**JERZY HABER INSTITUTEOF CATALYSIS
AND SURFACE CHEMISTRY
POLISH ACADEMY OF SCIENCES**

Leading National
Research Centers

DETAILED RESEARCH REPORT

year 2013

Leading National Research Centre

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

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

In 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.

In the reporting period, the Institute undertook several actions aimed at intensification of joint research between the consortium partners. Altogether 10 small research grants supporting research projects of Institute’s staff members implemented jointly with researchers from one of the partner institutions were funded. They comprised the following themes (names of the project leaders are provided in the brackets):

1. Strain fields inside a macroscopic wooden specimen subjected to humidity changes (Dr Leszek Krzemień).
2. Phonon properties of epitaxial layers of FeO on Pt(111) (Nika Spiridis DSc).
3. Combining FTIR and MAS NMR analyses as an effective method of studying structure of composites based on layered silicates and mesoporous silica (Professor Ewa Serwicka-Bahranowska).
4. Structure and dynamics of the binding centre in acireducton dioxygenases (Associate Professor Tomasz Borowski).
5. Determining the mechanism of ultrastabilization of the type Y zeolite using advanced spectroscopic (NMR i IR) and theoretical (DFT) methods (Professors Bogdan Sulikowski and Ewa Brocławik).
6. New generation of anticancer drugs: a hybrid system cobalamin – cisplatin (Dr Dorota Rutkowska-Żbik)
7. Investigating the effect of synthesis conditions on morphology, porosity and electrical capacity of nanostructural carbon materials as potential electrode materials (Dr Aleksandra Pacuła,
8. Investigating structure and superparamagnetic nanoparticles of iron oxide in relation to their biomedical applications (Associate Professor Tomasz Pańczyk)
9. Electrochemical monitoring of microorganism culture (Associate Professor Paweł Weroński)
10. Synthetic biodegradable polymer materials: application of a new class of nanohybrid – metalloporphyrin – heteropolycompound to obtain caprolactone (Dr Jan Połtowicz).

Altogether 12 yearly Smoluchowski Doctoral Scholarships were granted to support talented doctoral students.

The HEREDITAS centre, aiming at consolidation of cultural heritage research in the Krakow academic community, was launched. The first activity of the new centre was a two-day expert meeting ‘Identification, conservation and protection of art works made of polymeric materials’ organized to develop research programme of a grant proposal planned jointly by the Institute and the Faculty of Chemistry, Jagiellonian University.

Statutory Research

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)

Investigation aimed at synthesis of a composite material built of exfoliated/delaminated anionic clay mineral of hydrotalcite type and exfoliated/delaminated cationic clay mineral of montmorillonite type.

Ca-exchanged form of montmorillonite (Jelšovy Potok, Slovakia) and a synthetic magnesium-aluminium hydrotalcite (Mg:Al=2) were used for the synthesis. Both minerals were transformed into organic derivatives by ion exchange with organic species: decyltrimethyl ammonium cation $C_{10}H_{21}N(CH_3)_3^+$ (DTMA) in the case of montmorillonite and dodecyl sulphate anion $C_{12}H_{25}SO_4^-$ (DDS) in the case of hydrotalcite. This step aimed at an increase of the interlayer distance and hydrophobization of the solids, to facilitate swelling in an organic medium. In the next step both organo-derivatives were subjected to treatment with 1-octanol at 70^{o}C, aided by ultrasonication, to promote exfoliation/delamination. As a result, suspension of montmorillonite transformed into an iridescent solution, and that of hydrotalcite formed a clear solution. To investigate the effect of restacking, the solids were precipitated by addition of a polar solvent (acetone). Composite material was synthesized by mixing the colloidal solutions of delaminated minerals, ultrasonication and 16 h treatment at 180^{o}C in a microwave mineralizer. The resulting transluscent solution was treated with acetone to induce precipitation of the solid composite.

Physico-chemical characterization with XRD, XRF, FTIR, SEM, TG/DTG/DSC confirmed that the ion-exchange of starting minerals with organic species aiming at formation of organo-derivatives did occur. In particular, XRD demonstrated that the DTMA cations located in the interlayer space of montmorillonite assumed orientation parallel to the 001 plane, while the DDS anions present in the interlayer of hydrotalcite were oriented perpendicularly to the layers. Recovery of delaminated montmorillonite from octanol solution resulted in a solid with structure similar to that observed in the starting material, while the interlayer space of restacked hydrotalcite was 10% smaller than in the initial sample. Physoco-chemical characterization of composite precipitated from mixture of delaminated mieral organo-derivatives, in particular the XRD analysis which revealed the presence of reflections characteristic of montmorillonite and absence of features attributable to hydrotalcite, indicates that the composite may be envisaged as built of an organo-montmorillonite particles mixed intimately with dispersed hydrotalcite layers.

Results of this work will serve as basis for optimization of the methodology of layered minerals delamination and development of procedure for manufacturing of interstratified mineral composites.

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 PhD,
Katarzyna Luberda-Durnaś PhD, Marta Grzesiak-Nowak MSc)

Conducted research focused on the synthesis and structural characterization of new peroxocomplexes of Mo, W, and new polymolybdates of amines. For some of the obtained compounds tests of catalytic oxidation of cycloalkanes have been performed. In particular:

1) A number of syntheses of the peroxo-compounds with nicotinic, isonicotinic and picolinic acids were performed. Since it was noted that in the formed compounds N-oxide groups are incorporated, in part of carried out syntheses, nicotinic and picolinic acid N-oxide (nic-O and pic-O), and Na_2MoO_4 and K_2MoO_4, as a source of molybdenum, were used. So far, single crystals of NH_4(pic-O)$MoO(O_2)_2$ and polycrystalline isomorphic potassium salt were obtained. For the ammonium salt the crystal structure was determined (Fig. **a**). The potassium salt is in the process of structural studies.

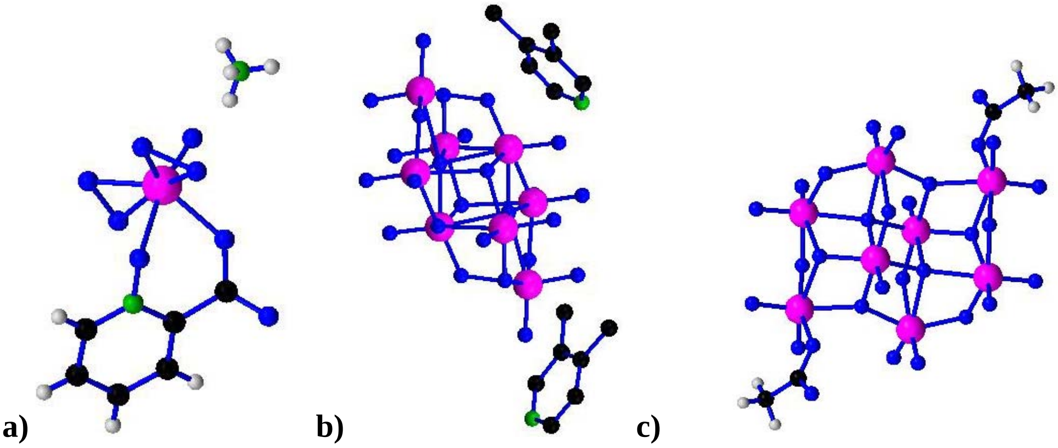
2) Studies on the synthesis of mixed molybdenum-tungsten peroxomolybdates were performed. Chemical analyzes, SEM and EDX studies, show that under applied conditions separation of compounds containing molybdenum and tungsten was observed.

3) For the purposes of catalytic tests, methods of synthesis of 3,4-dimethylpyridin (3,4-DMP) octamolybdates was 'fully elaborated'. In this study, besides 3,4-dimethylpyridine γ-octamolybdate, we obtained not reported yet in the literature salt $(3,4\text{-DMP})_4(\beta\text{-}Mo_8O_{26})$. It was structurally characterized by single crystal methods in the course of this study (Fig. **b**).

4) For future studies of catalytic properties, preparative work was foccused on obtaining new layered molybdates with high interlayer distance. The study focused on 4-propylaniline and 4-butylaniline molybdates. The study yielded in 3 new 4-propylaniline molybdates: β- Mo_8O_{26}, di(acetato)octamolybdate, layered pentamolybdate and 4-butylaniline (β-Mo_8O_{26}).

5) For some compounds, the catalytic tests of oxidation of cyclooctane, cyclohexane and cyclopentane, with oxygen from the air were performed. Investigations were conducted in cooperation with dr K.Pamin and dr J.Połtowicz (ICSC PAS).

The figure below, shows the refined asymmetric unit of: a) NH_4(pic-O)$MoO(O_2)_2$, b) $(3,4\text{-DMP})_4$(β-Mo8O26), c) anion di (acetato) oktamolibdenianowy. Colors of purple, green, black, blue and gray denote molybdenum, nitrogen, carbon, oxygen and hydrogen.



In conclusion, we obtained, and determined crystal structures of 5 new molybdates of aromatic amines, and one peroxomolybdate. For most of compounds catalytic oxidation tests were performed. The highest catalytic activity was observed in case of layered 4-propylanilinium pentamolybdate and 3,4-dimethylpyridinium β-octamolybdate.

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

(project leaders: Professor Piotr Warszyński, Assoc. Professor Paweł Nowak)

Dye pollutants from the textile industry are an important source of environmental contamination. It is estimated that 15% of the total world production of dyes is lost during dyeing process and is released in the textile effluents. One of the group of ubiquitous and hazardous contaminants are azo – dyes, such as rhodamine B. It is well known that azo dyes and their degradation products, especially aromatic amines are highly mutagenic and carcinogenic. Colored effluents may cause serious problem for human health and cause water borne disorders such as nausea, hemorrhage, ulceration of skin and mucous membrane, dermatitis, perforation of nasal septum, severe irritation of respiratory tract or cancer. Other problematic pollutants are methylene blue and Azure B. Therefore, it is necessary to reduce the concentration of dyes in water further used for drinking and domestic purposes. Moreover, in view of increasing restrictive requirements regarding the quality of drinking water is necessary to elaborate innovative methods of water purification.

In our research, the degradation of model organic compounds in the system, which is based on the combination of the UV-activated semiconductor catalyst and a strong oxidizing agent was examined. Detection of organic matter decomposition was carried out using spectrophotometry in the UV-VIS region with a suitable analysis wavelength for each substance in comparison with the parameter COD (Chemical Oxygen Demand) determined by the Standard Method PN-85/C-04578.02 and TOC (Total Organic Carbon). Spectrofluorimetric measurements were also performed.

As the result of the simultaneous action of the catalyst (TiO_2) and an oxidizing agent - sodium persulphate high conversion of the organic compounds was observed. It was substantially higher than in the case when the photocatalyst 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 was confirmed by both the spectrophotometric measurements and COD parameter on the other hand the results of TOC indicated that mainly colored, aromatic components were decomposed with high efficiency by the synergistic action of TiO_2 and $Na_2S_2O_8$. We examined two ways of oxidant dosing: continuous dosing and application of inorganic carriers with oxidizing agent. Several capsules with oxidant were synthesized (wax, PDMS capsules). We examined the release rate of the active agent from the capsules. The results proved that both methodologies of oxidant dosing lead to enhancement of azo-dyes decomposition.

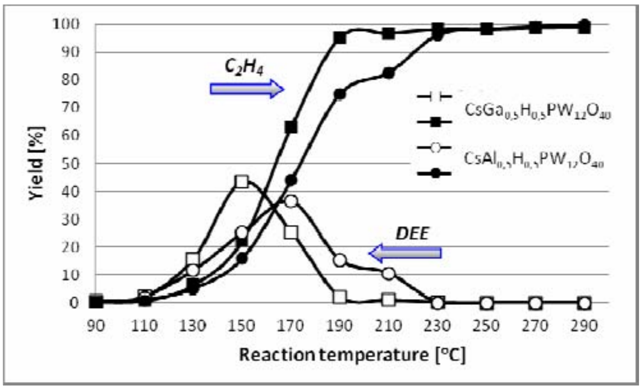
Synthesis, Physicochemical and Catalytic Properties of bi-Cationic Salts of Heteropolyacids

(Professor Adam Bielański, Anna Micek-Ilnicka DSc, Urszula Filek PhD,
Professor Małgorzata Witko, Assoc. Professor Renata Tokarz-Sobieraj)

The aim of the research was the synthesis and investigations of physicochemical properties of bicationic salts of Keggin heteropolyacids: $CsMe_{0,5}H_{0,5}PW_{12}O_{40}$ and $CsMe_{0,5}H_{0,5}PMo_{12}O_{40}$ (where Me=Al, Ga). Their activity was determined in the catalytic dehydration of ethanol. The catalytic results for bi-cationic salts were compared with those obtained for mono-cationic forms of the same salts. Apart from the experimental research, theoretical calculations were performed for the investigated salts.

The bi-cationic salts were obtained by the addition of fixed amounts of gallium or aluminium nitrates (at 50°C for 2h) into water solution of heteropolyacids $H_3PW_{12}O_{40}$ (HPW) and $H_3PMo_{12}O_{40}$ (HPMo) and then slow addition of Cs_2CO_3 solution under a constant stirring. This solution was subsequently evaporated and dried at 60°C for 2h. The salts were investigated using a comprehensive XRD analysis, thermal analysis and infrared spectroscopy to determine their crystallinity and thermal stability, and to identify structural vibrations. Surface morphology and at. % of the individual elements were examined using a scanning electron microscope. The catalytic tests of ethanol dehydration over solid bi-cationic salts were carried out in the gas phase in the flow microreactor at temperatures 90-290°C. Theoretical modeling started with the calculation of the electronic structure of mono-cationic (Ga, Al, In, Cs) salts of molybdenum and tungsten heteropolyacids. In addition, for each of the compensating cations, a mechanism of acid site formation proposed in the literature was considered. Also, initial calculations (with no crystallographic data available) for mixed Cs-Al and Cs-Ga salts were performed.

The Keggin structure of investigated salts (CsGaHPW, CsAlHPW, CsGaHPMo and CsAlHPMo) was confirmed by IR spectra. Microscopic images and EDX analysis confirmed the homogeneity of the samples composition. Thermal analysis showed that the content of crystallization water for each sample was about 11 H_2O/KU. Ethylene, diethyl ether (DEE) and acetaldehyde were the products of catalytic ethanol dehydration. In all cases, the catalytic conversion of alcohol increased with the increasing reaction temperature. The bi-cationic salts of HPW showed higher conversion of alcohol at 190°C (greater than 90%) compared with the salts of HPMo (below 50%). For the salts CsAlHPMo and CsGaHPMo, which indicated the comparable activities, in the temperature range 250-290°C acetaldehyde was the major dehydration product. On the other hands CsGaHPW salt exhibited a higher activity compared with CsAlHPW salt, at 190°C in almost 100% yield to ethylene (figure). An interesting catalytic effect for bi-and mono-cationic salts of HPMo was observed. The conversion of ethanol over those salts was higher than for HPMo and decreased in the order: CsGaHPMo, CsAlHPMo >> GaPMo, AlPMo > HPMo. Analysis of the electronic structure of Al, Ga, In and Cs salts and the mechanism of acidic centres formation showed that the acid properties correlate with the width of the band gap in the order: Ga > In > Al.



The catalytic results allowed determining the influence of the type of the bi-cationic Cs-Ga or Cs-Al systems on catalytic activity in ethanol dehydration. The calculation of electronic structure of bi-cationic salts should be continued.

Materials with Variable Porous Structures: Synthesis, Physicochemical and Catalytic Properties, Spectroscopic and Quantum-Chemical Studies

(Professor Ewa Brocławik, Assoc. Professor Mirosław Derewiński, Professor Bogdan Sulikowski)

Theoretical research in 2013 was aimed at detailed analysis and characterization of electron density and spin flow between the Cu(II) 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.

The analyses of the global reconstruction of electron density upon adsorption of the ligand 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 (within spin resolution, indispensable due to radical character of both NO and the center). The model for the adsorption of NO on copper site comprised the ligand interacting with Cu^{2+} cation coordinated by $[Al(OH)_4]^-$ group (T1). Our results confirmed that while the channel dominating total electron transfer between NO ligand and Cu(I) site is the π^*-backdonation one (enhancing NO activation), for the Cu(II) site the donation of unpaired electron (diminishing NO activation) dominates electron density transfer; it is effective solely within the α spin polarization.

The novelty of our results lies in the application of spin resolution to the analysis of electron transfer between the adsorbed NO and Cu(II) 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*.

In order to prepare innovating zeolite catalysts it is desirable to understand, on a molecular level, relationships between their structure, chemical composition, morphology and catalytic properties. The objective of our studies in 2013 was to modify zeolite Y, characterise the samples by a number of methods, and test them in transformation of α-pinene in the liquid phase. Terpenes encompass a number of hydrocarbons with various structures. Among them, α-pinene is one of the most important monoterpene hydrocarbons used for the synthesis of raw materials, like camphene, limonene and *p*-cymene. (Limonene is one of the products of α-pinene transformation.) Catalytic transformation of α-pinene is nowadays an industrial process, however, a catalyst used for this purpose exhibits several disadvantages. Accordingly, we have commenced studies aimed at preparation of aluminosilicates catalysts characterised by higher activity and selectivity.

In the period reported, our work was concerned upon introducing, purposely, the changes in the status of tetrahedrally coordinated aluminium. A series of zeolitic samples was therefore prepared by applying combined methods of modification, i.e., ion-exchange, calcination at elevated temperatures under different conditions, and extraction with diluted mineral acids. Physico-chemical characteristics of the samples were carried out using a number of methods: XRD, sorption of nitrogen, IR spectroscopy and solid-state NMR spectroscopy (^{29}Si, ^{27}Al & ^{1}H).

The objective of our studies remains in-depth characterisation of the changes introduced upon zeolite modification by various routes, and to establish which of them are positively affecting catalytic activity and selectivity. Finally, phenomena found might be, in the future to come, used for manufacturing of heterogeneous, zeolitic catalysts with enhanced properties and designed for use not only in the liquid, but in the gas phase as well.

New Materials for High Temperature Fuel Cells

(Michał Mosiałek PhD, Aneta Michna PhD, Magdalena Dudek PhD (AGH), Maciej Tatko MSc, Aneta Kędra MSc, Grzegorz Mordarski PhD)

Nowadays the solid oxide fuel cells (SOFCs) working in the intermediate temperature (IT) range (500–700°C) are the subject of intensive study. The performance of perovskite cathode materials can be improved by introducing the second active phase, for example silver. So far such composites were produced by two step sintering procedure. First perovskite cathode was sintered then saturated with silver nitrate solution containing also reducing agent and sintered again. Our goal was to simplify that process. The silver powder-perovskite powder composite was selected as the object of the study.

The $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) was used as perovskite cathode material, the $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) as en electrolyte and NiO–$Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) composite was used as a anode material. BSCF was prepared from nitrate solution by the Pechinni method. Then, the obtained product was calcined at 1100°C for 3 h and rotary-vibratory milled with the zirconia grinding media in dry ethanol. The Ag sol was prepared in one-step synthesis by reduction of silver nitrate by ethanol in the presence of polyvinylpyrrolidone (PVP), serving as the protective agent. Next BSCF powder was added to obtained silver sol and the solution was stirred for 40 min. The silver nanoparticles were evenly adsorbed on the BSCF oxide powder surface during stirring. As a result the silver nanoparticles with the average diameter ~40 nm, uniformly distributed on the BSCF skeleton were obtained (Fig.1). Finally the cathode was sintered in one-step process.

The BSCF and composite Ag–BSCF cathodes obtained by different methods were used for the sake of comparison of their catalytic activity in oxygen reduction reaction. The cathodes were tested both by the electrochemical impedance spectroscopy (EIS) in three electrode setup in argon oxygen mixtures and in the cells H_2|Ni–GDC|SDC|BSCF–GDC|Ag–BSCF|O_2. The cell with the composite cathode material obtained by new wet procedure exhibited 48% better performance in comparison with BSCF cathode. The EIS measurements reveal that the addition of silver improves the BSCF cathode performance in the low oxygen concentration region.

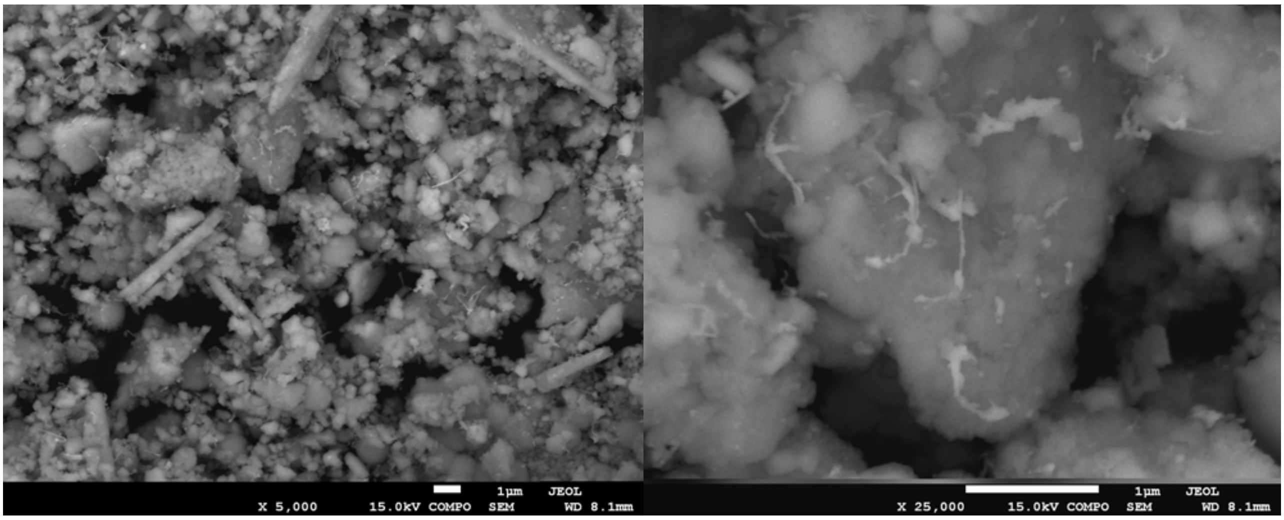
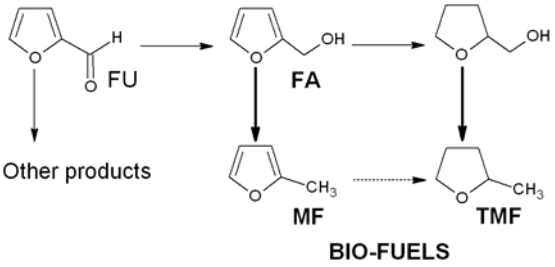


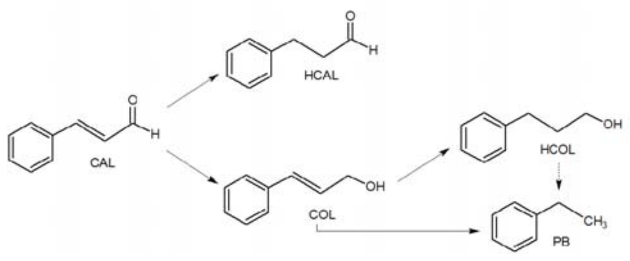
Figure 1. SEM images of Ag–BSCF composite powders

Catalytic Processes with Participation of Bio-Reagents

(Professor Alicja Drelinkiewicz, Żaneta Kalemba-Jaje MSc, Erwin Lalik PhD, Robert Kosydar PhD, Tomasz Szumełda MSc)

Studies concentrated on two catalytic processes dealing with the bio-reagents and in particular with the formation of bio-fuels. The first is ***transesterification of triglycerides*** with methanol yielding methyl esters (Biodiesel). Various organo-sulfonic acids (methanosulfonic, camphorosulfonic, lignosulfonic) doped polyanilines were tested as solid acid catalysts for methanolysis of triacetin (model triglyceride molecule) and castor oil and esterification of fatty acid (ricinoleic). The organo-sulfonic acids-containing catalysts exhibited much higher activity than that of alkyl-free sulfuric acid-containing counterpart related to increased hydrophobicity in close proximity to the active sites. This resulted also in stable and high activity during the reactions. Methanosulfonic acid-containing catalyst exhibited the best performance arising from the most advantageous effect of this type of alkyl-group.





Currently, a lot of interest in furan compounds called “sleeping giants: is paid to (i) catalytic processes concerning their production from the bio-mass derived sugars and (ii) their conversion to valuable chemicals and bio-fuels such as 2-methyltetrahydrofuran (TMF), 2-methylfuran (MF) and ethers (methyl, butyl) of cyclic tetrahydrofurans. They are the products of consecutive reactions during ***catalytic hydrogenation of furfural*** (FU) (Scheme). Reaction pathway in furfural hydrogenation is of similar type as the one in hydrogenation of α,β-unsaturated aldehydes, such as cinnamaldehyde (CAL). In both reactions, apart from the primary parallel reactions C=O and/or C=C hydrogenation also hydrodeoxygenation of unsaturated alcohols furfuryl(FA)/cinammyl (COL) can proceed yielding corresponding MF/propylbenzene products (PB), respectively.

Here liquid phase hydrogenation of both furfural and cinnamyl aldehyde was studied (20-60^{o}C, 1-6 atm H_2, toluene and iso-propanol solvent) on series of SiO_2 and carbon black (Vulcan XC-72) supported Pd-based bimetallic catalysts Pd-X (Pd-Pt, Pd-Au, Pd-Ir, Pd-Ru) of various Pd-X molar ratios. They were prepared by “water-in-oil” microemulsion method (non-ionic surfactant Triton and cyclohexane – oil phase). Using this method makes possible to achieve a good control of the size of mono- and bimetallic particles. The metal particles ca. 5-8 nm in average with a narrow size distribution were obtained in all prepared catalysts. The XRD, XPS, SEM (EDS) techniques showed the alloy structure of Pd-X particles, identified to be of “cluster-in-cluster” type in series of Pd-Au/C catalysts. The Pd was chosen as the base metal because of its known high C=C hydrogenation activity, whereas the second metal varied essentially in reactivity towards C=O reduction. The results of preliminary experiments showed that Pd-Pt/SiO_2 catalysts (Pd/Pt = 1:2, 2:1) exhibited enhanced reactivity towards C=C/C=O hydrogenation when compared with that of monometallic Pd catalyst. Among all studied samples, the Pd-Ir/C and Pd-Au/C were the most active catalysts towards hydrodeoxygenation reaction in iso-propanol or toluene solvent, respectively. The best selectivity to propylbenzene (ca. 40 %) was achieved on 2%(Pd-Ir)/C catalyst.

Structural, Electron Properties and Dynamics of Surface and Nanostructures Studied with Microscopic and Spectroscopic Techniques Radiation in the Ultra High Vacuum Conditions

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

The object of the studies were surfaces and nanostructures deposited from the gas phase by the molecular beam epitaxy. The studies were aimed to determine magnetic and catalytic functionality of the investigated structures. The main experimental techniques used for the present research, applied under ultra high vacuum conditions were: low energy electron and photoelectron microscopies – LEEM and PEEM, scanning tunnelling microscopy – STM, conversion electron Mössbauer spectroscopy – CEMS and photoelectron spectroscopy – XPS. The magnetic ex-situ measurements were carried out using the magnetooptic Kerr effect.

The most important sub-projects were related to:

- surface and interface properties in magnetic metal – oxide nanostructures,
- magnetic properties of epitaxial iron films on tungsten studied with spectroscopic and microscopic methods,
- oxygen adsorption on Fe/W(110),
- surface composition and electronic structure of catalyst.

In cooperation with Swiss Light Source in Paule Scherrer Institute the methodology of synchrotron based photoemission electron microscopy was developed.

In the topic of metal-oxide magnetic nanostructures we developed a growth method of polar oxide films by oxidation of single metal layers. The method was applied for growth of FeO(111) on MgO(111) and CoO(111), CoO(001) on MgO(111), MgO(001). In the CoO/Fe bilayers we studied the role of the film orientation on the exchange bias (EB) coupling. We showed that despite similar structural properties and stoichiometry of the CoO sublayers, the magnitude of the EB effect was by order of magnitude larger for Fe/CoO(111) than Fe/CoO(001). This effect was explained by an interplay of magnetic uncompensation of the CoO(111) films and small magnetocrystalline anisotropy of the iron layer. The Mössbauer measurements for Fe/MgO and Fe/NiO interfaces resulted in the identification of the chemical composition of iron interfacial oxides.

Magnetic properties, such as a mechanism and kinetics of the spin reorientation transition in epitaxial Fe films on W(110) were explained by using complementary synchrotron methods: nuclear resonance scattering of synchrotron radiation and photoemission electron microscopy based on the circularly polarized soft X-rays on the L Fe edge. X-PEEM was also used for identification of the chemical structure and morphology of 3d/rare earth metal nanostructures.

Based on the LDA calculations and CEMS measurements we interpreted the oxygen adsorption structure observed on Fe monolayer on W(110) and we showed that the transition from simple adsorption structures in the registry with the tungsten substrate to an oxide phase with a FeO stoichiometry occurs through complex intermediated phases.

The XPS spectroscopy was applied to study the electronic states of species involved in catalytic reactions for a broad range of materials such as high area powders, thin films, nanoparticles and in studies of catalytic model systems.

The results of X-PEEM studies will be useful by the commissioning of the first experimental beam-line at the Polish synchrotron source “SOLARIS”.

Studies on the Mechanisms of Catalytic Reactions of non-Haem Enzymes Oxidizing Hydrocarbons

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

Due to the growing demand for highly selective and non-toxic catalysts, enzymes are extensively studied both with respect to their direct applications as catalysts and synthesis of small molecule synthetic complexes operating according to the same paradigm as a given group of enzymes. In-depth understanding of the mechanisms of reactions taking place in the active sites of enzymes and/or biomimetic systems is one of the foundations for the rational design of such catalysts.

Two systems were studied with the help of quantum chemistry (DFT) or hybrid methods (QM (DFT) / MM): synthetic Cu(II) complex catalyzing oxidative cleavage of the C-C bond and acetyltransferase capable of acetylation of an antibiotic - chloramphenicol.

From among several tested reaction paths for the reaction between O_2 and the enolate Cu(II) complex the most likely mechanism for formation of an intermediate with a peroxide bridge between Cu(II) and the organic substrate was selected. This mechanism resembles a part of a catalytic c*ycle of Cu(II)-binding enzyme*-quercetin dioxygenase and includes: an organic substrate binding as a monodentate ligand to Cu(II), one-electron oxidation of the enolate to a radical, and finally formation of a bond between an organic radical and superoxide ion bound to the Cu(II) ion.

Acetyltransferase PA4794 from Pseudomonas aeruginosa not only catalyzes the N-acetylation of peptides, but also the O-acetylation of chloramphenicol, and interestingly, chloramphenicol binds in the AcCoA binding site and not in the canonical substrate binding site. Results of QM/MM and classical molecular dynamics simulations indicate that Tyr128 mediates the transfer of an acetyl group from AcCoA to chloramphenicol, and Cys29 plays only a structural role.

Gained insights into the course of the catalytic reactions can be the starting point for the design of new catalysts cleaving C-C bonds using molecular oxygen, as well as further research on acetylation of chloramphenicol.

Molecular Dynamics Methods in Studies of Biologically Active Systems

(Assoc. Professor Tomasz Pańczyk, Wojciech Płaziński PhD, Agnieszka Brzyska PhD)

Molecular dynamics allows for description of quite big systems at microscopic level. This is particularly important in case of biological systems which normally consist of hundreds or thousands atoms in a simulation box. Moreover, in such cases interaction with solvent (usually water) cannot be ignored. The key factor in molecular dynamics is application of possibly exact force field which can reproduce in reliable way possibly large number of parameters/properties known from experiment or quantum chemical calculations. Recently, strong attention is paid to interactions of carbon nanotubes with biologically active moieties. Enhancement of pharmacological activity of some drugs, being a result of interaction with carbon nanotubes, was confirmed. Carbon nanotubes are also considered as nanotransporters for anticancer drugs. Therefore, the aim of this study was development of a suitable methodology for analysis of carbon nanotube – drug conjugates and drugs absorption/adsorption/desorption on the surfaces or inside carbon nanotubes. Another aim of this study was implementation of biomolecular force field GROMOS 56aCARBO for use in GROMACS package.

A typical anticancer drug revealing strong activity is cisplatin. Very well known are also severe side effects accompanying administration of this drug. The carbon nanotube-cisplatin can thus serve as a model system which particular properties may help to draw general conclusions concerning the meaning of carbon nanotubes as biologically active moieties. As a result, the computational methodology for interaction of multi-walled carbon nanotubes with cisplatin was developed. Analysis of that model using molecular dynamics simulations and theoretical considerations allowed studying the structure of cisplatin inside the nanotubes, changes of their physical properties in reference to bulk solution and desorption dynamics. Concerning the implementation of the GROMOS 56aCARBO force field a modification of the default way of creation of nonbonded 1-4 pairs was proposed and automated program for generation of Lennard-Jones parameters for selected atoms (according to the rules of the force field) was developed. This program is accessible on the web page of GROMACS package.

The most important achievements at this stage of the studies are: determination of diffusion coefficient of cisplatin in the interior of carbon nanotube and its changes as function of the nanotube parameters, moreover, an analytical equation describing the rate of release of cisplatin from the nanotubes was derived. That equation was verified by comparing its predictions with the results from molecular dynamics. It also allows for prediction of the release rates for long times. Additionally, analysis of that equation leads to the conclusion that the release proceeds according to one-dimensional activated diffusion mechanism. The 56aCARBO force field was verified in a model system concerning the free energy changes of conformational transitions ${}^{4}C_{1} \leftrightarrow {}^{1}C_{4}$ in α- and β-D-glucose molecules.

The results obtained in this study are of fundamental significance. They are applicable in construction of complex systems tractable by molecular simulations. Particularly, they are important in design and theoretical studies of systems related to drug delivery technology. Detailed knowledge of microscopic properties of such systems allows for optimization of their properties or simplification of fabrication methods. The GROMOS 56aCARBO force field implemented in GROMACS package may be utilized in simulations of glycobiological systems. In such cases deformations of carbohydrate rings may have significant meaning.

Biomass Conversion: Dehydration of Bio-Butanol on Oxide-Type Catalysts

(Professor Ewa Serwicka-Bahranowska, Dorota Rutkowska-Żbik PhD)

Biomass is regarded as an alternative and renewable source of hydrocarbons. In this respect, bio-butanol, being produced in the process of biomass fermentation, might serve as a substrate for chemical synthesis. This is achieved through its de-hydration into butene, which, in turn, might be transformed into chemicals and commodities.

The aim of the research was to find and optimize oxide-type catalysts having high activity in dehydration of bio-butanol to butene.

As the investigated reaction proceeds on acidic sites, different types of acidic oxide-type catalysts were tested: a commercial Al_2O_3 (Puralox), tungstophosphoric heteropolyacid immobilized on montmoryllonite, Al_2O_3 (Puralox) modified with 1%WO_3, as well as Al_2O_3 (Puralox) doped with 2%CeO_2 and 7%ZrO_2.

The chosen catalysts were tested for de-hydration of butanol in a gas-phase flow reactor, under atmospheric pressure, in temperature range 150-400°C. The selectivity to different products: 1-butene, cis-butene, trans-butene, and butanal (being the main by-product of the process) was monitored with gas chromatography.

The majority of the used samples appeared active in the studied reaction reaching 100% conversion in temperature as low as 200°C. Typically, the process yields a mixture of different butene isomers (1-butene, cis-butene, trans-butene). Therefore, the interest was to find the catalyst, for which a composition of products was the furthest away from the thermodynamic equilibrium at a given temperature and pressure. In this respect Al_2O_3 (Puralox) modified with 1%WO_3 appeared the most promising.

In the next step, its studied samples were characterized with IR spectroscopy and ammonia TPD in order to correlate its catalytic activity with surface properties. Acid-base properties of 1%WO_3-Al_2O_3 were determined by pyridine and ammonia adsorption – see Table 1. No Brønsted acid sites were detected on the pure Al_2O_3, and its surface posses only Lewis acidity. The number of Lewis acid sites is practically not influenced by modification by WO_3. However, even such a small amount of WO_3 results in the considerable reduction of surface OH groups concentration and leads to the change in the reaction product profile.

Table 1. Brønsted and Lewis acid sites concentration in the selected systems

Temperature (^{0}C)	Brønsted and Lewis acid sites [μmol/g]*			
	Puralox Al_2O_3		Puralox Al_2O_3 + 1%WO_3	
	PyH^+	PyL	PyH^+	PyL
100	-	135	66**	116
200	-	73	0	72
300	-	42	-	37
400	-	21	-	17

* integral absorption coefficient for PyL complex = 2,22 cm/μmol, for PyH^+ ion = 1,67 cm/μmol, adopted from C.A.Emeis, J. Catal., 141 (1993) 347-354

** estimated value with high error due to the broad peak

Application of the Colloid Enhancement Method for the Determination of Topology and Electrokinetic Characteristics of Protein Monolayers at Solid/Electrolyte Interfaces

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

The goal of this work was to develop an efficient experimental method aimed at detecting protein monolayers at solid interfaces and to characterize molecule orientations under *in situ* conditions. The method, referred to as colloid enhancement (CE) is based on non-specific deposition of colloid micro-particles on protein layers. Its major advantage is that it enables measurements under wet, *in situ* conditions.

This technique was used to characterize bovine and human fibrinogen monolayers on mica produced by controlled adsorption under diffusion transport at pH 3.5. The surface concentration of fibrinogen N_f was determined by AFM imaging of single molecules adsorbed over the substrate surface. Negatively charged polystyrene latex microspheres, 820 nm in diameter were used in this study.

An anomalous deposition of negative latex particles on substrates exhibiting a negative zeta potential was observed, which contradicts the commonly used mean-field DLVO theory. Moreover, measurable deposition was observed even at low ionic strength 6×10^{-4} M NaCl, see Fig. 1 where the minimum approach distance of latex particles to the interface exceeds 70 nm. This confirms that fibrinogen molecules adsorb end-on on mica assuming extended conformations with the positive charge located mostly in the end part of the αA chains. This agrees with previous theoretical results reported in the literature. This unusual latex deposition on Fb monolayers was quantitatively interpreted in terms of the random site adsorption model.

These measurements unequivocally confirmed that the CE method can be used as an efficient tool for revealing protein adsorption mechanisms at solid/electrolyte interfaces that has a major significance for basic sciences.

A practical aspect of this work is that fibrinogen monolayers of well-defined coverage and molecule orientation can be produced in a reproducible way that can be exploited for efficiently perform immunological tests.

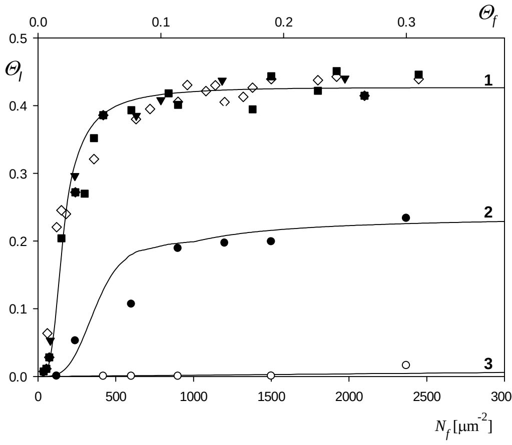


Figure 1. The dependence of the coverage of latex particles, Θ_l on the bovine fibrinogen surface concentration N_f [μm^{-2}], pH 3.5. The points denote the averaged experimental results obtained by optical microscopy and AFM for pH various ionic strength: (▼), 0.15 M; (◇),10^{-2} M; (■), 10^{-3} M; (●), 6×10^{-4} M; (○), 3×10^{-4} M. The solid lines 1-3 show theoretical prediction derived from the fluctuation theory, assuming deposition of latex on sites formed by at least two fibrinogen molecules.

Influence of the Liquid Film Size and Surface Electrical Charge on Kinetics of the Three Phase Contact Formation at Surfaces of Low Hydrophobicity

(*Professor Kazimierz Małysa, Jan Zawała PhD, Dominik Kosior PhD, Marcel Krzan PhD, Anna Niecikowska MSc)*

The study has been focused on influence of size of the liquid film formed by the colliding bubble and surface electrical charge of the interacting interfaces on kinetics of the three phase contact formation at solid surfaces of low hydrophobicity. Bubble collisions with solid surfaces (grain surfaces in flotation processes) are highly dynamic processes occurring within time scale of milliseconds. The three phase contact (TPC) is formed when the liquid film separating the solid and bubble surfaces can drain to its critical thickness and rupture during this short collision time. Electrostatic interaction between double layers of the interacting interfaces and van der Waals forces (DLVO theory) are the main factors determining stability of thin liquid films, while the film drainage velocity depends strongly on film size (radius).

Kinetics of the three phase contact formation on titanium dioxide (TiO_2) and mica surfaces was determined. Surface of the TiO_2 films deposited (PDV technique) on a glass slide was smooth and hydrophilic. The measurements were carried out also for slightly chemically hydrophobized (contact angles: θ_{adv}=40 and 60^o) surfaces. As size of the film formed by the colliding bubble is determined by the bubble diameter so the bubbles of different radius (R_B=0,2; 0,49 i 0,74 mm) were used in the experiments. Surface electrical charge of the interacting liquid/gas and liquid solid interfaces was modified via variation of the pH and adsorption of ionic surfactants. In distilled water (pH=5.8) the TPC was not formed at hydrophilic TiO_2 and mica surfaces because the wetting films formed by the colliding bubbles were stable due to repulsive electric interactions between similarly (negatively) charged liquid/solid and liquid/gas interfaces. Air bubbles in distilled water bear negative charge within wide range of pH, down to pH~2, while the isoelectric point (IEP) of $Ti0_2$ surface is located at pH 4.7. Therefore, at pH 3.5, i.e. at pH below the $Ti0_2$ IEP, the TPC was formed even at hydrophilic $Ti0_2$ surface due to the attractive electrostatic interactions which caused the wetting film destabilization (see Fig 1).

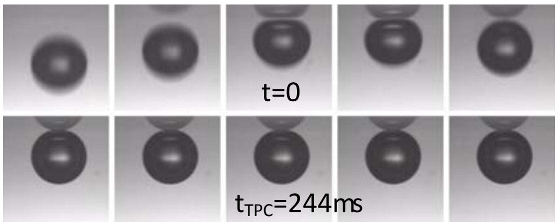


Figure 1. Sequences of photos showing the bubble 3rd collision (top row) and the TPC formation at hydrophilic TiO_2 surface (bottom row). pH=3.5, time interval between subsequent frames of each row Δt=0,96ms, distance from the capillary L=100mm.

When the TiO_2 surface was slightly hydrophobized then the TPC was formed even in distilled water (pH=5.8). Here also, the attractive electrostatic interactions, operating in the film at pH below the isoelectric point of the TiO_2 surface, facilitated the wetting film rupture and therefore the time of the TPC formation was shorten at $pH<pH_{IEP}$ (see Table). Data presented in the Table show also how strongly is the time of the TPC formation affected by size of the colliding bubble. The results obtained have implications and can be used for improvement of the flotation control and effectiveness.

pH	Time of the TPC formation at TiO_2 surface, $\theta_{adv}=40^o$		
	R_b=0,74 mm	R_b=0,49 mm	R_b=0,20 mm
5.8	462 ± 31 ms	133 ± 31 ms	9,6 ± 2,1 ms
4	229 ± 32 ms	95 ± 19 ms	7,9 ± 1,5 ms
3.5	92 ± 5 ms	114 ± 39 ms	6,9 ± 0,9 ms

Functional Polyelectrolyte Multilayers Films

(Project leader: Professor Piotr Warszyński)

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 2013 was to determine the effect of calcium ions on thickness and permeability of polyelectrolyte multilayers containing alginate (ALG) polyanions. Multilayer films containing various number of layers were formed using the sequential adsorption method with poly-L-arginine (PLArg) as the polycation. During their formation the multilayers were contacted with NaCl and/or CaCl2 rinsing solutions having various salt concentrations. The buildup process of PLArg/ALG multilayer films was monitored by Quartz Crystal Microbalance (QCM). The mass and thickness of formed multilayers were determined in-situ by the QCM-D (quartz crystal microbalance with dissipation) and correlated with the thicknesses of dried films measured by ellipsometry. We observed strong dependence of mass and thickness of the films on the concentration of calcium ions in rinsing solution. For example there was a fivefold increase of mass of the film when during its formation the 0.05 M solution of $CaCl_2$ was used instead of 0.15 M NaCl (see Fig. 1.). The increase of the mass and thickness of the film can be explained by crosslinking of alginate and enhanced adsorption of water in the crosslinked film since its dry thickness, measured by ellipsometry, is ten times smaller than measured by QCM in aqueous environment. The cyclic voltamperometry with three electroactive agents with different molecular mass was used to determine permeability of multilayers deposited at gold electrode. We observed the decrease in anodic and cathodic currents with increasing number of polymer layers in comparison with currents at bare electrode. We demonstrated that multilayers contacted with $CaCl_2$ solution were less permeable than those contacted with NaCl solution. However, the decrease of permeability was much smaller than increase of film thickness due to its crosslinking.

Our result will have the implication on the permeability of microcapsules prepared by crosslinking of alginate microdroplets.

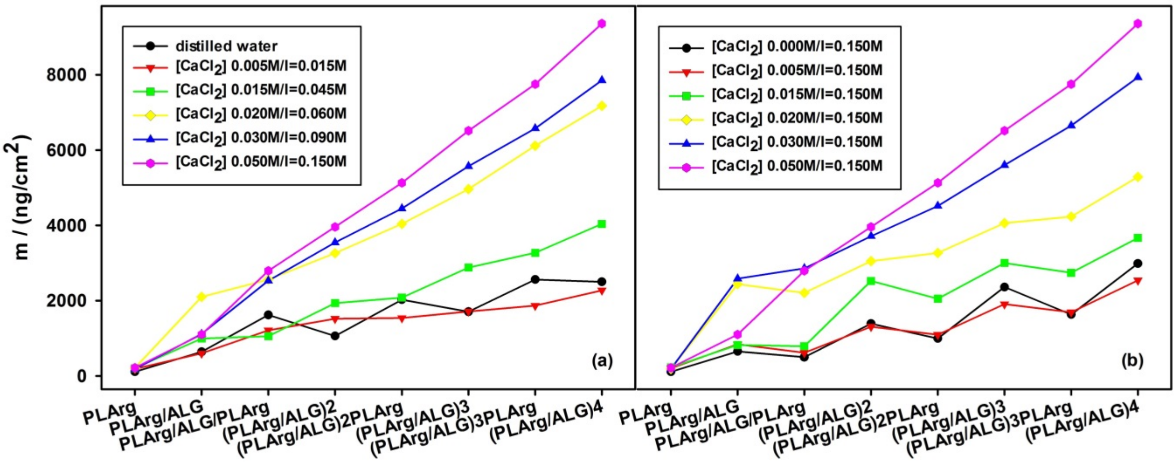


Figure 1. Mass (per surface unit) of PLArg/ALG multilayered films with increasing number of layers obtained for various rinsing conditions: (a) rinsing solutions with increasing concentration of calcium ions, (b) rinsing solutions with increasing concentration of calcium ions and with fixed ionic strength (0.15M).

Physical Properties of Paint Layers at the Conditions of High Relative Humidity

(Michał Łukomski PhD, Professor Roman Kozłowski, Łukasz Bratasz DSc)

The aim of the research was to determine dimensional changes and mechanical properties of paint layers at the conditions of high relative humidity when the glue binders become rubbery, as well as to establish risks of physical damage to these layers when passing from the rubbery to the glassy state during a relative humidity drop.

Polychrome wood belongs to the category of cultural heritage objects most susceptible to relative humidity and temperature fluctuations. The previously conducted studies on the impact of climatic conditions on damage development in the decorative layers on a wooden substrate resulted in establishing a safe range of relative humidity fluctuations around 50% - that is, in conditions typical of air-conditioned museums. However, very valuable collections of painted wood are located in castles and churches in which the average annual relative humidity exceeds 75%. In such conditions, the ground layer, which is part of the polychrome surface, becomes ductile and soft which substantially alters its sensitivity to climatic impacts.

Within the framework of the research work conducted, the main emphasis was on determining the mechanical parameters of the ground layer below and above the glass transition, at around 75% relative humidity. The tests were performed on rectangular samples with help of a testing machine coupled with a climatic chamber, which allowed humidity and temperature conditions in the environment of the sample to be to controlled accurately. Change in the rigidity, the elastic range, the humidity expansion coefficient, as well as the creep relaxation rate, and the creep extent were determined as a function of ambient relative humidity.

At the same time, damage development on the surface of the ground layer cast on a dimensionally stable glass substrate and subjected to varying humidity cycles in a climatic chamber - in which the material was passing through the glass transition of about 75% relative humidity – was monitored. The surface density of cracks was determined for various compositions and thicknesses of the ground layer as a function of the number of humidity changes, their amplitude and rate. The measurements showed that first fissures in the ground layer appears after just a few cyclic changes of the ambient relative humidity and the crack network density is inversely proportional to the layer thickness.

The research allowed the threshold for microclimate parameters to be determined above which irreversible deformation and physical damage of the paint layers of different thicknesses appear.

Research projects
of the Ministry of Science and Higher Education

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 goal 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 configuration of touching beads of various size. 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 and the conformation of the molecule. This allowed one to unequivocally determine conformations of this protein in electrolyte solutions and charge distribution for various pH. Knowing the charge distribution and molecule conformations one can quantitatively interpret the kinetics of fibrinogen adsorption derived from the in situ streaming potential measurements (see Fig. 1). As can be observed, the experimental data agree with theoretical results for the entire range of surface concentrations. It is also interesting to mention that for N_f smaller than 3000 μm^{-2} the surface concentration of fibrinogen it is a linear function of the square root of time that can be exploited for a precise determination of the bulk concentration of the protein.

These results have major significance for basic science indicating that for lower pHs fibrinogen adsorbs mostly in the end-on orientation that promotes an irreversible immobilization of negatively charged colloid and larger micro-particles on negatively charged substrates. This can also have consequences for biofilm formation on various substrates via bioparticle immobilization, e.g., bacteria, induced by fibrinogen adsorption.

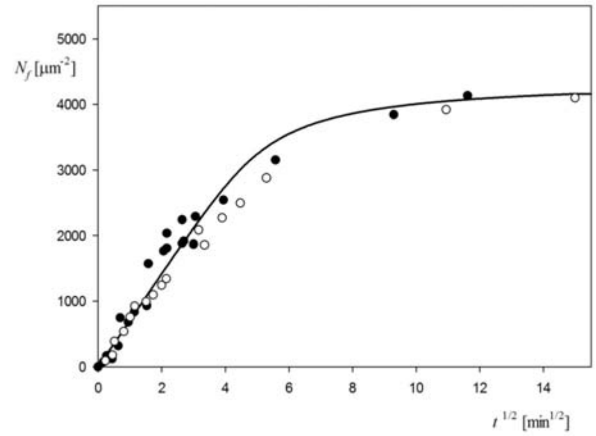


Figure 1. The kinetics of fibrinogen adsorption on mica under the diffusion-controlled adsorption regime. The points represent experimental results determined by streaming potential measurements for mica, c_b = 10 mg L^{-1}, pH 3.5 and 10^{-2} M, NaCl. The solid line denotes exact theoretical results calculated by solving the diffusion equation for the 3D RSA adsorption model.

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)

Development of new biocatalytic methods for synthesis of chirally pure secondary alcohols is an important task for fine chemical and pharmaceutical industry. Optically pure alcohols are universal synthons used for development of more complicated bioactive compounds that contain a chiral center. Biocatalytic methods are an interesting alternative to traditional chemical synthetics methods due to their high reaction enantioselectivity that stems from enantio-differentiating structure of enzymes' active sites.

Studies during the last year of the project focused on assessment of ethylbenzene dehydreogenase (EBDH) potential for its application in industrial scale synthesis of chiral alcohols. Previous results showed that the enzyme exhibits activity with a wide of substrates and is characterized by high enantioselectivity of hydroxylation. However it was observed that under reactor conditions EBDH loses it activity to quickly to be a viable industrial catalyst.

As the immobilization is known to stabilize enzyme activity, we tested effect of immobilization on EBDH activity in reaction conditions with several modified silica and crystalline cellulose support matrixes. Moreover, different types of reactor setups were assessed such as fed-batch reactors and flow-reactors with recirculation.

The studies were conducted in cooperation with Wrocław Technical University and Silesian Technical University. They allowed selection of the best support, i.e. unmodified cellulose Granocel matrix. The reactor tests and optimization of the reaction conditions allowed 84 fold elongation of enzyme activity from 4 h to 14 days. The enzyme working in such conditions is able to produce chiral alcohols in 2-5 mM concentrations. Moreover, it was shown that immobilized enzyme can effectively work with high (e.g. 10 mM) concentration of ferricyanide as a re-oxidation agent. Use of cheap $K_3[Fe(CN)_6]$ as the enzyme reoxidation agent instead of ferrocenium tetrafluoroborate eliminated a need to electrochemical reoxidation of reduced re-oxidant. However, we have developed an effective electrochemical oxidant recovery system both for batch and flow reactors. Such system is necessary for application where even trances of cyanides are not allowed (such as productions of pharmaceuticals).

The methods developed in the project are a content of Polish patent application (P.406286).

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 manganese oxides and mixed iron manganese oxides synthesis and also on the studies of catalytic properties of these oxides. The epitaxial structures of the oxides were obtained by metallic manganese oxidation at elevated temperature. The structures were characterized Low Energy Electron Diffraction (LEED), X-ray Diffraction (XRD), 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(100) spinel was performed either on Fe_3O_4(100) or MgO(100) substrates. The MnO(100) structure was obtained on MgO(100) and W(100). Additionally, Mn_2O_3(100) and MnO_2(100) were synthesized on MgO(100). MnO and Mn_3O_4 were doped with iron leading to the mixed manganese-iron oxides. It was found that surface of all manganese oxides was enriched with manganese ions of higher oxidation state (+3 or +4) than the lattice ones although the lattice composition and structure was correct.

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. When 0.1 ML of iron was added to the catalytic system (0.3 ML Mn), the mixed system showed higher resistivity to CO poisoning.

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 and/or iron 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 promising high efficiency environment-friendly next-generation electric power sources. Considerable efforts have been made in recent years to reduce the operating temperature of SOFCs to the intermediate temperature range 500-700°C. Nowadays the high overpotential of the oxygen reduction reaction at the cathode is still the threshold to make a further step forward. One of the possible solutions to that problem may be the addition of silver to the cathode material. Our investigations were focused on the possibility of applying metallic silver as a component of composite cathodes in the temperatures lower than 600°C.

The first stage of the project entitled: „The chemical stability of obtained composite cathode materials in presence of electrolytes and interconnectors recently used in fuel cells. Analysis of changes in the joint: cathode material|electrolyte during long-term operation of the fuel cell.” and “The characteristics of the oxygen reduction reaction at the interface: composite material comprising silver|oxide electrolyte by electrochemical measurements.”

The lack of interaction between examined composite materials with electrolytes: $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC), $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) and $Y_{08}Zr_{0.92}O_{1.96}$ (YSZ) was confirmed. The interaction between stainless steel SUS 430 and composite cathode materials Ag–LSCF and Ag-LSM was observed. The considerable amount of chromium was found in the tested composite materials after one week tests (Fig. 1).

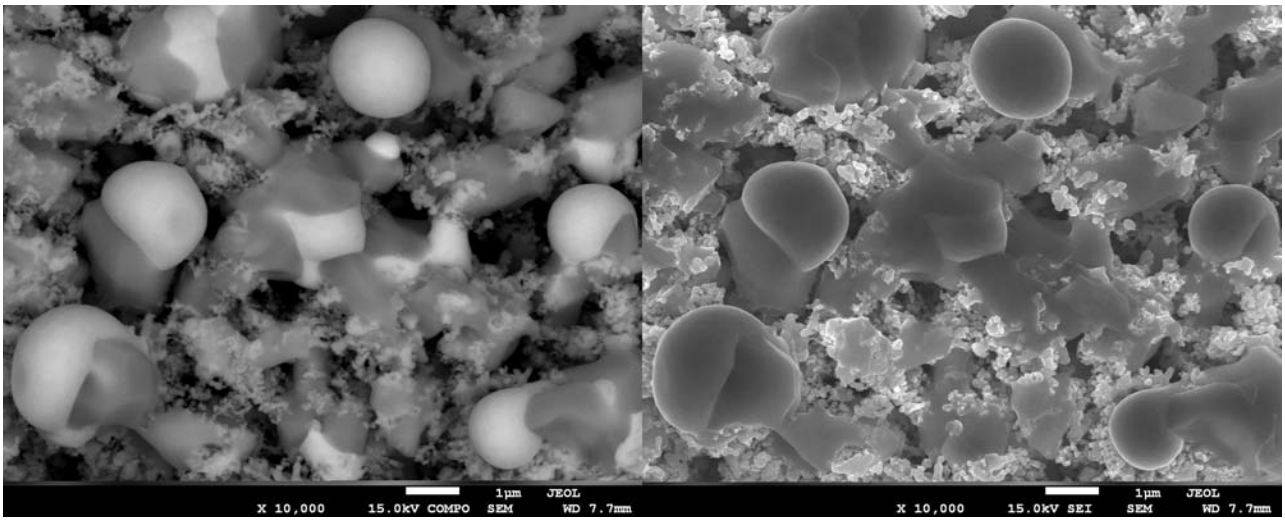


Figure 1. SEM picture of microstructure of the composite cathode Ag–LSCF: left in the COMPO mode, right in the SEI mode. The electrode contacting interconnector was heated for 144 h at 600°C. White balls contain only Ag whereas grey crystallites accompanying these balls contain Ag and Cr.

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 the determination of the mechanism of formation and stability of multilayer polyelectrolyte films with embedded casein and verification of their bioactivity, i.e., ability to bind the calcium ions

Polyelectrolyte multilayer films were built by sequential adsorption of polyelectrolytes (LbL) at surface of silicon wafers, quartz crystals (QCM) and germanium crystals (FTIR measurements). We found that 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). Analyzing experimental data we found that films formed with poly-L-arginine (PLArg) were much thicker (around 50%) than those built with poly-L-lysine (PLL). Additionally, dry films were 2 times thinner that the same films built in water environment; films constructed with α-casein were thicker that those with β-casein both in pair with PLL and PLArg.

We investigated the dependence of thickness of casein containing films on the ionic strength of the polyelectrolyte solution and on the 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 the charge reversal of casein. (PLL/cas)n films were also not stable in pH 11 due to the neutralization of PLL. Similarly, these films were more stable than ones with β-casein, when contacted with the solutions with various compositios. (PLArg/cas)n films were stable in base solutions (pH 11). During the QCM-D experiments we observed only a small decrease in the film thickness after applying solution having pH 11.

(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 that the (PLArg/cas)n films were stable in all conditions except for solution 1.5 M NaCl. In that solution removal of the film from support was observed.

To check the ability of casein to bind calcium ions, when it is embedded in polyelectrolyte films, the silicon plates covered with the PE films were immersed in the $CaCl_2$ solutions. After that the plates were measured by FTIR and XPS techniques. We found slightly shifts in FTIR spectra of casein of the maximum of the picks of amid I and amid II in direction of higher wavenumber. It suggested that absorption of casein in the multilayer film brought on a structuring in casein chains (to α helices). XPS data provided us the information about the contents of calcium ions in the casein/polyelectrolyte films. Using FTIR and XPS techniques we have confirmed that calcium ions can be incorporated to the casein built into polyelectrolyte multilayer films that means that casein is bioactive in such films. Obtained data are promising in context of our further investigations.

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)

Analysis of properties of molecular nanocontainers suspended in physiological fluid (0.145 mol L^{-1} NaCl solution in water) has been performed, Fig.1. The studies were focused on the effects of intermolecular interaction in: colloidal stability of suspension of the nanocontainers in solution, stability of the capped forms of the nanocontainers in intermolecular collisions, ability of performing the magnetically triggered uncapping and dynamics of drugs release (cisplatin) from the interior of the nanocontainers.

To that purpose the model and the force field for molecular dynamics simulations developed within previous research tasks have been utilized. The capped forms of the nanocontainers, containing the encapsulated cisplatin molecules, were subjected to detailed analysis. Particular attention was paid to stability of those capped forms in intermolecular collisions in solution. Various collision trajectories with various energies (collision temperatures) were studied. Also, the range of effective intermolecular interaction energy after collisions was analyzed. Influence of the direction of external magnetic field was probed by analyzing the slit sizes between magnetic nanoparticles and carbon nanotubes tips.

Results obtained in this study lead to several important conclusions. Namely: intermolecular collisions occurring at ambient conditions (temperatures of the order 300 – 310 K) do not lead to destruction of the capped forms of the nanocontainers and uncontrolled leakage of drug molecules do not occur, however, at higher temperatures (400 – 600K) these phenomena are likely to occur. The current chemical state of the nanocontainer, that is hydrophobic nanotube sidewalls and hydrophilic tips do not provide the colloidal stability of the nanocontainers, further chemical modification of the nanotubes sidewalls leading to reduction of hydrophobic interactions is necessary. The magnetically triggered uncapping occurs easily in assemblies of the nanocontainers, thus the intermolecular interactions do not affect those processes. As a result of magnetically triggered uncapping, the release of cisplatin proceeds according to activated one-dimensional diffusion mechanism. It was, however, found that in case of narrow nanotubes and high loadings of drugs the release might be apparently a non-activated process. This is due to the effect of dragging of drug molecules by the detaching magnetic nanoparticles. Then, the release pattern reveals two stages, the first (fast) corresponding to non-activated stage and the second (slow) obeying the activated diffusion mechanism, Fig.1.

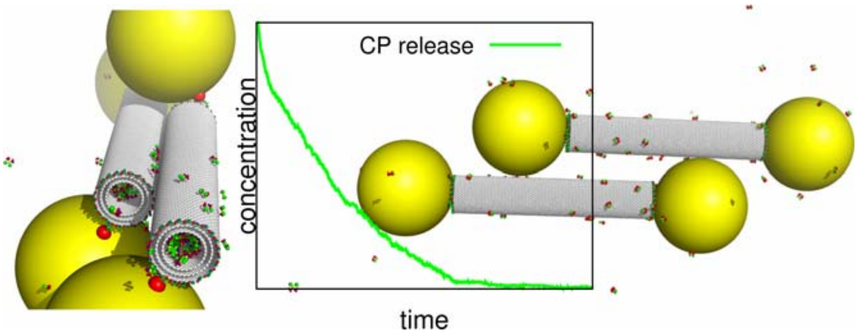


Figure 1. Two interacting molecular nanocontainers and the release pattern of cisplatin

The obtained results confirm the applicability of the considered system in the area of nanomedicine. It can act as a smart drug delivery system being able to initiate drug release in response to an external magnetic field.

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 solid surface and (ii) presence of air micro-bubbles on kinetic of the three-phase contact (TPC - solid/liquid/gas) formation.

In the reporting period experiments on time of the TPC formation (t_{TPC}) by the colliding bubble at hydrophilic and hydrophobized surfaces of fritted glass filters of defined porosity (pore diameters ranging between 16 and 40 μm). The motion of the bubble of radius R_b=0.74 mm and kinetics of its collision with investigated interfaces was monitored using high-speed camera. The distance between the bubble formation point and the interface was set in such a way that the bubble was still at the acceleration stage of its motion, and its impact velocity was smaller than the terminal one (~20 cm/s). The special procedure of the filter surface preparation was elaborated to obtain the glass porous surface: (i) without air ("no-air" case) and (ii) with air ("air" case). For the case (i) a special care was taken to minimalize the amount of air within the filter pores and at the porous surface, while for the case (ii) the condition of the filter contacting with air and immersing into aqueous phase favoured presence of air in pores of hydrophilic filter and at its surface (small overpressure in the filter < 1kPa).). It was found that air presence at hydrophilic porous surface affected significantly the collision course, the bouncing amplitude and time of the bubble immobilization (time needed for kinetic energy dissipation). In the case of hydrophilic surface, for "no-air" scenario the bubble was immobilized (captured) beneath the solid surface during the fourth collision, after about 45 ms. For the "air" case the kinetic energy was dissipated much faster, and the bubble was captured after 25 ms. Additionally, for "air" case the amplitudes of the bubble position oscillations and the bubble local velocity variations during the collisions were shifted towards smaller time values. In order to obtain more results supporting the experimental findings and hypothesis about the crucial role of air presence at solid surface for kinetics of the bubble collision, the numerical calculations were carried out. The behaviour of the bubble colliding with solid wall, where single pore filled with micro-bubble (height 11.4 μm) was present, was calculated numerically by solving the momentum and mass conservation equations. The results of numerical calculations stayed in pretty good agreement with experimental data. Both sets of data indicate that faster immobilization of the colliding bubble at hydrophilic porous surface was related to a quicker drainage and rupture of foam (water) film(s) formed locally between the colliding macrobubble and submicroscopic bubbles protruding from the hydrophilic surface pores. The phenomena observed were related to so-called capillary bridging mechanism. During the collision of the bubble with solid surface, where air was present, the air bridges were formed between colliding bubble and micro-bubble(s) protruding out the pores of fritted glass. As a consequence, part of the energy was consumed to overcome the capillary force acting at perimeter of the micro-bubbles present at the solid surface. In the case of hydrophobized fritted glass surface the observed effect of different kinetics of the bubble collisions with "air" and "no-air" surfaces was similar. In this case, however, the time of TPC formation (t_{TPC}) was determined. It was found that in the case of "no-air" surface the t_{TPC} was equal 22 ms, while for "air" case equal 2 ms, i.e. was significantly lowered.

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 transmetallation 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, the studied process 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. Present theoretical investigations were complemented with kinetic studies in solutions, monitored by UV-VIS spectroscopy.

Theoretical studies on magnesium ion exchange for the other metal ion are continued with stress put on the determination of factors, which are crucial for the process and control its effectiveness.

It appears that the reduced coordination number of magnesium in porphyrin type of compounds is one of the factors facilitating the initiation of the process of transmetallation of magnesium porphyrin by copper ions. Furthermore, the elucidated mechanism indicates the dependence of the reaction rate of the process on the solvent. The strength of magnesium – solvent bond in the initial complex may modulate its effectiveness. This finding is in agreement with experimental results, which postulate that the reaction is strongly influenced by the solvent.

The next factor influencing the rate of transmetallation is the type of chelating ligand, whose role is to activate magnesium ion. Based on already made experiments two chelators were chosen: acetate ion and acac ion. The performed calculations show that the influence of the chelating species is different and includes the interplay of two factors:

- Geometric: the binding of the chelating ligand to Mg(II) ion results in tetrapyrrole ligand deformation and Mg ion out-of-plane displacement. These changes facilitate binding of the incoming Cu(II) ion to the tetrapyrrole nitrogens. It was found that Mg out-of-plane displacement is larger for acac than for acetate species.
- Electronic: The nucleophilicity of the tetrapyrrole nitrogens is increased upon chelating. This facilitates electrophilic attack of Cu(II) ion onto tetrapyrrole nitrogens. The nucleophilicity of nitrogens was expressed as ESP charges, which quantify the electrostatic potential around a given atom. The effect is larger for acetate ion than for acac.

Finally, it seems that yet another factor is related to the respective conformation of the chlorophyll moiety and its potential ligands (solvent and chelating species). The preference for different facets of chlorophyll moiety was determined for both species. Acetate ion prefers “up” face of the tetrapyrrole, whereas solvent molecule prefers the opposite “down” face (where the phytol tail is attached). This observation was made on the smaller model of chlorophyll, which includes only pheophytin part, and thus requires further confirmation by applying the complete model enlarged by phytol tail.

The New Multi-Layered Systems with Controlled Architecture and Functionality

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

The project was implemented according to schedule. Studies were conducted on a mixture of two parallel adsorbing proteins.

Research aims to clarify the mechanism of parallel adsorption, and to develop a theory that describes well the experimental results.

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

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

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

AFM microscopy studies were performed in wet conditions.

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 the effective method of preparation of well-defined emulsions using membrane emulsification method. Such emulsions will be used as cores in encapsulation process. Membrane emulsification method is the low energy consumption process, which allows controlling size of the obtained emulsion droplets by the selection of membranes 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 2013 we focused on the task of the project concerning determination of the influence of process parameters on formed emulsions by membrane emulsification using apparatus built in our Institute last year. The series of studies of the influence of the shear force on the size of oil droplets formed in the membrane emulsifier were performed. Emulsion droplets were produced on the hydrophilic ceramic membrane with pore size of 4 micrometers. Freshly formed emulsions were characterized by droplet size analysis and the stability studies by Dynamic Light Scattering and direct microscopic observation. The effect of concentration and type of surfactant on the properties of the emulsion were also tested. Anionic SDS, cationic DTABr and nonionic Tween 80 surfactant were selected for that purposed. Figure 1 presents the dependence of average size of emulsion droplet on the surfactant concentration used in the emulsification process.

In the next stage of the project the membrane emulsification will be used to produce microcapsules containing anticorrosive agents. Such microcapsules can be used in the "smart" anticorrosive coatings, where the active ingredient is released from the capsules upon damage of the coating.

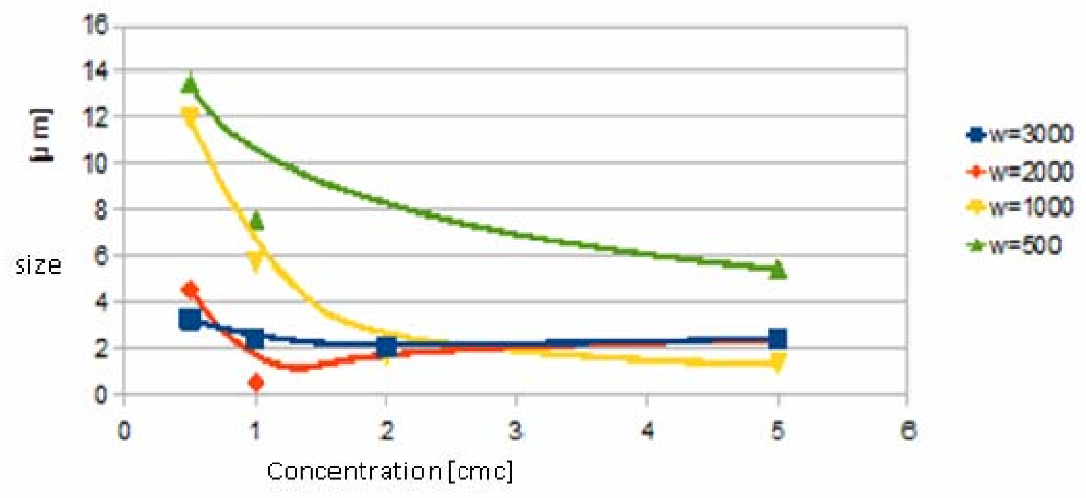


Figure 1. The dependence of the size distribution of the formed emulsion droplets on the concentration of Tween 80 surfactant used for emulsification.

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 during the bubble collisions with solid surfaces of low hydrophobicity. The three phase contact gas/liquid/solid is formed if a wetting film formed by the colliding bubble is ruptured during the collision time. Solid surface hydrophobicity and roughness, presence of surfactants (their kind and concentration), state of the adsorption layers at the film interfaces, magnitude and signs of electrical charge at the interacting interfaces are the most important parameters affecting stability of the wetting films. Electrostatic interactions between gas/liquid and liquid/solid interfaces of the wetting film can be either stabilizing or destabilizing forces, especially at solid surfaces of low hydrophobicity. Their magnitude can be modified through variations of the solution pH and adsorption of ionic surfactants. It was showed, in the experiments carried out, that preferential adsorption of cationic surfactants (n-alkyltrimethylammonium bromides - C8, C12, C16) at negatively charged bubble surface led to the wetting film rupture and the bubble attachment to hydrophilic, negatively charged mica surface. Moreover, the time of the bubble attachment depended strongly on solution concentration and state of the adsorption layer over surface of the colliding bubble. When the dynamic architecture of the adsorption layer (DAL), i.e. non-uniform distribution of the surfactant coverage, was established over surface of the colliding bubble, then longer time was needed for the bubble attachment. This is due to the fact that an additional time was needed in these cases to restore such adsorption coverage over top pole of the rising bubble, which caused the charge reversal from negative to positive and the film destabilization.

In 2013 A. Niecikowska M.Sc. was on the maternity leave and therefore the date of the grant fulfillment was shifted to 2014. Nevertheless, she worked out the data obtained earlier and prepared 3 posters presented at international conferences. She is also a co-author of 1 paper submitted for publication.

"Sonata Bis" Research Projects of the National Science Centre

Computer Aided Design and Prediction of Properties of Drug Delivery Systems Based on the Structure of Carbon Nanotubes

"Sonata Bis" research project NCN 2012/07/E/ST4/00763 [2013-2017]
(project leader: Assoc. Professor Tomasz Pańczyk)

Carbon nanotubes (CNT) reveal many properties which are potentially useful in drug delivery technology, these include: large inner volume, high mechanical stability and high aspect ratio which allows for facile penetration of cells membranes and moreover they are able to reach cell nuclei. Some unwanted properties of carbon nanotubes like toxicity or hydrophobicity can be reduced by a suitable chemical functionalization or size reduction. However, pristine carbon nanotubes do not reveal useful properties in terms of drug delivery vehicles. Therefore, various options of chemical or physical modification of carbon nanotubes are considered in order to find optimal structures revealing suitable properties. The aim of this work is detailed analysis of several theoretical concepts which can lead to designing of new CNT-based materials with extraordinary properties.

In the first stage of the project realization we focused on the development of the research methodology. It particularly concerns the theoretical backgrounds for modelling of CNTs interaction with organic ligands and colloid nanoparticles which can additionally reveal superparamagnetic properties. At this research stage we chosen the Congo red as the organic ligand interacting with CNTs. Congo red reveals ability to creation of supramolecular structures in aqueous solutions having a geometry of ribbon micelles. In the next stage of the studies the analysis of CNT-congo red conjugates will be performed as it is one of possible ways of pH dependent hydrophylization of CNT sidewalls. The methodology of characterization of spatial structure of Congo red ribbon micelles was developed. It is an important parameter allowing for analysis of structural changes in interaction with CNTs. Analysis of this parameter gives a measure of deviation from planar geometry and allows for full statistical description of those deviations as function of systems parameters. Another problem analyzed in this study was development of the research methodology for interactions of CNTs with colloid superparamagnetic nanoparticles. In this stage of the studies we focused on the methodology of determination of T_2 relaxivity. This is one of the most important parameters of magnetic nanoparticles. We developed totally new method based on molecular dynamics simulations with allows for analysis of the influence of various parameters on the T_2 relaxivity. These include zeta potential, Hamaker constant, magnetic anisotropy constant, presence of various functional groups or adsorption of water on the surface of nanoparticles. These parameters can affect the effectiveness of magnetic nanoparticles as contrast agents in magnetic resonance imaging, moreover, it is interesting whether the CNT-nanoparticle conjugates can act as such constant agents and thus become a nanotheranostic system.

The results obtained in this stage of the studies are mainly of fundamental significance. The developed methodology allows for further analysis of those classes of systems in terms of their application as drug delivery or diagnostic systems based on the structure of carbon nanotubes.

"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)

In the reporting period, a long-term monitoring of microclimate conditions and the concentration of dust in two size-fractions (0.3-1.0 microns and above 1.0 microns) in 3 new churches was initiated:

- 14*th*-century Gothic Collegiate Basilica of the Birth of the Blessed Virgin Mary in Wiślica equipped with a radiant heating,
- 20*th*-century Gothic-revival St. Joseph’s church in Krakow-Podgórze equipped with a pew heating system,
- 13*th*-century Gothic St. Mary's Basilica in Krakow equipped with electric storage heaters.

These three newly-monitored churches, and the remaining 7 monitored in the previous year add to a total of 10 churches planned in the project. In addition, in three churches where the monitoring was started last year:

- 13*th*-century 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,
- 15*th*-century Gothic church of St. Catherine of Alexandria in Krakow equipped with a radiation heating system,
- 20*th*-century Orthodox Church of St. Mary Magdalene in Warsaw equipped with a central heating system

Measurements were also carried out in the subsequent heating season in order to improve the statistics of the results. In all of the above -mentioned locations, the monitoring system consisted of at least two dust sensors at different locations spaced in the vertical profile, two temperature and relative humidity sensors, air speed and direction sensor, and CO_2 concentration sensor. In addition to monitoring the concentration of particulate matter inside the objects, the concentration of dust outside of the buildings as well as temperature and relative humidity of the outside air was measured.

In parallel with the long-term monitoring, short-term measurements (lasting about a week) are carried out with the use of a DustTrak DRX 8533 (TSI) aerosol concentration monitor measuring 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 a detailed chemical and morphological analysis. An initial comparison of the results of the gravimetric measurement conducted in St. Catherine’s of Alexandria church taken by means of this device confirms a very good agreement of the mass measurement (after an appropriate conversion) done by means of laser sensors measuring of the concentrations of particulate matter.

Results of the monitoring in 4 churches, in which the measurements were finished in the reporting period, are now subject of a detailed analysis encompassing the following issues: determining the air exchange rate between outdoors and indoors, and the related infiltration of the suspended particulate matter, sources of particle pollution indoors, increased turbulence of the air flow indoors and re-suspension of the deposited dust as a result of the church use, as well as mechanisms of the particle deposition on architectural surfaces.

New Pd-Pt/ Hybrid Nanocomposite Catatalysts 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.

Studies undertaken in 2013 concerned palladium and platinum catalysts synthesis and characterization of their physicochemical properties as well as investigation of their electrocatalytic activity towards ORR. In particular, the effect of Nafion ionomer (used as binding agent) on electroactivity of the investigated catalysts was evaluated. In all catalysts prepared by “water-in-oil” microemulsion method, the Pd nanoparticles of ca. 7 nm in size appeared regardless of the Pd content (ranging from 2 to 20 wt.%). Coating of the Pd/PPY samples with Nafion reduced their surface area and porosity. Chemical interaction due to Nafion acid functionalities affected the N-state of pyrrole as well as electron state of Pd in the Pd/PPY catalysts. These interactions played an essential role in the electroactivity of Pd/PPY for oxygen reduction reaction. For comparison, carbon black-supported (Vulcan XC-72) catalysts were also synthesized. The increased amount of Nafion relative to that of both investigated carriers reduced limiting current density. Simultaneously, an increase in the fraction of the undesired product hydrogen peroxide was observed when Vulcan XC-72 was used. Whereas in the case of PPY the half- wave potential shifted to a more positive value and the fraction of hydrogen peroxide remarkably decreased. This enhanced ability of the Pd/PPY catalyst towards oxygen reduction might probably arise from modification of Pd-sites reactivity induced by the presence of Nafion.

To date, the Nafion–Pt and Nafion–Pd interaction effect has not been taken into consideration in discussing the results of oxygen reduction reaction on Pt and Pd electrocatalysts. Therefore, the obtained results could contribute to a better understanding of factors responsible for catalysts activity in oxygen reduction reaction.

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 to determine the formation mechanism of hybrid multilayer films and to investigate the impact of the structure and surface properties of nanocomposites on their functionality and application in the field of modern materials. 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.

Determination of the impact of the model solid surfaces modification by polyelectrolyte mono/multilayer on the lipid bilayer formation was the main task for the current period. The technique of *layer by layer* assembly was used for the polyelectrolyte multilayer formation. Synthetic (PEI, PSS, PDADMAC) and natural (PLL, PGA) polyelectrolytes were used for the build up of multilayer films. Small unilamellar vesicles (SUV) were prepared by the extrusion method using polycarbonate membranes of the defined pore size of 100 nm. For the preparation of lipid vesicles following lipids were used: zwitterionic 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC), positively charged 1-palmitoyl-2-oleoyl-*sn*-glycero-3-ethylphosphocholine (chloride salt) (POPEC) and negatively charged 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phospho-L-serine (sodium salt) (POPS). The chosen lipids had the same hydrophobic chain with different ionic groups. The obtained SUV were characterized using dynamic light scattering and zeta potential measurements. The investigation of the formation of supported lipid bilayer (SLB) by quartz crystal microbalance with dissipation monitoring (QCM-D) was a very important step, which provided information about the mass and structure of adsorbed material during the deposition. The effect of polyelectrolyte multilayers of various thickness and surface charge used for the modification of QCM crystal surface on the vesicle fusion and the formation of supported lipid bilayers was investigated. We observed the formation of complete lipid bilayer by vesicle adsorption and rupture only for the following system: negatively charged lipids and gold sensor surface modified with PEI. In other cases we have observed adsorption only without the vesicle rupture.

The modification of hydrophobicity of quantum dots by using lipids was the next task for this year. Quantum dots were incorporated into hydrophobic parts of liposomes during their formation. Series of quantum dots of size from 1.6 nm to about 6 nm were used. Each type of quantum dots was successfully incorporated in the lipid systems, which was proven by registering of the emission spectra for liposomes with quantum dots with the spectrofluorimeter. Characteristic peaks corresponding to the quantum dots used, were observed. The next step was to investigate the deposition process of such modified liposomes on model solid surfaces. The results obtained confirmed the adsorption of liposomes modified with quantum dots on selected polyelectrolyte films deposited on the surface of the quartz crystal.

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. The ring conformation of the hexopyranose-based carbohydrate molecules is one of the central issues in glycobiology. The ring conformers (puckers) can determine the biological function and activity of carbohydrate and the dynamic equilibrium between puckers determines the macroscopic hydrodynamic properties of the carbohydrate polymers. Due to the extremely high free energy barriers separating particular ring conformers, most of the theoretical studies is focused on the detailed description of the free energy landscapes, neglecting the dynamic features of the conformational changes.

The reported study, based on the transition path sampling (TPS) simulations was aimed at filling this gap. We focused on the α-D- and β-D-glucopyranose molecules (GlcA and GlcB, respectively), treated as model systems. The results allowed for:

identifying the distinct local minima of the free energy corresponding to the states intermediate for the $^4C_1$ ↔ $^1C_4$ transitions;
assigning the time-characteristics to this transition and intermediate states;
performing the search for the optimal reaction coordinate based on the Peters-Trout approach (likelihood maximization).

Additionally, the structures corresponding to the $^4C_1$ ↔ $^1C_4$ transition states (TS) have been found; surprisingly, in the case of GlcA, the water dynamics has very little influence on the probability of the TS evolution either to $^4C_1$ or to $^1C_4$. The different result obtained for GlcB (large influence of water dynamics on the behavior of TS as well as the poor applicability of the Peters-Trout approach for calculation of the reaction coordinate) speaks for slightly different mechanisms of the $^4C_1$ ↔ $^1C_4$ puckering in molecules of GlcB and GlcA, probably with the larger contribution of diffusive transitions, characteristic for rough free energy landscapes in the case of GlcA.

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 the 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 are 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 2013, we focused on the preparation of nanocapsules containing hydrophobic anticancer agents Paclitaxel and on the determination of their cytotoxic/cytostatic activity. Nanocapsules were obtained by method developed previously in our lab, i.e., by direct encapsulation of emulsion droplets in the polyelectrolyte multilayer shells. The nanocapsules containing Paclitaxel with an average size of 100 nm were obtained. *In vitro* analysis of the effects of nanoformulations was performed using CT26-CEA, MC38 and 4T1 cell lines by various biochemical assays (MTT, LDH). Analysis of biological effects of empty as well as paclitaxel-containing nanocapsules show high activity of encapsulated drug. Figure 1 presents the comparison of the effects of paclitaxel encapsulated in nanocapsules (NP1PX, NP2PX), empty nanocapsules (NP1, NP2) and free paclitaxel (PX) on the viability of tested cells. The results show that our nanocontainers can be further considered as a promising delivery system for anticancer drugs.

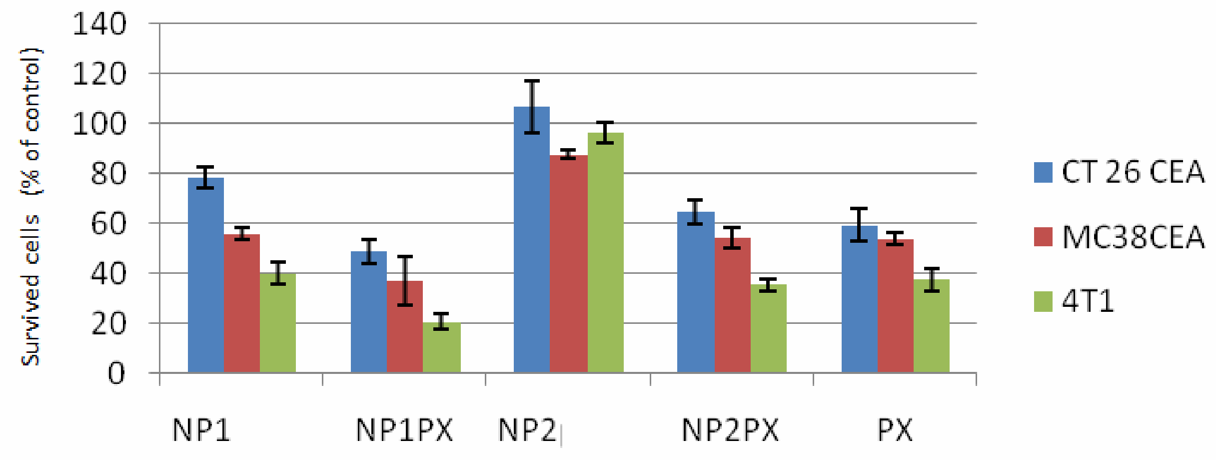


Figure 1. Comparison of the effects of paclitaxel encapsulated in nanocapsules, empty nanocapsules and free paclitaxel on CT26-CEA, MC38CEA and 4T1 cells viability.

The Mechanism of Regioselective Oxidation of Cholesterol Derivatives by a Novel Molybdenum Enzyme, Steroid 25-OH Dehydrogenase from *Stereolibacterium denitrificans*

"Sonata" research project NCN 2012/05/D/ST4/00277 [2013-2017]
(project leader: Maciej Szaleniec DSc)

The aim of the project is elucidation of the reaction mechanism for hydroxylation of cholesterol derivatives by steroid C25 dehydrogenase (S25DH). S25DH is molybdoenzyme and originates from a denitrifying bacterium *Sterolibecterium denitrificans.* It catalyzed hydroxylation of ternary carbon atom (C25) in cholesterol and its derivatives and the reaction does not requires molecular oxygen. Instead, the oxygen atom is most probably introduced from Mo=O ligand from molybdenum cofactor.

Studies of the reaction mechanism are conducted both with theoretical and experimental methods. As a first step of the theoretical modeling of the mechanism a homology model of the enzyme was constructed based on the crystallographic structure of ethylbenzene dehydrogenase, a prototype enzyme of that sub-class. The structure of catalytically active, oxidized molybdenum cofactor was achieved by QM:MM modeling within model of ethylbenzene dehydrogenase. The resulting homology models were subjected to minimization and molecular dynamics (MD) optimization of the active site. Two types of MD models have been used: with water molecules introduced into the active site and without solvent molecules.

The minimized models were used for docking of 20 substrates, potential substrates and known inhibitors of S25DH. This allowed analysis of the important intermolecular interactions in the active site as well as validation of the obtained homology models. Moreover, the parameterization of the whole molybdenum cofactor is underway. The parameterization of the cofactor will allow full MD optimization of the whole α subunit.

The experimental part of the project started with improvement of previously known aerobic purification protocol of the enzyme. An improved method utilized two IEX chromatographic steps (DEAE-Sepharose, Q-Sepharose) followed by affinity chromatography on Reactive Red column. The 0.1 mM ferrocenium tetrafluoroborate was used as a protectant in all chromatographic buffers. As a result an enzyme preparation was obtained with 4-fold enriched activity of S25DH compared to the enzyme obtained after first two step of purification.

Within the studies of substrate structure – enzyme activity relationship protopanaxatriol, dipterocarpol, cholic acid and stigmasterol was assayed for activity. The initial results suggest that the enzyme exhibits trace activity with stigmasterol.

Finally, the protocol of the enzymatic assay was optimized. The main problem of the assay is a very low substrates solubility in water. Therefore a range of solubilizing agents (beta-cyclodextrine. tert-butanol, saponins, DDM, CHAPS, 2-methoksyethanol) was assessed that can assist in solubilization of the substrates without their sequestration. A new activity assay turned out to be app. 6 times more sensitive than the assay reported in the literature.

"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.

Investigations of the fatigue processes carried out in the first phase of the project 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. The measurements showed that for the tensile strains of the magnitudes of 0.2 and 0.4 stabilization of the damage is observed after 75 000 and 170 000 strain cycles, respectively.

In the current phase of the research, the emphasis was laid on determining the impact of the wood annual ring structure on the crack network formation on the surface of the gesso as well as on assessing impact of the specific order of different strain cycles on the rate of damage development.

For the lime wood, commonly used in panel paintings, differences in the moisture related strain of the early and late wood are smaller than the average response of different samples to the same moisture change. In contrast, high strain concentrations are observed at the interface between the early and late wood, during both mechanical and humidity changes. These strains are transferred to the decorative layers, causing their fracture.

A systematic study of the fatigue process showed that the sequence of mechanical cycles has no effect on the rate of crack formation on the surface of the ground layer, whereas it is important at which humidity the sample was stored prior to doing measurements. This effect was analyzed by subjecting gesso samples on the wood substrate conditioned at different relative humidity to fatigue testing. The first results indicate that, at high humidity, stress in the sample decreases due to the ductility of the ground layer, which results in reducing the risk of fracture in the paint layer during stretching after reducing the relative humidity to 50%..

Monitoring the deformation of samples subjected to large amplitude humidity cycles confirmed a large change in the stress state of the ground layer after passing the high humidity cycle.

Quantitative assessment of the effect of the phenomena described above on the rate of damage development in the decorative layers will provide basis for an algorithm simulating the damage development in surfaces of historical objects in environments in which the objects are stored.

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)

Aqueous foams are extremely complex systems with a cellular internal structure, consisting of polydisperse gas bubbles separated by draining films. The main process taking places in such wet foams is a free drainage, due to the influence of gravitational acceleration, and viscous force between the adjacent bubbles. As result in absence of stabilizing agents the foam collapses. So far foams based on biopolymer have been considered as especially unstable.

The project aims to develop the new technology of generating of stable, but 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. Polysaccharides (chitosan, methyl cellulose or pectin) based "biofoams" could be used as unconventional agent for sterile dressing to prevent from infections and blisters during painless curing wounds.

The foaming potential of bio-surfactant solutions under influence of the solid particles were described by the foamability and foam stability tests in the foam column. 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.

It was found that the particles presence influence on BSA foam stability much more than methyl cellulose foam. The particles with diameter above 100 nm increased the stability and height of BSA foam. The initial height of foam was correlated with values of dynamic surface tension: the lower surface tension indicated the higher level of the foam.

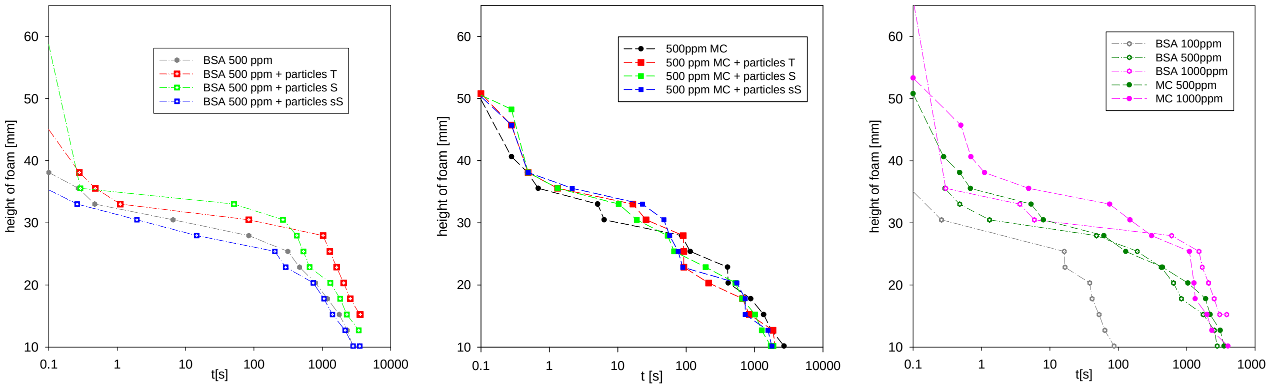


Figure 1. Bio-foam stability under influence of various solid particles in solutions of BSA and methyl cellulose (MC). (particles studied: T means TiO2 P90 Degussa, particle size ca. 2000nm, S = SidiShield C25 SiO_2, particle size ca. 200nm, sS => it's Elkem NanoSilica 999 SiO_2, particle size ca. 100nm)

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)

Most of the chemical processes are usually performed in organic solvents that are hazardous for natural environment. Due to their negative impact on natural environment it is the must to stop the use of organic solvents in chemical processes. Limitation of their use has already been forced by international treaties such as the Montreal Protocol. Perfect solvent should be non-toxic, biodegradable, non-volatile, able to dissolve a wide range of compounds, inexpensive and recyclable. Glycerol is highly promising in this respect. Glycerol is produced in huge quantities as a side product of transestrification of trigycerides. The exchange of volatile organic solvents used in chemical processes for the environmentally friendly compounds would have a great impact on the reduction of the use of organic solvents on industrial scale.

In Poland, glycerol or glycerol-based family of solvents has not yet found practical application as solvents in oxidation of phenol with hydrogen peroxide as oxidant and in the presence of metallocomplexes and heteropoly compounds as catalysts. 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 as catalysts in oxidation of phenols with H_2O_2.

First stage of the research consisted in the synthesis of water-soluble cationic metalloporphyrins MnTMPyP, FeTMPyP, CoTMPyP; MnTAP, FeTAP, CoTAP; anionic metalloporphyrins MnTPPS, FeTPPS, CoTPPS; anionic metallophthalocyanins MnPcS, FePcS, CoPcS, NiPcS, CuPcS and anionic metalosalens MnSalenS, FeSalenS, CoSalenS. The second group of synthesized compounds are manganese, iron and cobalt salts of tungstophosphoric or phosphomolybdic acids, $H_{3-2x}M_xPX_{12}O_{40}$, where X=Mo or W, x=½, 1, 1½. Synthesized samples were characterized by means of FTIR and UV-Vis spectroscopies and cyclic voltametry. They were applied as catalysts in the oxidation of phenol with H_2O_2 in the presense of glycerol as solvent.

Catalytic activity of cationic metalloporphyrins was studied in the oxidation of phenol in glycerol. For both groups of metalloporphyrins the following order of activity was established: FeP > MnP > CoP, where P=TMPyP or TAP. Similar order of activity was obtained for the same porphyrin metallocomplexes in the oxidation of phenol in acetonitrile.

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)

Primary goal is to establish structure-reactivity-relationship for oxides of Cr, Mo and W supported on silica and to explain how differences between the three elements affect the catalytic activity of their oxides. In our calculations we use a model of amorphous silica created through ab-initio molecular dynamics by dr Frederik Tielens from Université Pierre et Marie Curie in Paris. Secondary goal is to test and verify the periodic model of amorphous silica developed by dr Tielens and establish a solid base for future cooperation.

The research has a theoretical character and is conducted within periodic DFT method (employing VASP program) using PBE and PW91 functionals and plane waves as basis functions. Geometrical structures of MO_2 (where M=Cr, Mo, W) monomers anchored between two surface oxygen atoms were established. In the model of amorphous silica used there are 27 possible anchoring sites for each metal. Properties of NH_3 molecule adsorbed on surface Brönsted acid sites were also calculated. Additionally two surface modifications were considered: (i) creation of Si vacancy (27 possible structures) and (ii) substitution of Si center with Al cation (27 strustures). Further research will focus on monomer reactivity tests through adsorption of hydrogen and desorption of water.

Preliminary analysis of the results suggests that the main factor which influences the monomer reativity in redox reactions is the position of in-gap-states – additional energy states introduced by anchored monomer which are located within the band gap of the material. Additionally, the position of in-gap-states is correlated with the angle between monomer-surface bonds.

According to NCN rules, conducted research has basic character and obtained results have no immediate application in practice. However, due to a systematic description of a system with considerable importance in catalysis, the outcome of this project can form a solid fundation for further, more practical research.

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 goal of theoretical modeling in last period were heteropolyacids with Keggin structure, with formula $H_3PMe_{12}O_{40}$ (Me=Mo,W), modified by Cu ion in positionof central ion (CuW), addenda atom (PCuW) and compensating cations. Electronic structures of modified Cu-HPA were carried out within the DFT approach using the gradient corrected PBE, B-97D and B3LYP approach. The solvation effect was taken into account within COSMO approximation or by calculation of specific interaction of Cu^{1+}/Cu^{2+} ions with solvent molecules (H_2O, CH_3CN, DMSO).

Results of calculations show that Cu^{2+} ion introduced into the Keggin's anion has different charge, depending on the position, which it occupies in the structure. As a tetra-coordinated central ion, the charge on Cu^{2+} ion is substantially higher than charge on P in the reference (PW) system. In the position of addenda atom, surrounded by five oxygen ions, the charge of Cu^{2+} is much lower than on other addenda atoms (W/Mo). As a central ion Cu^{2+} (in CuW system) influences only closely localized oxygen atoms, which formed internal tetrahedron (inaccessible for substrates). Results of calculations for modified HPA in which one addenda atom was substituted (PCuW system) show that chemical character of introduced copper atom influences the nucleophilic character mostly of bridging oxygen atoms coordinated to introduced element. As show the Wiberg bond order analysis strong differentiation of metal-oxygen bonds in hole Keggin anion can be noticed in both, modified by copper ion systems. The changes are observed for interaction bonds between the internal tetrahedron-rest of Keggin anion as well as for metal-oxygen bonds in and between the triads (Me_3O_{13}). The introduction of Cu Keggin anion leads to systems with unpaired electron, which as shown the spin density analysis, is located almost entirely on the Cu cation.

Introducing of Cu^{2+} ions into Keggin anion results in new peaks between the valance and conduction band, that is characterized by *5d*-copper orbitals. The character of the main valence and conduction band stays almost the same, as the character of bands in the reference PW system. The valence band consists mainly of *2p*-orbitals of bridging oxygen with the small addition of addenda metal, whereas the conduction band consists mainly of addenda orbitals (W/Mo) with small amount of *2p*-oxygen orbitals. The calculated energy values for the solvent systems (with water as a solvent =80) show that introducing Cu into the system influences the energy of HOMO orbitals, which increases in order: PW (-6.89) < PWCu (-5.61) < CuW (-4.62). Smaller changes can be observed in LUMO energy orbital, which presents only slight decrease (0.1-0.25 eV) in systems modified with Cu^{2+}.

Interaction of Cu with sol vent molecule depends on charge on cooper ions and character of solvent. Cu^{1+} ion forms with water 2- 3-coordinated complexes whereas the Cu^{2+} forms six-coordinated complexes. With acetonitrile Cu^{1+} ion builds tetrahedron species Cu^{2+} octahedral complexes. Interaction of Cu^{1+} ions with DMSO ($(CH_3)_2SO$) molecule leads to the formation of four-coordinated complex with tetrahedral geometry.

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 this part of the project was to examine surface tension isotherms of quaternary ammonium salts surfactants: N,N,N-trimethyl-2-(dodecanoyloxy) ethaneammonium bromide (DMM-11) and N,N,N-trimethyl-2-(dodecanoyloxy)-1-methyl-ethane-ammonium bromide (DMP2M-11)) as well as dodecyloxycarbonylmethyl-*N*,*N*,*N*-trimethyl ammo-nium bromide (DMGM-12)) and dodecyloxycarbonyl-1-ethyl-*N*,*N*,*N*-trimethyl-ammonium bromide (DMALM-12)), to analyse the influence of ester bond ROC(O)- or carbonate one R-CO-O- on their adsorption. The dynamic surface tension measurements were performed by drop shape analysis, in a wide range of concentrations of investigated ester-quats, with ester (DMM-11, DMP2M-11) and carbonate bond (DMGM-12, DMALM-12) between polar and hydrophobic groups. The surface tension isotherms of DMM-11, DMP2M-11, DMGM-12, DMALM-12 are presented in Figure 1 together with isotherms of: C16TABr, C14TABr, C11H23COOH and dDDABr. The comparison of the surface activity of surfactants DMM-11and DMGM-12 having the same molecular weight, but different molecular structure, show, that DMM-11 having two -CH2- groups and ester bond between polar quaternary amine group and -C11H23- hydrocarbon chain is more surface active is. The surface tension isotherm of DMGM-12, with one CH2- group and carbonyl bond between quaternary amine group and -C12H25- hydrocarbon chain, is shifted a half order of magnitude to higher concentrations in comparison with DMM-11. The adsorption of DMM-11 and DMGM-12 isotherms correspond to ones for cethyl-trimethylammonium bromide (C16TABr) and tetradecyl-trimethylammonium bromide (C14TABr) respectively. Presence of additional CH3 group, close to the ester or carbonyl bond in DMP2M-11 and DMALM-12 diminishes the surface activity of both surfactants by about half of the order of magnitude in comparison with DMM-11 and DMGM-12 respectively. During adsorption we observed the changes of surface tension in neutral, acidic and alkaline conditions caused by the hydrolysis process. The strongest reduction of surface tension, in comparison with other investigated surfactants, is observed during adsorption of DMM-11. The initial and minimal values of surface tension of DMM-11 reach the minimal value of 23 mN/m at concentrations near cmc. Such low values of surface tension were obtained for dDDABr, having in the molecule one quaternary ammonium group and two dodecyl -hydrocarbon chain. Hydrolysis of DMM-11 leads to the formation of dodecanoic acid which, depending on pH of the solution, dissociate to dodecanoate anions. They can form electrostatic dimers with cationic surfactant ions that decrease the surface tension down to 23 mN/m, as the structure of the obtained DMM$^+$-dodecanoate$^-$ complex is similar to the dDDABr. One can expect that the interactions of those surfactants with polyelectrolytes can be driven by the pH of the environment.

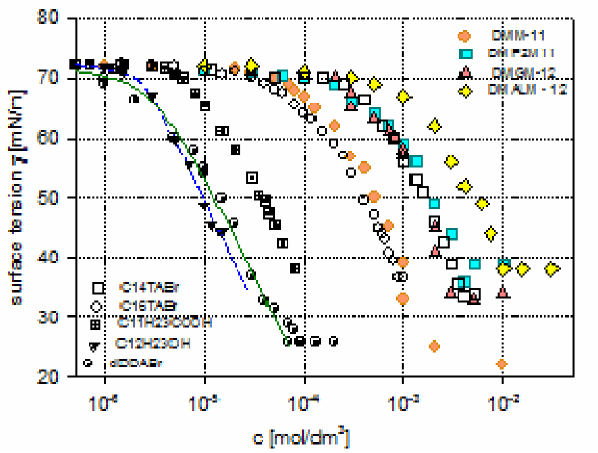


Figure 1. The experimental surface tension isotherms of ● DMM-11, ▲DMGM-12, ■ DMP2M-11, ♦ DMALM-12, together with isotherms for ○ C16TABr[28], □ C14TABr[28] • C11H23COOH [29] and dDDABr

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 (ARD) – 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.

With the mass spectroscopy the identity of the purified ARD:s was confirmed. Crystallization conditions were found and microcrystals for human and bacterial (*bacillus anthracis*) forms of ARD were obtained. Structures of both forms were solved with molecular replacement method using the known structure of ARD from mouse. In the active site of the bacterial ARD Cd ions are bound. In the crystals of human ARD ion of an unknown metal (probably iron) and the ligand, modeled in the structure as acetate, are bound in the active site.

Obtained structures will be the basis for further research on ARD, including further crystallization attempts and molecular modeling.

The Surface Chemistry Studies of the Hybrid Catalysts as the Method for the Explanation of Their Catalytic Properties in the High Pressure Dimethyl Ether Synthesis from the H_2/CO_2 Mixture

"Opus" research project NCN 2012/05/B/ST4/00071 [2013-2016]
(project leader: Assoc. Professor Ryszard Grabowski)

The aim of this project is to explain the interactions between CO_2 and the intermediates formed the reaction with the catalysts surface of the hybrid catalysts in direct synthesis of dimethyl ether (DME) from H_2/CO_2 mixture.

The investigations in the frame of the project have been started in 2013 year from the implementation of the first task – preparation the hybrid catalysts consisting of the metallic (Cu/ZrO_2) and acidic (montmorillonite K10) functions. Two different methods of the synthesis 10mols Cu/90moliZrO_2 catalyst were used: co-precipitation (with two precipitating agents Na_2CO_3 and NaOH) and citric method. Moreover, the metallic function of these bifunctional catalysts was modified with the addition of the promoters like Ga, Mn, Cr and Ag. It is well known that promoters can modify physicochemical and textural properties of the catalyst's surface and hence, their catalytic activity and selectivity to desired DME product. The determination of these relationships between these changes will be helpful in explanation of the role of the additives effect on metallic function in studied reaction.

The physicochemical characterization of the prepared catalysts was started from determination of their specific surface area by BET method. The catalysts obtained by co-precipitation method using Na_2CO_3 have low specific surface areas (1.4 to 2.9 m^2/g); for "citric" catalysts the values of specific surface areas are higher (40 to 62 m^2/g); for the third series (co-precipitation using NaOH) the BET measurements are in the progress.

The determination of the redox properties of the catalysts H_2TPR method are now in progress. For the catalysts synthesized by citric method, the reduction profiles of doped catalysts are different from undoped one; the shape and intensity of the profiles depend on the promoting metal.

The purchase of the planed research equipment allowing adaptation and extension the existing at the Institute of Catalysis IR cell was completed taking into account the character of the measurements planned in the project.

Novel Layered Porous Materials Based on Zeolite Nanoclusters for the Liquid-Phase Catalytic Processes

"Opus" research project NCN 2012/07/B/ST5/00771 [2013-2016]
(project leader: Assoc. Professor Mirosław Derewiński
acting project leader: Professor Bogdan Sulikowski)

Our objective is to design and develop viable protocols for the synthesis of new layered materials with the multimodal structure of pores. The starting materials are zeolite precursors, the so-called protozeolitic systems, formed in the early periods of synthesis and composed of nanoclusters ranging from few to several zeolite unit cells. These types of colloidal particles, containing few to several zeolite u.c., are formed by condensation of reactive silicate/aluminosilicate groupings around the organic templates, which are already present in the synthesis gels. Synthesis of monodispersed, stable colloid suspensions of protozeolitic particles, also containing the non-bonded silicate monomers and oligomers, is of paramount importance in the new hierarchic materials preparation protocols and constitutes the first stage of investigations.

Defining the conditions necessary for formation of nano-sized zeolite precursors, studies on their structure, finding relationships between the size and chemical composition of gels, preparation conditions and considerations of the suspensions stability have all been commenced. Studies on formation of colloidal suspensions of nanoparticles of the most important high-silica, medium-pore ZSM-5 have been carried out. This structure has been chosen taking into account its practical applications, high hydrothermal stability, broad range of the Si,Al isomorphous substitution in the unit cell, and generally high strength of the acid sites.

In the reporting period, by application of a diluted gel and gentle synthesis conditions (temp. $20\div50^{o}$C), the monodispersed suspensions of the Al-ZSM-5 (MFI) zeolite with different chemical compositions (Si/Al=12÷25), 5-6 nm size, containing few hundreds of TO_4 (T=Si, Al) tetrahedra and organic templates, were prepared.

The process of nanoparticles formation was monitored by DLS and XRD. Short-range structural ordering, characteristic for zeolites, was confirmed by FTIR in the framework vibration region and ^{29}Si & ^{27}Al MAS NMR spectra. The stability of suspensions was assessed by DLS and zeta potential measurements. Further detailed characteristics of the zeolite precursors are being made to optimize synthesis conditions and, simultaneously, modelling the properties of the nanoparticles synthesised.

Design, Synthesis, and Physicochemical Characterization of Ruthenium Catalysts and Their Application in Hydrogenation od Prochiral Ketones

"Opus" research project NCN UMO-2012/07/B/ST5/00770 [2013-2016]
(project leader: Dorota Duraczyńska PhD)

Preliminary work on the project included the purchase of equipment such as vacuum oven equipped with vacuum pump and accessories for drying the obtained samples of carriers and catalysts. In addition, a number of prochiral ketones and chemical reagents were also purchased that will be used in the hydrogenation reactions.

Dynamics of Oscillations in the Palladium/Hydrogen System

"Opus" research project NCN 2012/07/B/ST4/00518 [2013-2016]
(project leader: Erwin Lalik PhD)

The thermokinetic oscillations accompanying the sorption of hydrogen or deuterium in metallic palladium was discovered by the PI at the microcalorimetric laboratory of ICSC PAS in 2008. The main condition for the oscillations to occur is an admixture of ca. 10% vol. of inert gas (N_2 or noble gas) to the flow of H_2 or D_2 prior to its contact with Pd. The inert admixtures investigated previously included the nitrogen and the noble gases (He, Ne, Ar, Kr) except Xe. An empirical dependence of the mean Kr-normalized frequency on a parameter which is the product of the first ionization potential and the square root of atomic mass of IG (IG=inert gas; cf. Fig. 1) has been found to be linear. It is one of the assignments of the current project to use Xe as the inert admixture to H_2 or D_2 in order to verify the previously found empirical relation.

The experimental setup included gas flow-through microcalorimeter (Microscal) combined with mass spectrometer. Fine palladium powder (> 75 μm) was used as the sample (0.3201 g). The sorption/desorption cycles were carried out at the temp. 106ºC, at the flow rate of 3.2 cm^3/min, and with the molar fraction of H_2 0.94.

Fig. 1 shows that the new data point obtained for the H_2/Xe system (filled circle) is located exactly on the same straight line as the points for the rest of investigated systems, i.e., H_2/IG and D_2/IG. Possible reasons for the anomalous behavior of the H_2/He system has been previously discussed in one of previous papers by the current author.

The position of the newly obtained Kr-normalized frequency for H_2/Xe on the same straight line means that the linear dependence of frequencies on the product FIP*sqrt (*M*) has been thereby confirmed for the Xe/H_2 system. The presented data are preliminary, further experiments with the D_2/Xe system, as well as using palladium powder of various grain sizes and shapes are still in progress.

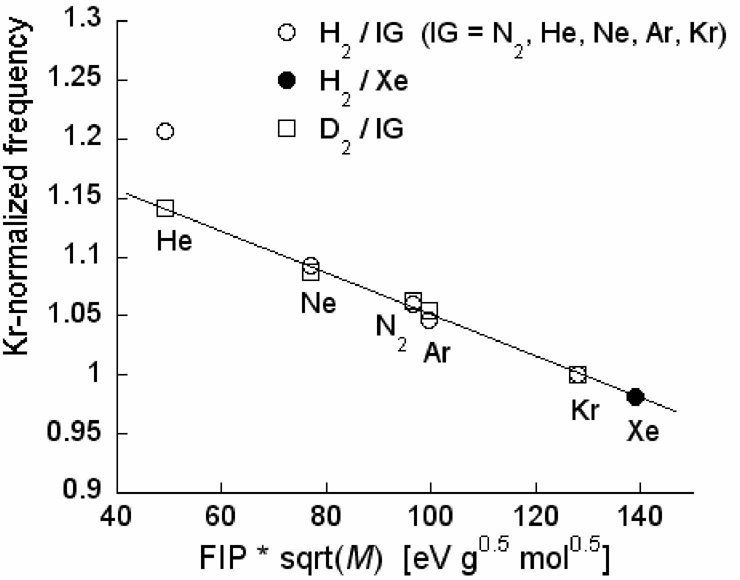


Figure 1. Empirical relation of the mean Kr-normalized frequency of thermokinetic oscillations of sorption of H_2 and D_2 in metallic Pd on the product of the first ionization potential (FIP) times square root of atomic mass sqrt(*M*) of the admixed inert gas.

Adsorption Mechanisms of Anisotropic Proteins under Controlled Transport Conditions

"Opus" research project NCN UMO-2012/07/B/ST4/00559 [2013-2016]
(*project leader: Professor Zbigniew Adamczyk*)

The deposition of positive amidine latex particles (98 nm in diameter, denoted as A100) on negative polystyrene latex particles (820 nm in diameter, denoted as L800) was studied using SEM imaging, micro-electrophoretic and the concentration depletion methods involving AFM. The role of ionic strength varied between 10^{-4} and 10^{-2} M, was determined. The number of deposited positive latex particles (surface coverage) was evaluated by a direct counting procedure exploiting the SEM images. This allowed one to calibrate the results obtained by measuring the electrophoretic mobility and the zeta potential of larger latex particles covered by a controlled amount of the positive latex (see Fig. 1). It was confirmed that the 3D electrokinetic model, developed for stationary and planar interfaces (see Fig. 1, the solid line) is applicable for spherical interfaces undergoing electrophoretic motion. This is significant because deposition processes on carrier particles proceed more efficiently compared to the deposition on planar interfaces.

Additionally, because the large slope of the zeta potential on the nanoparticle coverage dependencies indicate that the micro-electrophoretic measurements can be exploited for a robust determination of the coverage of nanoparticles on colloid carriers under *in situ* conditions. The results have significance for basic science indicating that the results obtained for curved interfaces (polymeric carrier particles) by the micro-electrophoretic method can be exploited for interpreting deposition of nanoparticle and proteins on planar interfaces and vice versa.

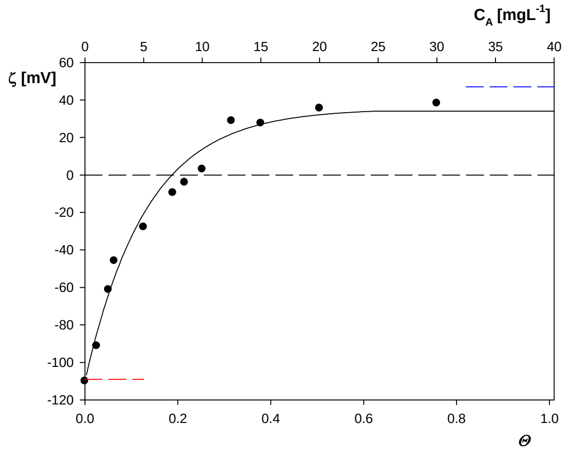


Figure 1. The dependencies of the zeta potential of L800 latex on the A100 latex coverage *Θ*, for ionic strength of 10^{-2} M. The solid lines denote the theoretical results calculated from the 3D electrokinetic model.

Structure and Properties of Protein Layers: from Biomolecules to a Functional Layer (A Combined Experimental and Simulation Study)

"Opus" research project NCN 4 ST5/ 00767 [2013-2016]
(*project leader: Barbara Jachimska DSc)*

The adsorption of bovine serum albumin (BSA) onto silica at various pH values was studied with QCM-D, MP-SPR and AFM measurements. These measurements allowed the determination of both the kinetics of adsorption and the maximum coverage of BSA as a function of pH. The maximum coverage of BSA was obtained for a pH range of 4.5-5.4, near the isoelectric point of the BSA molecules. At pH >5.4 or <4.5, the adsorbed mass decreased monotonically. AFM images demonstrated changes in the conformation of the BSA. Our measurements enabled us to distinguish among the various conformational states of the BSA molecule; these states were identified by dynamic viscosity studies. In particular, the compact N form prevailed at pH 4-9 and was characterized by an effective length L_{ef}=8.3 nm; the elongated conformations dominated at pH 4.0 with L_{ef}=18.1 nm (E-form) and at pH=3.0 with L_{ef}=26.7 nm (F-form).

Additionally, the adsorbed BSA films were characterized by contact angle measurements under diffusion-controlled transport. This approach demonstrated that the contact angle is sensitive to the amount of protein adsorbed on a silica surface. Comparisons of the QCM-D, MP-SPR and AFM data with other indirect methods (contact angle measurements) broadened the understanding of BSA adsorption patterns as a function of pH. The results obtained in our work confirm the essential role of the highly anisotropic charge distribution of BSA molecules in the adsorption process of this protein.

"Preludium" Research Projects of the National Science Centre

Modeling of Catalytic Activity of Biological Nanostructures – Non-heme Iron Dioxygenases

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

This project was devoted to the understanding and analysis of the mechanisms of reactions catalyzed by non-heme iron dioxygenase. Two closely related enzymes, which belong to α-keto acid dependent dioxygenase were selected as representatives: 4-hydroxyphenylpyruvate dioxygenase (HPPD) and hydroxymandelate synthase (HMS). Both proteins are of interest because using the same substrates: molecular oxygen and 4-hydroxyphenylpyruvate, catalyze reactions with initial steps occurring in the same manner, which lead to different products: homogentisate (HG) in case of HPPD and hydroxymandelate (HMA) for HMS (Fig. 1). Due to the fact that both enzymes have a similar tertiary structure, use the same substrates and catalyze reactions with a similar initial course, aroused interest to know the answer to the question: which factors determine their specificity?

Studies on HMS and HPPD are significant in terms of pharmacy, since HMS is required in the synthesis of macrocyclic antibiotics, such as vancomycin, whereas HPPD is involved in tyrosine catabolism. Disturbances in the functioning of HPPD lead to genetic diseases (tyrosinemia), which are treated by the administration of HPPD inhibitors. HPPD inhibitors are also used as herbicides, since this enzyme is involved in the biosynthesis of lyophilic cofactors necessary for photosynthesis.

To achieve the objectives, theoretical chemistry methods were used, covering quantum - mechanical calculations (QM) based on Density Functional Theory (DFT), molecular dynamics simulations (MD) and method combining molecular mechanics (MM) and QM (QM / MM).The studies started from MD simulations were aimed at modeling the structures of HMS and HPPD in complex with their last common intermediate: hydroxyphenylacetate (HPA Fig.1.). The MD results were used in building QM and QM/MM models. MD initial models were constructed based on the crystal structures of HMS and HPPD deposited in the PDB database (2r5v and 1CJX respectively). QM calculations were performed for various sizes of the HPPD and HMS models. Additionally for HPPD, studies with QM / MM method were performed in order to explain the experimentally observed inverse secondary kinetic isotope effect for hydroxylation.

One of the most important achievements of this project was to demonstrate the role of Ser201, which is involved in a hydrogen bond with the hydroxyl group of the substrate. In HMS and HPPD Ser201 adopts different conformations in the active site, causing various orientations of substrate with respect to the reactive Fe (IV) = O, thus determining the further course of HMS and HPPD reaction. Additionally, based on the QM/MM calculations, the mechanism of reaction catalyzed by HPPD was proposed, which is in line with the experimental findings.

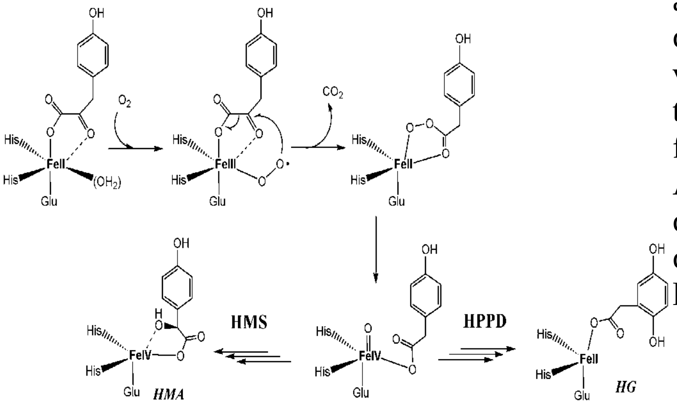


Figure 1. Reactions catalyzed by HMS and HPPD

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 on the phenomena occurring on the surface of these catalysts.

The study made so far on the Au-Me-O/TiO_2 systems were supplemented with an elemental analysis with XRF, the *steady–state achieving curves* were analysed to describe the surface phenomena occurring in the catalysts and also the set of H_2TPR curves was supplemented with the measurements of the co–deposited catalyst.

The XRF results (Table 1) showed that the real content of the catalysts' ingredients are very close to the nominal ones, though the gold content in the co-deposited catalysts is approximately 10% higher than in the sequentially deposited ones.

The analysis of the *steady–state achieving curves* showed that several phenomena occur while achieving the steady–state. The longest-lasting phenomenon (e.g. agglomeration of the smallest particles) is common for all doped samples and results in an activity decrease. on the other hand the phenomena which happen faster, have different influences, depending on the lower (Fe, Ni) or higher redox potential (Cu).

Table 1 Nominal {} and real content of catalalysts' ingredients

Dopant	Sequentially deposited		Co–deposited	
	Au	M	Au	M
––	{1} 0,81	–	{1} 1,15	–
Ni	{1} 0,82	{0,3} 0,27	{1} 1,11	{0,3} 0,26
Fe	{1} 1,01	{0,28} 0,24	{1} 1,12	{0,28} 0,24
Cu	{1} 1,08	{0,32} 0,34	{1} 1,13	{0,32} 0,35

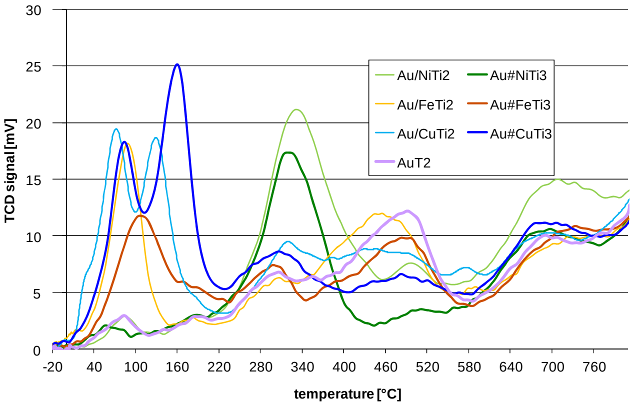


Fig. 1 H_2TPR curves of Au-MO_x/TiO_2 catalysts

To investigate the reducibility of the catalyst, TPR experiments of co–deposited catalyst were performed; results shown in Fig. 1. were juxtaposed with the sequentially deposited catalyst. The diagram shows that catalysts doped with the same base metal exhibit the same peak location, but only the reduction intensity is different. The integration of the curves showed that in case of Fe and Cu doped catalysts the amount of consumed hydrogen is the same, but the hydrogen consumption in case of the Ni–doped co–deposited catalyst is much lower.

The most significant achievement of the research is the description of the dependencies between the catalysts physical properties (reducibility, dopant content) and the activity in the CO oxidation, performed on catalysts treated in different atmospheres.

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 MSc, supervisor: Professor Piotr Warszyński)

The purpose of the project is to synthesize and to characterize biocompatible nanocarriers for water-insoluble neuroprotective drugs and to evaluate their cytotoxicity and neuroprotective effects on neuronal cells.

Nanocarriers were synthesized using 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, chitosan, alginic acid sodium salt) on the emulsion cores (e.g. IPM – isopropyl myristate, chlorophorm). Nanoemulsion-cores were stabilized by polyelectrolyte and surfactant (e.g. AOT – docusate sodium salt) complexes. The size distribution and zeta potential of nanocapsules were characterized by the dynamic light scattering (DLS) and the laser Doppler electrophoresis (LDE), respectively. The average size of synthesized nanocapsules ranged from ~80nm to ~100nm. Absolute values of their zeta potential were above 30mV. Additionally, nanocapsules were visualized using the scanning electron microscopy technique (SEM) (Fig. 1a). Surface of nanocarriers were also modified for maximum biocompatibility by copolymers of polyelectrolyte-polyethylene glycol. Biocompatibility of synthesized nanocarriers was evaluated against SH-SY5Y human neuroblastoma cells using MTT and LDH assays. The results obtained show that synthesized nanocapsules coated with most of selected polyelectrolytes (e.g. PLL and PGA) were non-toxic to SH-SY5Y cells (Fig. 1b).

Selected inhibitors of intracellular biochemical cascades leading to neuronal cell death (e.g. calpain inhibitors: MDL 28170, UDA – undecylenic acid) were encapsulated inside the cores of nanocapsules. The neuroprotective action of encapsulated active substances against neurotoxin (hydrogen peroxide) induced cytotoxicity was evaluated in the same cell line (SH-SY5Y cells). The degree of damage and neuroprotection was assessed using various biochemical and morphological tests (e.g. MTT, LDH). The data analyzed using analysis of variance (ANOVA) demonstrated statistically significant neuroprotective action of encapsulated MDL. That proves that our nanocapsules may be considered as candidates for neuroprotective drugs delivery systems.

Figure 1 a) The SEM micrograph of AOT(PLL/PGA)$_1$ nanocapsules; b) MTT reduction in SH-SY5Y culture after treatment with nanocapsules' cores stabilized by complexes of AOT and various polyelectrolytes.

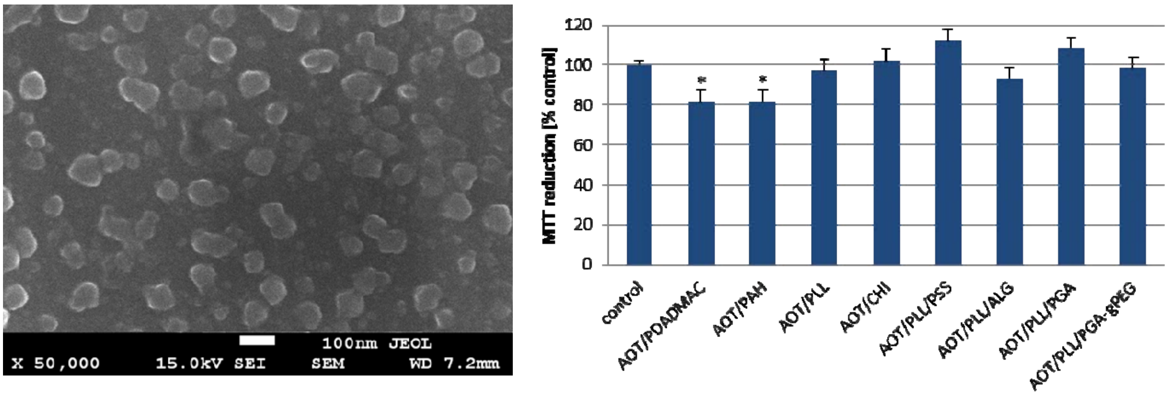


Figure 2 a) The SEM micrograph of AOT(PLL/PGA)$_1$ nanocapsules; b) MTT reduction in SH-SY5Y culture after treatment with nanocapsules' cores stabilized by complexes of AOT and various polyelectrolytes.

Improving the Method of Detection of Hydrogen Peroxide by Modifying Films Containing Prussian Blue Nanoparticles by Conductive Polymers and Reduced Graphene Oxide Sheets

"Preludium" research project NCN 2012/07/N/ST4/00350 [2013-2015]

(PhD student: Agnieszka Pajor-Świerzy MSc, supervisor: Professor Piotr Warszyński)

Successful monitoring of hydrogen peroxide (H_2O_2) is very important in many areas, such as environmental protection, various branches of industry and medicine. Therefore, the main objective of the project is to establish the scientific basis for the simple and universal electrochemical method of detection hydrogen peroxide. It is based on the immobilization of electro-catalytically active Prussian blue nanoparticles (PBN) in polyelectrolyte multilayers of various composition and structure, built on the surface of electrodes.

The Prussian Blue nanoparticles, with the size 10nm and the zeta potential –50mV, were synthesized by the reaction of $FeCl_3$ with $K_4[Fe(CN)_6]$ in 10^{-2} M HCl. Multilayer films consisting of polyelectrolytes and Prussian Blue nanoparticles was formed by the layer-by-layer (LbL) technique. This LbL method is based on the sequential adsorption negatively charged nanoparticles and positively charged polyions due to the electrostatic interactions. The most important advantage of this technique is the possibility to obtain films of controlled thickness. Conductive polymers were used to modify the polyelectrolyte layers with immobilized PBN in order to improve their electroactive properties by increasing amount of nanoparticles and enhancing the electron transfer from the film to electrode surface. The process of formation of multilayer films was monitored using Quartz Crystal Microbalance (QCM) technique. The electroactive properties of composite films were determined by the cyclic voltamperometry. Fig. 1 presents the comparison of the voltamperometric loops for electrodes covered with PE/PBN multilayer films modified with conductive polymers, polypyrrole (PPy) and polyaniline (PANi). It gives evidence of the enhancement of the PB redox current by conductive polymers.

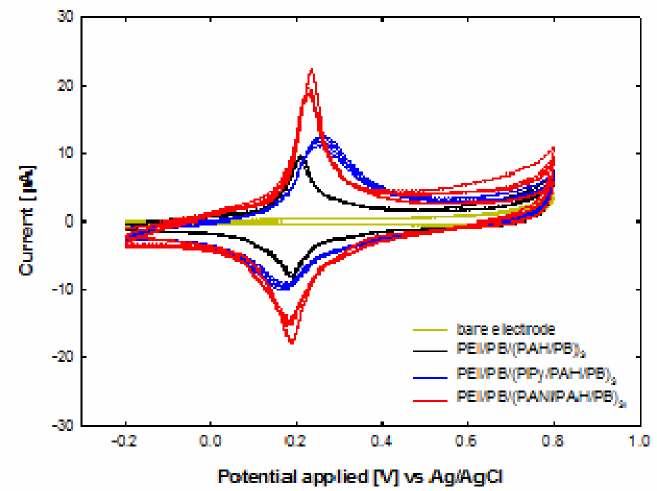


Figure 1. The comparison the voltamperometric loops for PE/PBN multilayer films modified with conductive polymers, polypyrrole and polyaniline.

We demonstrated by the cyclic voltamperometry that incorporation of PANi into the multilayer structure enhances the sensitivity for electrochemical detection of hydrogen peroxide by at least 40%. Therefore, such composite coatings can be considered as sensor layers for the monitoring of hydrogen peroxide.

Multilayer Polymer Films Containing Nanoparticles and Graphene as a Functional Coatings and Membranes

"Preludium" research project NCN NCN 2012/07/N/ST5/00173 [2013-2015]
(PhD student: Tomasz Kruk MSc, supervisor: Professor Piotr Warszyński)

The aim of this project is to develop the scientific background for the method of functionalization of polymer thin films produced using the "layer-by-layer" (LbL) technique to obtain coatings with specific properties. The functionalization of polymer films can be obtained by the incorporation of nano-objects with the specific properties (metallic, oxide, graphene, graphene oxide (GO) nanoparticles) in their structure or by modifying the surface of such films. That allows obtaining ultrathin films of selected properties (e.g. antibacterial, conductivity, antifungal) that may have application in many fields such as medicine, electronics or optics.

We selected metal or metal oxide (Ag, Cu/CuO) nanoparticles to obtain thin coatings with antimicrobial properties. Nanoparticles were synthesized by the reduction of metal salts with various reducing agents (hydrazine, sodium borohydride, formaldehyde, UV). The syntheses were carried out in micellar solutions of surfactants (SDS, CTABr, Tween 80) in the presence of stabilizing polymer such as PDADMAC, PVP, PVA. After synthesis all received size, zeta potential, stability, composition and nanoparticles were characterized. In the next step the multilayer films containing nanoparticles were formed by the LbL method. The formation of films was followed by QCM and the structures were characterized by various methods as ellipsometry, UV-Vis and SEM microscopy. The antimicrobial activity tests were carried out in the cooperation with the external laboratory (University of Warsaw and Łódź University of Technology). The following table gives the example of the results obtained for the multilayer coatings layers containing silver nanoparticles. They clearly illustrate the decrease of bacteria adhesion in the presence of increased amount of silver.

Table 1. Adhesion bacterial – luminometric method.

Carrier	E. Coli ATCC 10536 Peptone water diluted [RLU]	A. hydrophila LOCK0968 Peptone water diluted [RLU]	A. lannensis FMW1 Fruit-drink with sacharose [RLU]
(PEI/PSS)$_5$	25 300 ± 8 300	4 700 ± 2 505	4 800 ± 2 454
(PEI/Ag)$_1$	4000 ± 2 300	1 200 ± 1 000	1 000 ± 550
(PEI/Ag)$_2$	2 500 ± 1 100	1 000 ± 550	300 ± 78
(PEI/Ag)$_3$	1 600 ± 460	830 ± 67	33 ± 21
(PEI/Ag)$_4$	1 200 ± 340	340 ± 130	34 ± 11
(PEI/Ag)$_5$	690 ± 78	180 ± 58	28 ± 11
(PEI/Ag)$_5$*po 1roku	230 ± 56	1 300 ± 670	21 ± 14

The research will be continued by testing activity of the coatings against laboratory strains of Gram-positive and Gram - negative strains as well as clinical isolates of the resistant strains such as Staphylococcus epidermidis, Staphylococcus aureus, and Pseudomonas aeruginosa. As the final results proving antibacterial activity will be obtained by tests carried out in accordance with the ISO 22196 protocol.

Electrokinetic Characteristics of Interaction between Recombinant HSA Monolayers and Ionic Ligands

"Preludium" research project NCN NCN 2012/07/N/ST5/02219 [2013-2015]

(PhD student: Marta Kujda MSc, supervisor: Professor Zbigniew Adamczyk)

Extensive measurements of the physicochemical properties of recombinant human serum albumin (rHSA) have been performed. rHSA is a protein of unique biological functions. It plays a number of roles required to maintain homeostasis. It is a universal carrier for substances of a high biological importance: fatty acids, ions, hormones and vitamins. The specific structure and binding ability of a wide variety of ligands give it the potential importance in pharmaceutical formulations. Therefore, it becomes essential to examine the physicochemical properties of the recombinant form of human albumin, which is free of impurities and dimers and exhibits the reduced immunogenicity. For this purpose, a number of the following measurements have been performed:

- degree of purity of aqueous solution of rHSA monomers and the molar mass of the rHSA was estimated using the technique of gel electrophoresis SDS-PAGE in Laemmli system, with silver staining method.
- the diffusion coefficient of the protein and its hydrodynamic diameter was determined using the technique of dynamic light scattering (DLS).
- the electrophoretic mobility of the protein as a function of the ionic strength (10^{-3}-0.15M NaCl) and pH values in the range (3.5-9.0) was determined. The electrophoretic mobility was also converted to the zeta potential. (Figure 1 shows the relationship between the electrophoretic mobility of the protein as a function of ionic strength and pH).
- based on these measurements the isoelectric point of the protein equal to 5.4 was determined.

Thus, at pH < 5.4 rHSA has a positive surface charge to allow adsorption of the protein on negatively charged surfaces, such as mica surfaces. Adsorption studies will be undertaken in the next stages of the project.

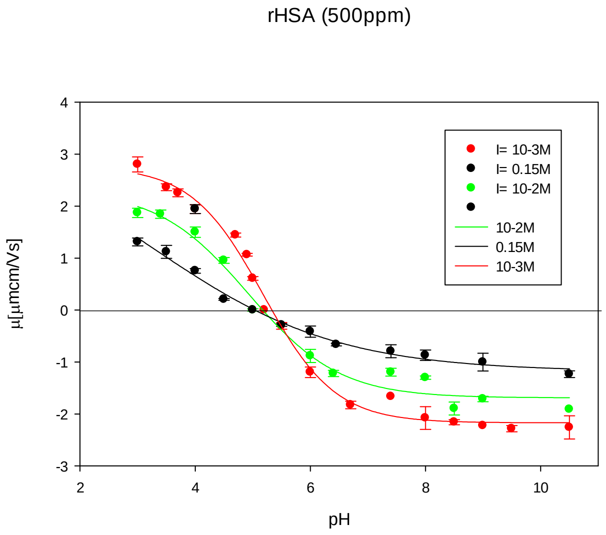


Figure 1. The dependence of the electrophoretic mobility of rHSA as function of ionic strength and pH.

"Harmonia" Research Projects of the National Science Centre

Visualizing the Local Reaction Kinetics: From the Mesoscopic to the Nanoscale

"Harmonia" research project NCN UMO-2012/06/M/ST4/00032 [2013-2015]
scientific cooperation between Poland and Austria
(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 and polycrystalline supports. The basic experimental method in the project is the high resolutions electron microscopy using a electrons originated fat the sample surface. The low energy electron microscope (LEEM) is also used in the project as a photoemission electron microscope (PEEM) both with laboratory and synchrotron excitation sources.

The applied research methodology allows structural, chemical and electronic characterization of surfaces on micrometer and nanometer scale and also monitoring of the surface modifications induced by surface reactions. The project is realized in the framework of trilateral cooperation of the Polish group with Technische Universität Wien and Swiss Light Source (SLS).

In the first stage of the project the microscope were adapted, installed and commissioned at the NanoXAS beamline at SLS. During two monthly experimental beamtimes a series of experiments were implemented on previously selected systems characterized with laboratory method such as scanning tunneling microscopy and photoelectron spectroscopy (XPS).

The experiments resulted in the elaboration of the LEEM and PEEM methodology for polycrystalline samples. We studies polycrystalline Pd and Pt foils for which we could identify orientation of single grains and perform local microscopic and spectroscopic measurements. We studied growth of iron oxides on the grains with different orientation and determined relation between the structure and morphology of oxide and substrate orientation. We studied also manganese nanostructures on single crystalline W(110) substrates. Using chemical sensitivity of X-PEEM we determined composition of the manganese oxides obtained by oxidation of submicrometer Mn islands. We showed a correlation between the thickness and morphology of the Mn adsorbate and the spatial distribution and oxidation state. For the magnetite films epitaxially grown on MgO(001) we studied the local variation of the surface stoichiometry between FeO and Fe_3O_4 using of this purpose both XAS and XPS microspectroscopy.

In the next project state the synchrotron results will be analyzed n detailed and verified using laboratory methods (mainly STM) which will give information in a different, namely atomic scale. The results of the X-PEEM studies will be exploited by the commissioning of the first experimental beam-line at the Polish synchrotron source “SOLARIS”.

"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 theoretical investigation of the structural and energetic aspects of metal ions (calcium, cadmium, copper and zinc) interactions with α-L-guluronic and β-D-mannuronic acids (in their anionic forms) was conducted. The study included the elucidation of the structures of the ion-uronate complexes and the estimation of the free energy profiles characterizing their stability.

Due to the inapplicability of the classical potentials of interactions between metal ions and uronic anions, 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 metal ion) are modeled with the accuracy of quantum mechanics while the remaining part with that of classical biomolecular force fields (e.g. the TIP3P model of water).

It has been concluded that the basic mechanism of calcium, cadmium and zinc ion binding by guluronate and mannuronate is the direct ('tight') interaction with one of the oxygen atoms belonging to the carboxyl group of uronate (1-SO mechanism). In the case of copper, the exceptional supremacy of the 2-SO mechanism (i.e. the coordination of ion by two oxygen atoms of carboxyl moiety) has been observed. The same (2-SO) pattern of binding is also possible for calcium, as both possible states (1-SO and 2-SO) differ only by a small (2.5 kJ/mol) value of free energy (1-SO is the preferred state). The remaining places in the first coordination sphere of metal ion are filled by oxygen atoms of water molecules. The mechanism of calcium binding is governed mainly by the Coulombic interactions, thus, the 1-SO and 2-SO states are separated by a relatively small barrier of the free energy, corresponding to the reorganization of water molecules in the first coordination sphere. Furthermore, the free energy difference estimated for the overall process of calcium ion binding is in agreement with the experimental data. Accepting the 1-SO mechanism as the preferred one for the majority of the bivalent metal ions remains in agreement with the recent results reported by other authors [Biomacromolecules 2012, 13, 1899−1907].

The influence of the polarization effects has been discussed in the context of calcium-guluronate anion interactions. The results of QM/MD simulations have been compared with those obtained when applying the classical force fields (e.g. GLYCAM06/TIP3P or GROMOS/SPC). The classical force fields appear to be responsible for lowering the free energy barriers which separate the 'free' and 'bound' states of metal ion. The statical geometry optimizations confirm the this effect can be ascribed to the polarization of the carboxyl moiety which can not be accounted for in the case of classical force fields (the atomic partial charges are fixed).

As there exist numerous hindrances concerning the experimental studies (as well as the data interpretation) of the basic features related to the uronate-metal complexes, our results (e.g. the values of thermodynamic parameters) may serve for the improvement in the interpretation of the existing data.

A New Method of Silver Sol Synthesis and Mechanism of Colloidal Particles Interaction with Heterogeneous Surfaces Determined by Electrokinetic Phenomena, AFM, Fluorescent Microscopy and QCM-D Techniques

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

The colloidal particle and polyelectrolyte interactions with the flat surfaces are the subject of intensive study. The adsorption of colloidal microspheres and charged polymers at solid/ liquid interfaces is of great significance to many processes such as nano-encapsulation for controlled drug delivery, cell adhesion, or formation of nanocoatings on textiles. However, the mechanism of colloidal particle and polyelectrolyte interactions as well as the kinetics of particle deposition and macromolecule adsorption were not yet fully established.

In 2013, the main subjects of this grant were as follows: to derive such thorough the characteristics of cationic polyelectrolyte - polydiallyldimethylammonium chloride (PDADMAC, molecular weight 160 kDa) monolayers on mica, and to determine the deposition kinetics of silver nanoparticles and fluorescent particles at solid/ liquid interfaces.

The *in situ* streaming potential measurements were applied to determine the formation and stability of PDADMAC monolayers on mica. The zeta potential was calculated from the streaming potential measured in the parallel-plate channel formed by two mica plates precovered by the polyelectrolyte. The studies of polydiallyldimethylammonium chloride monolayers were performed for a broad range of ionic strength 10^{-3}- 0.15 M and pH 5.8. The experimental data were expressed as the dependence of the zeta potential ζ on the PDADMAC coverage calculated using the convective diffusion theory. The obtained results were quantitatively interpreted in terms of the electrokinetic model postulating a 3D adsorption of macromolecules as discrete particles. These measurements allowed one to determine the coverage of PDADMAC as a function of zeta potential of mica. It was found that, for increasing the ionic strength, the limiting zeta potential for high PDADMAC coverage decreases from 45 mV for 10^{-2} M to 22 mV for 0.15 M. Furthermore, by using the same approaches the desorption kinetics of PDADMAC was studied. The stability of saturated PDADMAC monolayer against prolonged washing (reaching 24 h) was determined for 10^{-2}M and 0.15 M under *in situ* condition. This allowed us to determine the equilibrium adsorption constants for PDADMAC under different ionic strength, e.g. 72 cm^1 for 10^{-2}M.

Moreover, the kinetics of PDADMAC adsorption and desorption at gold-coated quartz crystal were investigated, as a function of polyelectrolyte concentration and ionic strength by the QCM-D method. The obtained results reveled, that the adsorbed mass of polyelectrolyte on gold surface increased linearly with bulk concentration of PDADMAC. Then, an abrupt stabilization of the adsorbed mass at a constant value was obtained e.g. (69.7, 125.5, and 127 ng/cm^2 for 20 min adsorption from PDADAMC solution with concentration equal to 5, 7, and 10 ppm in 10^{-2}M, respectively).

The deposition kinetics of negative silver particles and positive fluorescent particles on PDADMAC-modified mica were studied under diffusion-controlled transport conditions. The surface concentrations of both type of particles were obtained by a directly enumeration using AFM technique. Furthermore, the integrated intensity of fluorescence of particles covered PDADMAC was studied. This research has shown that there was almost no deposition of silver nanoparticles for the PDADMAC surface concentration up to 0.1, and then the maximum nanoparticle coverage was abruptly attained. On the contrary, the maximum surface coverage the positive particle as well as their fluorescence intensity abruptly decreased with increasing PDADMAC surface concentration.

The Advanced Theoretical Study on the Mutarotation Reaction of D-glucopyranose

"Iuventus Plus" research project MNiSW IP2012 00637 [2013-2015]
(project leader: Wojciech Płaziński PhD)

The mutarotation of carbohydrates is one of the fundamental chemical reactions, important in the context various fields of science. Although being the classical 'textbook' reaction, some of its details still remain unknown.

We plan to initiate the detailed computational investigation 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. glucose molecule and selected, catalytic, water molecules) are modeled with the accuracy of quantum mechanics while the remaining part with that of classical biomolecular force fields (e.g. the TIP3P model of water).

The very initial steps of the study, conducted so far, included:

(I) development and testing the protocol of the QM/MD simulations, combined with the metadynamics and/or transition path sampling methods;
(II) selection of the potential transition states structures, including the water molecules taking part in the ring-opening reaction (based on results published in [J. Am. Chem. Soc. 2006, 128 (15): 5049–5058].

Magnetic Responsive Drug Delivery Systems with the Controlled Release Properties

"Iuventus Plus" research project MNiSW IP2012 058972 [2013-2015]
(project leader: Krzysztof Szczepanowicz PhD)

`One of the major drawbacks of current conventional therapies is lack selectivity of preparations, since administered drugs are more or less equally distributed within the body. This results in many of the negative side effects due to the impact of the drug in the whole body, also on the healthy part of it. It seems reasonable to find the a route of controlled delivery of therapeutic, which would result in an action of the active substance only in strictly defined, pathologically changed place in the body. The solution of this problem is the drug targeting. The carrier transports the drug to its site of action and releases it.

These drawbacks of the current methods of conventional drug deliver are the main motivation of this project. The ability to deliver the drug selectively to the desired organ, tissue or cells can be achieved by various methods. One of them is called magnetic drug delivery system. Magnetic nanocarriers can be guided (remote control) and therefore, can transport the biological active matter with an optimum therapeutic concentration of pharmaceuticals to the desired tissue of the organism accurately and selectively, while the total dosage remaining unchanged. Therefore, the aim of the project is to develop the method of preparation of magnetically responsive nanocarriers for targeted drug delivery system and controlled release of therapeutic agents.

In 2013, we focused on the task of the project concerning the preparation of nanocapsules containing magnetic nanoparticles in polyelectrolyte shell. The nanocapsules were synthesized by method developed in our Institute i.e. direct encapsulation of emulsion droplets in the polyelectrolyte multilayer. Magnetic-responsive drug delivery system were prepared by the sequential adsorption of polyelectrolytes (layer by layer technique) using biocompatible polyelectrolytes (Poly L-lysine as the polycation and Poly Glutamic acid as the polyanion) and magnetic Fe_3O_4 nanoparticles. The polyelectrolyte nanocapsules with embedded magnetic nanoparticles of the average size of 100 nm were obtained. Figure 1 illustrates the influence of magnetic field on nanocapsules suspension.

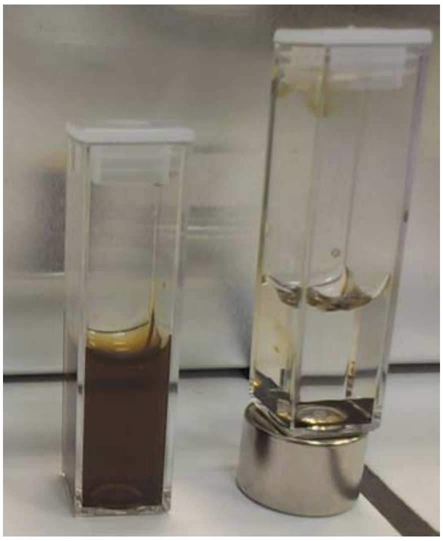


Figure .1 Nanocapsules suspension attracted by magnetic field.

"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 [2011-2013]
(project leader: Jan Zawała PhD)

The aim of the investigations carried out within "Mobilność Plus" framework was to determine main factors affecting stability of liquid film formed at liquid/gas and liquid/solid interfaces under dynamic conditions. The experiments were carried out using experimental set-up, elaborated at the University of Liege, Belgium, which allows monitoring dynamic phenomena occurring during the single bubble collisions with various interfaces resting or vibrating with control acceleration (determined by frequency and amplitude of oscillations). The experimental set-up consisted of: (i) square glass column with the capillary of inner diameter 0.025-0.075 mm sealed at the bottom, (ii) high-speed camera acquiring the picture with frequency 1000 Hz, (iii) precise system of gas dosage (syringe pump) and (iv) system allowing controlled induction of oscillations of the interface, i.e. electromagnetic shaker couple with wave generator, oscilloscope and accelerometer. The experiments were carried out in distilled water and silicone oils of defined viscosity and surface tension. The main parameters determined during experiments were (i) time of the bubble coalescence (t_c) at liquid/gas interface and/or time of the three-phase contact formation (t_{TPC}) at liquid/solid interface, i.e. the time span from the moment of the bubble first collision to the moment of liquid film rupture and (ii) degree of the bubble deformation during collisions and bouncing at the interfaces investigated.

The experiments carried out allow obtaining new and strong evidences, supporting the hypothesis that the degree of the bubble deformation during collisions, i.e. radius of the liquid film formed, is a factor of crucial importance for the collision outcome and timescale of the bubble rupture (coalescence of TPC formation). By the comparison of the results obtained for the interface being at rest and this vibrating with controlled frequency and amplitude the mechanism responsible for the bubble bouncing was explained. It was found that the probability of the bubble rupture or bounce depends on mutual interrelations between kinetics of drainage of the liquid film separating the bubble from the interface and kinetics of transfer of kinetic energy associated with the bubble motion to its surface energy, related to the bubble area variations at the moment of collision. If the transfer between the energies was faster that the time needed for the film to reach its critical thickness of rupture, the bubble was bouncing. In opposite situation, the bubble rupture was always observed. This situation was taking place always, when the kinetic energy was substantially dissipated (4 – 5 approach-bounce cycle of the bubble) and, consequently, the bubble deformation was small. Experiments carried out for vibrating interfaces allowed to observing effect of the bubble “immortality”. At the vibrating interface, supplying additional kinetic energy to the system, the bubble could bounce almost indefinitely at the interface. Additionally, its deformation ratio and the radius of the liquid film formed, was practically constant and higher than threshold value, below which the bubble rupture was always observed. Under such conditions formation of “immortal” bubbles was observed, even at the surface of distilled water, where, at resting interface, bubble ruptures in fraction of seconds (< 100 ms).

"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 2013 year the following tasks of this project have been started and accomplished, according to the project implementation schedule.

Task 1) The synthesis of the two series of the catalysts were completed: a) containing active copper phase supported on synthesized earlier chromites (with 5, 10, 15, 20 and 30 wt% of Cu, by impregnation method, thermal treatment: drying at 120°C - 10h, annealing at 350°C - 5h, in the flow of air), b) containing Cu and Ag deposited on TiO_2 and Al_2O_3 oxides (by impregnation method with thermal treatment as describe above); the amount of Cu was 2-6mmol/1g of the support, whereas for bimetallic systems the amounts of Cu and Ag were 0-1.5 metal mmol/1g of the support.

Task 2) Based on the literature review, the new method (sol-gel route) of preparation CuCr catalysts was applied, with ethanol as dissolvent and 1.2-propylene oxide as precipitant agent. The new catalyst, with Cu/Cr ratio equals 4 was prepared by this alternative method, followed by drying at 75°C - 40h and calcination at 500°C - 2h in the flow of argon).

Task 3) The physicochemical characterization was continued for: a) the synthesized chromites with common formula $Me_{II}Cr_2O_4$, where Me=Cu, Co, Zn, Ni, Mg, Fe i Mn, possesing the normal spinel structure, b) CuO/chromite support catalysts and c) Cu-Ag/oxide supports catalysts. This part of investigation included determination of the structure and texture by BET, XRD and SEM (for selected samples) methods, definition of the quantitative composition (by XRF) and determination of redox properties by H_2TPR method.

Task 4) The catalytic tests in hydrogenolysis of glycerol reaction were started, according to proposed earlier procedure for CuO/chromite catalysts, where $CuCr_2O_{4Adkins}$, $CuCr_2O_{4citric}$ and $FeCr_2O_4$ chromites were supports, and for Ag-Cu/oxide support catalysts. The conditions of tested reaction were as following: pre-reduction (150°C, 100 rpm, 2h), hydrogenolysis (200°C, 400 rpm, 5h, pH_2=15atm.). Because of the relatively low activity of the tested catalysts, both, the conditions of the reaction were changed: conditions of the pre-reduction (200°C, pH_2=5 atm.), time of the hydrogenolysis (20h, 26h), hydrogen pressure 40 atm. and temperature of the calcination (500°C). The highest selectivities to desired diols were obtained for 30wt%$CuO/CuCr_2O_4$, $2Cu/Al_2O_3$, $4Cu/Al_2O_3$, $6Cu/Al_2O_3$catalysts. Studies are in progress.

Task 5) The scientific care on the scholar included complex protection on first scholar of this project during writing the master thesis (master's thesis defense on 24.06.2013).

Task 6) The second recruitment of the next student took place (in accordance with appropriate procedure); from September 2013 the student started his research studies.

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)

Investigations in the Project concentrate on experimental variables determining activity of noble metals supported catalysts in recombination of hydrogen and oxygen to form water. This strongly exothermic reaction ($H_2 + 0.5\ O_2 = H_2O + 240$ kJ) is a safety problem in nuclear reactors because it is accomplished as a result of continuous H_2 formation in chemical and radiation processes. In the nuclear reactors the passive autocatalytic recombiners (PAR) are applied. They are composed of metallic plates which are coated with Pt deposited onto alumina, known as "wash-coat" catalysts. They must be able to catalyse the conversion of hydrogen at room temperature and must be resistant to humidity because of its high level in nuclear reactor.

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 mono- and bimetallic catalysts with various metal loading (0.2-4 wt %) 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 rate of hydrogen and oxygen recombination reaction is very high (explosion), difficult to be measured in the laboratory reactors. Introductory catalytic tests were carried out using various concentration of hydrogen in air and various flow rates of reagents in order to evaluate the conditions allowing comparison of catalysts activity in laboratory reactor.

Experiments performed during year 2013 dealing with catalytic performance (activity, stability) of supported monometallic (Pd, Pt) and bimetallic (Pd-Pt, Pd-Au) catalysts in the recombination of hydrogen and oxygen. The following aspects were studied:

a) preparation of catalysts using various oxide supports:
   Al_2O_3, SiO_2, MoO_3 and WO_3 supported monometallic Pd and Pt catalysts (0.25-2 wt %Pd or Pt); bimetallic Pd-Pt and Pd-Au catalysts with various metals ratio, montmorillonite (doped with Al and Zr) - Pd catalysts, palladium-P-$(WO_3)_{12}$ catalysts
b) characterization of catalysts properties; textural (surface area, porosity; BET) and metal phase (size of metal particles, their distribution in support; TPR, XRD, SEM, TEM, EDS)
c) measurement of catalyst activity; laboratory flow reactor (fixed-bed of catalyst)
d) evaluation of thermal effect during recombination of hydrogen and oxygen with microcalorimetric method (Microscal)
e) modeling of electron interactions in Pd, Pt-MoO_3, systems

The results of catalytic tests showed that all catalysts exhibited very high activity (almost complete hydrogen conversion) already at room temperature. The catalysts differed in stability measured during the catalytic test. This may be result of their sensitivity to water (formed in the reaction), determined among other by the type of support. A different aggregation ability of metal nanoparticles in the catalysts may be other property leading to decrease in activity. The results of microcalorimetric measurements showed various amounts of heat evolved depending on the type of metal nanoparticles (Pd, Pt, Pd-Pt, Pd-Au) in the catalyst. The best performance in terms of hydrogen conversion, the amount of evolved heat and thermal stability was exhibited by bimetallic Pd-Pt and in particular Pd-Au –containing catalysts.

Energy Efficiency of Museum and Library Institutions

Applied Research Programme HERIVERDE project NCBiR PBS2/A9/24/2013 [2013-2016]
(project leader: Professor Roman Kozłowski)

The project concerns the development of two tools supporting the energy efficiency of museums, libraries and archives occupying historical buildings: a software for a quantitative assessment of risk of damage to objects vulnerable to climate variations and a specialized module of the WUFI® Plus software which will make possible more precise modeling of microclimate and energy consumption in museums, libraries and archives. The tools do not exist in the collection care practice. They will be thoroughly tested through monitoring microclimate, energy consumption and dimensional change of model objects in the real-world conditions of selected buildings preserving collections, belonging to the project partners – the National Museum in Krakow and the National Library in Warsaw. The results obtained will be used to prepare the multivariate, energy-efficient strategies of climate management in these buildings.

The key task of the institute in the project is to model the water vapour movement, strains, and stresses in diverse library and museum objects in response to changing climate conditions, using the finite element analysis, supported by measurements of the physical properties of materials,. This research tool will enable a scientific assessment of the impact of microclimatic parameter fluctuations on the process of destruction of historic objects.

The project started in November 2013. A programme of measurements of water vapour adsorption and moisture dimensional response of materials constituting library objects: various kinds of papers, board, leather and parchment was initiated.

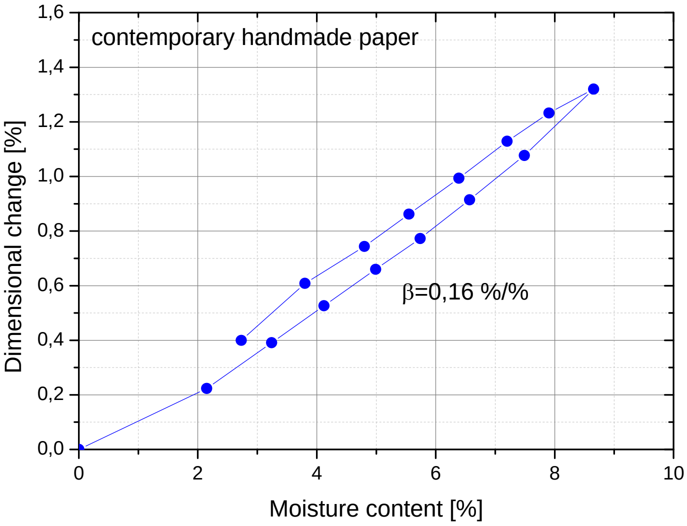


Figure .1 Dimensional change of a contemporary handmade paper as a function of water content; the moisture coefficient of dimensional change β is determined from the slope of the linear part of the plot.

"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 DSc)

The aim of the project is the development of a method for regioselective hydroxylation of cholesterol derivatives at the C25 carbon atom with a novel molybdoenzyme (S25DH). During 2013 the focus of the research was on two scientific goals: i) development of an S25DH overexpression system in *E. coli* (task 2) and ii) development of aerobic and optimization of anaerobic enzyme purification protocol from native bacteria in order to apply the obtained enzyme preparation in regioselective hydroxylation (task 3 and 4).

Research on development of an overexpression system focused on construction of artificial operons comprised of genes encoding all 3 subunits of S25DH enzyme (αβγ) as well as chaperon involved in molybdenum cofactor insertion into the enzyme. Two methodologies have been used: i) cloning of the native genes of all subunits, amplified from the genome of *Sterolibacterium denitrificans,* and ii) construction of an operon based on artificial genes, synthesized *de novo* and optimized for *E. coli* cells based on known sequence of the enzyme and chaperone. The obtained constructs were clone into expression vectors which were subsequently used for transformation of competent *E. coli* cells. Initial results show, that the obtained overexpression system produces recombinant α and γ subunits.

The research conducted within task 3 and 4 yielded two enzyme purification protocols: aerobic utilizing DEAE-Sepharose and Q-Sepharose ion exchange columns and anaerobic using DEAE-Sepharose and Resource Q column. Both methods provide enzyme preparation with enriched activity of S25DH, but the anaerobic purification, utilizing Q-Sepharose column is not able to separate S25DH from AcmB enzyme that exhibits different catalytic activity towards the same group of cholesterol derivatives. Additionally a rapid HPLC method was developed for analysis of protein profiles in the purification fractions. Such method, utilizing wide pore Poroshell RP-C18 column is a complimentary approached to SDS-PAGE electrophoresis.

The obtained enzyme preparations of S25DH were used for conversion of 7-dehydrocholesterol, choles-1,4-dien-3-one, α- and β-tocopherols, pegylated cholesterol (PEG-400) as well as sulphate and succinate cholesterol esters. In long time reactions in a batch reactor containing excess of electron acceptor $K_3[Fe(CN)_6]$ 7-dehydrocholesterol and cholest-4-en-3on were converted to C25 alcohols with high yields (50-100%). In case of tocopherols the activity tests showed high enzymatic activity but the non-specific oxidation reaction of the substrates and products with electron acceptor prevented identification of products of enzymatic reaction with LC-MS.

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. The activity of ICSC PAS was grouped into three tasks.

Within Task 2.1b ICSC PAS activity concentrated on development of the oxidation-active centers based on heteropolyacids. The following materials have been designed and prepared: anions based on normal Keggin structure (molybdophosphates with Co as compensating cations, Cu salt of tungstophosphoric acid, K salt of tungstophosphoric acid containing Cu as addenda atom, V modified molybdophosphoric acids supported on SBA-15 support) and anions based on trivacant lacunary Keggin (heteropolyanion containing a cluster of 4 Cu atoms).

Within Task 2.1c ICSC PAS activity concentrated on theoretical modeling of mechanism of C-H activation in methane molecule and its re-oxidation, in particular regarding the role of heteropolyanions in the oxidation step. The results of modeling of C-H activation in methane molecule on platinum metaloorganic complex show that the energy barrier for C-H rupture is relatively high and amounts to ca 45 kcal/mol and 27 kcal/mol for 4- and 3 coordinate forms, respectively. The results of heteropolyacids modeling show that catalytic properties of these systems strongly depend on their chemical composition. The results of calculation leads to the conclusion that central ion modification changes the redox properties of HPA systems (correlation between the energy of LUMO orbital and experimental data of redox potential). Changes in the position of addenda atoms results in the changes in nucleophilic character of oxygen sites in Keggin anion (correlation between oxidation power and a size of the gap between the valence and conduction bands in DOS spectra). The interaction of CH_3 radical leads to the formation of methoxy species CH_3O- or precursor of alcohol still bound with HPA structure (for interaction of radical with oxygen center or OH group, respectively). Interaction of CH_3 radical with Keggin structure leads to the elongation and weakening of metal-oxygen-metal bonds in HPA structure.

Task 3.1c aimed at elucidation of the mechanism of methane to ethylene transformation, being the first step of methane aromatization on MoO_3/ZSM-5 catalyst. Complete reaction pathway was modeled. After CH_4 physisorption, C-H bond in methane is activated. The process is facilitated by earlier reduction of the catalyst. Next, methane decomposition leads to the formation of CH_2 group bound to molybdenum ion. Two such groups recombine, and ethylene molecule is formed. Condensation of ethylene, leading to benzene formation, occurs in pores of the ZSM-5 zeolite. Next, the influence of size and composition of the active phase (Mo/C/O) on methane activation barrier was checked. It was found that the C-H bond rupture is the easiest on the cluster built from two or three molybdenum-oxygen octahedra. When the active phase changes its composition (from oxide to carbide), C-H activation barrier is further diminished.

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)

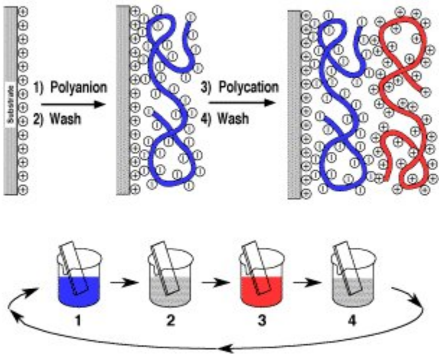
The F^3 Factory consortium believes that the EU chemical industry's competitive position would be significantly enhanced if it could operate modular continuous plant (F^3 Factory plant) for low to medium scale production rates. As such, the F^3 Factory project has united a wide variety of stakeholders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

The F^3 Factory project has two key aims:

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

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

Our aim in this project was validation of the F3 technology. Studies performed in our institute in 2013 concerned the evaluation of adsorption properties of the poly (acrylic acid) (PAA) using fluorescence measurements. Polyelectrolyte multilayers containing new type of PAA (from bio based process) and fluorescently labeled polycation (poly(allylamine) hydrochloride PAH) were formed using layer by layer technique (Figure 1). The dependence of the intensity of fluorescence vs number of layers were measured and the example of measured changes in intensity of fluorescence with the number of layers is presented in figure 2.



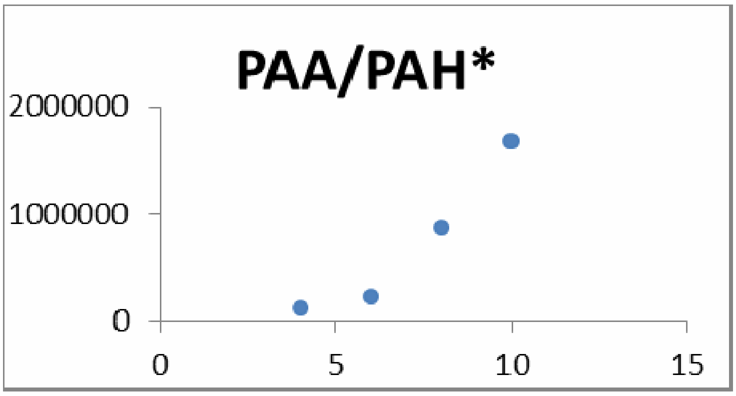


Figure 1. LbL technique

Figure 2. Fluorescent intensity with no of layers

Our studies proved that the bio-based polyacrylic acids obtained in the F^3 process had the same adsorption and multilayer forming properties as the reference synthetic PAA. Therefore, the F^3 method of PAA production was validated.

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 among one of the key enabling technologies in Horizon 2020 – EU Research and Innovation program. This presents a great challenge for education and knowledge dissemination in the field of nanoscience and nanotechnology. Therefore there is a need for evaluation of the existing educational systems in this emerging area with strong implications for European society and industry.

As a result, EU launched NanoEIS: Nanotechnology Education for Industry and Society project, whose aims 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 and teaching material development - for the latter task it acts as WP leader.

The examination of national curriculum for nanotechnology – related issues is done at secondary school level and at 1st, 2nd, and 3rd degrees of higher studies. It appears that nanotechnology is not taught as a separate course, nor is mandatory, in most European countries at secondary school level. Science education is rather concentrated around traditional disciplines, with nanotechnology presence limited to a chapter or topic in the national curriculum. It is nevertheless possible to be taught as a part of physics, biology, or chemistry classes. It might be integrated into science education in upper secondary schools in Poland, but there is a risk of omission due to the elastic curricula, which should reflect students' interests and teachers' background.

Full nanotechnology education is available at higher education level. Nanotechnology curricula were assessed for 1st, 2nd, and 3rd degree of higher studies. It is shown that the direct involvement of potential industrial employers in the teaching process is one of the key factors determining proper matching between the skills needed on the job market with the profile of university graduate.

The development of novel teaching and assessment tools for modern nanotechnology education is started. At first, a survey of the existing teaching materials, developed within earlier EU programs, was done.

HYPERCONNECT Functional Joining of Dissimilar Materials Using Directed Self-Assembly of Nanoparticles by Capillary-Bridging

EC 7th 310420 HYPERCONNECT project (CP) [2013-2015]
(project leader: Professor Piotr Warszyński)

Tomorrows micro-electronic devices will have to show more functionality and performance at smaller form factor, lower cost and lower energy consumption in order to be competitive on this multi-billion dollar market. Advanced system integration is thus inevitable, a trend bound to joining dissimilar materials with new packaging technologies. These processes must enable lower thermal resistances and higher interconnect density and device reliability under thermomechanical loading. HyperConnect project addresses these challenges by a radically new material joining process. Its design concept is to create a new functional connections between the different composite materials (such as ceramic materials and semiconductor, organic laminates with metallic paths). They take the form of necks with nanoparticles formed between the microparticles.

The main objective is to demonstrate superior electrical, thermal and thermomechanical performance and to combine design and technology with the support of simulation and testing. The central new idea comprises a sequential joint forming process, using self-assembly of nanoparticles, polymers and filler composite materials exploiting capillary action and chemical surface functionalization.

The partners in the project are scientific and industrial units from five European countries: IBM (Switzerland), Fraunhofer (Germany), LORD (Germany), Intrinsiq Materials Limited (United Kingdom), Angewandte Micro-Messtechnik (Germany), Conpart AS (Norway), SINTEF (Norway), J.Haber Institute of Catalysis and Surface Chemistry (Poland), Technische Universitaet Chemnitz (Germany) , Stiftinga Vestlandsforsking (Norway).

In the first year of the project we concentrated on the development of methodology of formation of alumina capillary using sol-gel approach. The necks were formed between model glass mili- and microspheres of alumina microparticles using aluminium isopropoxide as the alumina precursor. The dependence of neck geometry on the precursor concentration were established. Then nanoparticles of the material with high thermal\electric (SiC, AlN, Al_2O_3, cBN, Si_3N_4, Cu, graphene) conductance were suspended in the alumina precursor or polymer binder solutions and formation of necks were investigated. Figure 1 illustrated the example of necks formed between two glass spheres with 7% alumina precursor wthout and with addition of 1% wt. of graphene nanoflakes.

Figure 1. Necks formed 7% Al isopropoxide

Figure 2. Necks with graphene nanoparticles (1%)

The thermal or electric properties of the necks will be investigated at the later stage of the project. The results will be implemented in the electronics industry.

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 2013 several events were organized including the Working Group meetings: “*Synthesis, Kinetics and Catalytic Aspects of Biocolloids*”, La Valetta, Malta, “*Dynamics of Self-Assembly*”, Delft, Netherland, “*The balance of interactions in soft matter systems: Thermodynamics, structure and kinetics*”, Nicosia, Cyprus, “*Functionalized Surfaces and Nanobiocomposites*”, Szeged, Hungary, “*Dynamics of Liquid Interfaces*”, Potsdam, Germany. The annual conference of the Action took place during the ECIS 2013 Conference in Sofia, Bulgaria,. CM1101 School on Surface Analytical Techniques “Probing Macromolecules at Water-Solid Interfaces”, in Geneva, Switzerland, 14th European Student Colloid Conference and CM1101 training School, Potsdam, Germany, Pre-conference ECIS COST CM1101 Training Course “*Colloids and Medical Applications*”, in Sofia, Bulgaria. Additionally 16 STSM were organized. The official WEB page of the Action can be found at the address: http://projects.um.edu.mt/cm1101/ .

Projects of the Polish-Norwegian Research Programme

NANONEUCAR Nanoparticulate Delivery Systems for Therapies Against Neurodegenerative Diseases

The Polish-Norwegian Research Programme NANONEUCAR project 199523/64/2013 [2013-2016]
(project leader: Professor Piotr Warszyński)

Prevention and treatment of neurodegenerative diseases and stroke-related brain damage are major and unresolved problems of contemporary medicine. Despite the progress in understanding of molecular mechanisms of neuronal injury and preventing them, only few neuroprotective substances are used in the clinic and their efficiency in the treatment of stroke and neurodegenerations is not satisfactory. One of the major limitations to current neurodegenerative disease treatment is an inefficient delivery of neuroprotective drugs to the affected part of the brain.

The blood-brain barrier (BBB) is permeable by small (< 1000 Da), lipophilic molecules only. When a neuroprotective drug enters the brain, it may be partially brought back to the capillary lumen by multidrug resistance proteins. Moreover, some of the orally delivered neuroprotective drugs may influence the whole organism, thus causing peripheral toxicity and numerous adverse reactions.

The main project objective is to develop the new strategy of delivery of neuroprotectants by the nanocarriers, which are able to cross the blood-brain barrier without imposing side effect on its normal function. We will concentrate on developing various methodologies of encapsulation of neuroprotectants, adjusted to their physicochemical properties, for formation of nanocarriers with the size in the range (10 – 150 nm) and surfaces functionalized for targeted delivery. We will elaborate the mechanisms of internalization of nanocarriers of different structure and architecture of external layer in the “in vitro” models of BBB and in-vivo in wild type and transgenic mice models. The effects of some promising neuroprotectants and gene-delivery used in nanoparticulate formulations on viability of neuronal cells exposed to toxic agents will be examined. We hope that our nanocarriers will be used in future for therapies of stroke and neurodegenerative diseases as Alzheimer’s and Parkinson’s or schizophrenia.

The project consortium includes five scientific institutions: three Polish Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Science (ICSC) and Institute of Pharmacology (IPharm) Polish Academy of Science and the Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University (FBBB) and two Norwegian research institutes: SINTEF Materials and Chemistry (SINTEF) and the Laboratory of Molecular Neuroscience (LMN) at the University of Oslo.

FUNCLAY Synthesis and Functionality of Innovative Porous Clay Hybrid Nanostructures

The Polish-Norwegian Research Programme FUNCLAY project
210445/53/2013 [2013-2016]
(project leader: Małgorzata Zimowska PhD)

Metallic nanoparticles or their oxides play an important role in catalysis, optical or biomedical applications. This led the scientists to explore new supports, which will increase the degree of nanoparticles dispersion and availability. The promising group of materials used as a support are the ones derived from nano-modified clay minerals. The objective of this project is the development of a new generation supported catalysts for removal of VOC, the major pollutants of the atmosphere. In our project we would like to focus on the functionalization of the lattice of the porous silica materials based on clay minerals via direct site selected incorporation of heteroatoms.

This project is devoted to the design and development of functionalized porous materials based on ecofriendly clay minerals from smectite group for removal of volatile organic compounds, the major pollutants of the atmosphere. The stability and functionality of the new generation supported catalysts with selected heteroatoms will be performed.

Our investigation will focus on direct functionalization of purely siliceous mesoporous silica and porous clay heterostructure composites derived from layered clay minerals by site selected incorporation of iron into the structure.

The impact of such functionalization on the catalytic activity will be investigated in two types of catalytic reaction: removal of the volatile organic compounds (toluene) and the decomposition of ethanol. The position of iron and possible transformations in coordination and oxidation states occurring under synthesis and catalytic conditions will be investigated with the use of Mössbauer spectroscopy in comparison with infrared FTIR spectroscopy.

Projects of EU Structural Funds Programmes

MPD Krakow Interdisciplinary PhD Project in Nanoscience and Advanced Nanostructures

PO IG 1.1.2. MPD project [2008-2013]
(project leader: Professor Józef Korecki)

Project “Krakow Interdisciplinary PhD-Projects in Nanoscience and Advanced Nanostructures” has been 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. The Project Coordinator was Prof. Bartłomiej Szafran affiliated at Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, who is the partner in the Project. The project was 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 and finished December 31st, 2013 aimed 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. From the Institute side, the project was successfully implemented with five PhD thesis, namely:

1. Anna Wójcik PhD (supervisor: Assoc. Professor Tomasz Borowski) Selected iron-dependent dioxygenases as examples of biological nanostructures: computer modeling of catalytic activity (public defense October 4th, 2013)
2. Małgorzata Adamczak PhD (supervisor: Professor Piotr Warszyński) Surfactants, polyelectrolytes and nanoparticles as building blocks for surface nanostructures (public defense September 30th, 2013)
3. Dominik Kosior PhD (supervisor: Professor Kazimierz Małysa) Nanostructures and stability of thin liquid layers (public defense with distinction October 10th, 2013)
4. Katarzyna Luberda-Durnaś PhD (supervisor: Professor Wiesław Łasocha) Hybrid organic-inorganic layered materials - precursors of semiconducting nanostructures (public defense September 30th, 2013)
5. Ewa Młyńczak PhD (supervisor: Professor Józef Korecki) Surface and interface properties of metal-oxide magnetic nanostructures (public defense with distinction September 24th, 2013). For the first time this thesis was in the form of four papers published in recognized scientific journals.

In 2013 the PhD students of MPD were co-authors of eight publications in journals covered by Web of Science.

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.

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:

- 2nd year / 3rd year

K. Kubiak (supervisor: Z. Adamczyk) - The stability of silver nanoparticles on boundary surfaces-AFM and QCM study; Ł. Kuterasiński (supervisor: prof. M. Derewiński) - Nature of proton acidic centers in MFI type zeolites, isomorphic modified by boron; M. Gackowski (supervisor: prof. M. Derewiński) - Silica monoliths with zeolite nanoparticles as a model flow microreactors.3rd year / 4th year

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

- 4th year / 5th year

J. Dziedzic (supervisor: prof. P. Warszyński) - Photocatalytic decomposition of organic compounds in water enhanced by encapsulated oxidants; M. Krzak (supervisor: assoc. prof. P. Nowak) - High-performance anticorosive coatings prepared from composite meterial based on organic polymers; M. Nosek (supervisor: assoc. prof. P. Weroński) - Analysis of multilayer porous colloidal materials with controlled architecture; K. Onik (supervisor prof. M. Derewiński) -Hierarchic materials based on zeolites precursor as the basis of the modern catalytic systems; A. Pajor (supervisor: prof. P. Warszyński) - Elektroactive multilayers films with nanoparticles.

M. Oćwieja (supervisor prof. Z. Adamczyk) finished the project - Kinetics of silver particle adsorption on heterogeneous surfaces and morphology of silver monolayers, she publically defended the PhD thesis and received the PhD academic degree in chemical science in the field of chemistry.

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 main aims of the fourth year of the project was optimization of reactor conditions for the whole-cell PEDH system and elucidation of physicochemical parameters influencing final conversion in the reactor tests. Moreover, studies has been conducted on procedure development for implementation of PEDH-based technology in laboratory of the industrial partner.

In case of EBDH part the main focus of the project was on modeling of the reaction mechanism for para substituted phenols and anilins as well as on continuation of research on application of immobilized enzyme in batch synthesis of alcohols other than (S)-1-phenylethanol.

Modeling of PEDH reactivity required broadening of the kinetic database that contained results of test reactors for acetophenone derivatives (i.e. 4-Br, 4-OCH$_3$, 4-F, 4-NO$_2$, 4-Cl, 4-Ph, 4-Et, 4-OH and 4-mesyl derivatives). In order to reach equilibrium conversion limits the test reactors had to be analyzed for higher initial substrate concentrations (100-300 mM). This allowed better differentiation of substrates with different substituents and study of influence of their electronic characteristic not only on kinetics but also on the equilibrium point. The substituent electronic effect was described by Hammett σ, while thermodynamic effect was described by theoretically determined equilibrium constant (based on standard free enthalpy of the reaction). Two types of neural models were build – multiple layer perceptorn (MLP 5-3-1) and radial based function network (RBF 5-168-1). MLP network exhibited lower accuracy in prediction of product concentrations ($R^2 = 0.96$) than RBF ($R^2=0.99$) but it allowed analytical interpretation of relationship between input variables (σ, t, C_0, log P, log K) and product concentration. Analysis of response curves showed that electron-withdrawing substituents enhance conversion (linear relation) most probably due to stabilization of electron-rich transition state. The non-linear effect was observed for hydrophobicity (log P) and equilibrium constant (log K). The relationship for initial substrate concentration allowed determination of the optimal range for the highest conversion (150-200 mM). This experience allowed development of the procedure for the industrial partner that used cell extracts instead of the whole cells and resulted with first test synthesis in their laboratory.

Modeling studies f EBDH showed, that loss of enantioselectivity observed in case of para substituted alkylphenols and alkylanilines can be explained by the alternate reaction mechanism. Due to presence of a base (deprotonated carboxyl group of Asp485) residue in vicinity to p-substituent the carbocation intermediate product can lose a proton and spontaneously transform into quinone/imine product. This species in turn is able to react non-enantioselectively with a water molecule yielding both *S* and *R* alcohols. In consequence the relative reaction rate of the enantioselective hydroxylation with Mo-OH ligand and non-enantioselective hydroxylation by H_2O would decide about the chiral composition of the alcohol product. This theoretical hypothesis was supported by experimental evidences showing that changes of pH influences the enantioselectivity of the hydroxylation reaction. It was shown that increase of pH enhances the enantiomeric excess of the overall reaction.

Moreover, the immobilized enzyme was used in a stoichiometric batch reactor utilizing high concentration of $K_3[Fe(CN)_6]$ as electron acceptor for hydroxylation of 2-ethylthiophene. The reaction conducted in optimal conditions yielded 0.5 g/l product concentration.

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)

Systematic studies of silver particle deposition kinetics under diffusion transport on poly(allylamine hydrochloride) (PAH) modified mica were carried out. Monolayer coverage, quantitatively determined by AFM and SEM, was regulated within broad limits by adjusting the nanoparticle deposition time and the ionic strength of deposition. The stability of obtained silver films was determined in controlled release experiments also carried out under diffusion transport for pronged time periods reaching 240 hours. The decrease in the surface coverage of particles was followed by SEM and AFM imaging. The role of particle size, ionic strength and temperature was systematically studied. Typical release kinetics runs obtained for various particle sizes are presented in Fig. 1. As can be seen, the release rate significantly decreases with particle size. Thus, for the S1 sample (15 nm) the residue coverage of the monolayer after the time of 240 hours is only 30% of the initial value, whereas for the S3 sample (54 nm) it remains at the level of 90%. This means that in the latter case particle desorption was practically negligible.

These results were theoretically interpreted in terms of the random sequential adsorption model (RSA), which allowed one to determine the equilibrium adsorption constant K_a and the binding energy (energy minimum depth). For particles of the average size 15 nm and T = 298 K, the energy varied between -16.9 kT for ionic strength 0.1 M and -18.8 kT for ionic strength 10^{-4} M. For the largest nanoparticles 54 nm the energy varied between -17.7 kT for ionic strength 0.1 M and -20.8 kT for ionic strength 10^{-4} M. These results suggest that the interactions between surface and nanoparticles are mainly controlled by electrostatic attraction between ion pairs.

Our studies indicate that there is a possibility of a controlled release of silver nanoparticles from films formed at solid substrates, which can be significant for biological application, e.g., in respect to antibacterial activity.

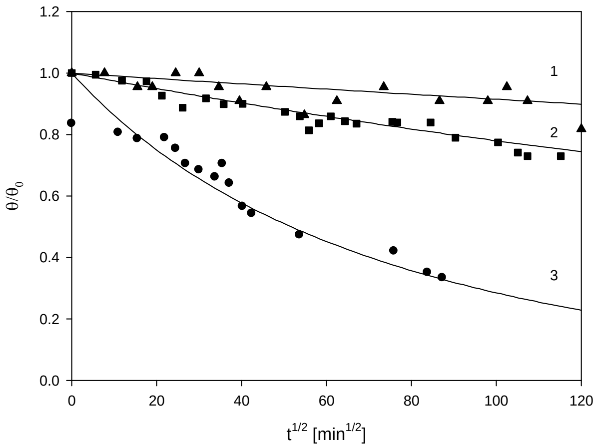


Figure 1. The kinetics of silver particle desorption expressed as the dependence of Θ/Θ_o on $t^{1/2}$. The initial coverage of particles $\Theta_o = 0.05$. The points denote experimental data obtained by AFM for $I = 10^{-2}$ M, pH 6, T = 298 K and particle size: 1) (▲) 54 nm, 2) (■) 28 nm, 3) (●) 15 nm. The solid lines denote the theoretical results calculated from the RSA model.

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

PO IG 1.1.2. VOX project [2009-2013]
(project leader: Professor Ewa Serwicka-Bahranowska,
principal investigator: Tadeusz Machej PhD)

Project aimed 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 were 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 2013 project entered its final stage. The activities concentrated on the experimental work associated with manufacturing of large volumes of active phase, in order to prepare four 50 kg charges of monolithic catalyst for scale-up tests, and on performing these tests in the pilot installation. On the basis of laboratory testing completed earlier, two catalyst formulations (**1** and **2**), containing copper and manganese as key transition metal elements, were selected for the preparation of the active phase. Active phase suspensions, in the amount of 50 dm^3 with formula **1** and 37 dm^3 with formula **2**, were prepared in the laboratories of ICSC PAS. In addition, optimization of washcoat composition and its preparation procedure were carried out. Covering the cordierite monoliths (two different cpsi values) with washcoat, and activity tests in pilot installation, were carried out in the company Katalizator sp. z o.o..

Results obtained during tests in pilot installation showed that both the formula **1** and formula **2** monolith catalysts were very active in total oxidation of model volatile organic compounds (toluene and ethanol), reaching T_{50} = 250^{o}C for toluene and T_{50} = 180^{o}C for ethanol, at VOC concentration of 1g/m^3 and GHSV = 10000 h^{-1}.

Results obtained during the project realization led to two patent applications.

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 2013:
According to the programme curriculum, series of lectures entitled “Philosophy” have started.
- in the second 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 second quarter of the year 5-day doctoral research workshop with invited lecturers was organized in Zakopane;
- in the fourth quarter of the year 2-day doctoral research workshop with invited lecturers was organized in ICSC PAS;
- in the fourth quarter of the year 20 members of faculty of partnership units completed 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

Organo-Clays as Intermediates for the Synthesis of Functional Hybrid Materials

Research project under Polish-Slovak Scientific and Technological Cooperation [2013-2015]
(project leaders: Małgorzata Zimowska PhD, Helena Pálková PhD)

Naturally occurring clay minerals from the smectite group, such as montmorillonite, are valuable, low-cost and environmentally friendly materials. However, appropriate modification of these layered silicates may significantly broaden their possible applications. One of possible montmorillonite modification is the exchange of inorganic cations, compensating the negative layer charge in the natural clay, for organic cations. It results in a material with significantly different properties than initial natural sample e.g. the surface changes from the essentially hydrophilic to increasingly hydrophobic depending on the intercalated surfactant. Moreover, clay minerals can be subjected to acid activation, which results in higher acidity and modification of structural and surface properties, very important in catalytic reactions. The purpose of the project was the preparation of organo-modified clays by cation exchange of calcium form of Ca-SAz montmorillonite by tetrabutylphosphonium cations (Bu_4P^+). Work focused on determination of the influence of Bu_4P^+ introduced between the layers of Ca-SAz montmorillonite on the stability of the structure upon acid treatment (6 M HCl) at 80 °C for 2-8 hours.

Acid activation affected the structure and textural properties of both calcium and organic derivative of montmorillonite. In Ca-SAz montmorillonite Ca^{2+} ions were exchanged for protons and the leaching of central atoms (Al, Mg) from the structure was observed. Based on chemical analysis from EDS patterns of Ca-SAz after 8 hours of treatment the amount of Al and Mg dropped below 10% of its initial value (Fig 1.). Structure decomposition increased also surface area from 70 m^2/g for initial Ca-SAz up to 467 m^2/g after 4 hours of acid treatment due to formation of amorphous partly protonated silica.

Loading of Bu_4P^+- caused significant decrease in the specific surface area (45 m^2/g) compared to Ca-SAz. Upon acid treatment the same changes were observed for Bu_4P^+-SAz i.e. gradual leaching of Al and Mg, and the increase of the specific surface area. However, the rate of decomposition was considerably lower for organic derivative and even after 8 h of treatment, around 50% of initial amount of Al and Mg were still present in the sample (Fig. 1.). Gradual decrease in the phosphorous content indicates de-intercalation of organic cation from the sample. The specific surface area of the organo-clays (Bu_4P^+-SAz) did not show such strong increase upon acid treatment as Ca-SAz, reaching maximum value of 244 m^2/g after 8 hours of treatment. The lower extent of decomposition of Bu_4P^+-sample confirmed higher stability of the structure of intercalated silicate. The extent of layer disintegration depends on the accessibility of the external and inner clay surfaces to protons of the acid. Thus, introduction of Bu_4P^+ cations hinders the attack of protons and improves the chemical stability of clay mineral.

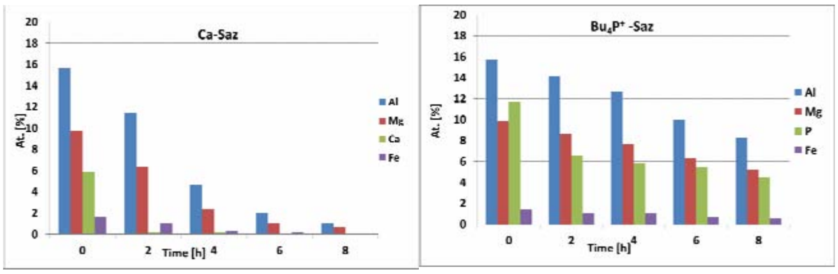


Figure1. The content of elements in Ca-SAz and Bu_4P^+-SAz after acid-treatment.

Polyoxometalates Immobilized on Mesoporous Silicas for Selective Oxidation of Alkanes and Alkenes

Research project under Polish-Ukrainian Scientific and Technological Cooperation
[2013-2014]
(project leaders: Professor Ewa Serwicka-Bahranowska)

The project aims at combining the versatile catalytic functions of a heteropoly metalate active phase with the unique pore structure offered by mesoporous silica supports. The main objective of the project is to develop efficient methods of immobilization/anchoring of heteropoly compounds onto mesoporous silica materials for their application as catalysts in liquid phase selective oxidation of alkanes and alkenes.

In the reported period research concentrated on immobilization of 12-molybdophosphate Keggin anion at the surface of functionalized mesoporous silica of SBA-15 type. The functionalized SBA-15 support containing protonated 3-aminopropyl groups was obtained by a new one-pot synthesis developed by the Ukrainian partner. Ion exchange with aqueous solution of $H_3PMo_{12}O_{40}$ was used for immobilization of heteropoly anions. The catalysts were characterized by means of XRD, chemical analysis, thermal analysis, SEM, FTIR, and nitrogen adsorption/desorption isotherms. Catalytic decomposition of ethanol was used as a test reaction for the assessment of acid/redox properties of the hybrid heteropoly anion/SBA-15 materials.

Physico-chemical characterization confirmed that the synthesized materials possessed ordered mesoporous structure typical of SBA-15. Chemical analysis demonstrated that up to15 wt. % of $PMo_{12}O_{40}^{3-}$ could be anchored by means of anion exchange. Catalytic decomposition of ethanol carried out in the temperature range 150-300^{o}C on the supported samples and unsupported $H_3PMo_{12}O_{40}$ shows that anchoring of 12-molybdophosphate anion at the surface of SBA-15 modifies the acid and redox properties of the heteropoly compound. In the supported samples, at temperatures $\leq$ 200^{o}C, the redox function prevails over the acidic one and the main reaction product is acetaldehyde. At higher temperature the acidic function becomes dominant and the increase of the catalytic activity is associated mainly with the enhancement of the dehydration pathway to ethylene, the yield of acetaldehyde remaining almost constant. At 300^{o}C the yields of ethylene and acetaldehyde are ca. 50 and 20%, respectively. In the reference unsupported $H_3PMo_{12}O_{40}$ the redox function is less pronounced and above 250^{o}C the yield of acetaldehyde declines to disappear completely at 300^{o}C, while the yield of ethylene, reflecting the catalyst acidity, grows rapidly to reach 100% at 300^{o}C. Liquid phase oxidation of cyclooctane with air showed that the unsupported heteropoly acid was more active than the hybrid heteropoly anion/SBA-15 catalyst.

Results of this work will serve as basis for manufacturing active and selective multifunctional catalytic materials with adjustable acid/base and redox functions, and controlled pore system architecture.

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 high efficiency. 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.

High temperature fuel cells can be powered by: hydrocarbons, carbon oxide, hydrogen and carbon. Direct carbon fuel cell use solid carbon as a fuel. Comparing to a hydrogen fuel cell, DCFC brings several advantages. 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 in Second stage „Initial tests” have been focused on the optimization of the performance (current density, density of power) 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.

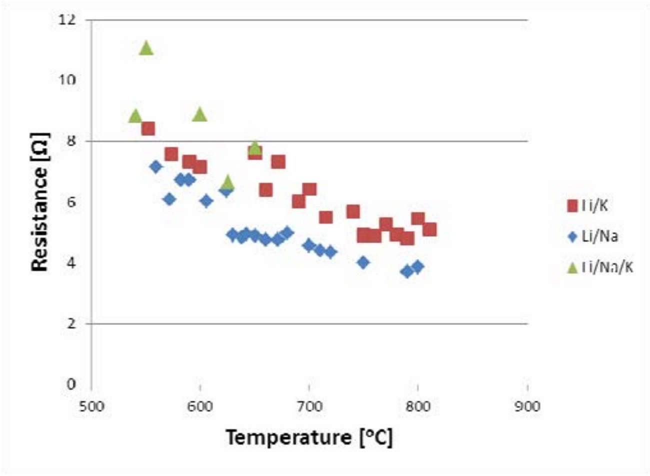


Figure 1. Temperature dependence of carbonate eutectic resistance

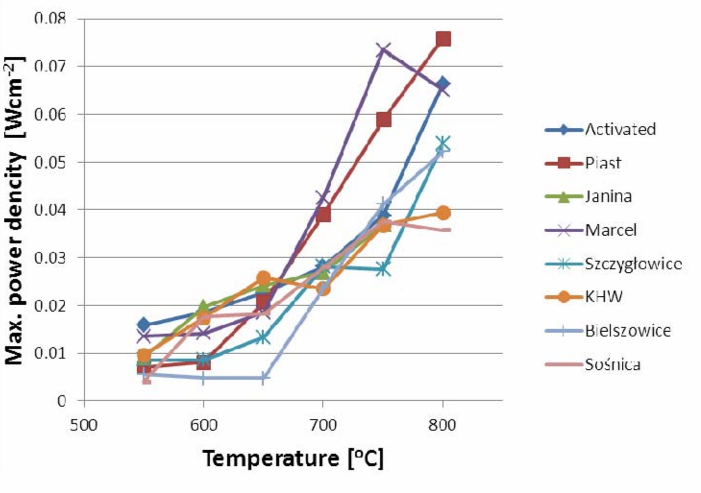


Figure 2. The maximum power density of fuel cells that use coals from Polish coal mines.

The goal of our investigations was to test the carbonate electrolyte fuel cells powered with carbon coming from Polish mines. Coals from mines were initially crushed and/or cleaned. Tests of molten carbonate fuel cells powered with coals from Coal Mines "Piast", "Janina", "Marcel", "Szczygłowice", "Bielszowice", and "Sośnica" were performed. For the sake of comparison, maximum power density test of fuel cell using high purity elemental carbon (activated carbon Norit SX2 ® AR) as a fuel was included too.