, $\langle [\eta] \rangle = 50$, $\varphi = 115^{\circ}$

Figure 1. Predicted conformations and charge distributions on the fibrinogen molecule

Modeling of kinetics and equilibrium of heavy metal ion sorption by materials of biological origin

Research project MNiSW N N204 271238 2010-2012]
(project leader: Professor Władysław Rudziński)

In 2012 the project was finished. The results obtained can be summarized as follow:

- Process of calcium equilibrium bonding: The models allowed one- or two-centres bonds of and effects of double electric layer (in context of Donnan gel) were proposed. The most advisable was the two-centres model assuming that alginates' carboxylic groups fixed heavy metal ions.
- The explanation of applicability of group of models and semi empirical expressions describing influence of pH and removed ion concentration (C) on biosorption yield (q) was proposed. These expressions expect the existing pH depended limit of biosorption yield (q) when removed ion concentration (C) is infinite.
- The systematic comparison of ion exchange mechanisms and competitive adsorption was carried out in context of pH depending metal ions fixation by biosorbents.
- The effects of conditions of noncontrolled pH (changed in time) of solution on biosorption kinetic (and, more general, adsorption) in model systems was described using the statistical rate theory (SRT).
- The metal ions/biosorbent systems were studied in view of surface heterogeneity effects and their rendering to ion exchange constant's idea.
- The effect of presence of calcium ions on other type divalent metal ions in binary and ternary (taking pH into account) systems was studied. The one- and two-centres metal ions bonding were considered.
- The interpretation of experimental thermodynamic data of bonding of divalent metal ions by alginates containing biosorbents was discussed. Two methods for differentiate apparent and real ΔH and ΔS values were proposed.
- It was stated that that the pseudo-second order (PSO) and pseudo-first order (PFO) equations (usually used for description of adsorption on solution/solid surface interface) can be also used for correlation the data measured for ion metal/biosorbent systems.
- The methods of generalization of equilibrium and kinetic models to case of multicomponent biosorption were studied and described. Beside of pH influence also the case of few types of metal ions (which could fix by the similar mechanism) presented in the system was discussed.

The described models contribute to better understanding the nature of biosorption processes and then can influence on the future directions of experimental studies.

Biocatalytic synthesis of chiral alkylaromatic and alkylheterocyclic alcohols by ethylbenzene dehydrogenase – theory and experiment

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

In 2012 the research aims were focused on the stabilization of the enzyme in immobilized form which would allow its application in electrochemical reactor. Initial conceptual steps on developments of the flow-reactors were also taken. QM:MM and MM modeling studies were used to investigate the reaction stereoselectivity as well as binding mode of a novel B-ethyl and N-ethylazaborine inhibitors. Theoretical studies were compared with chromatographic analyses (GC-MS, LC-MS) of reaction mixtures obtained for (*S*)- and (*R*)-d1-ethylbenznes.

In **task 1** two types of immobilization supports were studied: modified cellulose materials (granocels) developed by a research group of professor Bryjak from Wroclaw Technical University and metacryl polymer supports developed by professor Wiktor Bukowski from Rzeszów Technical University. Initial studies showed that both materials are promising being chemically inert to the reaction media (i.e. they were not reducing electron acceptor). The covalent immobilization was conducted on both materials but only trace binding on metacrylic materials was achieved. Immobilization on granocels also exhibited a significant loss of enzyme activity (1-13% of initial activity) due to partial binding of the protein on the support and also due to decrease of activity during immobilization procedure. Nevertheless, the stability tests reveled an increase of supported-enzyme stability with respect to homogenous enzyme by app. 30%.

In task 2 the modeling of reaction stereoselectivity was conducted with QM:MM method. The oxidation of ethylbenzene was investigated assuming pro-*S* or pro-*R* C-H activation as well as pro-*S* or pro-*R* OH rebound process. The products formed after oxidation of (*S*)-d1-ethylobenzene and (*R*)-d1-ethylobenzene were studied based on substrates custom-synthesized by project cooperators form Marburg.

The studies showed that C-H activation in pro-R orientation of substrates is associated with steric hindrance in the active site which leads to elevated activation energy. Meanwhile the OH rebound process is not so stereoselective mainly due to much longer C-OH-Mo distance compared to C-H-O in TS1. The isotopic studies showed that isotopic labeling of H to D at benzylic carbon atom influences reaction enantioselectivity, as (R)-1-phenylethanol has been observed in both reactions. Interestingly, in case of (*S*)-1-ethylbenzene-d1 reaction mixture non-labeled (R)-1-phenlethanol was detected along with a mixture of labeled and non-labeled (*S*) alcohol. In case of (*R*)-1-ethylbenzene-d1 a pure D-labeled (*S*) alcohol was formed along with a mixture of labeled and non-labeled (R) products. This studies were backed up by QM:MM calculations and VCD tests. The VCD test showed that labeled substrates were not enantio-pure and as a results it was not possible to provide an unequivocal explanation to the observed phenomenon.

As a result of promising immobilization results the modifications of electrochemical reactor system were undertaken. A new flow-reactor was planned based on HPLC pump, a glass FPLC column (3 ml volume, 3 MPa), UV-vis flow cell and tubular electrochemical cell equipped with oxidation electrode. The developed immobilized enzyme will be used in such reactor as a catalyst. The other project achievement was a successful QM:MM modeling of reaction stereoselectivity and modeling of binding mode of a new azaborine inhibitors.

Functional nanostructures of manganese oxides doped with other metals

Research project MNiSW 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 morphological, 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 the effort was focused on elaboration of methodology of mixed iron manganese oxide of spinel structure synthesis and also on the studies of catalytic properties of manganese oxide deposited on Pt(111). The catalytic system was investigated in the inverse supported model catalyst mode with the use of reaction titration approach. The systems were characterized Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Conversion Electron Mössbauer Spectroscopy (CEMS), Scanning Tunneling Microscopy (STM), Temperature Programmable Desorption (TPD) or titration reaction with Residual Gas Analysis (RGA).

The synthesis of Mn_3O_4 spinel structure was performed on Fe_3O_4(100) epitaxial substrate. The application of such well known structure substrate should intentionally force growth of Mn_3O_4 layer although in reality growth of spinel was confirmed by LEED up to only 3 ML. Then MnO(100) structure was obtained at the analyzed surface. The spinel structure was received again by annealing of the resulting layer in oxygen ($1\cdot10^{-5}$ mbar) at 820 K. The composition of the mixed iron-manganese spinel was dependent on the annealing time.

The catalytic performance of MnO was studied on Pt(111) substrate. The 0.1, 0.3, 0.5, 1.0 and 5.0 ML of manganese was deposited on Pt and then oxidized. The LEED analysis showed (19x1) reconstruction of MnO like structure on Pt(111). The XPS analysis confirmed formation of MnO. The titration reaction was performed for constant oxygen ($5\cdot10^{-7}$, $1\cdot10^{-6}$ and $5\cdot10^{-6}$ mbar) and changeable CO pressures at constant temperature (373, 393, 423 and 473 K). The titration reactions revealed low and high reactivity regions of the CO oxidation on MnO/Pt surface. It was found that MnO present at the Pt surface shifts the high reactivity region into higher CO pressures. This effect was significant and larger than one order of magnitude for CO pressure. The coverage of Pt(111) surface by manganese oxide was critical for CO oxidation below 0.5 ML. The observed effect collapsed above the mentioned value.

The presented studies showed new route for synthesis of spinel structure of mixed iron manganese oxide. This approach can be further applied for fabrication of magnetic and catalytic systems. The catalytic studies show positive impact of low amount of manganese on regeneration of CO poisoned Pt(111) surface. Such ability can be utilized in synthesis of the active catalysts.

Composite cathodes containing silver for solid oxide fuel cells SOFCs working at 600^{o}C and at lower temperatures

Research project MNiSW 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^{o}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 overpotential 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^{o}C.

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) cathode material was prepared. The characteristics of obtained material (phase composition, microstructure) was performed by XRD, SEM and EDS methods. Examination of the mechanism of oxygen reduction reaction at the silver electrode in the systems Ag|oxide electrolyte|Ag was continued (examined electrolytes: $Sm_{0.2}Ce_{0.8}O_{1.9}$ (20SDC), $Gd_{0,2}Ce_{0.8}O_{1.9}$ (20GDC), $Sc_{0.09}Zr_{0.8}O_{1-\delta}$ (9ScSZ), $Ce_{0.01}Sc_{0.1}Zr_{0.8}O_{1-\delta}$ (1Ce10ScSZ)). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Were used in the electrochemical tests. Measurements were performed at the rest potential and at different potentials in the range of -0.5 - 0.1 V. The largest impedance of the silver electrode was recorded at -0.2V. The inductive semicircle in the impedance spectra and the inductive loop in the voltammograms were observed in the case of negatively polarized electrode. The two compartment experimental setup for electrochemical measurements was build. The 20SDC, $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ (8YSZ) and 1Ce10ScSZ electrolyte discs (20 mm of diameter) for these measurements were prepared. The method of manufacturing cathode green tapes 0.1-0.5 mm thick was elaborated. The impedance of porous electrodes obtained by this method was measured in the system O_2|$La_{0.6}Sr_{0.4}Co_3$|20SDC|Ag|O_2. Composite cathodes Ag/$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-d}$ (LSCF) were prepared. Impedance of these cathodes was measured in the system O_2|Ag/LSCF|8YSZ|Ag|O_2.

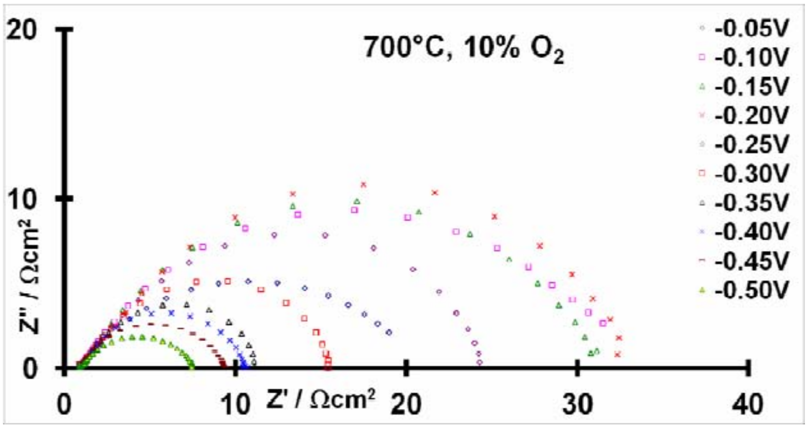


Figure 1. Impedance spectra of the negatively polarized silver electrode in the system O_2|Ag|20GDC|Ag|O_2 in the Nyquist representation

New methods for powder diffraction studies of structural materials, partially amorphous, disordered and of reduced dimensionality

Research project MNiSW N N204 329337 [010-2012]
(project leader: Professor Wiesław Łasocha)

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, set of filters, tests measurement were carried out. Suitable measuring programs were prepared, selection of the most appropriate sofware and hardware parameters.
- Studies have been undertaken for determination of lattice parameters for non-typical materials, including specimens of high texture and materials with large differences in the size of 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 objects of the study were samples of liquid crystals, greasy layered sediments and salts of carboxylic acids with long chains.

Among the tests performed, the attention should be paid to work on the structure of the barium salt of azelaic acid, made by 'charge flipping'. Studies using conventional packages do not form a reasonable model structures. The reasonable/comprehensive model of the structure was created only using the SUPERFLIP program, results pointed to the correct space group as well as the exceptionally large disorder in the structure.

Work was carried out on an independent verification of models of structures with non-diffraction methods. Support for powder diffraction methods were calculation methods, including methods of DFT (Density Functional Theory). Calculations of this type were carried out for a number of halogeno- or methylo- aniline polymolybdates. A further part of the study concerned the stability of the isolated octamolybdates, and the factors determining the choice of the actual model structure. An important element of the test sample was a selection of the structural elements responsible for the catalytic activity of some of the investigated compounds.

In the final stages, the structural studies based on the formalism PDF (pair distribution function) were carried out. Their goal was not only putting hypotheses regarding the construction of structural elements, but also the quantitative verification of models created by the refinement in a manner similar to the Rietveld method.

Further studies, designed to get the pre-start structural information, were carried out for a number of materials obtained on the basis of:

- tri-molybdates of transition metals (Zn, Co) after amorfization followed dehydratation,
- peroxomolybdates deposited on polymer media.

The main objectives of the project can be defined as "adapt and supplement the measurement and calculation procedures for essential elements (Ag lamp, DFT calculation methods, methods Charge Flipping, SEM and electron microscopy with precessing electron beam PED, FTIR method) allowing wider use of powder diffraction methods for structural characteristics of the new non-standard materials, based on laboratory radiation source".

Stability, functionality, and mechanism of creating polymer casein multilayer structures

Research project MNiSW 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

To build-up the polyelectrolyte multilayer films α- and β-casein as polyanion was chosen. As polycations poly-L-lysine (PLL), poly-L-arginine (PLArg) and chitosan were used. The sequential adsorption of polyelectrolytes (layer-by-layer technique) was applied to form films at surface of silicon wafers and quartz crystals covered with gold layer. We determined that films build-up with PLArg were much thicker (around 80 nm) than that with poly-L-lysine (30 nm). Unfortunately, we did not succeed to form the casein films with chitosan thicker then 6 nm due to weak adsorption of chitosan. That can be explained by the low positive charge of chitosan in the pH range above the isoelectric point of casein. For (PLL/cas)n and (PLArg/cas)n films the optimal conditions for film formation were at I = 0.15 M NaCl (films had maximum thickness)..

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. (PLL/cas)n and (PLArg/cas)n films were not resistant to solutions of pH 2 due to charge reversal of casein. (PLL/cas)n films were also not stable in pH 11 due to neutralization of PLL. In neutral conditions, films with α-casein were more stable than ones with β-casein, when contacted with the solutions with various composition. (PLArg/cas)n films were stable in base solutions (pH 11). During the QCM-D experiments we observed only small decrease in film thickness.

The (PLL/cas)n and (PLArg/cas)n films were also treated with NaCl (concentrations 0.015M NaCl, 0.15 M NaCl, 0.75M NaCl and 1.5M NaCl), HEPES and $CaCl_2$ (concentrations-2mM, 5mM, 20mM and 50mM). We found out that the (PLArg/cas)n films were stable in all conditions except for solution 1.5 M NaCl. In such solution removal of the film from support was observed.

To check the ability of casein to bind calcium ions, when it is embedded in to polyelectrolyte films, the silicon plates covered with the PE films were immersed in the $CaCl_2$ solutions. After that the casein layers were investigated by FTIR and XPS techniques. In FTIR spectra of casein we found slight shifts of the maximum of the picks of amid I and amid II in direction of higher wavenumber (to α helices). It suggests that absorption of casein in the multilayer film brings in a structuring in casein chains. XPS data gave evidence of the contents of calcium ions in the casein/polyelectrolyte films.

Using FTIR and XPS techniques we could confirm that calcium ions can be incorporated by the casein built-in polyelectrolyte multilayer films, that means that casein is bioactive in such films.

Studies of structure and properties of a magnetically triggered molecular nanocontainer

Research project MNiSW N N204 205240 [2011-2014]
(project leader: Assoc. Professor Tomasz Pańczyk)

Multiwalled carbon nanotube functionalized by magnetic nanoparticles through triethylene glycol chains (Fig. 1) was studied. The aim of the project was to study the role of magnetic anisotropy constant on the process of magnetically triggered uncapping of the nanotube.

For that purpose the dedicated model and force field have been developed which allow for studies of that phenomenon using molecular dynamics simulations. The mechanism of magnetization reversal due to interaction with external fields and coupling it with the standard newton mechanics were based on the Neel-Brown model and the overdamped Langevin dynamics. It was additionally assumed that the magnetization reversal proceeds according to coherent rotation model. Using the above assumptions several extra classes for the lammps code have been implemented.

The key results obtained in this stage of the studies concern: the energetic profile of the nanocontainer accompanying the uncapping transition, range of the magnetic anisotropy constant for which the magnetically triggered uncapping occurs within times of the order 10 ns, range of the magnetic field strengths leading to the uncapping and other effects like magnetic heating during the uncapping transition.

The obtained results confirm applicability of the considered system in the area of nanomedicine as a drug delivery system being able to release drug molecules in response to the external stimuli (magnetic field). The uncapping process is very fast though it depends on the mutual alignment of the nanocontainer and the field at the initial times. Fig. 2 shows typical uncapping profiles as functions of time, field strength and anisotropy constant K_a.

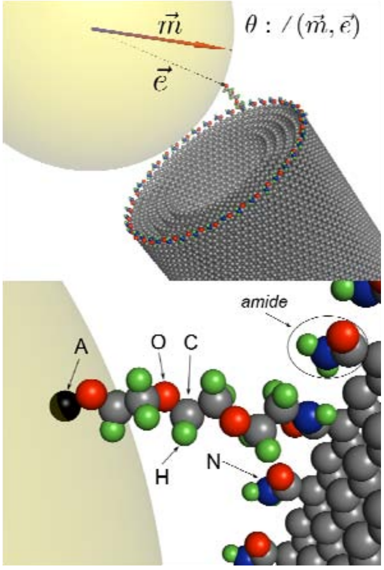


Figure 1 Model of the nanocontainer. $\vec{m}$ *- magnetization,* $\vec{e}$ *- easy axis*

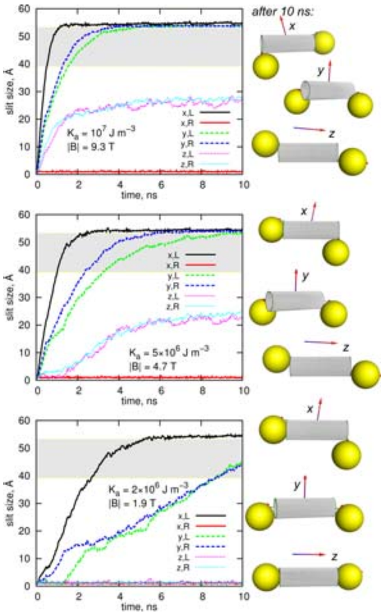


Figure 2 Temporal evolution of the structure of the nanocontainer

Influence of micro- and nano-bubbles at hydrophobic surfaces on kinetic and mechanism of the three phase contact formation in milliseconds timescale

Research project MNiSW N N204133640 [2011-2014]
(project leader: Jan Zawała PhD)

The aim of the project is to investigate influence of (i) roughness of the hydrophobic solid surface and (ii) presence of air micro-bubbles on kinetic of the three-phase contact (TPC - solid/liqid/gas) formation. In the reporting period experiments on time of the TPC formation (t_{TPC}) by the colliding bubble at Teflon plates of different roughness in high n-octanol and α-terpineol concentration were performed. Motion of the bubble of radius R_b=0.74 mm and its collisions with solid surface as well as the moment of the TPC formation was monitored using high-speed camera. The distance between the bubble formation point and the solid surface was sufficiently long and the bubble collides with solid plates with terminal velocity (15 cm/s). On the basis of movies recorded the effect of prolongation of the t_{TPC} in solutions of frothers of high concentration was confirmed. In the solutions of n-octanol and α-terpineol of concentration $1*10^{-3}$ M the spectacular effect of the t_{TPC} prolongation by 70 ms (i.e. over order of magnitude) in comparison to distilled water, was determined. The results obtained confirmed hypothesis that this effect is related to air presence at hydrophobic solid surface. The prolongation of the t_{TPC} is due to higher stability of foam films formed between colliding (macro) bubble and submicroscopic bubbles “captured” beneath the solid surface. Additionally, in the reporting period photos of surface of the fritted glass filters connected to the experimental set-up allowing application of different, control values of overpressure (P), were taken during the filters immersion in distilled water. In addition, pressure characteristics of the fritted glass filters were obtained, showing the dependence between magnitude of P and number and size of micro-bubbles formed at the filters surface. Figure 1 presents one of the characteristic of P obtained, i.e. P variations as a function of time, as well as photos of the filters surface corresponding to three P values marked. The formation of microscopic air bubbles can be noticed at the surface, which number and size is proportional to the P magnitude. The correlation between these two parameters was determined on the basis of image analysis. It was found that with increasing P in the range from 0 to P_{max} = 4 kPa, the size range of the micro-bubbles formed is wider – it increases form 20-200 to 20-700 µm. Moreover, the air surface coverage increases from 0% for P=0 to about 2% for P = P_{max}.

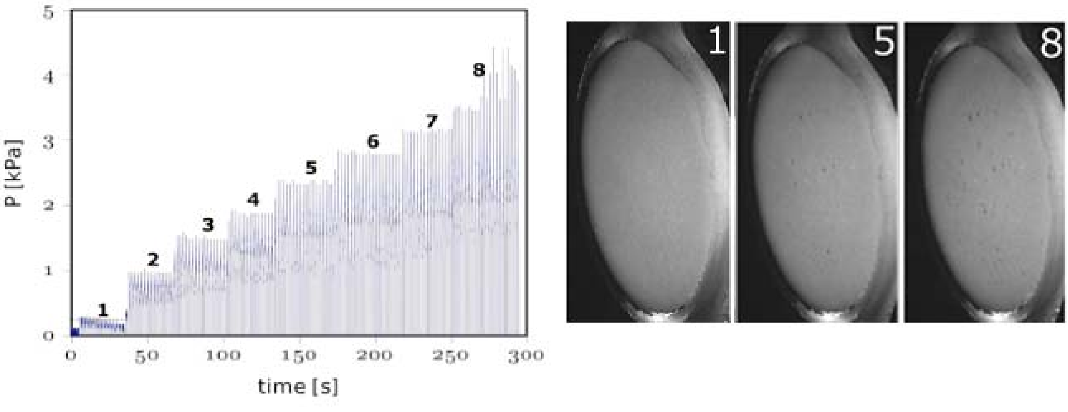


Fig. 1 Overpressure as a function of time and corresponding photos of the fritted glass filters , where formation of micro-bubbles can be noticed

Quantum-chemical studies on the mechanism of transmetallation reaction of porphyrin and its selected derivatives

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

The aim of the present project is the elucidation of the mechanism of transmetalation of porphyrin and its selected derivatives (chlorine, chlorophyll) by copper(II) and zinc(II) ions. On the one hand, it would enable for the detailed description of substitution of magnesium in chlorophyll by heavy-metals (mostly Cu(II)), which takes place in plants growing on 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.

Theoretical studies on magnesium ion exchange for the other metal ion are continued. The geometry and electronic structures of intermediate products, which are formed along the reaction, are determined.

The first step of the reaction is the activation of MgP complex, which occurs through Mg axial ligand exchange (here represented by acetonitrile – ACN) by acetate ion. This results in a considerable porphyrin ring deformation and shift of the central Mg ion over the porphyrin ring. In such a way tetrapyrrole nitrogens are exposed and their nucleophilic character is reinforced, what is manifested by the increase of their negative charge (from -0.28 to -0.63 on average). These atoms constitute targets for the electrophilic attack of the incoming ions (copper or zinc).

Further reaction proceeds through desolvation of Cu or Zn. The bimetallic systems of $(CH_3COO)MgPCu(ACN)_n$ where n = 3,2,1 and $(CH_3COO)MgPCu(CH_3COO)(ACN)_n$ where n = 2,1 have been then modelled. While the number of solvent molecules attached to the copper ion is decreased, Cu is gradually incorporated into poprhyrin center. Magnesium dissociation occurs when copper ion becomes desolvated.

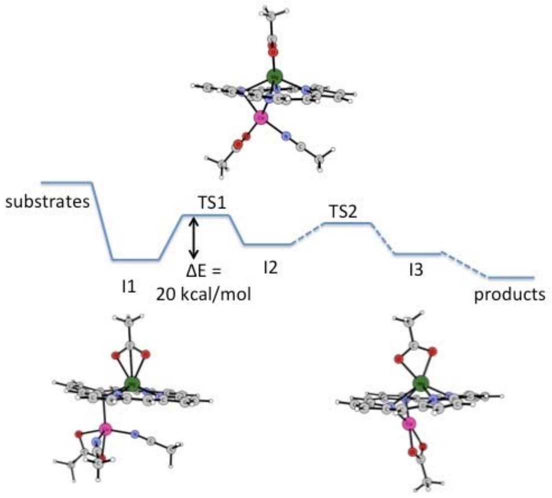


Figure. Schematic representation of the studied reaction profile

The new multi-layered systems with controlled architecture and functionality

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

The project was implemented according to schedule.

Competitive adsorption experiments were performed, for a mixture of particles of two different sizes.

The resulting layers were analyzed using atomic force microscopy, optical and electron microscopy. The results were used to determine the maximum coverages.

Parallel adsorption model was developed through the preparation of the kinetic part.

Particle adsorption kinetics were determined and the corresponding simulations were performed.

The results obtained were compared with each other. Based on the results were prepared poster presentations.

The study involved: dr Michał Ciesla, dr Aneta Michna; dr Marta Kolasińska-Sojka oraz mgr Marta Kujda i mgr Jadwiga Rzepa.

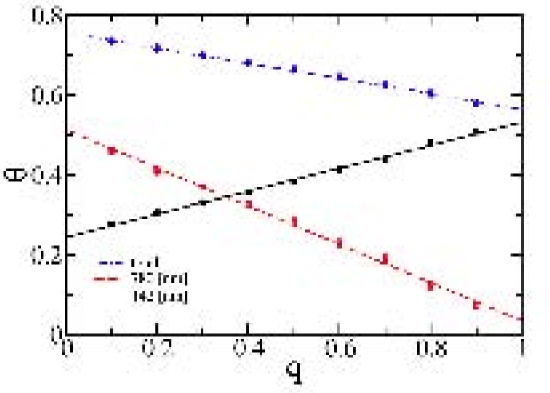


Figure 1 The maximal coverage ratio as a function of concentration both kind of particles.

Application of membrane emulsification for formation of nano- and microcapsules' cores

Research project MNiSW N N209 757340 [2011-2014]
(project leader: Professor Piotr Warszyński)

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

In 2012 we focused on the task of the project concerning the design and construction of a new membrane emulsifier unit. The unit consists: a pump, membrane module and mixers. Our membrane emulsifier possess ability to control all parameters influencing on the properties of the resulting emulsion. Pictures of the built membrane unit is shown in Figure 1 The system is equipped in a replaceable membrane with a pore diameter 80 nm, 100 nm, 200 nm and 4um. Preliminary tests of membrane emulsifier, concerning the impact of the flow rate of the oil phase on the size of the resulting emulsion droplets were performed. The results were in the good aggrement with prediction of theoretical model derived in the previous reporting period.

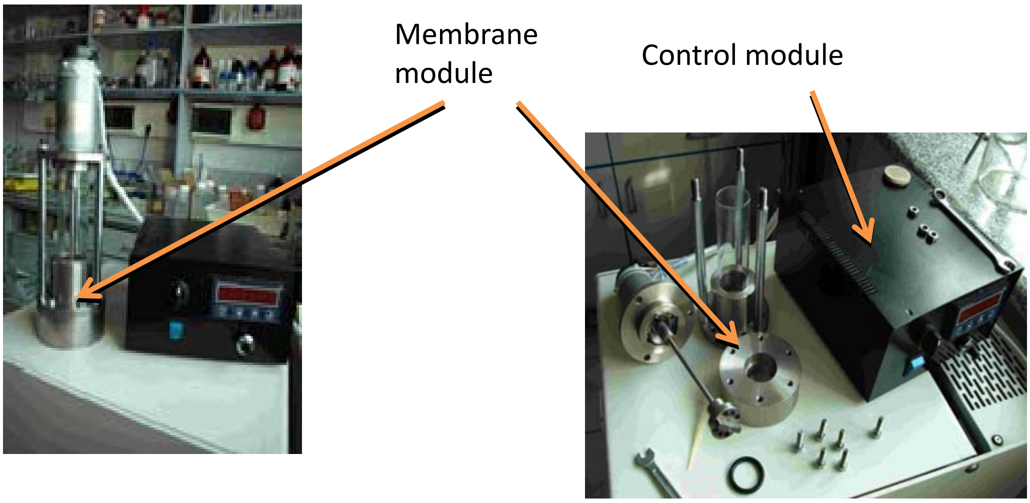


Figure 1. Membrane emulsifier

In the next period the membrane unit will be used to form capsules with polyelectrolyte shells for delivery of active compounds (drugs, anticorrosives, fluorescent markers)

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

Influence of cationic surfactants and pH at kinetic three phase contact formation at low hydrophobicity surface

PhD research project MNiSW N N204 179439 [2010-2012]
(supervisor: Professor Kazimierz Małysa, PhD student: Anna Niecikowska MSc)

The project aims at determination of influence of cationic surfactants and solution pH on kinetic of the three phase contact (TPC) formation (gas/liquid/solid) under dynamic conditions at surfaces of low hydrophobicity. The three phase contact gas/liquid/solid is formed, when a liquid film is ruptured during the time of the bubble collision with a solid surface. Stability of the liquid (wetting) films is affected by many parameters and hydrophilic/hydrophobic properties and surface roughness, presence of surfactants at the interfaces (their kind and concentration), electrical charge of the interacting interfaces are the most important ones. Electrostatic interactions between gas/liquid and liquid/solid interfaces can be either stabilizing or destabilizing force, especially at solid surfaces of low hydrophobicity. Electrical properties of the gas/liquid and liquid/solid interfaces can be modified through variations of the surfactant adsorption and/or solution pH.

In 2012 the PhD student –Anna Niecikowska MSc - gave birth to a daughter and had 1 year maternity live of absence. Therefore, the studies planned for 2012 were shifted to 2013.

Structural response of Roman cement mortars due to drying

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

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 was explanation of cracking mechanism in Roman cement mortars and pastes. The key research task, accomplished in the reporting period, was a comparative study of structural response due to drying for several binders which can be used in restoration works. Examinations using optical and scanning electron microscopy were also accomplished.

The research was focused on Roman cements which are currently produced from marls gained in Poland (Folwark) and Austria (Gartenau and Wietersdorfer & Peggauer), French natural cement Prompt and natural hydraulic lime (NHL5), and covered pastes (materials with no aggregate) and standard mortars (materials with the addition of aggregate).. In order to prolong sufficiently the workable life of materials based on Roman cements, two procedures retarding setting were used – chemical retardation and addition of a small amount of water to de-activate some of the cement hydraulic phases. Compositions of the pastes and mortars were determined according to constant flows suitable for manufacturing of cast architectural details and façade renders, respectively.

The risk of cracking was determined by comparing the drying shrinkage and the elongation at failure. Generally, the ultimate shrinkage exceeded the elongation at failure for all materials based on Roman cements. Therefore, these materials are generally susceptible to cracking on drying. This is in particular valid for the Roman cement pastes. The risk of cracking is the least for the shortly cured pastes of Prompt and Folwark cements. In turn, the risk of cracking is considerably reduced in mortars rich in aggregate. In these materials, a high risk of cracking was observed only for shortly cured mortars of the Austrian cements, retarded through the partial de-activation. As the drying shrinkage was reduced with the curing time and the mechanical parameters increased for materials based on the natural hydraulic lime NHL 5, long curing is recommended to limit the cracking risk. The microscopic examinations revealed that most cracks were formed in the cement matrix along unhydrated cement grains and aggregate grains. Only for materials of matured structure of the cement matrix, a part of cracks are formed in unhydrated cement grains.

The results obtained during two years of the project’s implementation were used in the doctoral thesis which was defended in November 2012.

"Sonata" Research Projects of the National Science Centre

Impact of heating historic churches on transfer and deposition of dust

"Sonata" research project NCN 2011/01/D/HS2/02604 [2011-2014]
(project leader: Marcin Strojecki PhD)

The research project is carried out in the framework of a scientific consortium in cooperation with the National Institute of Museology and Collections Protection in Warsaw. The aim of the project is to identify the intensified flows of heat, dust and moisture occurring during different heating strategies of historic churches and for various heating systems.

The project has been proceeding according to the schedule. The preliminary laboratory tests involving checking and calibration of the purchased laser dust sensors were completed. Analysis of the results showed a very good agreement of the measurements performed with the use of these sensors with the measurements obtained using standard cascade impactors. The resulting correlation coefficients were 0.99 and 0.95, respectively, for the particle size fraction of 0.3-1.0 μm and above 1.0 μm, pointing to a high reliability of the purchased dust sensors.

The second phase of the project involving installation and a long-term monitoring of the microclimate conditions in 5 selected churches (in the first year of the project) was preceded by a preliminary long-term survey. It consisted of installation of a very extensive monitoring system in two different churches equipped with two different heating systems and checking in the real-world conditions how to plan and arrange such measurements in other objects.

The first system consisting of 6 dust sensors, 5 temperature and relative humidity (T/RH) sensors, 1 ceiling surface temperature sensor, 1 ultrasound anemometer, 1 CO_2 concentration sensor was installed in March 2011 in a 13th-century brick-masonry church of the Assumption of the Blessed Virgin Mary and St. Wenceslaus in Krakow-Mogiła equipped with a heating system blowing hot air at the floor level. The second monitoring system consisting of 7 dust sensors, 4 air T/RH sensors, 1 ultrasound anemometer and 1 CO_2 concentration sensor was installed in the 15th-century wooden church of St. Bartholomew the Apostle in Krakow-Mogiła equipped with a pew heating system. The sensors were deployed in both the horizontal and vertical profiles in order to check whether there were differences in the distribution of particulate matter in the interior of the churches. The sensors measuring the concentration of CO_2 was installed in order to determine the rate of exchange of indoor and outdoor air and indirectly to estimate the number of the faithful visiting the church. In addition, 1 dust and 1 T/RH sensors measuring temperature and relative humidity of the outside air were installed inside a bell tower located near the two churches, in order to have a reference point of the external climatic conditions.

Analysis of the results obtained during the nine-month monitoring period provided information on both the spatial distribution of particulate matter in the interiors of the churches and their microclimatic conditions. The results showing a fairly uniform spatial distribution of particulate matter enabled optimization of the monitoring system, i.e. reduction of the number of sensors needed for reliable measurements. This allowed the number of monitored churches to be increased, so currently the measurements are carried out in 7 churches

Parallel to the long-term monitoring, short-term measurements (lasting about a week) are carried out with the use of a DustTrak DRX 8533 (TSI) aerosol monitor, which measures the weight of the dust content in 5 size fractions: PM1, PM2.5, PM4, PM10 and TPM (total particulate matter). In addition, the dust deposited on the filter and macroscopic dust samples collected from various locations in the monitored churches have been subjected to detailed chemical and morphological analysis.

New Pd-Pt/ hybrid nanocomposite catalysts for oxygen reduction in polymer electrolyte membrane fuel cell

"Sonata" research project NCN 2011/01/D/ST5/04917 [2011-2014]
(project leader: Monika Góral-Kurbiel PhD)

Current research involves investigations of polymer electrolyte membrane fuel cells. These devices use hydrogen and oxygen to produce electrical energy. Over the last several years, there has been a growing interest in fuel cell technologies due to their numerous advantageous properties. For example, they do not contribute to the greenhouse effect and water is the only formed by-product. However, a large-scale commercialization of fuel cells faces some significant barriers, such as a high cost of energy production and low durability. The aim of the project is to perform investigations of electrocatalysts for the oxygen reduction reaction, ORR at the cathode in direct methanol fuel cell. It is planned to use a conducting polymer – polypirol, PPY as a support material for Pd, Pt and Pd-Pt nanoparticles. Additionally, hybrid nanocomposite composed of PPY and Keggin or Dawson type heteropolyacids will be applied as the support material. Due to the application of bimetallic Pd-Pt system instead of commonly used Pt, a cost of production could be reduced. Moreover, an improvement of catalyst resistance to poisoning by carbon monoxide and methanol is expected with simultaneous preservation of metal centers activity. Nanocomposite of heteropolyacid and PPY should ensure electron and proton transfer. Furthermore, strong electron interactions caused by the presence of a conducting polymer, should lead to the modification of electron properties of metallic nanoparticles.

Studies undertaken in 2012 concerned palladium catalysts synthesis and characterization of their physicochemical properties as well as investigation of their electrocatalytic activity towards oxygen reduction reaction, ORR. In order to obtain Pd nanoparticles of well defined properties, they were synthesized using water-in-oil microemulsion method, based on the metal particles formation in “water droplets”. This favors the formation of small metal crystallites with a narrow size distribution. Using this technique, palladium particles of 5-8 nm in size were prepared and subsequently immobilized in PPY matrix. This conducing polymer was synthesized by the oxidative polymerization with ammonium peroxydisulfate in aqueous acidic media. Catalysts with various palladium loadings, from 2 to 20 % (w/w) were investigated. They were characterized by different methods, such as BET, XRD, XPS, IR and SEM. Electrocatalytic activity of the prepared materials towards ORR was investigated in 0.5M H_2SO_4 using rotating ring disc electrode voltammetry and cyclic voltammetry techniques.

Analysis of the obtained results leads to the conclusion that electrocatalytic activity towards ORR was improved with increasing palladium loading. Simultaneously, electroreduction potential was shifted to more positive values. However, this behavior was observed only up to the optimal metal loading which was found to be ca. 10% (w/w). With higher palladium loadings, there was no further increase of activity. The observed electroactivity of Pd/PPY catalysts was influenced by various effects, such as: palladium particles aggregation (proved by microscopic studies) and their penetration into polymer matrix (XPS studies). Moreover, increasing palladium loading led to a higher selectivity to water – a desired product of ORR.

Although conducted studies were fundamental, some new effects were explored (i.e. metal particle dispertion effect and metal loading effect). This could contribute to a better understanding of factors responsible for catalysts activity and their deactivation in oxygen reduction reaction. Consequently, it could be expected that obtained results would influence practical applications of the investigated systems in fuel cells.

Functionalization of the polymer films as a tool for attainment of the novel materials of broad utility spectrum

"Sonata" research project NCN UMO-2011/01/D/ST5/04913 [2011-2014]
(project leader: Marta Kolasińska-Sojka PhD)

The scientific goal of the project is the functionalization of polymer films by determining the formation mechanism of multilayer films and to investigate the impact of the hybrid structure and surface properties of nanocomposites on their functionality and application in the field of modern materials with complex structure. Nanocomposites are obtained by the sequential adsorption of oppositely charged polyelectrolytes and/or nanoparticles or liposomes from their solutions. Nanoparticles used are hydrophilic nanoparticles of gold and silver and hydrophobic quantum dots. Quantum dots show broad absorption band while their fluorescence emission band is narrower with much higher stability than for conventional fluorescent dyes. As they are much more stable in hydrophobic solutions there is a need to embed them into amphiphilic structure (as lipid vesicles) to enable their incorporation into hydrophilic coatings. Moreover, such strategy allows one to eliminate the cytotoxicity of quantum dots in the composites used as biomaterials.

Our studies were focused on the characterization of polyelectrolyte films made from biocompatible components (PLL/PGA) and comparison of obtained results with similar ones, done for multilayers built from model, synthetic polyelectrolytes (PAH/PSS, PDADMAC/PSS). It was observed that in the case of PLL/PGA films, one could select proper conditions (i.e. pH of the polyelectrolyte solutions), that the resulting structures show exponential growth in both the thickness and weight. Additional electrochemical studies of permeability allowed to find that although such multilayers are much thicker, there is no decrease of selected electroactive agents' diffusion through films' volume, which proves their "porous" structure. One should keep it in mind when designing the polyelectrolyte capsules that can be used for the controlled release of active agents.

Another part of studies was focused on the optimalisation of conditions needed to obtain lipid bilayer on the surface of polyelectrolyte films by fusion of lipid vesicles. All these studies were done using a quartz crystal microbalance. One observed the fusion of lipids used (SOPC: SOPS) and formation of lipid bilayer under certain restrictions, such as the concentration of vesicles used cannot be higher than 0.05 mg/ml and the temperature used should be kept constant, above the phase transition temperature of the selected lipids. Preliminary studies on the incorporation of hydrophobic quantum dots in nonpolar parts of the vesicles were done. The presence of quantum dots in the vesicles was confirmed by recording the emission spectra with the fluorometer. The current work focuses on optimalization of the bilayer formation process from such modified vesicles, because they tend to deposit on the surface of polyelectrolyte films without the fusion, i.e., as vesicles.

In addition, optimalization of the conditions for the formation of nanocomposite films of selected polycations and negatively charged nanoparticles of gold and silver was performed. In the cases studied one observed linear increase of adsorbed mass with increasing number of layers of polycations and nanoparticles used.

Conformational changes of the pyranose rings: computer simulations

"Sonata" research project NCN UMO-2011/03/D/ST4/01230 [2012-2015]
(project leader: Wojciech Płaziński PhD)

The study was focused on the dynamics and thermodynamics of the conformational changes ($^1C_4$ chair ↔ $^4C_1$ chair) in molecules of the selected carbohydrates consisting of the six-membered pyranose rings. This type of conformational change (ring puckering) is especially important in many physical and glycobiological processes but, due to the fact that they can be observed in relatively long (microseconds) timescales, it is hard to study them by using standard experimental and theoretical methods.

The standard molecular dynamics (MD) methods is not an effective method in this case, due to the long time required to observe even single event of conformational change (microseconds). In order to collect sufficiently large amount of data, we combined the MD technique with the *Transition Path Sampling* (TPS) method. Furthermore, the parallel tempering (replica-exchange) molecular dynamics approach was used to identify the puckering-related free energy profiles.

The free energy profiles corresponding to the selected carbohydrates (e.g. α- and β-D-glucose, α- and β-D-idose, α- and β-D-talose, α- and β-D-altrose) were obtained. The $^4C_1$ chair is the most stable conformation in nearly all cases except of α-D-idose. The algorithms of the TPS method were modified to tackle the issue of carbohydrate puckering (e.g. the so-called shooting point bias algorithm was introduced).

The obtained results contribute to the understanding of mechanisms governing the conformational changes in carbohydrate rings. Additionally, the developed algorithms may be used to study other conformational changes in related systems.

Targeted drug delivery systems - synthesis and functionalization of nanocarriers

"Sonata" research project NCN 2011/03/D/ST5/05635 [2012-2017]
(project leader: Krzysztof Szczepanowicz PhD)

The nanocapsules can be used in specific drug delivery systems as they can penetrate the cell membrane. Moreover, they can be functionalized to achieve “intelligent targeting”, i.e. delivery to the specific cells or organs. It would allow minimizing one of the main drawbacks of currently used pharmacological formulations that is lack of selectivity, therefore, it should eliminate side effects of applied therapeutics due to elimination of their toxic effects in the whole body.

The main aim of this project is the development of scientific background and elaboration of the technique of therapeutic agents incorporation inside biocompatible nanocapsules with functionalized shells for targeted drug delivery. That aim will be achieved in a few fundamental steps. First of them will be development of the method for encapsulation of active components followed by capsule functionalization for targeted drug delivery in order to achieve “intelligent targeting”, i.e. delivery to the specific cells or organs. Final step will be biological tests: cytotoxicity and verification of selective action of prepared nanocarriers with model cells. The work is carried out simultaneously in two centers which possess necessary facilities in this type of study: Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences and the Department of Biochemistry, Biophysics and Biotechnology, Jagiellonian University .

In 2012, we focused on the preparation of nanocarriers containing new anticancer agents (Taxol, Dpm44T). Nanocapsules were obtained by method developed previously in our lab, i.e., direct encapsulation of emulsion droplets in the polyelectrolyte shells. Emulsion containing active substance stabilized by AOT/Polycation interfacial complex with an average droplet size of 100 nm were obtained, then such droplets were encapsulated in a polyelectrolyte shell using layer-by-layer technique and saturation method. Figure 1 shows the average size of nanocapsules with 5 bilayers of PLL / PGA.

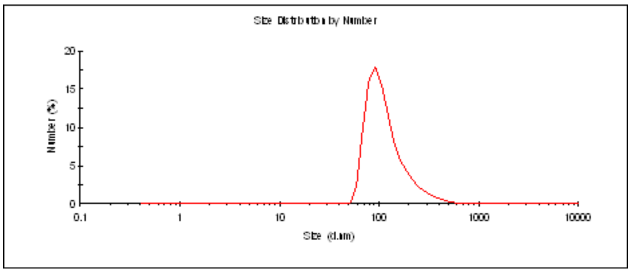


Figure 1. Size distribution of the polyelectrolytes nanocapsules AOT(PLL/PGA)$_5$ containing Dpm44T

"Opus" Research Projects
of the National Science Centre

Mechanism of damage of panel paintings taking into account growth ring structure of wood and real word climate fluctuations

"Opus" research project NCN UMO-2001/01/B/HS2/02586 [2011-2014]
(project leader: Łukasz Bratasz PhD)

Uncontrolled variations of temperature and relative humidity are principal hazards to the preservation of polychrome wood as they induce stresses in the multilayer structure of wood, glue, gesso and paint layer and lead to physical damage of these materials. The project provides next step in establishing with precision the allowable fluctuations of air parameters, undertaking wide research on the fatigue phenomenon in the polychrome layers on wood, that is, damage resulting from large number of strain cycles in the material even under the yield point.

Preliminary investigations of the fatigue processes produced fatigue curves for the polychrome layer on wood, that is, relationships between the strain leading to the first crack on the polychrome layer and the number of cycles causing cracking at that strain. Then, computer modelling was used to assess magnitude of relative humidity variations causing the critical strain levels. The described, pioneering investigations have demonstrated the key importance of the fatigue processes in the damage occurrence in the polychrome layer on wood and pointed to the necessity of accepting a „dose" of strain cycles as a measure of the cumulative risk of damage. The research was limited, however, only to the first phase of the process and namely that of the formation of the first crack on homogenous undamaged polychrome layer. In fact, real historic polychrome layers are almost always cracked, and sometime show areas delaminated from the substrate. A frequent observation is a stabilisation of crack and delamination patterns induced by the impact of the same environment. The phenomenon is described as "adaptation" or "acclimatization" of objects to microclimatic conditions in which the objects are displayed.

During the first year of the project implementation we analysed the damage development in a polychrome layer subjected to a large number of strain cycles until the "equilibrium" of the damage pattern corresponding to the acclimatization of the object to a given magnitude of the damaging impact was reached. The methodological approach used consisted in subjecting specimens of polychrome on wood to a large number of strain cycles induced mechanically with a parallel monitoring of crack and delamination development. The mechanically induced strains were imitating strains induced by climatic fluctuations. The damage monitoring was carried out by using Digital Speckle Pattern Interferometry which records small, even a few-nanometer strains of the objects.

Results of performed study indicate that both the rate of damage accumulation and the level of "stable damage pattern" achieved depend on the amplitude of repeated strain cycles. The measurements show that for the magnitude of strain equal 0.2 and 0.4 stabilization of the damage is observed after 75 000 and 170 000 strain cycles respectively. The consecutive, already started phase of the study, is focused on assessing impact of the specific order of different strain cycles on the rate of damage development. Determination of this relationship will constitute the basis for the algorithm simulating the damage development for artworks stored in museum conditions.

New development in technology of stable and biodegradable foam generation - for industrial and biomedical applications

"Opus" research project NCN 2011/01/B/ST8/03717 [2011-2014]
(project leader: Marcel Krzan PhD)

Foams are used in many technological applications, which include cleaning, water purification and waste treatment, ore flotation, drilling oil, fire fighting as well as production of food or ultra light nanocomposites. Aqueous foams are dispersions of gas bubbles in a surfactant solution. The main process taking places in wet foams is a free drainage. The liquid flows through the foam, driven by the gravity and capillarity. It is strictly linked to the foam stability, which is of great industrial relevance.

The project aims to develop the new technology of generating of bio-inspired, easy degradable polysaccharides and/or proteins based aqueous foams stabilized by micro-, nano- or colloidal dispersed particles. The particles as components should block the drainage of the liquid from the film layer enhancing foam stability, elasticity and yield stress. Such "biofoams" as easily decomposable can be an alternative to presently used foams based on the anionic surfactants. It could be applied as stabilizing factors in industry (in various kinds of froth flotation or in oil industry as the drilling fluids). Biofoams also could be used in pharmaceutical, cosmetic, personal care and biomedical applications, based on the unique and specific attributes of some natural polysaccharides and proteins. The chitosan "biofoam" could be used as unconventional agent for sterile dressing to prevent from infections and blisters during painless curing wounds.

It is generally accepted that the dynamic surface tension is a main determining factor for the biopolymer foamability, since the faster rate of decreasing s directly reflects a faster adsorption, i.e. better stabilization against coalescence. Therefore a series of dynamic surface tension measurements were conducted with the solutions of various selected proteins and polysaccharides. As expected, we observed that $\sigma(t)$ decreased faster with increasing the biopolymer concentration for each studied compound. We determined the values of the initial slopes of the curves, (i.e. $d\sigma/dt_{t=0}$), in order to characterize the rate of surface tension decrease when a new surface is created (as it is during the foaming process). Our measurements let us estimate the foamability potential of studied biopolymers.

The foamability and foam stability tests in the foam column for studied biopolymers solutions were also performed. Heights of the foam and solution columns were started to be measured automatically, immediately after the gas injection, and the profiles of the foam height decay were determined as a function of the time. The initial height of the foam describes the solution foamability, i.e. "ability" of the system to form foam, while the durability of the foam fraction characterizes its stability. The obtained results were in good agreement with the predictions basing on the data from dynamic surface tension.

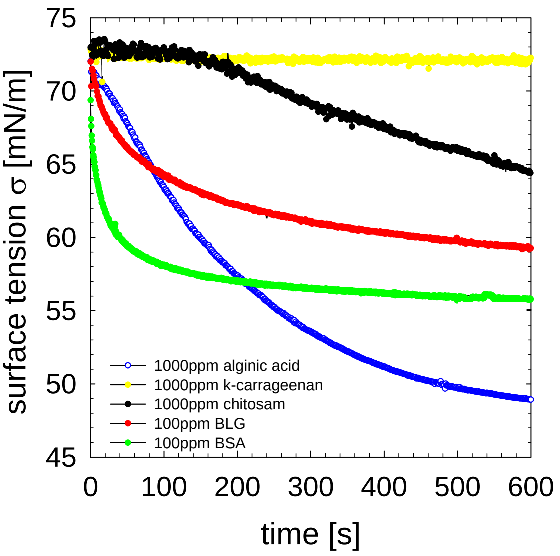


Figure 1. The dynamic surface tension variations for studied biopolymer solutions (at pH 5.8)

Influence of glycerol as non-toxic and biodegradable solvent on the mechanism of phenol oxidation

"Opus" research project NCN UMO-2011/03/B/ST5/01576 [2012-2015]
(project leader: Katarzyna Pamin PhD)

The oxidation of phenol to hydroquinone and catechol is an important reaction on the industrial scale and moreover it serves as a utilization method to convert phenol pollutants into more biodegradable molecules. Transition metal complexes like metalloporphyrins, metallosalens, metallophthalocyanines and polyoxometalates have received much attention in the field of catalytic oxidation and they all are good candidates for catalytic centers.

The present study has concerned the synthesis of anionic complexes like metalloporphyrins, metallophthalocyanines, metallosalens and polyoxometalates modified by transition metal ions. Anionic porphyrin TPPS and phthalocyanine PcS ligands were prepared by policondensation of appropriate monomer, followed by sulfonation and finally introduction of the suitable transition metal. Anionic salenS ligand was synthesized by condensation of sulfonated salicylaldehyde with ethylenediamine. Next, prepared ligand was metalated with manganese, cobalt or iron salts. Moreover, the series of manganese, cobalt or iron salts of dodecatungstophosphoric acid $M_xH_{3-x}PW_{12}O_{40}$ and dodecamolibdophosphoric acid $M_xH_{3-x}PMo_{12}O_{40}$, where x=1; 2; 3, were synthesized.

Synthesized samples will be characterized and applied as catalysts for oxidation of phenols with hydrogen peroxide in glycerol and glycerol-based solvents which are biodegradable media manufactured from renewable sources.

Properties of chromium(VI), molybdenum(VI) and tungsten(VI) monomeric oxo species on amorphous silica and Al-modified silica from periodic DFT simulations

"Opus" research project NCN 2011/03/B/ST4/01223 [2012-2014]
(project leader: Robert Gryboś PhD)

Project aims at description of properties of group 6 metal (Cr, Mo, W) di-oxo monomers grafted on the surface of amorphous silica.

Structure of monomers and probe molecules (needed in further parts of the project) was optimized, along with the structure of the amorphous silica surface. Also a full vibrational analysis for silica was performed. Three monomers were placed on the surface in such a way as to close a chain of 6 -O-SiO_2-O- units, and their geometry was optimized.

Energy of adsorption MO_3 (M=Cr, Mo, W) monomer from the gas phase onto the silica surface with transformation into MO_2 and liberation of water molecule depends on the metal. Chromium exhibits lowest adsorption energy (-2.21 eV), while tungsten – the highest (-3.36 eV). Adsorption energy for molybdenum is -3.08 eV.

Obtained results will be compared with adsorption of monomers on other sites on amorphous silica.

Physicochemical and catalytic properties of heteropolyacids modified with copper ions. Theoretical calculations vs. experiment

"Opus" research project NCN 2011/03/B/ST4/01216 [2012-2015]
(project leader: Assoc. Professor Renata Tokarz-Sobieraj)

The aim of the present project is the full description of theoretical and physicochemical properties of heteropolyacids HPA modified by transition metal ions by using the wide spectrum of experimental techniques as well as quantum-chemical calculations. Primary goal is to describe the properties of heteropolyacids modified by copper ion(s) (Cu-HPA) in which copper ion(s) occupy the position of central ion, addenda atom(s) or compensating cations.

The researches were started on molybdenum and tungsten heteropolyacids with Keggin structure $H_3PMe_{12}O_{40}$ (Me = Mo, W). The center of such structures is tetrahedron PO_4, surrounded by twelve MeO_6 octahedrons (addenda metals with six oxygen atoms, grouped in four Me_3O_{13} units).

In the reporting period a series of heteropoly compounds, containing Cu ions as compensating cations, have been synthesized and characterized. Materials with different composition of copper ions, with general formula $Cu_nH_{3-n}PW(Mo)Mo_{12}O_{40}$ (x = 0, 1, 2, 3) were chosen as particularly suitable for the synthesis. The materials were characterized with x-ray diffraction measurements (XRD) and thermal analysis (TG/DSC). XRD analysis confirmed that the synthesized solids possessed the expected structures, that changes for different Cu composition. The synthesized salts were single phase materilas. In addition the results show that the tungsten salts have a higher crystallinity than the molybdenum heteropolyacid copper salts.

The DFT calculations are carried out using both the cluster (local) and periodic (non-local) models. The cluster model is performed using the Turbomole code and will serve to describe the properties of the active centers. Periodic calculations are performed with the VASP code and are used to describe the secondary structure of heteropolyacids.

In the reporting period calculations with different types of functionals both gradient and hybrid have been tested. Started the calculations for (a) systems with copper ion in the position of the central ion with general formula $CuW(Mo)_{12}O_{40}^{n-}$, where n = 6, 7, for Cu^{2+} i Cu^{1+} respectively (b) systems with copper ions in position of addenda atom with formula $PCuW_{11}O_{39}^{5-}$.

Literature search of cooper salts of molybdenum and tungsten heteropolyacids have been performed. Literature data emphasize the high acidity of the copper salt of HPA. The cooper salts were tested in different type of catalytic reactions such as: dehydration of ethanol, oxidation of isobutene, isomerization of xylene, dehydration of 1-butanol.
Hypothetical mechanisms (that will be tested in calculations) of formation of acid centers in studied Cu-HPA cooper systems were proposed:

$$[Cu(H_2O)_m]^{n+} \leftrightarrow [Cu(H_2O)_{m-1}(OH)]^{(n-1)+} + H^+$$
$$Cu^{n+} + 1/2\ H_2 \rightarrow Cu^{(n-1)+} + H^+$$

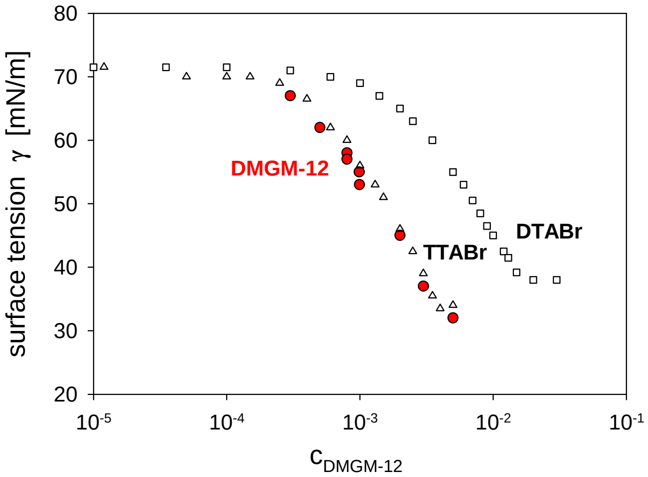
Mechanism of ionic surfactant - polyelectrolyte interactions in the process of formation of new generation of nanocarriers

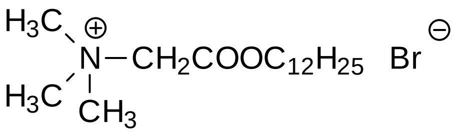
"Opus" research project NCN UMO-2011/03/B/ST4/01217 [2012-2016]
(project leader: Professor Piotr Warszyński)

The aim of the project is to develop the basic understanding and to elaborate theoretical description of the mechanism of formation of cationic surfactant/polyelectrolyte interfacial complexes depending on the molecular structure of surfactants and synthetic or natural polyelectrolytes. These complexes stabilize nano- or microemulsion drops and form the anchoring layer for build-up of polymer film of controlled thickness - the shell of nano- or microcapsules. For the purpose of this study a number of structural groups of simple and gemini – type quaternary ammonium salts (ester derivatives in combination with n-alkyl, and alkoxymethyl substituents) and also dicephalic type derivatives was designed.

Synthesis of the planed structures is based on the quaternization reaction of tertiary amines. In this reaction the substituted 2- aminoethyl esters and N,N – disubstituted derivatives of α-amino acids (glycine) reacted with alkyl bromides. Glycine mono derivative (DMGM-12) was obtained in the following stages. In a first step dodecyl alcohol reacted with chloroacetyl chloride in a dichloromethane solution to form corresponding dodecyl chloroacetate, which in the next step reacted with dimethylamine in diethyl ether to form N,N-dimethylglycine dodecyl ester hydrochloride. The third step involved neutralization of hydrochlorides with saturated aqueous solution of $NaHCO_3$ and extraction with diethyl ether. In the last step quaternization reaction of N,N-dimethylglycine dodecyl ester with methyl bromide in diethyl ether solution was conducted to form final product - n-dodecyl N,N,N-trimethyl-aminoacetate bromide- DMGM-12.

We investigated the interfacial behavior of aqueous solutions of synthesized surfactant DMGM-12. The dynamic and equilibrium surface tension of investigated solutions at free surface was determined. The surface tension isotherm of DMGM-12 is shown in the Figure 1 together with the isotherms of dodecyltrimethylammonium bromide - DTABr and tetradecyltrimethylammonium bromide - TTABr. As we can see adsorption isotherm of DMGM-12 coincides with adsorption isotherm of (TTABr). It means, that influence of ester group in the carboxylic chain on surfactant adsorption is similar as the CH_2 group influence.





$$\mathrm{(H_3C)_2\overset{\oplus}{N}(CH_3)-CH_2COOC_{12}H_{25}\;\;Br^{\ominus}}$$

Figure 1.Surface tension isotherm of DMGM-12 (full circles) together with the isotherms of DTABr (empty squares) and TTABr (empty triangles).

Structure and function of acireductone dioxygenases – experimental and computational studies

"Opus" research project NCN NZ1 04999 [2012-2017]
(project leader: Assoc. Professor Tomasz Borowski)

The purpose of this research project is to obtain the molecular structure and elucidate the mechanism of the catalytic reaction of acireductone dioxygenases – metalloenzymes encountered in almost all forms of life and responsible for one stage of a methionine salvage pathway. These enzymes are unique in that their product specificity and 3D structure depend on the identity of a metal ion bound in the active site. The ongoing research activities include expression and purification of the enzymes, kinetic studies, protein crystallization and molecular modeling. This research project commenced in the second half of 2012 and up to now the expression and purification procedure has been worked out.

"Preludium" Research Projects of the National Science Centre

Modeling of catalytic activity of biological nanostructures – non-haem iron dioxygenases

"Preludium" research project NCN DEC-2011/01/N/ST4/02330 [2011-2013]
(PhD student: Anna Wójcik MSc, supervisor: Assoc. Professor Tomasz Borowski)

The main goal of this project is to provide insight into the mechanisms of reaction catalyzed by representative iron dependent dioxygenases, in order to determine factors responsible for their high specificity. The studies, conducted with theoretical chemistry methods, focus on two related enzymes: 4-hydroxymandelate synthase (HMS) and 4-hydroxyphenylpyruvate dioxygenase (HPPD). Both enzymes catalyze transformation of the same organic substrate, and as currently believed, their catalytic reactions run through the same intermediates until the point they diverge giving products hydroxylated in different positions (Fig. 1). HMS and HPPD belong to a group of α-ketoacid dependent dioxygenases. They catalyze reactions involving molecular oxygen and 4-hydroxyphenylpyruvate (HPP) as substrates and leading to hydroxymandelate (HMA) and homogentisate (HG), respectively. HPPD is involved in tyrosine metabolism, as well as in biosynthesis of plastoquinones and tocopherols. HPPD inhibitors are used in treatment of genetic diseases associated with impaired degradation of tyrosine, because they prevent the accumulation of toxic metabolites. HMS is responsible for synthesis of hydroxyphenylglycine, which is needed in the synthesis of macrocyclic peptide antibiotics, including vancomycin.

Molecular Dynamics simulations (MD) for the complexes of HMS and HPPD with hydroxyphenylacetate, which is their last common intermediate, were carried out, based on the crystal structures (PDB code: 2R5V and 1CJX, respectively for HMS and HPPD). The purpose of the MD simulations is to derive reliable models for the enzyme-HPA complexes, whose structures are currently not known. Based on MD simulations extended models of active sites were constructed and used in quantum-mechanical (QM) calculations with Density Functional Theory (DFT) methods, involving hybrid exchange-correlation functional: B3LYP.

Results obtained from QM studies shed some new light on the mechanism of the reaction catalyzed by hydroxymandelate synthase (HMS). Detailed investigation carried out for HMS enzyme showed that Ser201, present in both enzymes, plays an important role in the specificity of the reactions catalyzed by HMS and HPPD. In the active sites of HMS and HPPD, Ser201 forms hydrogen bonds with substrate and other partners, with the latter influencing orientation of Ser201. Different conformations of Ser201 in HMS and HPPD catalytic sites enforce different substrate orientations and in consequence influence the reaction specificity of these enzymes. Studies for HPPD are in progress.

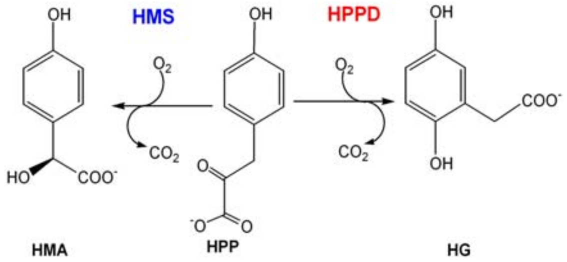


Figure 1. Reactions catalyzed by HMS and HPPD

The influence of base metal oxidation state in Au-Me-O/TiO_2 systems on the interaction between gold nanoparticles and the support

"Preludium" research project NCN 2011/03/N/ST5/04313 [2012-2013]
(PhD student: Jan Mizera MSc, supervisor: Assoc. Professor Ryszard Grabowski)

Since the discovery of the catalytic activity of gold nanoparticles being active in many reactions such as oxidation, hydrogenation and dehydrogenation there have been only sparse commercial application of these catalysts. The problem encumbering them is the relatively low time- on- stream stability caused by the reduction of the Au oxidation state and accumulation of carbonates and formates on the gold active sites. A route leading to obtaining a stable catalyst would be through changing the interaction between the gold nanoparticle and the support so that the catalyst would become resistant to the mentioned phenomena. The idea of the project is to modify an active catalyst (Au/TiO_2) with metal oxides having different reducibility and ability to mix with gold and TiO_2 (Fe, Ni, Cu, Ag) to recognize their influence on the properties of gold nanoparticles and broaden the view, which the gold catalysts are regarded.

The study made so far on the Au-Me-O/TiO_2 systems were supplemented by an FTIR study of the reference catalyst, then the activity examination in the propane oxidation reaction and also by carrying out a TPD –DTA and XRD examination of CuO/TiO_2 and FeO_X/TiO_2 catalysts in order to ascertain the possibility of formation of dopant metal titanates.

The FTIR (Fig. 1) showed that the CO molecule doesn't adsorb on the Au/TiO_2 reference catalyst. Thus the peaks observed on the doped catalysts origin from the presence of the dopants, which probably cause defects in the TiO_2 structure. Although the tallest peak at 2175 cm^{-1} refers to β–centres on Ti^{+4}, the results show that the adsorption on these centres occurs only when the catalyst is doped with another base metal.

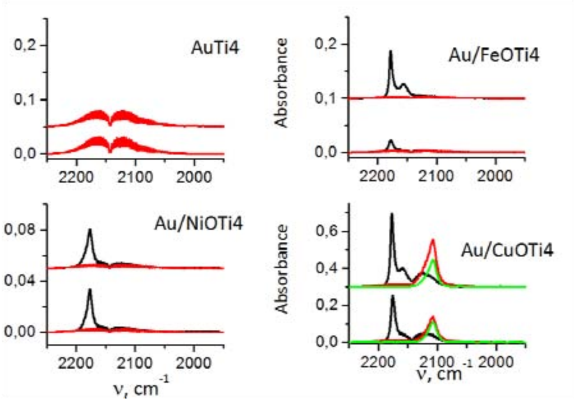


Fig. 1 FTIR investigation results

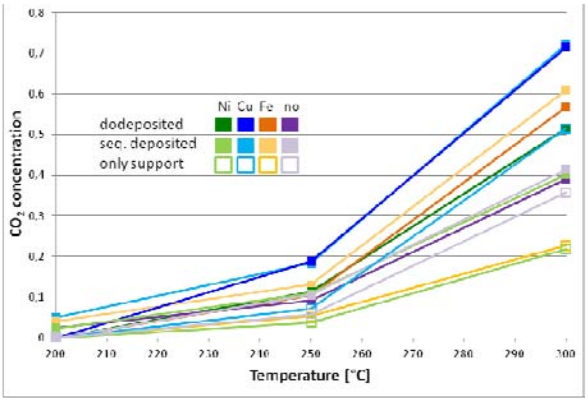


Fig. 2 Catalytic results of propane oxidation

The TPD–DTA and XRD investigations on CuO/TiO_2 and FeO_X/TiO_2 didn't enable to adjudicate the matter of titanate formation on the doped catalysts. The XRD measurements exhibited no presence of binary oxides in samples calcined at 400°C and the DTA investigation suggests only a possibility of the occurrence of an exothermic solid state reaction at 400–550°C.

The propane oxidation catalytic results (Fig.2) showed that the most active catalysts are doped with Cu, the Fe- doped are also quite active. The activity of the Ni-doped one depends on the preparation method; it's higher or equals that of the reference catalyst. The activity comparison of the catalysts (Au/MeO+TiO_2) and their supports (Au/MeO+TiO_2) showed that the most active gold nanoparticles are in the iron doped catalyst. The activity of the rest of the catalysts results from the high activity of their supports.

The hints given by this investigation allow a more precise determination of the influence of the dopant metals on the catalytic potential of the Au/TiO_2 system.

Synthesis of biocompatible nanocarriers for selected neuroprotective agents

"Preludium" research project NCN 2011/03/N/ST5/04808

(PhD student: Mariusz Piotrowski, supervisor: Professor Piotr Warszyński)

The aim of the project is to develop scientific methodology for the synthesis of biocompatible nanocarriers for neuroprotective drugs and to investigate the effect of encapsulated model drugs on neuronal cells.

Nanocarriers for neuroprotective agents were synthesized according to the layer-by-layer (LbL) technique, applied for the adsorption of various polyelectrolytes (e.g. PLL – poly(L-lysine hydrobromide), PGA – poly(L-glutamic acid) sodium salt) on the emulsion core (e.g. IPM – isopropyl myristate). Nanoemulsions were stabilized by polyelectrolyte - surfactant (e.g. AOT – docusate sodium salt) complexes that exhibit suitable surface properties. Nanocapsules were characterized for particle size and zeta potential. The size distribution (hydrodynamic diameter) of nanocapsules was evaluated by DLS (Dynamic Light Scattering). The zeta potential was measured using LDA (Laser Doppler Electrophoresis). The example of the results of physicochemical characterization of IPM/AOT/(PLL/PGA)$_n$ nanocapsules is presented in Figure 1. The average size of synthesized nanocapsules measured was ~80nm (n=1) and was increasing with the number of adsorbed layers to ~100nm (n=10) (Fig. 1a). The observed layer to layer variations of zeta potential provide evidence for formation of consecutive layers (Fig. 1b). Zeta potential values ranging from below ~-30mV for the polyanion layers to above ~30mV for the polycation layers indicate electrostatic stabilization of the nanocapsules suspension providing their long-term stability.

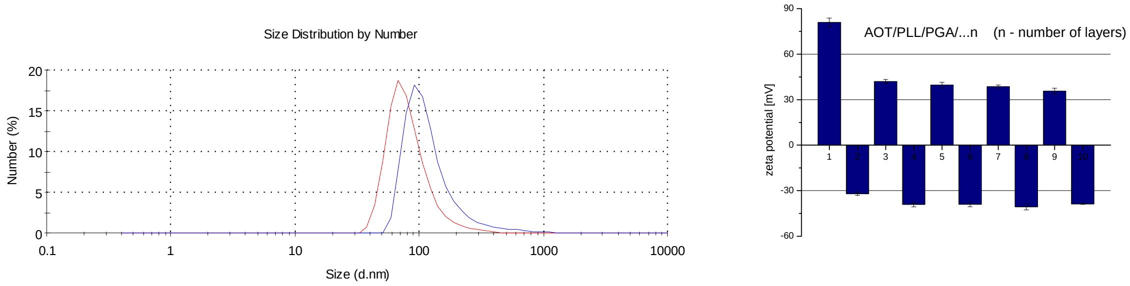


Figure 1 a) Size distribution of IPM/AOT/(PLL/PGA/…n) (n=1, n=10) nanocapsules; b) Layer-to-layer variations of zeta potential of IPM/AOT/(PLL/PGA/…n) (n=1,…,10) nanocapsules.

Surface of nanocarriers will be further modified for maximum biocompatibility (e.g. through the use of copolymers of biocompatible polyelectrolyte-polyethylene glycol). Additionally, nanocapsules will be visualized using the scanning electron microscopy technique (SEM). Inside the cores of nanocapsules selected inhibitors of intracellular biochemical cascades leading to neuronal cell death (e.g. caspase or calpain inhibitors) will be encapsulated. Evaluation of the effectiveness of nanoencapsulated active substances, preceded by cytotoxicity tests of empty capsules will be carried out on human neuroblastoma SH-SY5Y cells. The degree of damage and neuroprotection will be assessed using biochemical and morphological tests (MTT, LDH, etc.). The data will be analyzed using analysis of variance (ANOVA) to demonstrate the statistical significance.

"Iuventus Plus" Programme Research Projects of the Ministry of Science and Higher Education

The selected aspects of interactions between α-L-guluronic acid, β-D-mannuronic acid and bivalent metal ions

"Iuventus Plus" research project MNiSW IP IP2011 042471 [2012-2013]
(project leader: Wojciech Płaziński PhD)

The main purpose of the study was to investigate the structural and energetic aspects of calcium ions interactions with α-L-guluronic and β-D-mannuronic acids (in their anionic forms). Study included the elucidation of the structures of the ion-uronate complexes and the estimation of the free energy profiles characterizing their stability.

The investigation was performed by using the molecular dynamics (MD) method, according to the QM/MM (quantum mechanics/molecular mechanics) protocol which means that part of the system (e.g. the uronate molecule and the calcium ion) are modeled with the accuracy of quantum mechanics while the remaining part with that of classical biomolecular force fields. This allow for increasing the accuracy of computations of the crucial part of the system with simultaneous considering the presence of water environment. Up to now the following tasks were completed:
(i) Performing the QM/MD simulations of the systems containing the α-L-guluronate/calcium ion and β-D-mannuronate/calcium ion pairs (~20 ps).
(ii) Designing and performing the Umbrella Sampling protocol for recovering the free energy profiles associated with the process of association/dissociation of ion to/from α-L-guluronate poly(α-L-guluronate) according to the so-called egg-box model.

The results allowed for: (i) finding out the preferential pattern of calcium ion coordination (bidentate binding involving two oxygen atoms of carboxyl moiety); (ii) the positive verification of the structural model of calcium alginate obtained during the previous study and developed by using the classical, biomolecular force fields.

As there exist numerous hindrances concerning the experimental studies (as well as the data interpretation) of the basic features related to the uronate-metal on complexes, our theoretical data are the significant contribution to the knowledge about the studied systems.

A new method of silver sol synthesis and mechanism of colloidal particles interaction with heterogeneous surfaces determined by electrokinetic phenomena and AFM, fluorescent microscopy and QCM-D techniques

"Iuventus Plus" research project MNiSW IP2011 0353 71 [2012-2014]
(project leader: Aneta Michna PhD)

The mechanism of colloidal particles interactions with surfaces is important for many natural and practical applications because such interactions lead to adsorption, deposition and adhesion processes. However, the mechanism of colloidal particle interactions, as well as the kinetics of particle deposition on solid/ liquid interfaces were not yet fully understood.

The main goals of the project were: to synthesize the monodisperse silver sol without using any toxic reagents and additional stabilizers, to purify the obtained silver sol, and then to understand and develop the aspects of mechanism of silver nanoparticles and fluorescent latexes deposition at solid/ liquid interfaces. Finally, the effective method of nanoparticle detection at heterogeneous surfaces (mica covered by different amounts of polyelectrolyte) will be obtained.

In 2012, a green method was developed for the synthesis of silver nanoparticles by using modified Tollens procedure. A sol was obtained via the reduction of silver nitrate using glucose as reducing agent. After the synthesis the sol was purified using stirred filtration cell. The silver suspension was thoroughly characterized in the bulk. Bulk characteristics of silver suspension involved the extinction spectra, diffusion coefficient (hydrodynamic diameter), and electrophoretic mobility (zeta potential) measurements determined by UV-Vis spectroscopy, dynamic light scattering (DLS) and laser Doppler velocimetry (LDV) techniques, respectively.

Properties of poly(diallyldimethylammonium chloride) (PDADMAC), a strong cationic polyelectrolyte, having the molecular weight of 160 kDa as well as commercial fluorescent latex particles were also characterized by using DLS and LDV methods.

The obtained sol showed a visible excitation band near 434 nm, attributed to the surface plasmon excitation of silver nanoparticles. The average hydrodynamic diameter of silver particles was 70 nm, which was independent of ionic strength (10^{-5}-$5x10^{-3}$ M) and pH (3-9). Furthermore, the electrophoretic mobility of metal particles attained the value of -3.3 μm cm/V s for ionic strength range (10^{-5}-10^{-2} M) and pH 3-9.

However, the electrophoretic mobility of PDADMAC decreased with ionic strength from 6.5 for $I=10^{-3}$ M to 2 μm cm/V s for I=0.15 M. Its diffusion coefficient (measured by DLS) was 2.58 $x10^{-7}$ cm^2 s^{-1} for $I=10^{-3}$ M and 1.31 $x10^{-7}$ cm^2 s^{-1} for I=0.15 M. The decreased diffusion coefficients with increasing solution ionic strength suggested that in low ionic strength, the PDADMAC chain is rather extended. On the other hand, in higher ionic strength polyelectrolyte chain will be bent (circle shape).

Furthermore, it was stated that zeta potential of fluorescent latexes decreased with ionic strength (pH 5.5), assuming the value +45 mV for 10^{-4}M, +40 mV for10^{-3}M, +34,5 mV for 10^{-2}M, and +13,6 mV for 0.15 M. However, the average hydrodynamic diameter of latex particles was 250 nm, which was independent of ionic strength (10^{-4}-10^{-2}M), pH (5.8).

It was concluded that stable silver nanoparticles can by produced without using stabilizers and toxic reagents. Furthermore, the thorough bulk characteristics the silver nanoparticles, fluorescent latexes and polyelectrolyte can be applied to establish the optimal conditions to study the mechanism of particle deposition at heterogeneous surfaces.

"Mobility Plus" Programme Research Projects of the Ministry of Science and Higher Education

Factors determining stability of the liquid films formed at liquid/gas and liquid solid interfaces under dynamic conditions

"Mobility Plus"programme research project MNiSW [2011-2012]
(project leader: Jan Zawała PhD)

The project aim is to obtain new data which will be helpful in better understanding of mechanisms of stability of liquid films formed at various interfaces under dynamic conditions. In the reporting period the collisions of the bubble of radius R_b=0.78 mm with water/air interface were observed using high-speed camera. The experiment was carried out in the set-up elaborated at the University of Liege, allowing recording of bubble collisions with (i) resting water/air interface and (ii) vibrating interface, where the surface waves of control frequency and amplitude were induced. It was found that in distilled water, when the interface was at rest, the bubble bounced 4 times before rupture. Accordingly, the coalescence time (t_c), calculated form the moment of first collision to the moment of the bubble rupture, was equal 0.075 s. In contrary, at the vibrating interface, spectacular elongation of the t_c was observed. The bubble could bounce at the interface practically indefinitely. This means, that even in the distilled water, the t_c increased by several orders of magnitude (tc > 10s). Analysis of the recorded movies showed that the prolongation of the t_c was correlated with constant maximum deformation of the colliding bubble beneath the vibrating interface. The comparison between maximal value of the horizontal bubble diameter (d_h) during subsequent collisions of the bubble with interface at rest and vibrating interface is presented in Fig. 1. As can be observed, in the case of surface at rest, the d_h decreases with collision number. It was moreover the smallest during 4th, i.e. rupture, collision. For vibrating surface dh was practically constant and independent on collision number. The results obtained showed that the coalescence of the bubble during its collision with water/air interface takes place only, when the radius of the liquid film, i.e. the layer of liquid separating the bubble from the interface, is small enough to drain to the critical thickness of rupture during time of collision. When this condition is not fulfilled, the bubble bounce backward. The results obtained are additional evidence that radius of the liquid film, is parameter of crucial importance for film stability under dynamic conditions.

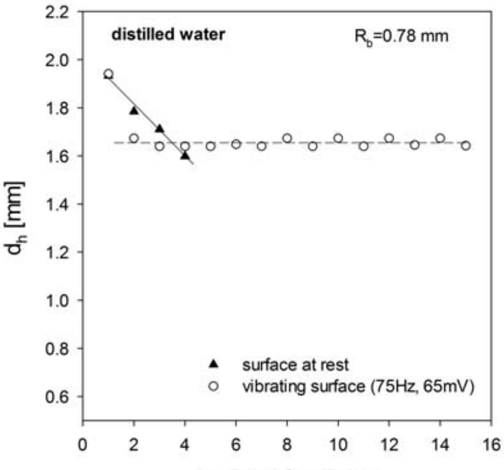


Figure 1. Bubble deformation as a function of collision number during bubble bouncing at resting and vibrating water/air interface

"Homing Plus" Programme Research Projects of the Polish Foundation for Science

Structure and electric properties of the composite films containing conductive nanoparticles

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

Scientific goal of the project was to determine the mechanism of nanocomposite multilayer films formation and to investigate the influence of the structure and surface properties of the nanocomposites on their functionality and applications in novel chemical sensors.

Nanocomposites were obtained by sequential adsorption technique of oppositely charged polyelectrolytes and/or Prussian blue nanoparticles from their solutions. The nanoparticles were chosen because of their electroactive nature and its ability to catalyze hydrogen peroxide decomposition. Thus, they can be used as an active agent in the chemical sensors for hydrogen peroxide detection.

Formation of nanocomposite films was studied using quartz crystal microbalance, surface topography of selected nanocomposites was obtained by AFM technique, their structure was studied by spectroscopic ellipsometry and, finally, electrochemical characterization of selected nanocomposites was done. Electrochemical technique used was cyclic voltammetry, basing on the reversible electrochemical redox reaction of Prussian blue (reduction to Prussian White).

It was found that both: the structure and electrochemical properties of nanocomposite films containing Prussian Blue depend on the first, anchoring PEI layer. In the case that it is adsorbed from a solution of lower pH, which ensures complete dissociation of PEI, the aggregation of embedded nanoparticles is not observed, which means that they maintain their size (c.a. 10nm in diamater) upon deposition, which enhances the current response. In addition, a linear increase of the oxidation and reduction current with the number of Prussian blue layers present in the multilayer film was observed. The effects of ionic strength of polycation solutions used during the deposition on the current characteristics of the hybrid films was studied in the range of 0.015 up to 1.5 M NaCl. It was found that the higher the ionic strength used during the film formation was, the bigger currents were generated by the target structure. The effect of the type of polyelectrolyte used was also determined. For that purpose films were made using three different polycations: PAH, PDADMAC or PAA. Same as in the case of PAH, linear dependence of generated currents on the number of layers of Prussian blue in the film was observed for both other polyelectrolytes. Current values were similar in all three cases, i.e., the differences in the studied parameters, resulting from the use of these polycations were less than the experimental scatter for any of the polycations.

Electrochemical studies in the presence of hydrogen peroxide were also carried out. The reaction of reduction of H_2O_2 to OH^- was observed as the most reliable in the system used for the detection of H_2O_2. In the investigated range of concentrations of H_2O_2, there was a linear decrease in reduction current with increasing concentration of H_2O_2 in the range from 0.5mM to 50mM of H_2O_2. This means that the investigated films can be used not only to detect the presence of hydrogen peroxide, but also to determine its amount, according to the calibration curve.

Performed studies prove that Prussian blue nanoparticles take part in the process of electrochemical decomposition of hydrogen peroxide which makes the studied films good candidates for electrochemical sensing.

"Pomost" Programme Research Projects of the Polish Foundation for Science

Selective hydrogenolysis of glycerol to glycols via acetol on heterogeneous metal/metal oxides based catalysts

"Pomost" programme research project FNP POMOST/2011-3/7 [2011-2014]
(project leader: Katarzyna Samson PhD)

During 2012 year the following tasks of this project have been started and accomplished, according to the project implementation schedule.

Task 1) The synthesis of the chromite supports with common formula $Me_{II}Cr_2O_4$, where Me = Cu, Co, Zn, Ni, Mg, Fe i Mn, possessing the normal spinel structure. The chromite spinels were obtained by application of citrate precursor method, using a stoichiometric quantity of solutions of metal salts and citric acid. All samples were drying at 130°C for 8 h and then pre-calcined at 400°C for 5 hours, in the stream of air. The final thermal treatment consisted of annealing the sample in air or hydrogen/argon mixture taken place at 600-900°C, during different time (5-20h), depending on the chromite. The confirmations of the spinel structure were done using X-ray diffraction analysis (from 73 to 100% of spinel phase, depending of the chromite). For all synthesized chromites BET and porosity measurements were done (4-60m^2/g) and reducibility by H_2TPR method was determined (the profiles of reducibility depend on the chromite). Thus obtained chromites will be the supports for copper active phase for catalysts using in hydrogenolysis of glycerol reaction.

Task 2) The next step in the preparation was the synthesis of the catalysts including copper active phase deposited on prepared earlier chromite supports. On the basis on the literature data, five concentrations of active copper phase: 5, 10, 15, 20 and 30wt% of CuO were deposited on each spinel support. The 45 obtained catalysts were prepared by impregnation method with aqueous solution of copper nitrate of the chromite supports, followed by drying (10h, 120°C) and calcinations under the flow of air (5h, 350°C).

Task 3) After the preparation step, the physicochemical characterization of prepared catalysts was started. For all the synthesized catalysts BET measurements were planned (determination of specific surface area and porosity). For three checked catalytic systems, including CuO (5, 10, 15, 20, 30w%) supported on Cu, Co and Zn spinels, both the specific surface area and porosity decrease with increase of amount of copper active phase. The preliminary measurements by XRD and H_2TPR methods have been accomplished for chosen systems (at the beginning for Cu/copper chromite prepared by citric method and Cu/copper chromite prepared by Adkins method).

Task 4) Design of experimental set-up for catalytic tests. In the last period the experimental set-up for catalytic measurement (gas chromatograph GC with purchased, dedicated capillary columns and “batch” reactor) was built. Then, the calibration procedure including: the identification of all liquid reagents of the hydrogenolysis of glycerol to glycols (methanol, ethanol, 1 and 2 propanols, acetol, ethylene glycol, 1.2 and 1.3 propandioles) and quantitative calibration (using the mixture of chemicals above-mentioned) was carried out. The best results obtained for DB-PS624 capillary column in HP gas chromatograph. The same procedure is planned for all gaseous products of tested reaction: methane, ethane, propane, butane and carbon oxides. For catalytic tests in hydrogenolysis reaction the “batch” reactor of 100 ml volume with mixing and pressure (for our reaction: 14 atm. of hydrogen) and temperature (for our reaction: 200°C) control was chosen.

Strategic Research Projects
of the National Centre for Research and Development

Catalysts for recombination of hydrogen and oxygen in nuclear reactors. Catalysts activity as a crucial parameter determining safety of recombiners performance

Strategic research project NCBiR SP/J/7/170071/12 2012-2015]
(project leader: Assoc. Professor Alicja Drelinkiewicz)

Research work started in October 2012. Present investigations concentrate on experimental variables determining activity of noble metals (Pd, Pt) supported catalysts in reaction of hydrogen and oxygen present in atmosphere in nuclear reactors. This reaction is a safety problem in nuclear reactors because recombination of hydrogen and oxygen is accomplished as a result of continuous evolving of hydrogen in various chemical and radiation processes. In commonly used procedure in the nuclear reactors, the passive autocatalytic recombiners (PAR) are applied in order to remove this hydrogen. They consist of catalyst, most frequently platinum, which is very well known to be active in reaction of hydrogen and oxygen producing water. Typically, in nuclear reactors several PAR reactors (30-40) are located. They are composed of number of parallel metallic plates which are coated with active metal (Pt or Pd) deposited onto alumina, known as “wash-coat” type catalysts. The name “passive” indicates that the PAR reactors must be active in hydrogen conversion without additional energy sources and without the personal action. They must be able to catalyse the conversion of hydrogen at room temperature and their activity is result of convective flow of hydrogen-containing air. In addition, catalyst in the PAR reactors must be resistant to humidity because of high water vapor level (up to 50 % vol) in the atmosphere in nuclear reactor.

Reaction of hydrogen and oxygen recombination ($H_2 + 0.5\ O_2 = H_2O$) catalysed by the PAR reactors is an highly exothermic process. The formation of one water molecule is accompanied by the 240 kJ energy. However, this reaction could also proceed in hydrogen – air mixture without the catalyst when the temperature of gas mixture is high, ca. 550^0C. This process presents explosion of hydrogen and could also proceed in PAR reactors, especially when the concentration of hydrogen in air is high and the catalysts of very high activity are located in the recombiners.

In the present project, the research work has been undertaken in order to evaluate experimental variables determining activity of noble metal catalysts (palladium, platinum) supported on various carriers, among them inorganic oxides or metallic plates. The catalysts with various Pd loading (0.5 – 4 wt %) supported on alumina and silica were prepared by means of commonly used impregnation method and a new method termed as “water-in-oil” microemulsion method. The latter procedure allows preparing the catalysts of well controlled size of metal nanoparticles and controlled surface concentration of metal on the support surface. The reaction between hydrogen and oxygen presents an explosion and as a result its rate is very high, difficult to be measured in the laboratory reactors. Introductory catalytic tests were carried out using various concentration of hydrogen in air (0.5 – 3 % vol.) and various flow rate of gas reagents in order to evaluate the conditions allowing comparison of activity for various catalysts.

Influence of surfactants on the cellulose hydrolysis

Strategic research project NCBiR SP//E/4/65786/10 [2011-2012]
Uniwersytet Warmińsko-Mazurski w Olsztynie
(project leaders: Professor Zbigniew Adamczyk, Małgorzata Nattich-Rak PhD)

The aim of this work was determining the influence of inorganic salts on the effectiveness of cellulose hydrolysis processes and the influence of surfactants on the dispersion degree of and size distribution of cellulose micro-crystals. This allows one to select an optimum composition of salts and surfactants promoting a high dispersion desirable from a practical point of view. The efficiency of hydrolysis and dispersion processes was determined by comparing the results using reference cellulose samples. In Fig. 1 typical size distributions of cellulose micro-crystals are shown obtained by laser diffractometry for samples treated by 2% solution of sodium dihydrophosphate (NaH_2PO_4) at various temperatures. The most significant changes in microcrystal size (relative to the reference sample) were observed for the temperature 180°C and the treatment time of 2h. A similar size distribution is also obtained for the temperature of 160°C, which is more efficient from a practical point of view because of lower energy consumption. It was also proven in this series of experiments that a twofold increase in the treatment time by NaH_2PO_4 (samples A1 i A5) results in a rather insignificant increase in the dispersion degree.

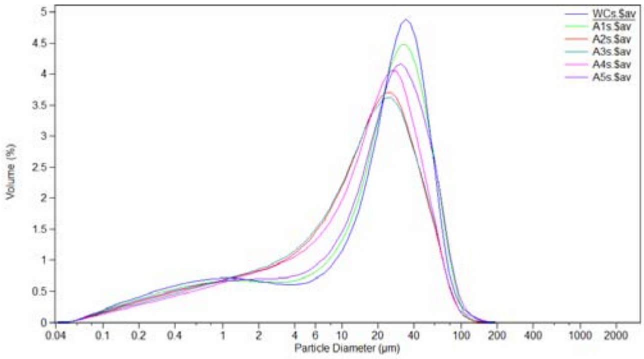


Figure 1. Size distributions of micro-crystalline cellulose determined by laser diffractometr Beckman Coulter for various temperatures: for WCs,T = 100°C for A, T = 120-200°C.

In the second series of experiments the influence of various surfactants (CTAB and SDS, Wellaxon and PEG) on the cellulose dispersion was investigated. Extensive experiments carried out using the laser diffractometer and scanning electron microscopy enabled one to demonstrate that best effects are obtained for the samples having the composition: 2% H_3PO_4+0.005% CTAB+10g cellulose (the average size of microcrystals after treatment was 20 µm) and 2% H_3PO_4+0.005% SDS+10g cellulose (the average size of microcrystals after treatment was 21 µm). In this way, a 30% reduction in the initial average size of cellulose micro-crystals was attained. The obtained results have practical significance since investigations of cellulose degradation in the presence of surfactants have not been carried out in the literature.

"Leader" Programme Research Projects of the National Centre for Research and Development

Regioselective oxidation of cholesterol derivatives with a novel molybdoenzyme – 25-OH cholesterol dehydrogenase

"Leader" programme research project NCBiR LIDER/33/147/L-3/11/NCBR/2012 [2012-2015]
(project leader: Maciej Szaleniec PhD)

Project has started in November 2012. The aim of the project is a development of method for regioselective hydroxylation of cholesterol derivatives at C25 carbon atom with a novel molybdoenzyme.

The first action within the Project was recruitment of the Team members, Agnieszka Rugor and Natalia Zawada and their training (in technology transfer a& project management skills – training organized by NCBiR and Innovation Brooker by Cracow University of Economics as well as in molecular biology)

The action conducted within task 1 “Cultivation of *S.denitrificans* bacterium” encompassed up-scaling of fermentation from lab scale to 16 l and than to 100 l in facilities of a group of prof Włodzimierz Grajek from Department of Biotechnology and Food Microbiology, Poznań University of Life Science. The fermentation yielded 382.5 g of fresh cell mass.

Within task 2 “Development of CholDH overexperssion system” Ms Natalia Zawada was trained in cultivation of genetically modified *E.coli* strain.

Within task 3 “Enzyme purification and optimization of purification protocol” the tender on anaerobic glove-box was carried out and successfully resolved. Moreover, a plan of interior glove-box equipment arrangement has been made.

EC 6th Framework Programme Research Projects

NANOREP II Surface modification of nano- and micron size plastic modifiers

EC 6th FP ERA-NET MNT project SPR NANOREP II [2008-2012]
(project leader: Professor Piotr Warszyński)

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 2012 was to select silanes for surface modification of silica nanoparticles to increase their compatibility with polymer coatings or thermoplastic. On the other hand to increase scratch resistance of plastic parts the nanoparticles should be build-in the structure of polymer. Therefore, the silanes containing chemical groups, which could form bonds with polymer during polymerization or curing stage were used for modification. 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 modified silica nanoparticles with the average size of 100 nm was mixed with monomers and then polymerization was performed. Good dispersion of AES modified nanoparticles in the resulting polymer was obtained. The scratch test performed by the project partners indicated some improvement of the scratch resistance of composite samples.

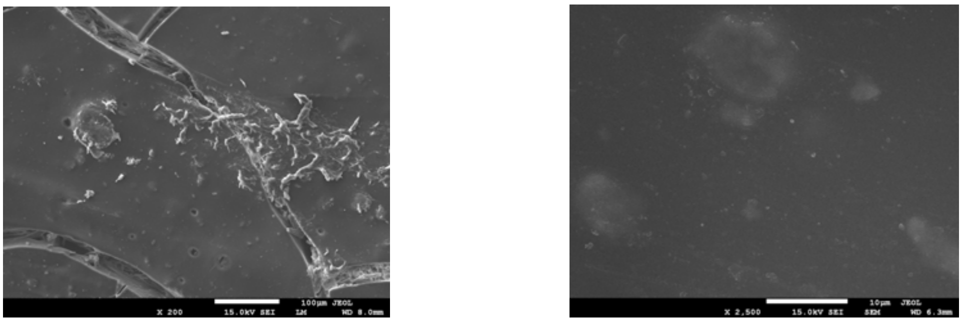


Figure 1. SEM image of samples of polyamide-6 with AES modified silica particles

EC 7th Framework Programme Research Projects

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

EC 7th FP NEXT-GTL project (IP) [2008-2013]
(project leader: Professor Małgorzata Witko)

The aim of the project is the development and optimization of catalysts for natural gas conversion. The stress is put on a number of possible processes, among which selective oxidation of methane to CH_3OH/DME on metal-carbene complexes and heteropolyacid hybrid systems, or methane aromatization on MoO_3/ZSM-5 are the most investigated. ICSC responsibility covers the synthesis of modified heteropolyacid components and theoretical description of electronic structure of the studied catalysts and reaction modeling.

In the reporting period a new series of heteropoly compounds, containing V as an element responsible for the enhancement of the redox functionality, has been synthesized and characterized. The materials were characterized with ICP-OES, XRD and TG/DSC. Materials of the $H_{3-x}(PMo_{12-x}V_x)O_{40}$ series (x=0, 1, 2) were chosen as particularly suitable for the synthesis of hybrid catalysts, in which they were supposed to act as an oxygenating component, responsible for the selective oxygen insertion.

Calculations were focused on description of oxidative properties of regular and modified tungsten heteropolyacids (HPW) with Keggin anion geometry. Catalytic properties of HPA as oxidative catalysts depend strongly on their ability to provide oxygen or hydroxyl group as a reactant. The results of calculations (creation of oxygen vacancies by removal of O/OH ions from structurally different positions) show that energy of vacancy formation is a function of defect location: lower values of energy for oxygen removal are obtained for the bridging oxygen (coordinating two addenda atoms) than for terminal oxygen atoms (bound with only one addenda atom). The energy needed for removal of OH group is always smaller than corresponding values for the removal of O ion. Moreover, the calculations show that modification of Keggin ion changes energies of vacancy formation. The obtained results show that the effect of the central atom is substantially smaller than the influence of the addenda atom. In addition, the process of oxygen activation on selected metal centers (Mn, Co, Fe, Cu, Zn) in modified HPA was investigated. The results of modeling leads to the conclusion that molecular oxygen does not adsorb on Cu and Zn ions. At Mn, Co and Fe the adsorption of O_2 molecule results in formation of superoxo species. In all cases upon adsorption the oxygen molecule becomes activated: together with elongation of O-O bond, a weakening of the bond (in comparison with isolated O_2 molecule) is observed.

Theoretical investigation into methane aromatization process on MoO_3/ZSM-5 were continued. The influence of the dispersion of the active phase of the catalyst (which in the initial phase is MoO_3, later reduced and then converted into molybdenum oxocarbide) on the first phase of methane aromatization, which is C-H bond activation, was examined. To study the influence of the size and chemical composition of the active phase, different models of molybdenum oxide and molybdenum (oxo)carbides, which might fit ZSM-5 crystal structure, were constructed. When methane activation occurs at molybdenum oxide, the C-H activation is preferred at the edge of the cluster built from multiple MoO_8 octahedra. When the process occurs in the center of the cluster, the energy needed to split C-H bond increases. Clusters consisting of two or three molybdenum octahedra are of optimum size for the process. When the active phase of the catalyst is changed from pure molybdenum oxide to molybdenum oxocarbide, the increasing content of carbon, especially substituting doubly coordinated oxygen atoms, lowers C-H activation barrier.

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

EC 7th FP NMP3-LA-2008-214261 MUST project (CP) [2008-2012]
(project leader: Professor Piotr Warszyński)

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 was 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 Institute of Catalysis and Surface Chemistry in 2012 year was the development of the nanocontainers containing anticorrosive components and the experimental verification of their protective ability.

The nano- and microcontainers were formed using various procedures as the polyelectrolyte layer-by-layer encapsulation of microemulsion cores or emulsion droplets formed by membrane emulsification. As the anticorrosive components 2-Mercaptobenzothiazole (MBT) and 2-methylbenzothiazole (BT) were used. The second component was also used as an oil phase. For capsules preparation 0.1 ml BT solutions with 0,34g/ml concentration of AOT was added to 200ml of aqueous PDADMAC solution during continuous mixing. The concentration of MBT in oil phase was 4%. The average drop size of obtained emulsion was around 100nm with polydispersity index 0,2. Zeta potential of emulsion was 68 ± 5mV. The formation of the multilayer polyelectrolyte shells on such prepared cores were performed by sequential adsorption of polyelectrolytes from their solutions without the intermediate rinsing step. The PDADMAC/PSS polycation/polyanion pair were chosen to form PE shells. Release of MBT from nanocapsules were determined using a dialysis technique in alkaline solution at pH 10 and 13. Analysis of the MBT content in release medium was performed by UV-VIS spectrometry in the wavelength range: 190 – 500 nm. Figure 1 shows the example of the MBT release profiles from the capsules with various thickness of polyelectrolyte shell. The electrochemical impedance spectroscopy measurement confirmed that in the presence of encapsulated MBT high corrosion resistance is maintained with time.

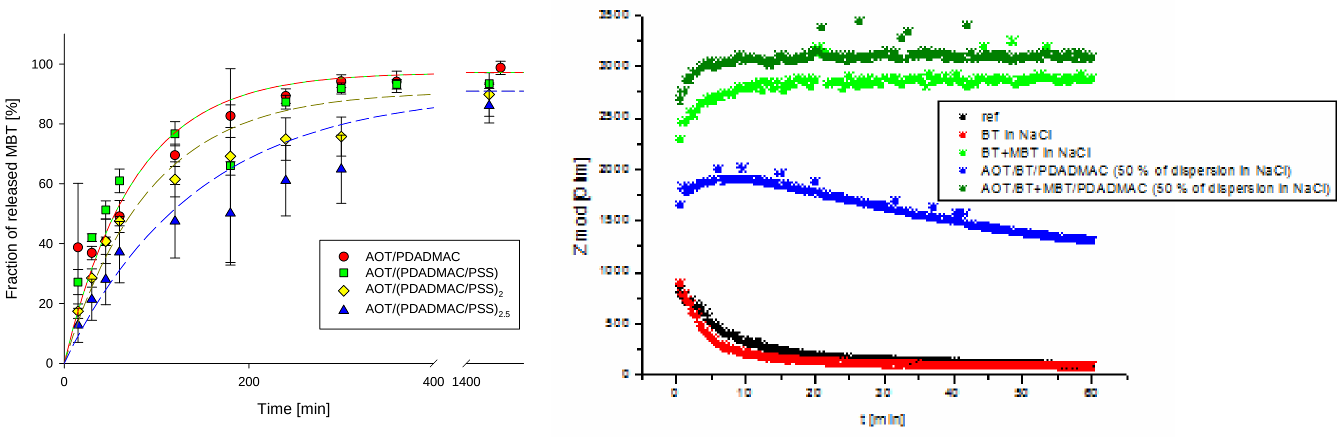


Figure 1. Left – The release profiles of MBT from nanocapsules with polyelectrolyte shells of various thickness. Right – the modulus of the impedance measured at the frequency of 1 Hz for AA2024 panel in the suspension of different concentrations containing capsules with the solution of MBT in BT.

ROCARE Roman Cements for Architectural Restoration to New High Standards

EC 7th FP 226898 ROCARE project (CP) [2009-2012]
(project leader: Professor Roman Kozłowski)

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 finished ROCARE project were scaling up of the production, laboratory studies to fully understand optimum conditions of mortar processing and handling, and broad dissemination measures.

Research elucidating the mechanism of shrinkage cracking of Roman cement pastes and mortars, which was the key research task of the institute, was finalized in the reporting period. The primary feature of this mechanism is the time-dependent stress development in mortars layers subjected to restrained shrinkage during drying. Such situation is experienced by render layers laid on the brick masonry and, after sufficiently long curing, exposed to a low relative humidity environment. Therefore, stress relaxation in the restrained Roman cement pastes and mortars during drying was investigated. No mortar failed, irrespectively of the curing time and related ultimate drying shrinkage. Reduction in the ultimate stress levels when compared to the stress corresponding to the mortar shrinkage in the absence of relaxation was measured. In contrast to the mortars, all pastes failed in the restrained shrinkage tests, which indicated that the pastes exhibited shrinkage exceeding elongations at failure even when slow stress development enhanced the deformability of the material.

The institute led Workpackage 3 “Dissemination and marketing”. During the reporting period two key dissemination activities were accomplished. The manual on best practice in the application of Roman cements was prepared and made accessible on the project website at http://www.rocare.eu/. The manual was designed to best advice and attract the end-user group. Its structure and content aims at a clear presentation of scientific information to the conservation practitioners. Parts 1-3 serve as general reference chapters on various detailed issues of Roman cement history, manufacturing, chemistry and application. Part 4 – the glossary on the deterioration patterns and restoration treatments – is particularly extensive and important as it sets up a common language describing the decay phenomena of Roman cement stuccoes and thus helps to avoid communication problems between scientists and conservation practitioners. Similarly part 5 – frequently asked questions - constitutes a tool for presenting research on physical and mechanical properties of Roman cement based materials in a way relevant to the practitioners.

The second key dissemination activity was international conference ‘Natural cements in European cultural heritage: history, properties, applications and conservation’ organized in Paris, jointly with ICOMOS France, the Laboratoire de Recherche des Monuments Historiques, and supported by the Ministère de la Culture et de la Communication. The conference focused on the natural cements in France with detailed presentation of two historic production centres in the regions of Rhône-Alpes and Marseille, and on the scientific and practical outcome of the ROCARE project. A bi-lingual English/French book of abstracts was published and all presentations were made available at the website of the ROCARE project.

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 F^3 project (IP) [2009-2013]
(project leader: Professor Piotr Warszyński)

The F³ Factory consortium believes that the EU chemical industry’s competitive position would be significantly enhanced if it could operate modular continuous plant (F³ Factory plant) for low to medium scale production rates. As such, the F³ 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 F³ Factory premise is that the operation of a modular, continuous F³ 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 F³ 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 F³ Factory mode of production therefore combines the best of these two conventional production modes.

Our aim in this project is validation of the F3 technology. Studies performed in our institute in 2012 year concerned the evaluation of adsorption properties of poly(acrylic acid) PAA in presence of impurities arising from polymerization process. The adsorption properties of PAA polymer were studied with a quartz crystal microbalance QCM (adsorption on gold surface) and on colloidal particles $CaCO_3$. We demonstrated that investigated impurities did not affect the final adsorption properties of the PAA polymer.

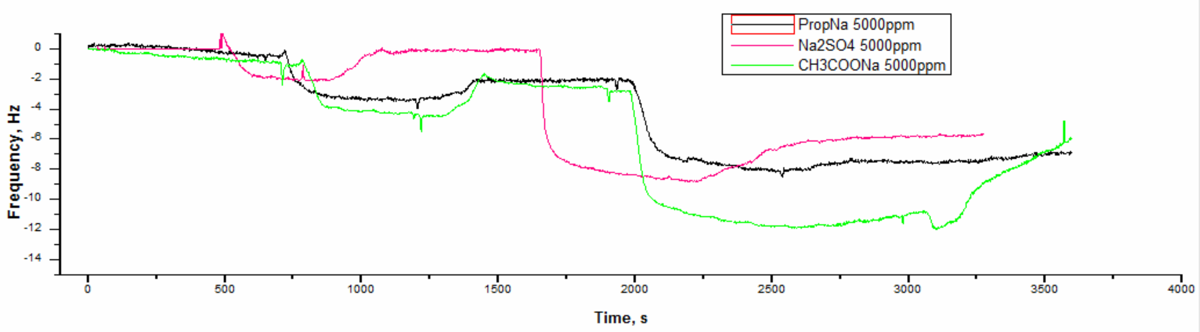


Figure 1. Measured changes in frequency of a quartz crystal during adsorption process of PAA in presence of selected impurities

NanoIES Nanotechnology Education for Industry and Society

EC FP7-NMP-2012-CSA-6 NanoIES project (CSA) [2012-2015]
(project leaders: Professor Józef Korecki, Dorota Rutkowska-Żbik PhD)

Nanotechnology is an emerging area with strong implications for European society and industry. It is a challenge for the education system to integrate this interdisciplinary and trans-sectorial subject into curricula shaped mostly along classical disciplines.

Therefore, the main goals of the just started NanoEIS project are

a) to make, based on a thorough assessment of employer needs, recommendations for curriculum contents as well as for best practice strategies to implement them;
b) evaluate how nanotechnology education has been integrated into secondary schools and universities;
c) develop novel teaching and assessment tools for modern nanotechnology education.

ICSC is mainly involved in assessment of EU education in nanotechnology at university level (with stress put on the third degree education) and teaching material development - for the latter task it acts as WP leader.

During the first two months of project duration, the legal issues related to the project were solved: Management Board and Advisory Board were elected and the Consortium Agreement was agreed and signed by all partners. The examination of national curriculum for nanotechnology – related issues is started.

EU COST Actions

Colloidal Aspects of Nanoscience for Innovative Processes and Materials

EU COST Action CM1101 [2012-2016]

(chair: Professor Piotr Warszyński, grant holder representative: Lilianna Szyk-Warszyńska PhD)

Colloid chemistry is a steadily growing field of immense importance. The enormous diversity of the colloidal processes involved in novel materials and their applications in both advanced technologies and everyday life cannot be overstated. There is a compelling need for exchange, coordination and cooperation in the European colloid community. The CM1101 COST Action combines coherently the outstanding European expertise in this field, including: theoretical modelling and experimental formation of functional and patterned interfaces; self-assembly of molecules and colloidal particles; synthesis and up-scaling of novel nano-colloidal and bio-colloidal materials; the kinetic and catalytic aspects of these novel materials; and their applications in chemical, pharmaceutical and food industries, as well as in nano-devices such as sensors, assays, photonics and bio-fuel cells. This includes many of the Grand Challenges in energy, health and environmental protection. The Action provides a platform for coordination of national programs and will stimulate academia-industry cooperation. Its main deliverables will be the increased networking in colloid chemistry through the organization of scientific events (conferences, workshops), Training Schools and STSMs. Through an extensive mobility program targeted to early-stage researchers, it will encourage their involvement in the research at the international level.

The activities of the Action are organized in the six Working Groups (WGs). They correspond to the six basic subdomains of colloid and interface chemistry: (i) interfaces; (ii) colloidal interactions; (iii) synthesis of colloids; (iv) kinetics of colloidal processes; (v) products; and (vi) devices. The subjects of Working Groups 1 and 2 are related to fundamental aspects of interfaces and colloids related to molecular processes at interfaces; self-assembly and multi-particle interactions in colloids and theoretical modelling of such systems and processes. Working Groups 3 and 4 is focused on chemical processes: synthesis of nanoparticles and other nano-colloidal materials, as well as on the respective kinetic and catalytic aspects. Finally, the activities of Working Groups 5 and 6 are dedicated to applications for development of colloid-based products and devices.

In 2012 several events were organized including the Working Group meetings: "*Discussion on Hydration Forces*" in Sofia, Bulgaria, "*Bubble and Drop Interfaces 2012"* in Krakow, Poland, "*Nano-biocolloidal materials and non-equilibrium self-assembly*" in Barcelona, Spain. The annual conference of the Action took place during the ECIS 2012 Conference in Malmoe, Sweden. CM1101 Training School on Interfaces was organized in Regensburg, while the 11th European Summer Training School on Scattering Methods Applied to Soft Condensed Matter was also partially supported by the Action. Additionally 10 STSM were organized. The official WEB page of the Action can be found at the address: http://projects.um.edu.mt/cm1101/.

Projects of EU Structural Funds Programmes

MPD Krakow Interdisciplinary PhD Project in Nanoscience and Advanced Nanostructures

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

Project "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, International PhD Projects Programme coordinated. The Project Coordinator is Professor 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 (Włochy), 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 Ostrawa, (Czech Republic), Institute of Physical Chemistry , Bulgarian Academy of Sciences (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. Currently the project enters into the final implementation phase which should bring in the next year five PhD theses, namely:

1. supervisor: Professor Ewa Brocławik, PhD student: Anna Wójcik MSc. Project title: Computer modeling of biological nanostructures. The student accomplished her research program at the University of Stockholm to April 30, 2012.
2. supervisor: Professor Piotr Warszyński, PhD student: Małgorzata Adamczak MSc. Project title: Surfactants, polyelectrolytes and nanoparticles as building blocks for surface nanostructures. The student is accomplishing her research program at SINTEF Material and Chemistry since September 1, 2012.
3. supervisor: Professor Kazimierz Małysa, PhD student: Dominik Kosior MSc. Project title: Nanostructures and stability of thin liquid layers. The student is accomplishing his research program in Germany since September 2012 to March 2013.
4. supervisor: Professor Wiesław Łasocha, PhD student: Katarzyna Luberda-Durnaś MSc. Project title: Hybrid organic-inorganic layered materials - precursors of semiconducting nanostructures. The student is preparing the thesis.
5. supervisor: Professor Józef Korecki, PhD student: Ewa Młyńczak MSc. Project title: Surface and interface properties of metal-oxide magnetic nanostructures. The PhD procedure was started on January 12, 2012. The student participated in synchrotron measurements at Swiss Light Source. The PhD thesis is planned in the form of publication collection. Two of them have been already published.

In 2012 the PhD students of MPD were co-authors of five publications in journals from the JCR list and presented 16 papers at the international and national conferences. The PhD programs are realized according to their schedules.

ISD Interdisciplinary PhD Studies "Advanced Materials for the New Technologies and Energy of the Future"

PO KL 4.1.1. ISD project [2009-2015]
(project leader: Assoc. Professor Renata Tokarz-Sobieraj)

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). In the Institute the following 17 individual PhD projects are running:

II year

- K. Kubiak MSc (supervisor: Professor Z. Adamczyk) The synthesis of new layered materials based on silver nanoparticles
- Ł. Kuterasiński MSc (supervisor: Assoc. Professor M. Derewiński) Hierarchic porous materials as the basis of the modern refinery processes

III year

- P. Batys MSc (supervisor: Assoc. Professor P. Weroński) Surface and transport properties of nanoparticle multilayers
- A. Dziedzicka MSc (supervisor: Professor B. Sulikowski) Modified zeolites as a catalyst for terpene transformation
- M. Grzesiak MSc (supervisor: Professor W. Łasocha) MOF`type structures: materials for catalysis and crystal engineering
- Ż. Kalemba-Jaje MSc (supervisor: Assoc. Professor A. Drelinkiewicz) Transesterification of triglycerides with methanol in presence of solid polymer acid catalysts
- A. Miłaczewska MSc (supervisor: Assoc. Professor T. Borowski) Research of structure and catalytic mechanism of activity of selected nonheme metalenzymes
- P. Niemiec MSc (supervisor: Assoc. Professor R. Tokarz-Sobieraj) Theoretical description of modified heteropolyacids
- A. Szymańska MSc (supervisor: Professor W. Łasocha) New polymetalates and peroxocomplexes as materials for applications in catalysis, medicine and industry
- D. Szepietowska MSc (supervisor: Professor B. Sulikowski) Selected heteropolyacids salts as a catalysts for transformation of terpenes
- M. Tatko MSc (supervisor: Assoc. Professor P. Nowak) New, highly conductive ionic conductors based on lantanide metal oxides for high-temperature solid oxide fuel cell

IV year

- J. Dziedzic MSc (supervisor: Professor P. Warszyński) Photocatalytic decomposition of organic compounds in water enhanced by encapsulated oxidants
- M. Krzak MSc (supervisor: Assoc. Professor P. Nowak) High-performance anticorrosive coatings prepared from composite material based on organic polymers

- M. Nosek MSc (supervisor: Assoc. Professor P. Weroński) Analysis of multilayer porous colloidal materials with controlled architecture
- M. Oćwieja MSc (supervisor: Professor Z. Adamczyk) Kinetics of silver particle adsorption on heterogeneous surfaces and morphology of silver monolayers
- K. Onik MSc (supervisor: Assoc. Professor M. Derewiński) Hierarchic materials based on zeolites precursor as the basis of the modern catalytic systems
- A. Pajor (supervisor: Professor P. Warszyński) Electroactive polyelectrolyte multilayer films with embedded nanoparticles

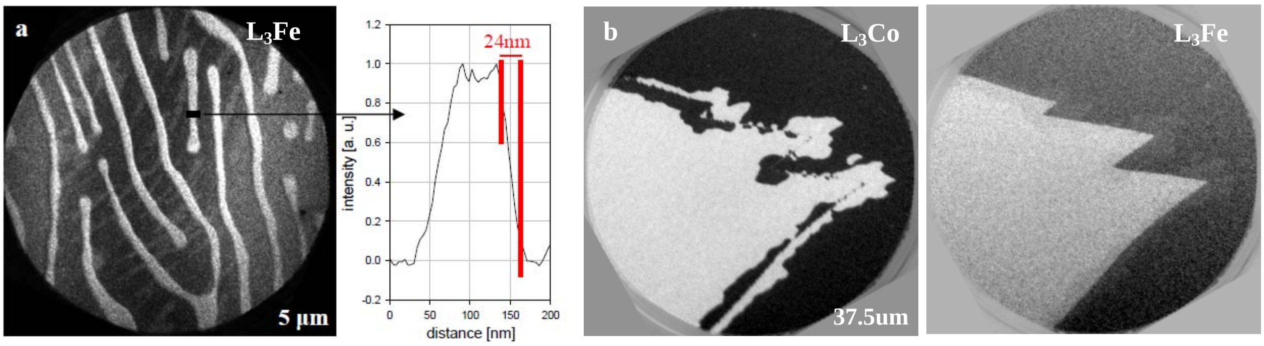
SPINLAB National Centre of Magnetic Nanostructures for Applications in Spin Electronics

PO IG .2. 2. SPINLAB project [2009-2012]
(project leader: Professor Józef Korecki)

The task was focused on adaptation for synchrotron requirements and performance tests with synchrotron radiation of the Spectroscopic Photoemission Electron Microscope (ELMITEC SPE-PEEM III), purchased in the frame of the SPINLAB project.

Optical and mechanical components essential for adaptation the microscope to synchrotron were purchased. The microscope was supplied with additional UHV chamber enabling *in situ* sample preparation and characterization, equipped with molecular beam epitaxy (MBE) system, quartz monitor, LEED-AES spectrometer, ion-gun and quadrupole mass spectrometer. Additionally, the imaging chamber was equipped with MBE evaporator for material deposition during imaging. The microscope was installed at Swiss Light Source at the NanoXAS beamline. Extensive microscope performance tests have been carried out under X-PEEM regime using all accessible modes of operation: imaging with chemical contrast (XAS-PEEM, XPS_PEEM), imaging with magnetic contrast (XMCD-PEEM, XMLD-PEEM) and micro-spectroscopies (uXAS, uXMCD, uXMLD, uXPS).

The test measurements (6-week beamtime) were carried out in a wide range of temperature (between ~100K - ~1200K) on a row of model samples, such as metal-oxide multilayers, patterned and self-organized nanostructures, magnetic and non-magnetic, ferromagnetic and antiferromagnetic, prepared *in situ* and outside of the UHV system. Typically, the images were collected with ~50 nm resolution. The best resolution value achieved during the tests was 24 nm (Fig. a). The images intensity in the absorption mode was high enough to observe near-surface processes in real time (with chemical and magnetic sensitivity). Good chemical and magnetic contrast was also observed for layers buried as deep as 5nm below the surface (Fig. b). It should be emphasized that not only ferromagnetic but also antiferromagnetic domains materials were also observed (using linear magnetism dichroism).



a) XAS-PEEM image collected at the L_3Fe edge of Fe islands prepared on W(110), and the intensity profile representing the best resolution achieved during the tests. b) XMCD-PEEM images collected at L_3Co and L_3Fe edges at the same place on the sample showing magnetic domains present in the 2nmCo/~3nmAu/20nmFe/W(110)layered system. The image taken at the L_3Fe edge originates from an iron layer buried ~5nm below the surface.

BIOTRANSFORMACJE Biotransformations for pharmaceutical and cosmetics industry

Task. 6. Biocatalytic methods of synthesis of chiral alcohols

PO IG 1.3.1 BIOTRANFORMACJE project [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 alkylaromatic alcohols: ethylbenzene dehydrogenase (EBDH) and phenylethanol dehydrogenase (PEDH). The first aim was to develop reactivity models using neural networks and QSAR methodology for both enzymatic systems. The second aim was to immobilize both enzymes and test them in process conditions.

For modeling of EBDH the already developed methodology was applied, that connects physicochemical descriptors of substrates with experimentally measured reaction rates by means of neural networks. The obtained models forecasted relative specific activity with 95% accuracy and was able to differentiate inhibitors from substrates.

In case of PEDH the alternative approach was used. Due to complex reaction system (biocatalysis in a whole cells, system with cofactor regeneration) the series of batch reactor experiments were conducted and conversion of different substrates was monitored with HPLC. The kinetics of conversion of app. 50 mM acetophenone and its 4-Br, 4-OCH$_3$, 4-F, 4-NO$_2$, 4-Cl, 4-Ph, 4-Et, 4-OH and 4-mesyl derivatives was collected and the neural model predicting conversion in time was established. The model used substrate characteristics (electronic and hydrophobic) as well as reactor parameters (conversion time, initial substrate concentration) as input values and allowed interpolation of conversion functions with 95% accuracy.

In order to obtain biological material for research and immobilization the cultivation of E.coli system and subsequent over-expression of PEDH was conducted in 200 l fermentor. The obtain material was purified and the covalent immobilization was conducted on supports obtained from the project partners. The immobilization on modified silica materials (SBA-S, MCF, MH) yielded materials with 30-50% of the initial activity. The materials were characterized by high stability to refrigerated storage and multiple use in short enzymatic tests. Moreover the modified granocel supports were also tested, but the obtained materials were of lower activity (14-35%). The best support, granocel modified with DEAE groups with dvinyl sulphone linker, allowed conversion of 5 subsequent 50 mM acetophenone reaction batches to be converted with 50% of the initial batch activity.

In case of EBDH the immobilization on silica materials was studied. The tests showed, that the reaction system is incompatible with materials functionalized with amine groups due to redox reaction with electron acceptor. Unfortunately the materials functionalized with glicydyl groups showed insufficient binding of the enzyme (trace activity). Therefore, the NH$_2$-silica materials were used for immobilization with surface oxidized with excess of ferrocenium tetrafluoroborate which resulted with biocatalysts 3 times more active with respect to that immobilized on untreated silica. In addition the factors stabilizing enzyme activity during immobilization, such as temperature, electrolytes (NaCl), presence of the product were tested.

The obtained results allowed identification of parameters influencing the conversion rate, which will help in planning of the reactions in a bigger scale (PEDH models) and will further elucidate mechanism of EBDH catalytic reaction. The reactions preformed with immobilized enzyme or whole-cell system allowed an scale-up and easy separation of pure chiral alcohols.

FUNANO Functional nano- and microparticles - synthesis and applications in innovative materials and technologies

POIG 1.1.2.FUNANO project [2009-2014]
(project leader: Professor Zbigniew Adamczyk)

Hematite, the most stable of iron oxides, is widely used as synthetic pigment in paints, ceramics and as an anti-corrosion agent. It has significance for catalysis in the Haber process, the Fischer-Tropsch synthesis, the desulfurization of natural gas, oxidation of alcohols, production of butadiene, etc. It is also used in photovoltaic cells (water splitting) and in processes of chlorophenol and azo dyes photodegradation. Many practical applications of hematite involve thin films deposited on various surfaces, which serve as gas, alcohol or humidity sensors, electrodes in lithium batteries, photo-anodes, etc. In this work hematite nanoparticles were synthesized according to the modified Matijević method based on the forced hydrolysis of ferric chloride in an acid solution. The average size of hematite particles (determined by AFM and dynamic light scattering) was 22 nm. The nanoparticle monolayers on mica were produced under diffusion-controlled transport from suspensions of various bulk concentration and ionic strength at pH 3.5, where the particles exhibited a positive zeta potential, opposite to the mica zeta potential. In Fig. 1 the kinetics of hematite particle deposition is shown. The particle coverage was determined *ex situ* using the AFM (full points) and SEM (hollow points) imaging. As can be seen, by varying the ionic strength, one can systematically adjust the maximum coverage of hematite monolayers within wide limits from 0.12 to 0.45 (for I = 3x10^{-2} M, NaCl). It should be noted that these values agree with theoretical predictions derived from the random sequential adsorption model (depicted by solid lines in Fig. 1). Hence, deposition of hematite nanoparticles at an ionic strength of 3x10^{-2} M creates the most favorable conditions for producing uniform monolayers of the highest coverage. This has a special significance because such monolayers exhibit a high positive charge (for pH < 9), thus they can be used as convenient supporting layers for catalytically active noble metal (Au, Ag, Pt) or oxide particles, usually negatively charged.

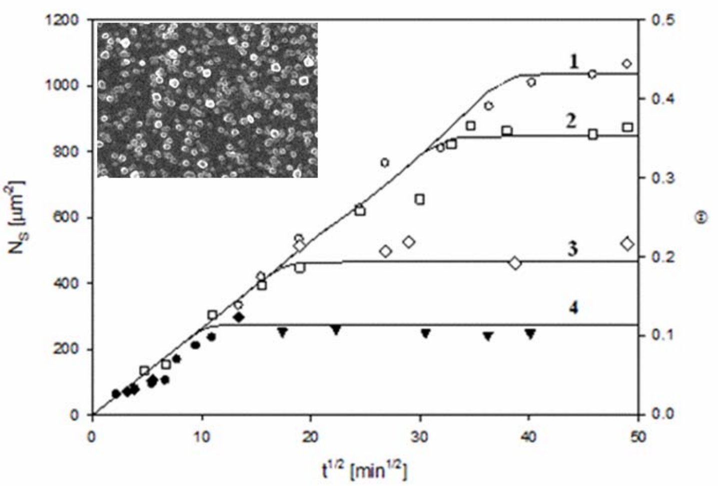


Figure 1. The kinetics of hematite particle deposition at mica determined for various ionic strengths using AFM (full points) and SEM (hollow points). Particle size 22 nm, deposition conditions: pH= 3.5, T = 293 K, c_b = 20 ppm. The points denote experimental results obtained for: 1) (●,○) I=3x10^{-2} M, 2) (□) I=10^{-2} M, 3) (♦,◊) I=10^{-3} M, 4) (▼) I=10^{-4} M. The solid lines denote the theoretical results calculated from the RSA model. The inset shows the SEM image of the hematite monolayer on mica.

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 project [2009-2013]
(project leader: Professor Ewa Serwicka-Bahranowska,
principal investigator: Tadeusz Machej PhD)

The 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 $[(M^{2+})_{1-x}(M^{3+})_x(OH)_2](A^{n-})_{x/n}\cdot m\,H_2O$, whose specific structure allows for uniform mixing of catalytically active elements at atomic level.

In the reported period the optimisation of the catalyst active phase composition and synthesis conditions was has been completed. 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. On the basis of the laboratory scale catalytic tests two catalyst formulae have been chosen for further testing in the pilot set-up. Next stage involved synthesis of large volumes of selected active phase formulations, in order to prepare four 50 kg charges of monolithic catalyst for industrial scale tests.

ISD Interdisciplinary PhD Studies MOLMED
Molecular sciences for medicine

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

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 performed in the year 2012:

According to the programme curriculum, series of lectures entitled “The experimental techniques in molecular sciences” and “Diseases of civilization” have started.

- in the second quarter of the year 5-day doctoral research workshop with invited lecturers was organized in Ochotnica Dolna;
- in the third quarter of the year the employees of four partnership units were invited to participate in the internship competition. A total of 4 individuals were selected to pursue 3 month postdoctoral training;
- in the fourth quarter of the year 20 members of faculty of partnership units started language course in English in order to improve their language skills.

PhD students conduct research work in the appropriate partnership unit/s, receive monthly fellowships, make purchases of materials and equipment necessary for their work. In addition, they participate in scientific conferences in Poland and abroad, where they present the results of their research in the form of oral and poster presentations. The progress of the project is supervised by the Programme Board consisting of 8 members – two representatives from each partnership unit.

Other International Research projects

Fe monolayers on W(110): adsorption and magnetism

Research project within the Polish-Austrian Scientific and Technological Cooperation [2009-2012]
(project leader: Professor Józef Korecki)

The tree-year project (funded over two years due to the maternity leave of the main Austrian project researcher) has been completed. Project aimed at the structural, electronic and magnetic properties of gas-phase adsorbates and iron nanostructures on a W(110) substrate studied by the hyperfine interaction spectroscopies.

The adsorption of the molecular oxygen on the Fe(110) surface was investigated by the classical surface methods such as: low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) and by the nuclear methods, namely conversion electron Mössbauer spectroscopy (CEMS) and nuclear resonance scattering of synchrotron radiation (NRS).

Several structures of the adsorbed oxygen were identified, both already reported in the literature and the new ones. The first structure, the (2x2) one, appears at the exposure of 0.4–1.2 Langmuirs (L) that results in the 0.25 oxygen coverage. Oxygen atoms are adsorbed at the so called long-bridge positions. The same LEED structure emerges occasionally under the residual gases adsorption. Further oxygen exposures (up to 5 L) caused the c(3x1) or the so called "split c(3x1)" structure. In fact, this structure corresponds to the big oblique surface unit cell with a complicated diffraction pattern coming from two mirror structural domains. The next structure, (3x2), that appeared at the oxygen exposure of approximately 10 L, resulting in the coverage of 0.66 ML, was not reported before. Finally, the onset of the oxide formation was recognized at about 100-200 L, when the symmetry of LEED images changed to the hexagonal one.

The electronic structure of the consecutive adsorption stages was studied by means of NRS at the beamline ID 18 at ESRF Grenoble. It was found that, for the (2x2) structure, the oxygen proximity reduces the surface electric field gradient, whereas there is no modification of the surface magnetic moments for the all initial oxygen adsorption stages. Meaningful changes of the NRS spectra were observed starting from the (3x2) structure, which was interpreted as the result of the electric charge transfer from iron to oxygen. Such a transfer indicates the onset of the strong chemical Fe-O bond formation, being a first stage of the oxidation.

In the frame of the project the reactivity of the Fe(110) surface and pseudomorhpic Fe monolayer on W(110) was compared. It was concluded that the first and second Fe layers present different reactivity and that the characteristic (2x2) structure shows up only on the second layer, while the only observed structure at the early adsorption stage on the Fe monolayer is (3x2).

The effects of the project are the date concerning the oxygen adsorption on the Fe(110) surface, Fe/W(110) monolayers and morphology and magnetic properties of ultrathin layers and nanostructures of Fe on W(110).

Visualizing the local reaction kinetics: from the mesoscopic to the nanoscale

Research project within the Polish-Austrian Scientific and Technological Cooperation [2012-2013]
(project leader: Professor Józef Korecki)

The project is aimed at studies of correlations between structure (in a wide sense), morphology and the course and kinetics of the surface reactions for model catalysts, which are metal and oxide nanostructures on single crystalline supports. The project result will be the new knowledge on the reactivity and reaction kinetics depending on the surface structure and orientation, morphology and chemical composition for selected model catalysts.

The project implementation depends on the funding from the National Science Centre under the Harmonia-project that was recently submitted.

Metal and oxide epitaxial nanostructures as seen by nuclear resonance scattering of synchrotron radiation

Research project within the Polish-French Scientific and Technological Cooperation Programme POLONIUM [2010-2012]
(project leader: Professor Józef Korecki)

The two-year project, aimed at application of the nuclear resonance scattering of synchrotron radiation (NRS) to studies of the electronic structure and dynamics of crystal lattice in metal and oxide epitaxial nanostructures, has been finalized. In cooperation with the team of the beamline ID 18 at ESRF Grenoble, following the 6th FP European Project DYNASYNC we have been studying nanostructures by the NRS technique under ultra high vacuum conditions.

The last phase of the project concerned the analysis of phonon spectra for epitaxial FeO films on Pt(111). Figure 1 presents phonon density of states (DOS) retrieved from the inelastic NRS measurements as a function the FeO thickness. In the whole thickness range the phonon spectra are distinctly different from the bulk FeO. The most characteristic DOS features are: (i) a sharp peak and a cut-off in the high energy part of the spectrum for the thinnest and thickest films, (ii) a clear correlation between the spectra broadening at intermediate thickness (6 ML – 10 ML), and magnetic properties that appear in the same thickness range, (iii) a phonon hardening at the thicknesses above the magnetic anomaly that is illustrated in Fig. 1 by the vertical dotted lines which visualize the shift of the main peak with increasing thickness and (iv) a remarkable increase of the phonon densities for the energy range E<10 meV for thinnest films (1 ML and 2 ML). An explanation for such a behaviour can be specific structure of the first and second FeO monolayer on Pt(111). A large misfit of the interatomic distances in the FeO(111) and Pt(111) surfaces and the resulting huge epitaxial stresses are reflected in considerable structural modifications.

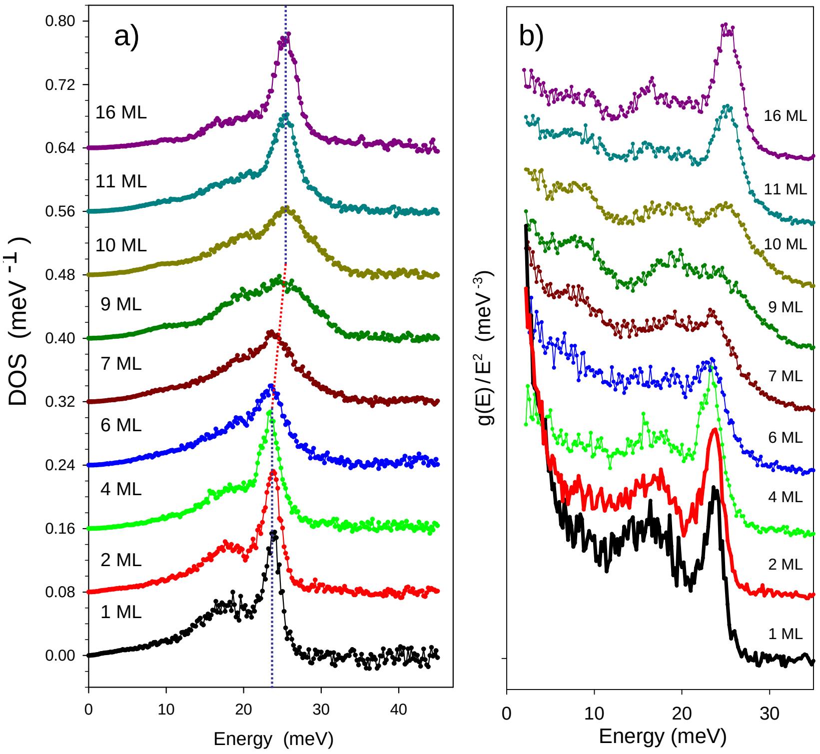


Figure 1. Normalized phonon density of states for FeO films on Pt(111) as a function of the film thickness (left) and reduced DOS'es, divided by energy square (right).

Projects of the Consortium "Coal Fuel Cells" under auspices of the Ministry of Economy

Molten Carbonate Electrolyte Direct Carbon Fuel Cell (DC-MCFC)

Research project of the Consortium "Coal Fuel Cells" under auspices of the Ministry of Economy [2012-2013]
(project leader: Grzegorz Mordarski PhD)

Direct carbon fuel cell (DCFC) converts chemical energy of solid carbon fuel to electricity directly with a high efficiency. Contrary to a hydrogen fuel cell, DCFC uses solid carbon directly as a fuel. That brings several advantages. The theoretical thermal efficiency of DCFC is slightly over 100% due to the entropy change of the cell reaction: $C + O_2 = CO_2$ which is slightly positive.

Comparing to hydrogen, carbon is more convenient for storage and transportation and presents lower hazard of explosion. Almost all the carbon-rich materials, such as coal, natural gas, petroleum, and biomass can be easily converted or purified to the fuel of DCFC.

Depending on electrolyte, DCFCs are classified into several categories. One of them is DCFC with electrolyte consisting of molten carbonate (DC-MCFC). This type of fuel cell has become the object our investigations. Our efforts have been focused on the design of DCFC devices (First stage “Start”) and the improvement of cell performance (Second stage “Initial tests”).

The purpose of the tasks carried out in the First stage was the verification of the possibility of building a high-temperature fuel cell based on liquid electrolyte with solid carbonates powered by coal. That goal was achieved through the construction of small-size cell and the stand for testing. Operation of this cell powered by elemental coal has been proved by preliminary tests.

Figure 1. Installation of the fuel cell

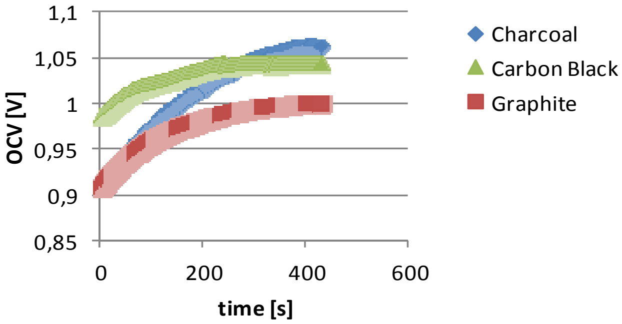


Figure 2. The course in time of the open circuit voltage of the fuel cell powered by charcoal, Carbon Black. and graphite

To improve the unit cell performance and stability molten carbonate fuel cell matrices were fabricated using combined tape casting method. $LiAlO_2$ powder mixed with carbonates was used to produce in single process mechanically stable matrix. Such produced matrices showed good microstructural stability during eight thermal cycle tests in the air atmosphere at 923 K.

Our current efforts are focused on the optimization of the performance of the small-size fuel cell by the selection of the following parameters: optimum operating cell temperature, anode and cathode material, composition of carbonate eutectic mixture, composition and flow rate of the anode and cathode gas mixtures, catalyst material, the amount and composition of the composite fuel.