JERZY HABER INSTITUTEOF CATALYSIS
AND SURFACE CHEMISTRY
POLISH ACADEMY OF SCIENCES

DETAILED RESEARCH REPORT

year 2015

Leading National Research Centre

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

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

In July 2012 the Institute as a member of Marian Smoluchowski Kraków Research Consortium „Matter-Energy-Future" received a status of The Leading National Research Center in physics for the period 2012-2017. Apart from the Institute, the Marian Smoluchowski Kraków Research Consortium consists of: Faculty of Chemistry of the Jagiellonian University, Faculty of Physics, Astronomy and Applied Computer Science of the Jagiellonian University, Faculty of Physics and Applied Computer Science of AGH University of Science and Technology, and The Henryk Niewodniczański Institute of Nuclear Physics Polish Academy of Sciences.

During the year 2015 the Institute undertook a series of activities aiming at intensifying joined research activities of employees of the institutions partaking in the Consortium. A competition for three grants supporting joined research projects of the employees of the Institute with researchers of other partner institutions of the Consortium was proceeded and the following projects received founding:

1. "New catalysts for conversion of furfural to saturated alcohols – biofuel components" (dr Robert Kosydar, cooperation with the Chemistry Department of the Jagiellonian University)
2. "Studies on interaction between proteins modified with biologically active compounds and their receptors" (dr hab. Barbara Jachimska, cooperation with the Chemistry Department of the Jagiellonian University)
3. "Novel lactose esters" (dr Maciej Guzik, cooperation with the Chemistry Department of the Jagiellonian University)

Six one year-long PhD stipends, "Smoluchowski Doctoral Scholarships", were granted to the most talented students of the PhD studies lead by the Institute.

The Institute hosted as visiting professors researchers from abroad, who gave lectures and seminars for employees and PhD students of the Institute. The researchers who visited the Institute were the following:

1. Dr Josep Grau-Bove, University College London, UK
2. Prof. Jarosław Majewski, Los Alamos Neutron Scattering Center, USA
3. Dr Emiliy Zholkovskyy, Institute of Bio-Colloid Chemistry National Academy of Sciences of Ukraine, Kiev, Ukraine.

The Institute participates in a FOKUS action entitled "ArtMet", which is coordinated by the Faculty of Chemistry of the Jagiellonian University and is devoted to interdisciplinary research of metal objects.

Statutory Research

Catalytic Materials and Processes for Sustainable Development

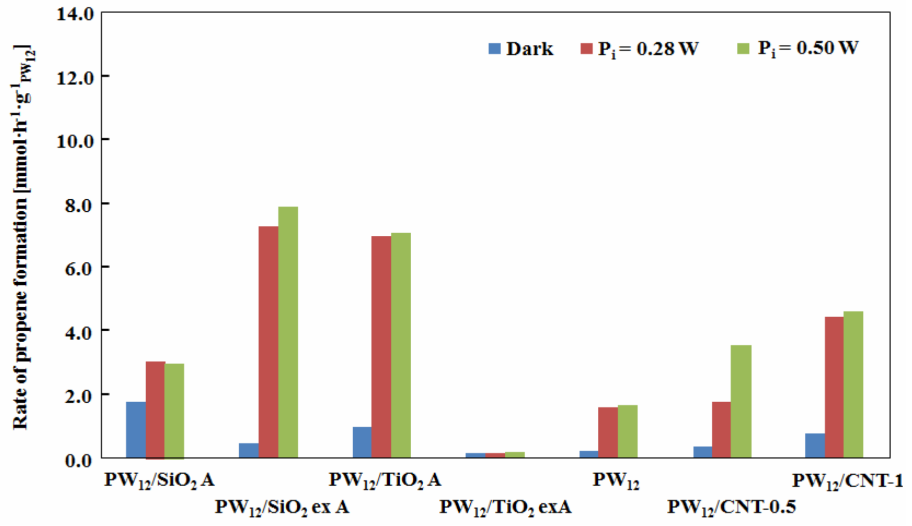
Heteropolyacid-oxide Systems; their Physicochemical Properties and Catalytic Conversion of Isopropanol

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

The isopropanol conversion to form propene (C3) and diisopropyl ether (DIPE) is considered a useful reaction to characterize the acidity of a catalyst The selectivity to these products mainly depends on the acidity-basicity of the solid catalyst. Some bulk and surface properties of the catalysts have been studied and the effect of light has been investigated by taking into account that the (photo)reactivity can depend on the features of the support and the formation of a pseudo-liquid phase, both related to the presence of HPA.

Catalytic and photocatalytic tests for 2-propanol dehydration to propene were successfully carried out by using binary materials obtained by supporting a Keggin heteropolyacid $H_3PW_{12}O_{40}$ (PW_{12}) via hydrothermal conditions (abbr. ”A”) and solvothermal treatment (abbr. “exA”). The commercial SiO_2 (Mallinckrodt), TiO_2 (Evonik P25) and additionally multiwall carbon nanotubes CNT (Sunnano) or home solvothermically prepared SiO_2 and TiO_2 were used. Both photocatalytic and catalytic 2-propanol conversion was studied in gas-solid regime by using a continuous reactor working at atmospheric pressure and 60-120 °C. For photo-assisted runs this reactor was also illuminated with UV light (power 0.28W and 0.5W). This conversion was also studied by performing FTIR spectra of the gas-phase over the HPA-oxide system. Propene and diisopropyl ether were the main reaction products.

Our measurements allowed comparing the catalytic and photocatalytic activities of new performed binary samples containing heteropolyacid in propanol conversion. It was confirmed that Keggin heteropolyacid species played a key role both for the catalytic and the photo-assisted catalytic reactions. The illumination with UV light enhanced the reactivity of these binary materials (heteropolyacid-oxide) compare to no-illuminated materials.



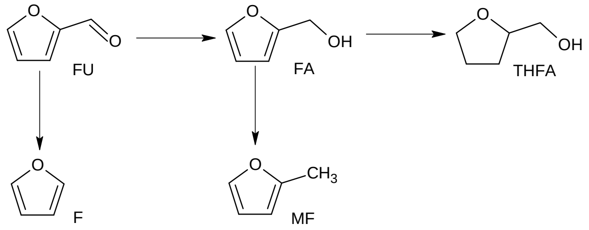
The rate of propene formation for PW_{12}/TiO_2 A and PW_{12}/SiO_2 exA was significantly (seven times) increased upon UV light (see figure). The apparent activation energy of 2-propanol conversion was determined in the range 60-120 °C and it decreased in the presence of light for all of the catalysts used.

In the future basing on our catalytic and photocatalytic results we would like to explain role of heteropolyacid in these binary materials because such huge increase of photoactivity versus the activity without light is very promising.

Catalytic Processes with Participation of Bio-reagents

(Professor Alicja Drelinkiewicz, Erwin Lalik PhD, Robert Kosydar PhD, Leszek Matachowski PhD, Aleksandra Pacuła PhD, Monika Góral-Kurbiel PhD, Mateusz Kołodziej MSc, Tomasz Szumełda MSc)

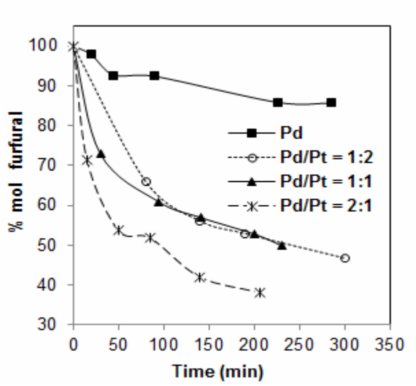
The aim of studies is a role of MoO_3 - based support for hydrogenation of furfural, bio-reagent, generating number of technologically important products and for oxygen reduction reaction in fuel cell.

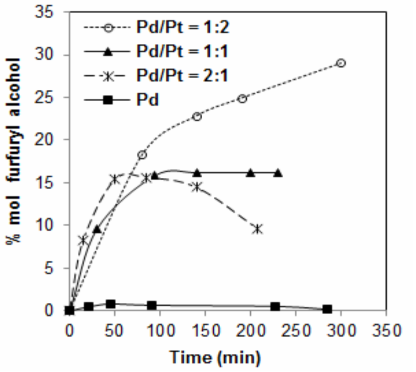


The main reaction is furfuryl alcohol formation and its hydrogenation to THF. Besides, decarbonylation reaction generating furan and CO is commonly observed, resulting in catalyst deactivation by these products.

The research work concentrated on liquid phase hydrogenation of furfural (60^oC, 6 atm H_2, toluene) on two series of bimetallic Pd-Pt catalysts, 2 wt % Pd+Pt, Pd/Pt = 2:1; 1:1; 1:2 molar ratio. Series I is represented by Pd/P-MoO_3 and bimetallic Pd-Pt/P-MoO_3 catalysts obtained by calcination (air, 700^0C, 20 h) of Pd or Pd-Pt salts of heteropolyacid $H_3PW_{12}O_{40}$, followed by reduction with H_2 at 250^0C (3h). Series II is represented by Pd/SiO_2 and Pd-Pt/SiO_2 catalysts prepared by the reverse “water-in-oil” microemulsion method. Catalysts were characterized by BET, XRD, XPS, SEM (EDS) techniques.

The obtained results confirmed the alloy Pd-Pt phase in both series catalysts (XRD). Metal particles in series I (Pd-Pt/P-MoO_3) catalysts are 20-30 nm in size, while in series II (Pd-Pt/SiO_2) the particles of definitively smaller size, 8-10 nm appeared. In hydrogenation of FU catalysts of series I of very low surface area (2-3 m^2/g) displayed very low activity, 3-4 % FU conversion. The Pd-Pt/SiO_2 catalysts displayed much higher activity. A very high initial activity of Pd/SiO_2 strongly decreased during the reaction due to poisoning of catalyst by products of decarbonylation reaction. Deactivation of Pd-Pt/SiO_2 catalyst was definitively weaker. They exhibited much higher selectivity to FA formation compared to Pd, because of lower reactivity to THFA formation.





The electroreduction of oxygen, reaction in fuel cells, was studied on Pd/P-MoO_3 and Pd-Pt/P-MoO_3 catalysts. The samples were mixed with electroactive carbon Vulan XC72. All studied catalysts exhibited activity for oxygen reduction. The activity of Pd-Pt was higher and the potential of oxygen reduction was positively shifted compared to those for monometallic Pd electrocatalyst. The Pd/Pt ratio did not essentially affect electrocatalytic performance of the samples.

New Peroxo-compounds of Mo (VI), W (VI) and V (V). Synthesis, Structural Studies and Applications in Oxidation Processes

(Professor Wiesław Łasocha, Dariusz Mucha PhD, Katarzyna Luberda-Durnaś PhD, Barbara Bożek PhD, Marcin Oszajca PhD, Adrianna Borowiec MSc)

The aim of the studies was to obtain new compounds of the type of peroxocomplexes and polyoxocompounds of metals: Mo (VI), W (VI) and V (V) with amines and selected inorganic cations. These compounds have been subject of structural, physico-chemical and catalytic studies.

Among the research conducted in 2015 worth mentioning are:

a) We conducted research on obtaining of new compounds from the group of peroxo- molybdates with nicotinic and isonicotinic acids and inorganic cations. As a result a new peroxo- compound with nicotinic acid was obtained. We were not obtained, however, new compounds with an isonicotinic acid as pure crystalline phases.

b) We have studied new compounds of molybdenum, formed in the reactions with an excess of aliphatic amines: 1,2-diaminopropane, 1,3-diaminopentane, and diethylamine.

c) New compounds of molybdenum were studied which have formed by reactions in aqueous solutions in the presence of selected aliphatic amines and in the presence of excess acetic acid.

Description of the most important results:

- • We have obtained and investigated new oxodiperoxomolybdate of sodium $Na_2[MoO(O_2)_2(C_6H_4NO_2]_2.2H_2O$ containing nicotinic acid N-oxide group built-in cyclic anion (Figure 1a). Lattice parameters of obtained compound: a=8.0647(2), b= 11.9155(2), c=11.6799(3)Å, β=109.585(3)°, V=1057.44Å SG $P2_1/n$.
- • Fully tested was a new hybrid molybdenum oxide with the formula $MoO_3(N_2C_3H_{10})$. In this chemical compound there are polymeric chains of the type -Mo-O-Mo-O-. Each atom Mo(VI) in addition connects to two terminal oxygen atoms and two nitrogen atoms of the 1,2-diaminopropane molecule (Fig. 1b).Lattice constants are: a=8.72458 b=11.04544 c=7.37513Å, V=710.72$Å^3$, SG Abm2.
- • It was obtained a new compound $NH_4[Mo_2O_6(H_2O)(CH_3COO)]$, in which there are infinite double- molybdenum-oxygen chains. Half of the molybdenum atoms are coordinating by acetate anions (Fig. 1c). Basic crystallographic data: a=9.1636(3) b=14.2706(4), c=7.40978(18)Å, V= 968.977, SG Pnc2. Similar compound was obtained using the nicotinic acid.

The use of the obtained results.

We plan to use the selected monophasic compounds in catalytic tests, including the reactions of catalytic oxidation of organic compounds, in particular hydrocarbons such as cyclooctane and limonene using air and gaseous O_2. Hybrid Mo(VI) oxide with 1,2-diaminopropane will be tested in the epoxidation reactions.

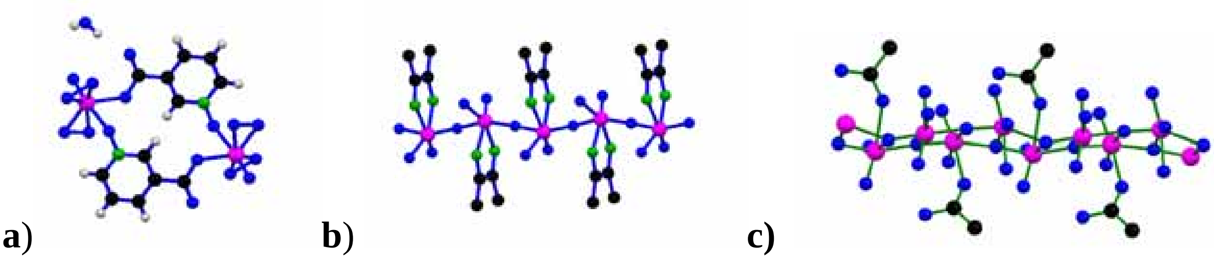


Figure.1 New perokso- and polyoxo molybdates synthesized in this study. Colors of magenta, green, black and blue represent molybdenum, nitrogen, carbon and oxygen.

Studies on the Transformation of Furfuryl Alcohol towards Bio-components for Fuels and Plastics

(Dorota Rutkowska-Żbik PhD, Assoc. Professor Ryszard Grabowski, Tadeusz Machej PhD, Michał Śliwa PhD, Katarzyna Samson PhD, Małgorzata Ruggiero-Mikołajczyk PhD, Łukasz Mokrzycki PhD, Wojciech Rojek MSc)

The aim of our study was to design a catalyst for hydrogenolysis of furfuryl alcohol to 2-methylfuran (DMF) and to study which parameters of the catalyst are responsible for their high selectivity and/or activity. In such a way our studies may contribute towards the production of DMF from biomass.

Chromites of Ni, Co, Fe and Cu were obtained by citric acid method, copper chromite was additionally obtained by so-called „Adkins" method, whereas Fe/SiO_2, Fe/Al_2O_3, Cu/ $CuCr_2O_4$ catalysts were obtained by impregnation of solid carriers. The synthetized catalysts were characterized by the following physico-chemical methods: XRD for the phase compositions, BET for the specific surfaces, H_2-TPR for the reducibility of the prepared samples, and XPS for the composition and oxidation state of the metal component of the active phase. Acid-base properties were additionally measured by carrying the test reaction of isopropanol decomposition using pulse method (pulses of 0.5 μL isopropanol, fixed-bed flow reactor, T = 200^{o}C, TCD-GC analysis). Next, the catalysts were tested in the hydrogenolysis of furfuryl alcohol and furfuryl aldehyde in a flow reactor under atmospheric pressure, in the range of temperatures 150° - 400°C. The selectivity towards the main products of hydrogenolysis (2-methylfuran and furan) as well as by-products (methane, ethane, butane) was measured.

Two main isopropanol decomposition products were identified: propene (which is formed on the acid sites) and acetone (which is formed via dehydrogenation on the basic sites) when model reaction was carried on the tested samples. The propene:acetone ratio depended on the type of catalys. For the $NiCr_2O_4$, $CuCr_2O_4$, $50Fe/SiO_2$, $CoCr_2O_4$, and $MnCr_2O_4$ systems the amount of acetone was considerably higher, with $CuCr_2O_4$ possessing the most basic character. For the Fe/Al_2O_3 and $FeCr_2O_4$ samples, propene prevailed; for iron chromite is was the only detected product. The obtained results were correlated with the catalytic activity of the studied materials. For furfurol hydrogenolysis, the samples, which exhibited basic character, were selective mostly to furan (S_{furan} = 100% vs the highest amount of acetone detected for isopropanol decomposition over $CuCr_2O_4$). DMF is the major product of furfuryl alcohol dehydrogenolysis over "acidic" catalysts. Similar relationship was observed for furfural dehydrogenolysis, with the exception of the $FeCr_2O_4$ and Fe/Al_2O_3 catalysts. For the latter, the catalytic activity was due to other properties, probably to the iron oxidation state, as indicated by the results of XPS experiments.

The performed studies aim at the optimization of the composition and the properties of the catalyst, which will be selective towards 2-methylfurane from furfuryl alcohol derived from hemicellulose. DMF is identified as a promising bio-additive for fuels. The design of the active and selective catalyst, which would enable to produce DMF from biomass and the determination of the factors governing its catalytic properties, would become an asset to the worldwide research leading to novel routes towards production of bio-component of fuel from biomass.

Hydrogenation of Acetol in the Presence of Metallic Catalysts Supported on Mesoporous Silicas

(Professor Ewa Serwicka-Bahranowska, Dorota Duraczyńska PhD, Alicja Michalik-Zym PhD, Bogna D. Napruszewska MSc, Roman Dula PhD, Małgorzata Zimowska PhD, Robert P. Socha PhD)

The aim of the research was the synthesis, characterization and the application of heterogeneous ruthenium catalysts supported on SBA-15 type mesoporous silica and the application of new materials in the hydrogenation of acetol to 1,2-propanediol. This reaction constitutes an important process from a technological point of view since the resulting diol is used as solvent, antifreeze, deicing agent and approved food, cosmetic and pharmaceutical additive. Moreover, it plays a key role in processes vital for transformation of renewable feedstock, such as catalytic hydrogenolysis of glycerol or upgrading of bio-oil. Unfortunately, current industrial technologies and laboratory procedures involve homogeneous catalytic systems and require the use of elevated pressures and temperatures, very long reaction times or the utilization of homogeneous catalysts. Such mode of operation implies high energy consumption, and generates problems with separating catalysts from the reaction mixture.

In this study, a series of ruthenium catalysts containing various contents of active phase i.e. 0.2 wt.% Ru/SBA-15, 0.5 wt.% Ru/SBA-15, 1 wt.% Ru/SBA-15 and 2 wt.% Ru/SBA-15 was prepared by simple wet impregnation procedure. These new materials were thoroughly characterized with the use of X-Ray Powder Diffraction (XRD) technique, X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and High-Resolution Transmission Electron Microscopy (HRTEM); textural properties were also determined. The test reaction was carried out under mild conditions of pressure and temperature (ie. 1 bar H_2 and room temperature); water was used as solvent. The catalytic activity of 2 wt.% Ru/SBA-15 was compared with that of 2 wt.% Ru/SiO_2.

The obtained results demonstrate that Ru/SBA-15 materials are excellent, recyclable, heterogeneous catalysts capable of efficient liquid phase hydrogenation of acetol at ambient temperature and pressure, using water as a solvent. Analysis of the conversion data points to the general trend – the higher Ru content the more active the catalyst, although the effect is not proportional to the active phase loading. Based on the SEM/HRTEM data it appears that the observed results are most likely due to differences in particle size and distribution of ruthenium nanoparticles supported on SBA-15 and SiO_2 carriers. Moreover, these compounds are easily separated from the reaction mixture and can be used in subsequent catalytic cycles.

These results are the starting point for further work aimed at the use of these active compounds in the hydrogenation of the C=O, C=C and C≡C groups. Development of recyclable heterogeneous catalysts exhibiting high catalytic activity under mild conditions of pressure and temperature is an attractive research direction.

Heteropoly Compounds as Catalysts for Oxidation of Cyclohexanone to ε-Caprolactone with Molecular Oxygen

(Professor Ewa Serwicka-Bahranowska, Katarzyna Pamin PhD, Jan Połtowicz PhD, Joanna Kryściak-Czerwenka PhD, Bogna D. Napruszewska MSc)

Baeyer-Villiger reaction is widely applied in organic chemistry for oxidation of cyclic ketones to appropiate lactones. The goal of our study was the synthesis, physico-chemical and catalytic characterization of iron salts of tungstophosphoric and molybdophosphoric acids in oxidation of cylohexanone to ε-caprolactone with molecular oxygen. Oxidation of cyclohexanone leads to the synthesis of caprolactone which is substrate to obtain a biodegradable polymer.

Synthesized compounds were analyzed using different spectroscopic methods like FTIR, UV-Vis, differential thermal analysis DSC and cyclic voltammetry. All synthesized heteropoly compounds were active in investigated oxidation reaction. In the case of iron salts of molybdophosphoric acid, all salts were more active than parent heteropolyacid and their activity and conversion of substrate was increasing upon the increase of the iron content in the catalyst structure. The following order of activity for iron salts of molybdophosphoric acid was obtained:

$$Fe_{1.5}PMo > Fe_{1}PMo > Fe_{0.5}PMo > HPMo$$

In the case of the iron salts of tungstophosphoric acid, similarly as in the case of iron salts of molybdophosphoric acid, all compounds demonstrated higher activity than the parent heteropolyacid. Moreover, all the iron salts of tungstophosphoric acid were also more active than respective iron salts of molybdophosphoric acid. The catalytic activity of the series of iron salts of tungstophosphoric acid $Fe_{1}PW$ was varying in the following manner:

$$Fe_{1}PW > Fe_{0.5}PW > Fe_{1.5}PW > HPW$$

Summarizing, the study demonstrated that, irrespective of the nature of the addenda atoms in heteropoly compounds, insertion of iron in the form of compensating cation has a beneficial influence on the catalytic performance in the oxidation of cylohexanone. The most active among all synthesized catalysts was the $Fe_{1}PW$ catalyst.

Results of this work form the basis for further optimisation of the catalyst for oxidation of cyclohexanone to ε-caprolactone with molecular oxygen.

Selective Hydrogenation of Benzene on Metal Catalysts

(Professor Ewa Serwicka-Bahranowska, Jan Połtowicz PhD, Katarzyna Pamin PhD, Alicja Michalik-Zym PhD, Małgorzata Zimowska PhD)

The study aimed at investigation of the catalytic performance of selected metal catalyst in the hydrogenation of benzene to cyclohexene. Hydrogenation of benzene is an important industrial process for the synthesis of cyclohexene which is in the next step hydrated to cyclohexanol. Cyclohexanol is a key intermediate for the production of polyamide polymers like Nylon-6 and Nylon-66. The hydrogenation of benzene in the liquid phase using typical metal catalyts (e.g. nickel) leads to the formation of cyclohexane. The reason for that is the high catalytic activity of such catalysts, which does not permit the reaction to stop at the stage of cyclohexene formation. The difficulty of the process consists in a suitable choice of the reaction conditions and the catalysts, so that the hydrogenation of benzene is stopped after formation of cyclohexene and its further hydrogenation to cyclohexane is prevented.

In the first stage metal catalysts such as ruthenium black, nickel catalyst, rhodium catalyst and ruthenium-nickel were studied. The most active catalyst was ruthenium black and this metal catalyst was chosen for further studies. In the second stage of our studies the catalytic activity of different ruthenium containing catalysts in the hydrogenation of benzene to cyclohexene was examined. The majority of catalysts are the catalytic systems containing ruthenium deposited on different supports, including Ru on Zn-Al hydrotalcite, Ru on active carbon, Ru/SiO_2 and Ru/ZrO_2. The catalyst containing ruthenium in its structure, namely ruthenium porphyrin RuTPP(CO)(MeOH), was also studied in this reaction.

Among the investigated ruthenium-containing catalysts the most active was ruthenium black and this catalyst was also the most active of all studied metal catalysts.

These results are the starting point for further work aimed at the use of metal catalysts for selective hydrogenation of benzene, with focus on the optimization of the metal component dispersion.

Photocatalytic Activity of Layered Minerals Pillared with Transition Metal Oxides

(Professor Ewa Serwicka-Bahranowska, Professor Piotr Warszyński, Assoc. Professor Paweł Nowak, Alicja Michalik-Zym PhD, Bogna D. Napruszewska MSc, Elżbieta Bielańska PhD, Roman Dula PhD, M. Rogowska)

The study aimed at synthesis, physico-chemical characterization and comparison of photocatalytic properties of two types of TiO_2/montmorillonite composites, differing in the manner of titania insertion into the mineral structure.

TiO_2-montmorillonite composites were synthesized using conventional pillaring method and a new procedure, involving inverse microemulsion method. The resulting materials were characterized with XRD, XRF, SEM, Raman spectroscopy and N_2 adsorption/desorption methods. Synthesized composites were tested in the photocatalytic degradation of two model organic compounds: rhodamine B and methyl orange. Photocatalytic efficiency of the composites was compared with the performance of a commercial product TiO_2 P25.

Pillaring of montmorillonite led to the formation of well ordered structures, in which neighbouring layers were firmly bound by intercalated titania pillars. Procedure employing inverse microemulsion yielded disordered, partly delaminated „house of cards” structures, containing dispersed TiO_2 nanoparticles. In both composites titania nanoparticles showed the anatase structure. Experiments with photocatalytic degradation of cationc (rhodamine B) and anionic (methyl orange) dyes demonstrated that both photocatalysts led to complete decoloration of dye solutions, the pillared montmorillonite showing higher activity. Both composites were less active than the reference TiO_2 P25, but binding of TiO_2 nanoparticles within the layered mineral structure facilitated the recovery of the photocatalyst from aqueous environment due to a quicker and more efficient sedimentation.

Results obtained in this study form basis for further work on the design of photocatalytically active composites based on layered minerals and transition metal oxides.

The Mechanism of Oxygen Reduction Reaction on Selected Cathode Materials Devoted to the High-temperature Fuel Cells

(Michał Mosiałek PhD, Assoc. Professor Paweł Nowak, Maciej Tatko MSc, Aneta Kędra MSc, Grzegorz Mordarski PhD, Elżbieta Bielańska PhD, Małgorzata Ruggiero-Mikołajczyk PhD)

The oxygen reduction reaction (ORR) is a four-electron reaction, proceeding through many intermediate steps. The goal of the research was to reveal which of the intermediate steps in ORR at the investigated materials is the rate-determining step and to propose the methods to improve the catalytic activity of them.

The object of the research was the materials described in the report from the statutory research in the year 2014. They were composite materials, composed of samarium strontium cobaltite $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) and lanthanum strontium ferrite $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF). Those composites show unusual resistance to temperature shocks, what is very important from the point of view of their possible application in fuel cells. As an electrolyte we applied cerium samarium oxide $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC), material showing very high ionic conductivity in the range the lowest temperatures applicable in the high-temperature fuel cells. The mechanism of the ORR was investigated with the application of the cyclic voltammetry and electrochemical impedance spectroscopy methods. The possibility to optimize the procedure of investigated materials preparation was investigated too.

The composite sintered at the temperature of 1000 °C showed the lowest reaction resistance (so, the highest catalytic activity) among the composites sintered at the temperatures: 900, 950, 1000, 1050 and 1100 °C. Comparing to the composites sintered at lower temperatures, composite sintered at 1000 °C is roast-sintered well enough, showing simultaneously relatively high specific surface area, and relatively high contribution of mesopores, which enables effective oxygen diffusion. The later material was selected to the investigations of the ORR mechanism.

Up to five characteristic features (parts of a semicircle) related to the particular steps of ORR, may be discerned in the impedance spectrum of the SSC-LSF composite electrode on which the ORR proceeds. Three of them, which impedance appears in the high frequency range show no dependence of oxygen concentration what is characteristic for the processes of charge transport in the electrolyte. The capacitance, correlated with those processes is very low (from 1.6×10^{-8} to 4.3×10^{-6} F cm^{-2} in the temperature of 700 °C in pure oxygen). Those values are typical for the capacitance connected to intergranular boundaries. The resistance connected with the semi-circle registered in the range of middle frequencies depends on the pressure of oxygen according to the formula: $\log(R)=a-m \log(P_{O2})$, with the coefficient m assuming the value between 0.05 and 0.15. The value of the coefficient m, equal to 0.125 may be connected with the reaction $O_{ads} + 2e \leftrightarrow O^{2}$,in which transfer of the second electron is slower than the transfer of the first one. The process registered at the lowest frequencies showed values of resistance similar to the previous one. The coefficient m for that process assumed the values close to 0.5, characteristic for the process of oxygen dissociative adsorption: $O_2 \leftrightarrow 2O_{ads}$. One of the later processes was the rate-determining step, depending on the conditions (temperature, oxygen partial pressure).

The described cathodic material may be applied in the high-temperature fuel cells. The catalytic activity of the material may be increased by deposition of the nanoparticles catalyzing the adsorption of oxygen at the surface.

Physics and Chemistry of Surfaces and Nanostructures
– Experiment and Theory

Enzymatic and Biomimetic Reactions Mechanisms – Theoretical Approach

(Assoc. Professor Maciej Szaleniec, Assoc. Professor Tomasz Borowski, Maciej Guzik PhD)

The aim of the task was to investigate the reaction mechanism catalyzed by benzylsuccinate synthase (BSS) based on the crystal structure of the apoenzyme.

The project was conducted in cooperation with a group of prof. J. Heider from Marburg University, that conducted experimental part of the study. The following questions were formulated and tackled with theoretical modeling: 1) what is the geometry of substrates (toluene and fumaric acid) in the enzyme active site, 2) which of the postulated mechanisms is most probable and agrees with isotopic experiments (labeling and KIE), 3) what factors are responsible for reaction enantioselectivity (BSS catalyzes synthesis of only (R)-benzylsuccinate).

In order to obtain enzyme-substrate complex (ES) the molecule of the product, i.e. (R)-benzylsuccinate, was docked into the active site of BSS. This provided a preferential protonation state of the carboxylic groups of the product and an initial pose for further modeling of the complex (EP). The molecular dynamics (with CHARMm force field) was used to relax crystal structure of the BSS and to accommodate the product molecule in the active site. The geometry which was characterized with the lowest total energy was cooled down to 0K and used in further studies. The product molecule was replaced with substrates both in pro(S) and pro(S) configuration and the geometry of both ES complexes was minimized. The analysis of total energy and ligand binding energy revealed slight thermodynamic preference of the BSS for binding of fumarate in pro(*R*) orientation (by 7 kcal/mol).

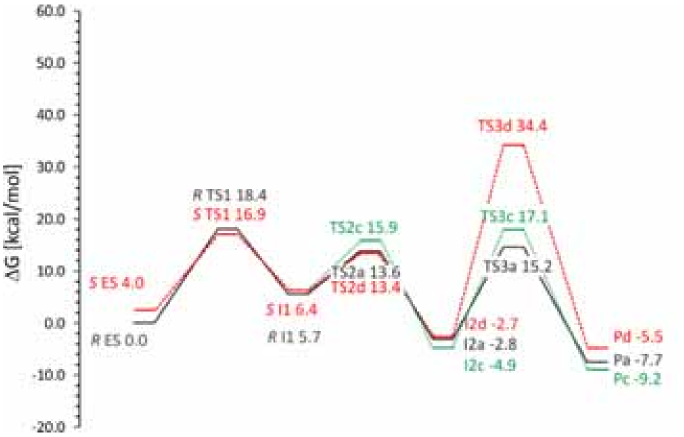


Figure. 1. 3 different variants of the reaction catalyzed by BSS: black line – pro(R) pathway with attack on distal C atom of fumarate, line red and green – pro(S) pathway, line red – attack on proximal C atom of fumarate, green line – attack on distal C atom of fumarate.

Based on geometry of ES complex the cluster model was constructed and used in quantum chemical studies of 5 different variants of the reaction. The calculations were conducted with DFT (B3LYP+D2 at 6-31G(d,p)/6-311+G(2d,2p) + solvent correction (with IEFPCM) and thermal corrections to Gibbs free energy computed at 6-31G(d,p)). The calculations confirmed there is a preference for benzoil radical attack on the distal, with respect to Cys493, C atom of fumarate. The analysis of Gibbs free energy reaction profile showed that TS1 (radical activation of C-H of toluene) is the rate limiting step, but the radical quenching step (TS3) is associated with a very similar barrier. The calculated isotope effects for both process with respect to ES are indistinguishable (6.9 and 6.7) although the KIE for TS3 calculated with respect to I2 is very close to the value observed in experiment (4.0). The calculations also confirmed lower thermodynamic probability of formation of pro(*S*) ES complex. Moreover, they also revealed kinetic factors influencing enzyme enantioselectivity, i.e. the barrier of TS2 (C-C coupling step) in pro(S) configuration is lower for proximal attack on C=C of the fumarate, which results with prohibitively high barrier of the radical quenching step (TS3d).

Results obtained for BSS may be a starting point for a search for biocatalysts for stereoselective coupling of toluene and fumarate.

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

(Professor Ewa Brocławik, Professor Bogdan Sulikowski)

Quantum chemical modeling was aimed at the characterization of electron density and spin flow in the adducts of NO and ammonia-modified Co(II) sites in zeolites. The dependence of spin- and orbital-resolved electron transfer channels on ammonia co-adsorption (revealed by the analysis of multi-configuration wave function in terms of configurations corresponding to electronic resonance structures) explained the role of electron transfer from NH_3 lone-pairs in the mechanism of the vital NO transformations.

The dependence of the identity and efficiency of the charge transfer upon co-adsorption of donor ligands revealed that not only the number of NH_3 molecules but also the spin and electronic status of the system are crucial for enhancing NO activation: for native Co(II) site no backdonation is registered while triggering-on π^*-back donation depends not only on the number of NH_3 molecules but also on the spin state of the system. The most interesting theoretical result was the analysis of many-configuration wave function in terms of resonance structures (corresponding to electromers with various charge-transfer characteristics) for cobalt complexes with the $\{Co(II)\text{-}NO\}^8$ core. Resolution of multi-configuration wave function (by means of localized active orbitals) into configurations corresponding to resonance structures $Co^{II}NO^0$, $Co^{III}NO^-$, $Co^{I}NO^+$, enabled quantitative assignment of the NO activation to the dominant contribution of the $Co^{III}NO^-$ charge-transfer form.

The objective of experimental studies was to establish relationships between the modification of type Y zeolites and their activity and selectivity in transformations of α-pinene in the liquid phase. Starting from NaY, a series of samples was prepared by applying various methods of modification: ion exchange with ammonium ions, calcination in the broad range of temperatures and extraction with mineral acid solutions. Some samples were also modified by solid-state ion exchange of additional, external source of aluminium. The samples were characterized by XRD, sorption of nitrogen, FT IR spectroscopy and solid-state ^{29}Si and ^{27}Al MAS NMR spectroscopy. Quantitative deconvolutions of NMR spectra were used for monitoring the status of silicon and aluminium, and the transformations of aluminosilicate framework at different temperatures and calcination conditions were documented. Physicochemical characteristics of modified FAU and HEU type zeolites were correlated with the catalytic properties in isomerization of α-pinene.

Solid-state NMR studies of natural mesolite (NAT) were carried out and the geometric features of a zeolite framework were considered to assign ^{29}Si and ^{27}Al MAS NMR spectra. Qualitative and quantitative description of all the silicon sites was provided. The 1D ^{27}Al MAS NMR spectra were complex and could not be assigned directly to the three aluminium atoms present in mesolite. It was however demonstrated, for the first time in literature, that by using 2D ^{27}Al 3MQ MAS NMR spectroscopy all three magnetically and crystallographically framework aluminium sites can be clearly resolved. The subtle changes in aluminium content in the pristine and dealuminated mesolite samples were successfully monitored. Finally, in-depth studies on dealumination of natural zeolite clinoptilolite (HEU) under various conditions led to the preparation of active and selective catalysts for isomerization of α-pinene in the liquid phase.

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

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

The aim of this study is to determine the relationship between the atomic and electronic structure of epitaxial nanostructures and their properties functionalized for magnetic and catalytic applications. The applied technique of the molecular beam epitaxy allows to obtain metallic and oxide structures over a wide range of compositions, as well as to stabilize metastable phases that do not occur in nature. A special attention was on metal-oxide heterostructures both in bi-layered and multi-layered systems. In such systems it is possible to model the catalytic properties of corresponding heterogeneous metallic catalysts on oxide supports. On the other hand, systems including combination of a ferromagnetic metal and an antiferromagnetic oxide are basic building blocks of spintronic devices such as spin valves or RAM memories. Model studies on single-crystalline samples are compared with analogous polycrystalline systems.

The most important research task concerned thin film oxide FeO and MnO structures. We used a comprehensive experimental methodology including structural and magnetic characterization such as low-energy electron and photoelectron microscopy (LEEM and PEEM, respectively), scanning tunneling microscopy (STM), conversion electron Mössbauer spectroscopy (CEMS) and photoelectron spectroscopy (XPS). We also continued the development of the synchrotron based microspectroscopic methods.

We correlated the structural and magnetic properties of ultrathin FeO (111) films on Pt (111). The research was conducted both using laboratory methods and synchrotron radiation – the nuclear inelastic scattering. It was found that the structural properties of the FeO films are different from those of the bulk oxide with the FeO stoichiometry, i.e. wustite. We showed that the phonon density of states for the monolayer thickness exhibits a linear dependence on energy for the low energy range, which is typical for two-dimensional systems. With increasing thickness a gradual transition from the two-dimensional to three-dimensional behavior was observed. For the few monolayer thickness a long-range ferromagnetic order was established which has no correspondence in the bulk. The observed FeO film properties witness a stabilization of a metastable FeO phase, which does not occur naturally. This phase was justified by first principles DFT calculations.

Manganese oxide are widely used in catalysis owing their many oxidation states. Epitaxial films of manganese oxides were prepared by oxidation of metallic Mn layers, also as mixed oxide with other 3d metals. Mn oxides with MnO and Mn_3O_4 stoichimetry were stabilized, as well as mixed manganese and iron oxides with the $Fe_{3-x}Mn_xO_4$ stoichiometry in a spinel structure. The magnetic and electronic structure was determined using CEMS and XPS.

The iron (II) containing catalytic systems designed for oxidation of organic compounds were studied. The electronic states of the elements at the surface of FeO/SiO_2 and $FeCr_2O_4$ previously used in the catalytic tests were investigated by photoelectron spectroscopy (XPS/ESCA). In case of $FeCr_2O_4$, the oxidation process leads to partial hydroxylation (ca. 25%) of the chromite surface and formation of the coordination bonding between chromium (III) and organic carbon. The Fe^{2+} ions show hydroxylation ratio comparable to that for the surface (ca. 28%) and much lower than observed for FeO/SiO_2 after the same catalytic test (ca. 70%). Therefore, the oxide surrounding of Fe^{2+} ions is much better stabilized in chromite than in the oxide system.

The new research possibilities in the above topics are opening up with the commissioning of the spectroscopy beam-line at National Synchrotron Radiation Center Solaris.

Studies of the Influence of Microscopic and Physicochemical Parameters on the Ability of Control the Properties of Systems with Biomedical Importance

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

The aim of the studies was analysis of the influence of various microscopic and physiocochemical parameters on the ability of control the phenomena occurring in systems with biomedical importance. Particularly, we focused on the systems which, in some circumstances, can act as drug delivery systems. These mainly were: structure of carbon nanotubes, size of biocompatible metallic nanoparticles, influence of pH on adsorption/desorption effects of selected molecules on the surfaces of carbon nanotubes, meaning of the catalytic role of water in processes of structural transformations in hexapyranozes, conformational stability of biomolecules, adsorption and morphology of protein layers on biocompatible surfaces and swelling of PAMAM dendrimers.

The above aims have been achieved by: analysis of the influence of carbon nanotubes and functionalized metallic nanoparticles sizes on the energy of dispersion interactions between these components and ability of biding of doxorubicin molecules on the surface and in the inner cavity of carbon nanotubes with various chirality parameters. Moreover, by applying the transition path sampling method, we determined and analyzed reaction paths, corresponding to the ring-opening process involving alpha- and beta-glucopyranose molecules and occurring in the aqueous environment. We also focused on the dendrimer monolayer structure at silica surfaces. We used Multi Parametric Surface Plasmon Resonance (SPR) and Quartz Crystal Microbalance with dissipation energy (QCM-D) to investigate the conformational behavior of the 6th generation of PAMAM molecules.

The most essential results coming from the performed studies were following: showing that a key factor governing the potential applicability of composite systems carbon nanotube – metallic nanoparticle is their size. Nanoparticles with diameters not greater than 40 Å can adsorb reversibly on the surfaces of nanotubes, whereas bigger nanoparticles will adsorb very strongly and irreversibly. Adsorption of doxorubicin on the nanotubes surfaces turns out to be weak, the same was found for encapsulation of doxorubicin in the inner cavity of carbon nanotubes. Thus, it is necessary to develop additional modifiers in order to enhance the stability of the system. It was shown that the ring opening process may involve both one or two water molecules; the first possibility is the more probable one. The reaction is initiated by deprotonation of anomeric hydroxyl moiety; the subsequent step, i.e. the protonation of the ring oxygen atom, is necessary for the final ring cleavage. The MP-SPR measurements allow determining the mechanisms of dendrimer adsorption, e.g., the reversibility and orientation of molecules at interfaces for a wide range of concentrations. From the combination of the QCM-D and MP-SPR data with the assumption that the excess mass measured in QCM-D compared to the MP-SPR mass is due to trapped water molecules, we estimated the fraction of the water in the dendrimers film. The structure of resulting films is strongly dependent on the deposition condition.

The systems composed of carbon nanotubes and functionalized metallic nanoparticles or PAMAM dendrimers reveal useful properties as drug delivery systems. They also offer ability of incorporation of extra factors implementing the controlled release of drugs, eg. pH change. Similar properties can be found in the case of adsorption of doxorubicin in the inner hollow space of carbon nanotube. Practical realization of such functional composite systems needs, however, further studies. The pyranose ring-opening reaction is common in nature and significant in the context of biological systems. Explaining its mechanism may be crucial for understanding the action of carbohydrate-degradating enzymes as well as for the nature of anomeric equilibria.

Theoretical Calculations of Catalytic Activity of Heteropolyacids Salts

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

The aim of the presented study was to describe the geometric and electronic structure of heteropolyacids salts, compounds used in not only in the selective oxidation but also in other reactions, which require acidic catalysts. The structure of HPA salts allows for many different modifications of compensating cations (e.g. alkali metals, transition metal cations, elements of main group, organic cations) and of stoichiometry (result of total or partial replacement of protons in tungsten or molybdenum heteropolyacids (Me_xH_3-XPW (Mo)) that provide an opportunity to tailor their catalytic properties. The aim of the calculations was to determine the influence of geometric structure of heteropolianions, its chemical composition and the nature of the compensating cation on the acidic and oxidative properties of various salts.

Calculations were carried out using both cluster and periodic model. In the cluster approach two models were taken into consideration: i) solvated metal cations (to demonstrate differences in activity of various cations, eg. Co^{2+}, Mn^{2+}, Fe^{2+}, Al^{3+}, Ga^{3+}) and ii) hydrated metal cations connected with tungsten or molybdenum Keggin or Dawson anions (to demonstrate the influence of heteropolyanions geometry, addenda atom or central ion on properties of various salt). Periodic model was used to determine the geometric structure of heteropolyacids salt.

The results of cluster calculations show that acidic properties (measured by the energy of proton formation) of the studied salts depend on chemical character of compensating cations and addenda atoms as well as on the geometry of heteropolyanion, while do not depend on the character of central ion. Salts of elements of main group show a stronger acidic properties than systems with transition metal cations. Salts with Keggin anions are characterized by stronger acidic properties than systems with Dawson heteropolyanion.

Oxidative properties of studied salts systems were modeled by description of adsorption and activation process of oxygen donor (O_2, H_2O_2 molecules) on solvated (coordinated with H_2O and CH_3CN) compensating cations (Cs^{1+}, Fe^{2+}, Co^{2+}, Mn^{2+}, Al^{3+}, Ga^{3+}). The results of calculations show that adsorption and activation (elongation and weakening of O-O bond) is easier on transition metal cations than on alkali metal and elements of main group.

Due to the fact that for many salts there are no experimental data available regarding the crystallographic structure, the main goal of calculations using periodic model was to find the optimal size of crystallographic unit cells of a series of salts of the phosphotungstic acid. It is possible to devise optimal cell size theoretically, by finding a relation between cell volume and total energy and fitting it to the Murnaghan equation. In first approximation, the cubic system was assumed for all considered salts. Optimal cell sizes were obtained for pure acid and the following salts: $Li_3PW_{12}O_{40}$, $Na_3PW_{12}O_{40}$, $K_3PW_{12}O_{40}$, $Rb_3PW_{12}O_{40}$, $Cs_3PW_{12}O_{40}$, $Ag_3PW_{12}O_{40}$, $AlPW_{12}O_{40}$, $GaPW_{12}O_{40}$, $InPW_{12}O_{40}$, as well as for mixed salts $Cs_{1.5}Al_{0.5}PW_{12}O_{40}$ i $Cs_{1.5}In_{0.5}PW_{12}O_{40}$. In comparison to available experimental data for pure acid and the potassium salt, calculations overstate the cell size, most probably due to neglecting of van der Waals interactions.

The calculations will be continued. In the next step, salts which do not crystallize in the cubic system (e.g. magnesium salt) will be investigated. Also the influence of van der Waals interactions on the cell size will be studied. Obtained results will be used to construct reliable periodic models of heteropolyacid salts in order to explore their catalytic properties.

Nanostructures of Soft Matter

Topology and Electrokinetic Properties of Protein Monolayers on the Solid Substrate/Electrolyte Interfaces. Determining Conformations of Albumin Molecules Using the Micro-particle Deposition Method

(Professor Zbigniew Adamczyk, Jakub Barbasz PhD, Piotr Batys PhD, Anna Bratek-Skicki PhD, Marta Kujda PhD, Aneta Michna PhD, Maria Morga PhD, Małgorzata Nattich-Rak PhD, Monika Wasilewska PhD, Assoc. Professor Paweł Weroński)

The colloid particle deposition method was applied in order to characterize human serum albumin (HSA) monolayers on mica adsorbed under diffusion transport at pH 3.5. The surface concentration of HSA was determined by a direct AFM imaging of single molecules. The electrokinetic characteristics of the monolayers for various ionic strength were done by *in situ* streaming potential measurements. In this way the mean-field zeta potential of monolayers was determined. It was shown that the initially negative potential changed its sign for HSA surface concentrations above 2800 μm^{-2} that was interpreted as overcharging effect. The monolayers were also characterized by the colloid deposition method where negatively charged polystyrene microspheres, 810 nm in diameter were used. The kinetics of particle deposition and its maximum coverage were determined as a function of the HSA monolayer surface concentration. An anomalous deposition of particles on substrates exhibiting a negative zeta potential was observed, which contradicts the mean-field theoretical predictions. This effect was quantitatively interpreted in terms of the random site sequential adsorption (RSSA) model, see Fig. 1.

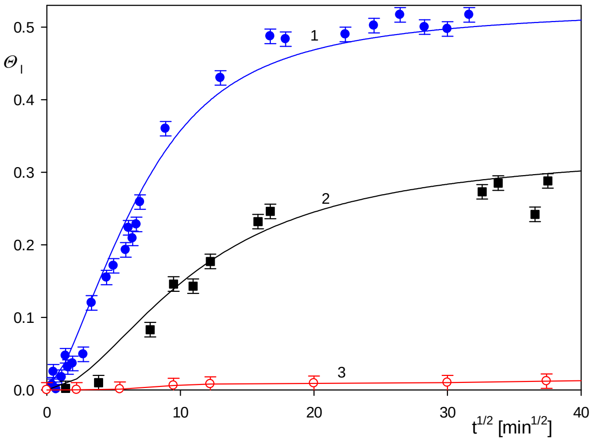


Figure 1. The kinetics of latex particle deposition on HSA (human serum albumin) monolayers of various surface concentration N_a determined by optical microscope imaging for ionic strength 0.15 M, pH 3.5, bulk latex concentration 0.5% (5,000 mg L^{-1}). The points denote the experimental data obtained for $N_a = 5x10^3$ [μm^{-2}] (●), $N_a = 3x10^2$ [μm^{-2}] (■), N_a = 60 [μm^{-2}] (○). The solid lines 1-3 show the theoretical results calculated by using the RSSA (random site sequential adsorption) model.

It was also confirmed that for high ionic strength of 0.15 M, the HSA monolayers can efficiently immobilize colloid particles even for the coverage as low as 0.01 mg m^{-2}. In this way, a unique functional relationship between the particle coverage accessible from optical microscopy measurements and the HSA surface concentration could be formulated. Based on this relationship a robust method for quantitatively determining the coverage of albumin under *in situ* conditions for the low range inaccessible to conventional methods was proposed. It can also conclude that the results can be exploited as useful reference data for the analysis of deposition phenomena of bioparticles at protein monolayers that has practical significance for a regulation of the bioadhesive properties of surfaces.

Influence of Ionic and Non-ionic Surface active Substances on Kinetics of the Three Phase Contact Formation at Hydrophilic and Hydrophobic Solid Surfaces

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

The studies have been aimed at determination of influence of a preferential adsorption of different surface active substances surface at solution/gas interface (bubble surface) on kinetics of the three phase contact by the bubble colliding with hydrophilic and hydrophobic solid surfaces. Bubble collisions with solid surfaces (grain surfaces in flotation systems) are highly dynamic processes occurring within the milliseconds timescale. During the bubble collision with the solid surface the three phase contact is formed if the liquid film separating the bubble and solid surfaces is ruptured during the collision time. Adsorption of surface active substance at the bubble surface affects the bubble rising velocity (terminal velocities are significantly lowered) and can vary drainage kinetics and stability of the wetting film formed during the bubble collisions with the solid surfaces.

Influence of various surface active substances on kinetics and mechanism of the three-phase contact (TPC) formation by the bubble colliding with hydrophobic (polytetrafluoroethylene – Teflon) and hydrophilic (muscovite mica) solid surfaces was studied. The experiments were carried out in solutions of non-ionic (n-hexanol and n-octanol), cationic (n-octyl-(OTABr), n-dodecyl-(DDTABr) and n-hexadecyl-trimethylammonium (CTABr) bromides, and anionic (sodium hexadecyl sulfate (SHS)) surface active substances (SAS) yo determine influence of type of the SAS polar group. The time of the TPC formation (t_{TPC}) and timescale of rupture of the thin liquid film separating the colliding bubble and a solid surface was determined using high-speed video recordings. The t_{TPC} was defined as the time span from the moment of the bubble first collision up to the liquid film rupture and formation of the TPC (dewetted) hole. It was shown that the influence of SAS on the kinetics of the TPC formation could be completely different depending on the hydrophilic/hydrophobic properties of the solid surface. At the Teflon surface the TPC was formed always, both in distilled water and in SAS solutions of various composition and concentration. Moreover, the t_{TPC} was significantly pro-longed at higher SAS concentrations, independently on the SAS type (ionic, non-ionic). These results show that air was present at the hydrophobic Teflon surface and the TPC formation was air-induced, i.e. the TPC was formed due to rupture of local foam films formed between the colliding bubble and nano-/micro-bubbles present at the hydrophobic solid surface. At the mica surface the wetting film was stable and the TPC was never registered in distilled water as well as in solutions of non-ionic and anionic surfactants. However, the TPC was formed at the mica surface in solutions of cationic surfactants, but the t_{TPC} values were decreasing with increasing cationic surfactants concentration. These data show that at the mica surface the TPC formation is undoubtedly electrostatically driven. The bubble attachment to negatively charged mica surface was possible only when the negative electric charge at the bubble surface was reversed, what can occur only in cationic SAS solutions.

Results of these studies have implications for optimization of the flotation separation processes. Efficiency of the flotation separation is strongly dependent on kinetics of the elementary flotation processes, that is, on kinetics of the three phase contact (TPC) formation and attachment of mineral grains to bubbles.

Functional Polyelectrolyte Multilayers Films

(Professor Piotr Warszyński and coworkers)

Functional polyelectrolyte multilayers formed on macroscopic surfaces or nano- and microsize particles or droplets are new materials with potential broad 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 2015 was to determine the effect of various multivalent cations on properties of polyelectrolyte multilayers containing alginate (ALG) polyanions. The multilayers were prepared by the layer by layer deposition method with incorporated ALG hydrogel obtained after crosslinking of ALG with different cations (Ca, Ba, Gd, Al). The PLArg/ALG multilayer film formation was confirmed with set of methods: quartz crystal microbalance with dissipation monitoring (QCM-D), ellipsometry, Fourier transform infrared spectroscopy with attenuated total reflection (FTIR ATR) and electrochemical techniques cyclic voltamperometry (CV) and electrochemical impedance spectroscopy (EIS). The results indicated that crosslinked multilayers had greater mass per unit area than their non-crosslinked counterparts. They were strongly hydrated (from 50-85 mass %) and crosslinked ones had an average 10% more water than non-crosslinked. The films stability was evaluated with EDTA solution treatment indicating partial delamination of last layer. Electrochemical methods proved to be very useful for the evaluation of barrier properties of PLArg/ALG films. Two models (homogenous membrane and membrane with pinholes) were applied to describe the permeability of multilayers and it was found that homogenous membrane model is better for description of PLArg/ALG films permeability. Fitting experimental data with electrical equivalent circuit proposed for EIS results evaluation based on homogenous membrane model gave similar permeability results to ones obtained from alternative method (CV) what additionally confirmed validity of the homogenous membrane approximation. The partition coefficients between membrane and solution estimated from EIS results were larger than unity, what indicated accumulation of probe within membrane. Viability tests showed that multilayers regardless ion type (crosslinking or not) used during the multilayer build-up, did not inhibit cells proliferation (MTT tests) neither caused their morphological changes (visualisation test of THP-1 cell line differentiation), therefore, the PLArg/ALG multilayers proved to be a promising material for cell adherent coatings. The results of our work can also be used to design the biocompatible coating of controlled permeability and microcapsules for use as theranostic carriers of hydrophilic or hydrophobic therapeutic agents and contrasts in medical imaging.

Physics and Chemistry in Cultural Heritage Protection

Model Development for the Particulate Matter Deposition in the Interiors of Historical Buildings

(Professor Roman Kozłowski, Łukasz Bratas DScz, Leszek Krzemień PhD, Michał Łukomski DSc, Marcin Strojecki PhD)

The research aim has been to develop a general model of transport and deposition of suspended particulate matter in the interiors of historical buildings, and, basing on the outcome of the modelling, refine the methodology of reducing soiling of historical surfaces, furnishings and collections for various building usage patterns.

The modelling consists of size-resolved particle concentration measurements in a historical building diagnosed and separation of the particle penetration and deposition losses by solving mass conservation equation relating the outdoor and indoor particle concentrations (C_{out} and C_{in}, respectively) with the use of a 'forward marching' scheme with time step Δt, corresponding to the measurement interval of particle concentrations:

$$C_{in}(t_2) = C_{in}(t_1)+P\cdot C_{out}(t_1)\cdot AER(t_1)\cdot\Delta t - C_{in}(t_1)\cdot[AER(t_1)+k]\cdot\Delta t \qquad (3)$$

where *AER* is the air exchange rate, *P* is the particle penetration factor and *k* is the deposition loss rate. *AER* is determined by fitting exponential decay curve to the difference between the recorded indoor and outdoor concentration of CO_2, after people present in the building left it. The analysis is carried out for periods with negligible indoor emission.

The elaborated approach was used to analyze multi-year experimental studies of indoor particle number concentrations in historical churches. Large indoor and outdoor particle concentration variability helped to separate the effects of penetration and deposition losses. For example, liturgical services regularly generated high indoor particle concentrations, owing to the burning of incense. During the particle concentration decay after the services, losses due to deposition could be reliably determined, whereas the events of high outdoor aerosol concentrations with no emission of particles indoors allowed the penetration factors to be precisely determined.

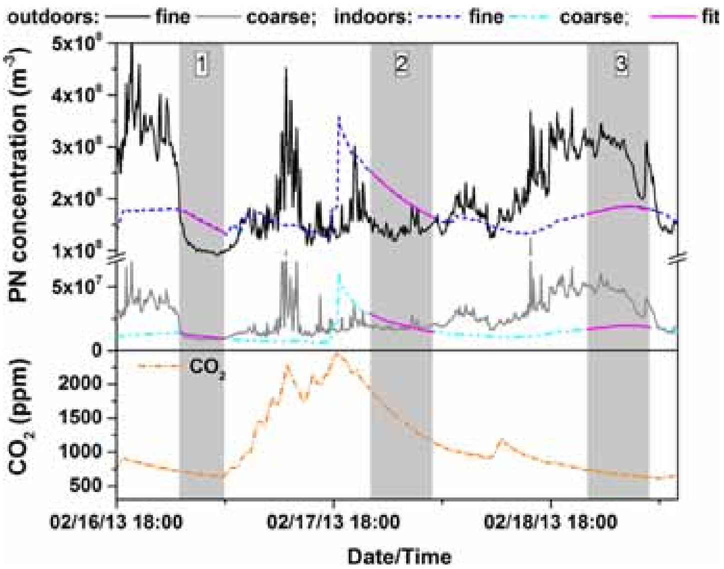


Figure 1. Number concentrations of fine (0.3-1 µm) and coarse (above 1 µm) particles measured indoors and outdoors at a church. Two events of low outdoor PN concentrations (1 and 2) and one event of high outdoor PN concentration (3) were used to determine particle deposition and penetration, respectively. The decay of indoor-generated CO_2 concentration was used to determine AERs during the events.

The model is a significant advance in the field, as it allows robust values of the deposition loss rate *k* and the penetration factors *P* in historical buildings to be determined, key parameters in evaluating the soiling risk indoors, even when the air exchange dominates the particle loss process.

"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)

Drug delivery systems, based on the architecture of carbon nanotubes, are extensively studied because of very useful mechanical and physicochemical properties of carbon nanotubes. An interesting concept is application of carbon nanotubes as transporters of drugs encapsulated in their inner cavities or on the sidewalls. Therefore, the aim of this part of the studies was modeling of several molecular architectures containing carbon nanotubes, model anticancer drug molecules (cisplatin and doxorubicin) and another component being sensitive to the environment parameters and allowing control of the molecular structure of the system. We focused on application of the pH change from physiological 7.4 to acidic one occurring in tumor tissue. This phenomenon is well-known in the literature and it is due to enhanced metabolism and oxygen deficiency in tumor tissue (hipoxy).

Two types of systems were studied: (i) carbon nanotube covalently linked to gold nanoparticles functionalized by hydrazone bonds containing chain molecules and (ii) carbon nanotube – dye molecules revealing pK_a values in the range 5-7. About 10 various dyes have been studied but only 4 of them revealed more or less interesting properties.

The obtained results suggest that application of dyes which charge distribution changes in the pH range 5-7 may lead to pH controlled drug release from the inner cavity of carbon nanotubes. Co-adsorption of dyes and doxsorubicin on the sidewalls of nanotubes is less effective. We observed binding of doxorubicin at neutral pH and its release in acidic pH only for methyl red and neutral red. However, the observed effects were quite weak. Definitely more promising is application of blocking effect for doxorubicin by layers of dyes incorporated to the nanotube in a second impregnation cycle. In this case we obtained very interesting and promising results, particularly for neutral red and p-phenylaniline used as blockers. However, in the case of p-phenyloaniline the stability of the blocked form at neutral pH is quite low. Blocking of carbon nanotubes by functionalized gold nanoparticles leads to very promising results as well. We found that hydrolysis of hydrazone bonds at acidic pH does not lead to spontaneous unblocking of carbon nanotube. The systems stay in the capped formas a result of strong dispersion interactions and steric anchoring of linkers. However, incorporation of cisplatin to the inner cavity of carbon nanotube leads to significant reduction of energetic barriers for detachment of gold nanoparticles. This is because cisplatin forms a kind of condensed phase in the interior of the nanotube and that effect prevents anchoring of the linkers in the nanotube interior after hydrolysis of hydrazone bonds.

The obtained results are of significant importance in the area of development of drug delivery systems. The considered systems are able to release the drug molecules spontaneously when they enter acidic environment of tumor tissue or lysosome. The molecular architecture of these systems is quite simple. So, it is possible to directly apply the obtained results in fabrication of pH sensitive drug carriers.

2-Oxoglutarate Dependent Oxygenases in the Biosynthesis of Pharmacologically Active Alkaloids - Structure, Catalytic Mechanisms and Rational Redesign

"Sonata Bis" research project NCN 2014/14/E/NZ1/00053 [2015-2020]
(Assoc. Professor Tomasz Borowski)

Within this project we pursue a tightly integrated structural, biochemical and computational studies on two groups of 2-oxoglutarate dependent dioxygenases involved in biosynthesis of tropane and morphinian alkaloids: anisodamine / scopolamine (H6H enzyme) and codeine / morphine (CODM, T6ODM and PODA enzymes). Structures of these proteins are not known, as are the detailed mechanisms of their catalytic reactions.

The project started in the middle of last year. On the experimental ground, we tested various protocols for protein production, a method for qualitative and quantitative analysis of H6H reaction products was worked out, and for the purified H6H enzyme the catalytic activity was confirmed. Within computational studies and with the use of cluster models, the mechanism of dioxygen activation leading to reactive ferryl species was revisited, and a mechanism of codeine demethylation was studied.

"Sonata" Research Projects of the National Science Centre

New Pd-Pt/ Hybrid Nanocomposite Catatalysts for Oxygen Reduction in Polymer Electrolyte Membrane Fuel Cell

"Sonata" research project NCN 2011/01/D/ST5/04917 [2011-2016]
(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 cathodic oxygen reduction reaction, ORR in fuel cell. It is planned to use a conducting polymer – polypirol, PPY as a support material for Pd, Pt and Pd-Pt nanoparticles. Due to the application of bimetalic 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. Additionally, hybrid nanocomposite composed of PPY and Keggin or Dawson type heteropolyacids will be applied as the support material. Nanocomposite of heteropolyacid and PPY should ensure electron and proton transfer.

Studies undertaken in 2015 concerned palladium-platinum catalysts synthesis and characterization of their physicochemical properties as well as investigation of their electrocatalytic activity towards ORR. Pd-Pt nanoparticles were synthesized using water-in-oil microemulsion method, which favors the formation of small metal crystallites with a narrow size distribution. Using this technique, metal particles of ca. 6 nm in size were prepared and subsequently immobilized in PPY matrix. For comparison, carbon black-supported (Vulcan XC-72) catalysts were also synthesized. The conducing polymer was synthesized by chemical polymerization in aqueous acidic media. Catalysts with constant palladium loading of 10 wt.% (the optimal metal loading which was estimated in previous studies) and various Pd: Pt molar ratios, i.e. 95:5, 90:10, 80:20, 90:10, 70:30, 50:50 and 30:70, were investigated. They were characterized by different methods, such as BET, XRD, XRF, XPS, FTIR, TEM and HRTEM. Electrocatalytic activity of the prepared materials towards ORR was investigated in 0.5 M H_2SO_4 using rotating ring disc electrode voltammetry and cyclic voltammetry techniques. Analysis of the obtained results lead to the estimation of the optimum Pd: Pt molar ratio, namely 50:50 in tested catalysts. They exhibited higher activity and selectivity than Pt nanoparticles deposited on carbon black Vulcan XC-72 (system commonly used in fuel cells).

The next step of studies undertaken in 2015 was optimization of the synthesis conditions of nanocomposites composed of PPY and heteropolyacids, HPAs of Keggin type, $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ or Dawson type, $H_6P_2W_{18}O_{62}$. The conducing polymer was synthesized by chemical polymerization of pyrrole carried out in the presence of HPAs (HPA: pyrrole molar ratio of 0.33) in CH_3NO_2 and CH_3CN as the reaction media. Additionally, some preliminary studies were undertaken to evaluate the effect of the HPA presence on the electroactivity of 10 wt.% $Pd_{50}Pt_{50}$/PPY catalyst in ORR. In the preparation of the catalysts tested in ORR a commonly used method is based on the preparation of a suspension composed of the catalyst powder and Nafion ionomer (used as binding agent). Here, HPAs were introduced to the catalyst suspension dropped on the electrode surface. Modification of 10 wt.% $Pd_{50}Pt_{50}$/PPY catalyst with HPAs, in particular with $H_3PMo_{12}O_{40}$ resulted in the enhancement of its activity in ORR. Therefore, the obtained hybrid nanocomposites HPA-PPY will be used to synthesize Pd-Pt/HPA–PPY catalysts in order to investigate their electrocatalytic activity towards ORR.

Conformational Changes of the Pyranose Rings: Computer Simulations

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

Conformation of the pyranose rings: transition path sampling study

The study is 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.

We performed the first systematic calculations using the three carbohydrate-dedicated force fields to investigate the kinetic features of the hexopyranose ring flexing. The rate constants calculated by using both the GROMACS $56A6_{CARBO}$ and GLYCAM force fields suggest that the chair-chair conformational rearrangements in the hexopyranose rings occur at timescale ranging from about 1 microsecond up to several tens of microseconds (α-glucose) or from 0.2 up to 80 miliseconds (β-glucose). The chair-boat transition occur on a slightly ($56A6_{CARBO}$) or significantly (GLYCAM) smaller timescale. Except of the extremely large values suggested by GLYCAM for the $^4C_1 \rightarrow {}^1C_4$ transitions in β-glucose, the obtained values are in agreement with the experimental estimation. The exceptionally high free energy barriers separating the particular ring conformers and inherent to the GROMOS $53A6_{GLYC}$ force field hinder the possibility of any unbiased rearrangement in the ring at the timescale of μs. Following that, the timescale of the $^4C_1 \rightarrow {}^1C_4$ transition can be estimated as larger than hundred of seconds, i.e. much above the experimental values. Overall, the timescales of the 4C1 → 1C4 rearrangement are dependent on the force field and increase in the following order:

$$\text{56A6CARBO} < \text{GLYCAM} \ll \text{53A6GLYC}.$$

The timescales for the 4C1 → B/S rearrangement can be ordered as follows:

$$\text{GLYCAM} < \text{56A6CARBO} \ll \text{53A6GLYC}.$$

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 is lack of selectivity, therefore, it should eliminate side effects of applied therapeutics due to elimination of their toxic effects in the whole body.

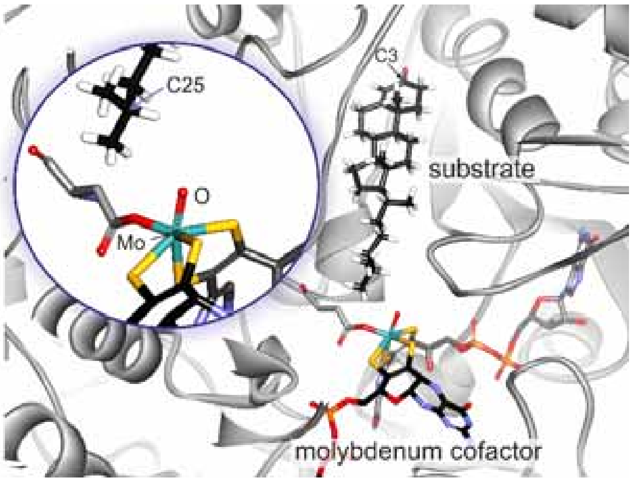
The main aim of this project is the development of scientific background and elaboration of the technique of therapeutic agents incorporation inside biocompatible nanocapsules with functionalized shells for targeted drug delivery. That aim will be achieved in a few fundamental steps. First of them will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

In 2015, we focused on the preparation and modification of nanocapsules containing macromolecular active substance. Nanocapsules core were obtained by complexation of DNA Plasmid (model substance) with appositively charged polyelectrolytes. Such macromolecular complexes (polyplexes) were encapsulated in the polyelectrolyte multilayer shells. The polyelectrolyte multilayer shell was constructed by sequential adsorption of polyelectrolytes (layer-by-layer) method and saturation technique. Polyelectrolyte multilayer shells were constructed with biocompatible and biodegradable polyelectrolytes: poly-L-lysine as polycation and poly-L-glutamic acid as polyanion. The average size of synthesized nanocapsules was 100 nm. The obtained nanaocpasules were further modified by pegylation. Pegylated polyelectrolytes (PGA-g-PEG) with various grafting ratio and PEG chain length were synthesized. Such pegylated polyelectrolytes were used to form external pegylated layer of the nanocapsules

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: Assoc. Professor Maciej Szaleniec)

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(VI)=O ligand from molybdenum cofactor.



The studies of the mechanism are conducted both with use of theoretical and experimental methods. The theoretical studies of the enzyme continued research on homology model of α subunit. Using obtained previously structures of enzyme substrate complexes a series of MD simulations has been conducted. The simulation aimed at elucidation of dynamic behavior of selected substrates in S25DH active site. The statistical and conformational analyses of the results of MD simulations together with Gibbs free energy of ligand binding (calculated with Poisson-Boltzman and Generalized Born methods) allowed detailed description of substrates binding modes and quantitative estimation of their interaction with active site residues.

The parameters obtained in MD simulations were correlated with kinetic constants obtained from kinetic studies conducted for 3 selected substrates. This allowed determination of factors responsible for differences in observed reaction rate, such as binding mode and frequency of catalytically active conformation in the active site. Postulated factors may be responsible for the observed differences in enzyme activity. Based on the experimental results of S25DH reaction rates for four 3-ketosterols, three 3-OH-sterols and one succinate ester, substrates were divided into two groups: 3-ketosterols with higher and 3-OH-sterol or ester with much lower rates of hydroxylation.

In the next step the initial QM:MM model was prepared and main steps of the reaction pathway were investigated yielding ES, EP complexes as well as the structure of intermediate product. The obtained results showed, that the radical form of intermediate product is more stable than the carbocation one. This result is different from that observed for ethylbenzene dehydrogenase. Based on optimized geometry of ES complex a QM-only cluster models were constructed. Two models were formed: i) a minimal model contacting part of the molybdenum cofactor, Asp residue that coordinates Mo and Lys residue that forms H-bond with Asp as well as isooctyl cholesterol side chain representing the substrate (83 atoms in total); ii) extended model that contained also residues surrounding the substrate (198 atoms). These two models were used to investigate the reaction mechanism in details. The initial results predict higher transition state barriers than for EBDH, which is in agreement with experimentally observed lower reaction rate of S25DH compared to EBDH. Moreover, a radical character of C-H cleavage step and intermediate product was proposed along with quasi-carbocation nature of OH rebound process. Finally a possibility of the oxidative dehydrogenation process was also demonstrated as an alternative process to substrate hydroxylation.

Mechanism and Kinetics of Bubble Coalescence at Undisturbed and Vibrating, with Controlled Frequency and Amplitude, Liquid/gas Interfaces

"Sonata" research project NCN 2013/09/D/ST4/03785 [2013-2017]
(project leader: Jan Zawała PhD)

The aim of the investigations carried out within the project framework is to investigate a mechanism determining probability of bouncing of a single gas bubble during its collision with surfaces of pure liquids. The investigations are focused on fundamental phenomena underlying stability of thin liquid films formed under dynamic conditions. In order to verify the work hypotheses the experiments were carried out using experimental set-up, 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 0.025-0.150 mm sealed at the bottom, (ii) high-speed camera acquiring the picture with frequency 1000-5000 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 and accelerometer.

In the reported period the experiments were carried out in silicone oils of precisely determined physicochemical properties (viscosity, surface tension), in order to determine threshold (excess) acceleration needed to significantly prolonged the colliding bubble lifetime at liquid/gas interface in comparison with stagnant system (no oscillations of the liquid/gas interface). The air bubbles were formed at the glass capillaries of different inner diameters. The bubbles formation was controlled by the precise gas dosage system allowing adjustment of chosen time interval between subsequent bubble detachments. The diameters of the capillaries used vary within the range 0.025-0.15 mm, so the equivalent radii of the detaching bubbles were 0.60-1.2 mm. It was found that for each bubble size there is specific value of amplitude and frequency of the liquid/gas interface oscillations (i.e. oscillations acceleration), below which the bubble lifetime is comparable with the stagnant system, but above which significant prolongation (by several orders of magnitude) of the bubble lifetime at the liquid surface is observed. Moreover it was found that larger the bubble, smaller the threshold acceleration needed for lifetime prolongation effect. This observation is strong additional proof for correctness of the postulated mechanism of the bubble bouncing and coalescence during collisions with liquid/gas interfaces where the liquid film is a parameter of crucial importance. It shows that the radius of the liquid film, determined by the tendency of the bubble to be deformed at the moment of collision (impact), is a key factor determining the collision outcome (rupture or bounce). Due to lower internal pressure (Laplace pressure), much smaller acceleration is needed to deform bubble of larger size and to create a liquid film large enough not to drain to the critical thickness of rupture during the collision time.

New Protein Bilayer System Based on Antigen-Antibody Interactions – *In situ* Physicochemical Characteristics

"Sonata" research project NCN 2014/13/D/ST4/01846 [2015-2017]
(Project leader: Monika Wasilewska PhD)

Immunoassays are important application areas of proteins immobilized on solid substrates. Common adsorbed proteins are immunoglobulins G (IgG) or their active fragments, which specifically bind to its antigen with high affinity. Although immobilized antibodies play a critical role in immunoassays, the mechanisms of the immobilization processes are poorly understood. Little *in situ* research has been done on how IgG adsorb on immobilized proteins monolayers. There is lack of systematic investigations of the relationship between the immobilization conditions and resulting protein coverage, local distribution and orientation of these adsorbed protein and their bioactivity. Therefore, the main goal of this project is to elucidate mechanisms of IgGs adsorption and develop the protocol for a reliable, and sensitive method for detection of trace amounts of antibodies based on physical attachment of antibody to fibrinogen monolayers.

The main research task realized during reporting period was physicochemical characteristic of anti-fibrinogen immunoglobulin G in electrolyte solutions. The influence of the ionic strength and pH on the electrokinetic and hydrodynamic properties (electrophoretic mobility, diffusion coefficient, isoelectric point, and uncompensated charge of protein) was determined.

Additionally preparation and physicochemical characterization of fluorescent dye labeled IgG was realized. The influence of the dye on electrophoretic mobility, diffusion coefficient, isoelectric point, and uncompensated charge of labeled protein was investigated.

Adsorption of IgG molecules on fibrinogen monolayers was theoretically studied in terms of MC-RSA simulations. Bilayers were created in two steps. Firstly the fibrinogen monolayer was built using RSA. Algorithm was stopped after number of iterations corresponding to dimensionless time of 10^5. Then the IgG particles were put randomly on fibrinogen, according to RSA rules. IgG particles can have two possible orientations: up, and upside-down, with equal probabilities.

"Opus" Research Projects
of the National Science Centre

Influence of Glycerol as Non-Toxic and Biodegradable Solvent on the Mechanism of Phenol Oxidation

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

The purpose of the study is the use of glycerol or glycerol-type solvents as solvents for phenol oxidation reaction with hydrogen peroxide in the presence of transition metal complexes 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. Metallocomplexes are known as efficient catalysts in different oxidation processes and therefore they have been chosen for phenol oxidation reaction in glycerol.

The purpose of the present study is to explain how the application of glycerol as alternative solvent influences the catalytic activity of ionic cobalt, manganese and iron porphyrins in the liquid-phase oxidation of phenol. Cationic MnTMPyP, CoTMPyP, FeTMPyP and anionic MnTPPS, CoTPPS, FeTPPS metalloporphyrins were synthesized, characterized and applied in the liquid-phase oxidation of phenol with H_2O_2 performed in a thermostated glass reactor at 80^{o}C for 1 hour. Synthesized samples were characterized by means of FTIR, UV-Vis spectroscopies and cyclic voltammetry.

All synthesized catalysts were active in the investigated reaction and their catalytic activity depends on the nature of active centers. For both catalytic series the highest catalytic activity is observed for iron complexes. It is not a surprise that iron catalysts are the most active in this reaction since in phenol oxidation by Fenton reagent iron plays a key role. Catalytic investigations of ionic metalloporphyrins in phenol oxidation in glycerol as solvent demonstrated that glycerol can be an alternative to volatile organic solvents. Our study could help to replace toxic organic solvents for non-hazardous “green” solvent like glycerol.

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 to describe the electronic structure and catalytic 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 impact of a Cu atom in the HPA structure was studied by considering a series of heteropolyanions with different geometry and chemical composition. The studied groups contain the following systems: i) derived from normal Keggin anion with general formula $PMe_{12}O_{40}^{n-}$, ii) derived from lacunary Keggin or Dawson anions, with general formula $PMe_{11}O_{39}^{n-}$ i $P_2Me_{18}O_{62}^{n-}$, where one/few addenda atom(s) was/were replaced by cooper ion(s), iii) “sandwich-like" systems with Weakly & Finke structure, where copper ions form metallic cluster between two lacunary Keggin anion, iv) heteropolyacids salts with various content of Cu ions.

Properties of various HPA were studied within the DFT approach (with the gradient PBE and hybrid B3-LYP potentials) using cluster model and applying the Turbomole code. Optimized geometries, densities of states, IR spectra, various population analyses, as well as the character and energy of boundary orbitals were determined. The Natural Orbital Chemical Valence method was used to investigate the mechanism of Cu ions interaction with solvent molecule and small inorganic substrates. The solvation effect (water and acetonitryle) can be treated by the COSMO approximation (COnductorlike Screening MOdel), where the solute molecule forms a cavity within the dielectric continuum of permittivity .

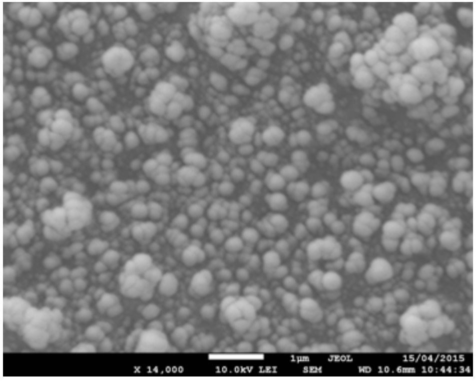
The results of calculations, of modified Cu-HPA, show that changes in chemical composition lead to the changes in physicochemical properties of the studied system. Introducing of Cu^{2+} ions into various heteropolyacids anion, results in new peaks, composed mainly from 3d Cu orbitals, close to the Fermi level. Both, the charge and the spin density of the Cu ion, introduced in HPA structure, depends on the geometry of heteropolyanion and type of other addenda atoms (Mo/W). The theoretical modelling of solvation effect showed that the solvent molecules (for example. CH_3CN, H_2O) do not adsorb on the copper ion. Cu ion exists, in heteropolyanion structure, as a five-coordinated metallic center. Cu cations introduced into HPA anions in the position of addenda atom become potential adsorption sites of small molecules (OOH, H_2O_2, NO), making possible their activation by the metal center. The results of calculations modelling the interaction of copper ions with small reagents, indicated a tendency for a spontaneous adsorption, which take place as a results of donation and back donation process between ligand (reacting molecule) and HPA skeleton. In all studied systems the electron flow is larger in back donation process than in donation process.

Theoretical study were carried out equally with experimental studies involving the synthesis and characterization of the physicochemical properties of heteropolyacids.The catalysts were tested in the dehydration of ethanol reaction, in the gas phase, in the range of 90-310° C. Additionally the modified catalysts Cu-HPA were used as a catalysts in the oxidation of ethanol, in the range of 90-310° C. Experimental data showed low activity of studied systems, in the investigated reactions. Among the tested systems the greatest activity showed copper salts.

Mechanism of Ionic Surfactant - Polyelectrolyte Interactions in the Process of Formation of New Generation of Nanocarriers

"Opus" research project NCN 2011/03/B/ST4/01217 [2012-2015]
(project leader: Professor Piotr Warszyński)

The purpose of the project is to develop the mechanism of surfactant/polyelectrolyte complex formation in order to apply them in the process of nanocapsules creation. Developing a better understanding of these systems is a matter of importance because of their potentially wide use in a variety of industrial applications including pharmaceuticals, cosmetics, coatings, enhanced oil recovery, and detergency. We considered both experimentally and theoretically adsorption of selected cleavable cationic esterquad surfactants. We studied derivatives having –O-CO- bond between quaternary amine and hydrophobic tail: (DMM-11) and (DMP2M-11)), and derivatives with –CO-O- bond: (DMGM-12)), and (DMALM-12)). These compounds are stable in the acidic conditions but in neutral and basic pH undergo hydrolysis resulting in either dodecanoic acid or dodecanol as surface active products. The extended “surface quasi two-dimensional electrolyte” (STDE) model of ionic surfactant adsorption was applied for the description of hydrolysis influenced surface activity of surfactants. As the result, good theoretical description of the data was obtained. We found that surface activity of the mixture resulting from the esterquat hydrolysis increases with time and it is higher for derivative with –O-CO- bond with respect to the inverted arrangement derivative with –CO-O- bond. That is a consequence of strong synergistic effect between the cationic esterquat surfactant and the anionic product of its hydrolysis - dodecanoate ion. We also found that addition of side CH_3 into esterquat head-group slows down the hydrolysis that leads to the lower surface activity of the resulting mixture. The kinetic measurements of equilibrium surface tension of pure surfactants solution, and their mixtures with polyelectrolytes, provide data to obtain adsorption isotherms, which allow determination of the range of surfactant and polyelectrolyte concentration in which surfactant – polyelectrolyte complex is formatted. We found that mixtures of surfactants with polyanions exhibit the synergetic effect on the surface tension. The biggest effect was observed in the case of the least hydrolyzed DMALM-12, the smallest for the most hydrolyzed DMM-11, when the surfactant charge is neutralized by dodecanoate anion. Surfactant/Alginate mixtures exhibit much higher surface activity than those with PSS. DMGM-12/ PAA (PGA or CAR) complexes exhibit similar surface activity. As the cores of microcapsules swollen micelles of selected surfactants were used. Capsules were formed by sequential adsorption of oppositely charged polyelectrolytes (LBL). Physicochemical properties of microcapsules were determined by dynamic light scattering (DLS), zeta potential, and AFM measurements. The example of SEM image is presented below.



The crucial information obtained in this project will be determination of the influence of surfactant structure, the kind of introduced groups (ester groups) on the adsorption mechanism of these compounds at the interface and the ability to create surfactant ion - polyelectrolyte complexes. Developing of the theoretical model of surfactant-polyelectrolyte interactions will enable describing prediction of the surface properties of their complexes, which can lead to their better selection depending on the practical application

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.

In the previous years, a method for reconstitution of the enzyme with a selected transition metal was developed, an analytical HPLC method for detection and quantization of organic products of the catalytic reactions of Fe- and Ni-ARD was worked out. Stoichiometry of the enzymes was examined for human and bacterial (*bacillus anthracis*) forms confirming dependence of the reaction specificity on the identity of the bound metal ion. Mossbauer spectroscopy measurements were done for Fe-ARD in the native form and in a complex with the substrate. Crystals of ARD enzymes were obtained and their structures were solved. Moreover, reaction mechanisms of two synthetic inorganic complexes catalyzing model reactions for ARD were scrutinized with DFT methods.

In the last year, the experimental studies included the following: a) synchrotron measurements of nuclear inelastic scattering (NIS/NRVS), which were conducted in ESRF (Grenoble) for the native form of Fe-ARD and its complex with the model substrate; b) a method for protein production on a minimal broth supplemented with ^{57}Fe was worked out; c) the synthesis route to the stable and convenient to store form of ARD substrate was finalized and the substrate was characterized with spectroscopy (IR, Raman, UV-vis, NMR) and crystallography methods. Computational studies included: a) calculations of oscillatory, electronic and NMR spectra for the enzyme substrate; b) molecular dynamics simulations for Fe-ARD and its substrate complex; c) calculation of Mossbauer spectra parameters for active site models of Fe-ARD; d) computations of reaction paths for ARD enzymes. Synthesis of so far obtained experimental and computational results allowed us to formulate a hypothesis explaining the observed relationship between the identity of the metal ion bound in the enzyme active site and the outcome of the enzymatic reaction. According to this hypothesis, the key feature of the metal ion is its red-ox potential for the M^{2+}/M^{3+} pair. More specifically, Fe^{2+} plays a role of one electron donor during the decisive reaction step – cleavage of the O-O bond, and hence enables a mechanism involving hemolytic cleavage of the O-O bond, which yields to products observed for Fe-ARD. Other ions, e.g. Ni^{2+}, Co^{2+}, have much higher red-ox potential, and as a result the O-O cleavage is a heterolytic process coupled to evolution of the substrate into the products characteristic for Ni-ARD. Additionally, we performed computational study on the nitroxygenation reaction catalyzed by quercetin dioxygenase – an enzyme catalyzing a reaction very similar to that characteristic for Ni-ARD.

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 clarify the relationship between the catalyst physicochemical properties and theirs operation based on dimethyl ether (DME) synthesis reaction from the H_2/CO_2 mixture.

Works on this project were continued in 2015. Catalysts having the composition $10molCu90molZrO_2$, obtained by co-precipitation (using a variety of precipitating agents: Na_2CO_3, NaOH), as well as citric method were modified by promoters such as Ga, Mn, Cr, Ag, in an amount of 3% by weight. The obtained samples were characterized by: H_2TPR, BET, specific adsorption of N_2O (Cu specific surface area) and XRD. For the studied catalysts changes in the reducibility properties, textural and surface copper surface area were observed. These changes depend both on the preparation method and type of the introduced promoter. The addition of the promoters leads to the changes in the reduction profiles and in lowering of the maximum reduction temperature.

The changes in the specific surface area, depending on the preparation method, are described by the following inequality:

$$\text{NaOH method} > \text{citrate method} > Na_2CO_3 \text{ method}$$

The catalysts obtained using NaOH method exhibit the highest pore volume as well as they have the highest Cu specific surface area.

As comes out from the catalytic results selectivity to DME depends on preparation method of metallic function as well as on the montmorillonite modification. So far the best results were obtained for the hybrid catalyst synthesized with NaOH method, doped by Ga or Cr and montmorillonite modified by HPW. Preparation method of the catalyst has strong impact on CO_2 conversion. Carbon dioxide conversion is the highest for metallic function obtained by NaOH method. Catalytic tests carried out on the hybrid catalysts consisting of $CuZrO_2$ metallic function doped by promoters Ag, Cr, Mn, or Ga, and the montmorillonite acidic function pure or modified by molybdenum or tungsten heteropolyacid, showed that the introduction of the promoters in metallic function and modification of the acidic function improves performance of the hybrid catalysts. The suitable combinations of these two components can lead to the preparation of the catalyst for industrial scale.

In the frame of this project vacuum setup was build for to study infrared adsorbed species, for studies planned in the project. This setup is currently used to determine changes, which appear after modification of montmorillonite K-10 by heteropolyacid. As part of these studies IR spectra of adsorbed methanol on the surface of the hybrid catalyst of the acid function were carried out. These studies showed that heteropolyacid changes the acidic properties of montmorillonite K-10 and have an impact on subsequent dehydration reaction of methanol into DME and that HPW/K10 is a little better in this role than HPMo/K10.

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]
(previous project leader: Professor Mirosław Derewiński,
acting project leader: Professor Bogdan Sulikowski)

The main objective of this project is the synthesis of novel layered materials with unique hierarchical structure of pores. The main cognitive aim of the project is elaboration of a new, effective route for preparation of aluminosilicate materials with multimodal pore arrangement, containing micro- and mesopores of various dimensions, starting from the suspensions of protozeolitic species. We expect that such new layered and hierarchic structures will allow performing catalytic transformations of (mainly organic) molecules much more effectively, first of all where used in the liquid phase processes.

After successful preparations of monodispersed suspensions of nanoparticles containing aluminum, we have elaborating synthesis of similar structures containing exclusively iron and silicon. Our aim was to prepare materials with lower strength of the acid sites. A route giving a stable, monodispersed suspensions of protozeolitic Fe-MFI species was developed, with the particle size about 14 nm. Due to lower iron stability, lower temperatures of calcination were used, and calcination in the ozone atmosphere. Moreover, removing of the organic templates by extraction with alcohol was carried out.

Suspensions of protozeolitic nanoparticles with different amounts of aluminium and iron were used for the preparation of mesoporous lamellar materials. Physicochemical characterization with several methods, enabling estimation of morphology, structure, adsorption and acid properties, was carried out. The H4 hysteresis loop was characteristic for these materials containing slit pores between the layers. Simultaneously, the presence of microporous was documented, in analogy to standard zeolites. Solid-state ^{29}Si and ^{27}Al MAS NMR spectra were acquired. It was shown that partial dealumination occurred upon calcination of the mesoporous materials. These extraframework aluminium species were characterized by 1D and 2D (3MQ) ^{27}Al MAS NMR, quadrupolar coupling constants were obtained. Analysis of NMR data gave further evidence of the presence of zeolitic nanoclusters exhibiting characteristics similar to the ZSM-5 type zeolite.

The catalytic properties of mesoporous samples were studied extensively under different conditions in the liquid phase. Catalytic transformations of α-pinene were tested in a batch reactor at 50-120 ^{o}C under atmospheric pressure. The presence of acid sites was necessary for the reaction studied, and conversion was related with the content of aluminium in the mesoporous samples. Intrinsic activity and selectivity of aluminium acid sites showed superior activity of mesoporous materials in comparison with the properties of standard, micron-sized ZSM-5 zeolite and an amorphous aluminosilicate.

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

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

According to the schedule of the research project (Task Plan) the following tasks were carried out:
1. Purchase of equipment (task completed). The following pieces of equipment were purchased:
a) Vacuum oven with accessories (vacuum pump, necessary tubing and connections)
b) Burette for accurate hydrogen dispensing while conducting catalytic tests
c) Sample collecting vessel

2. Preparation of modified carriers (task completed). The gel-type FCN resin were prepared according to previously published two stage procedure. In the first stage of preparation the GMA resin was obtained by suspension polymerization of the mixture of glycidylmethacrylate (20 mol%), styrene (77mol%) and diethylene glycol dimethacrylate (3 mol%). In the next step the beads of GMA resin were functionalized by S,S-diphenyletylenediamine, R,R-diphenyletylenediamine and (1S,2S)-N,N′-dimethyl-1,2-diphenyl-1,2-ethylenediamine.

3. Characterization of modified carriers (task completed). The modified carriers were characterized by scanning electron microscopy (SEM, EDS, STEM), Fourier transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD).

4. Preparation of ruthenium catalysts (task completed). The synthesis of Ru (0) catalysts deposited on modified polymer resins was performed.

5. Characterization of ruthenium catalysts (task completed)
Ruthenium catalysts were characterized by scanning electron microscopy (SEM, EDS, STEM), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS).

6. Catalytic studies (work in progress)
Catalytic studies included optimization of hydrogenation reaction conditions for 8 prochiral ketones (acetophenone, acetol, methyl ethyl ketone, cyclohexyl methyl ketone, ethyl phenyl ketone, methylacetophenone (CH_3 group in ortho, meta and para position).

Dynamics of Oscillations in the Palladium/Hydrogen System

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

Electrical measurements have been carried out *in situ* during oscillatory sorption of hydrogen and deuterium in metallic Pd powder. A special arrangement to the microcalorimetric cell has been applied, making it possible to use the impedance spectroscopy and chronoamperometry to measure changes in resistivity or conductivity of the powdered bed of Pd concurrently with the thermokinetic oscillations accompanying the sorption of hydrogen. Several sorption/desorption cycles have been recorded.

Figure 1 shows aperiodicity in changes of resistivity of palladium compared to periodic oscillations of the rate of heat evolution accompanying the sorption of D_2 in Pd. The figure represents data from three experiments. In vivid contrast to the exact reproducibility in thermokinetic frequency (the blue and the dotted lines), the changes in resistivity (solid red, green and black lines) are only relatively reproducible, in a sense, that certain features in their curves appears to correlate repeatedly with the thermokinetic frequency. These may consist of either rising or plunging, but still coinciding with the ascending parts of the thermokinetic time series.

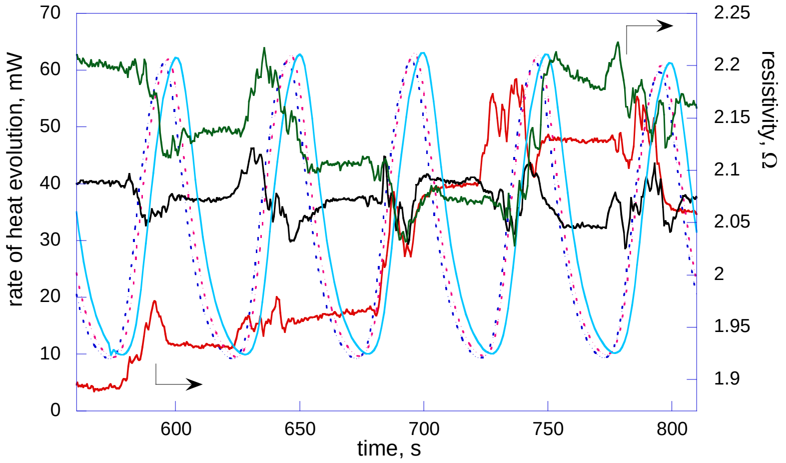


Figure 1. Mathematical (deterministic) chaos in resistivity of Pd powder (solid red, green and black lines) accompanying thermokinetic oscillations (solid blue and dotted lines) in sorption of D_2 in Pd in three separate sorptions at 75 °C. It can be seen the Pd resistivity either climbs or drops with the progress of sorption, but always in sync with the periodic oscillations of the rate of heat evolution. Deterministic character of the aperiodic resistivity changes has been confirmed using a method previously proposed by the author [E. Lalik, J. Math. Chem. 52 (2014) 2183.].

Such limited reproducibility seems to be a characteristic of chaos, and it was possible to confirm the deterministic character of the aperiodic resistivity curves using a mathematical method previously proposed. A similarly chaotic behavior has been observed in the chronoamperometry. Figure 2A shows the Pd conductivity peaks (red) coinciding with the maxima in thermokinetic oscillations (green) during sorption of deuterium. Panel B represents the Fourier transformation of both curves shown in the Panel A. It is clear that the frequency of peaks in conductivity is the same as the frequency of oscillations in the rate of heat evolution.

Since the current flow in Pd powder is determined by the resistivity of the inter-grain contacts, we suggested that a periodical appearance of intermediate hydrogen species might take place on the Pd surface and be responsible for the oscillatory heat evolution on the sorption.

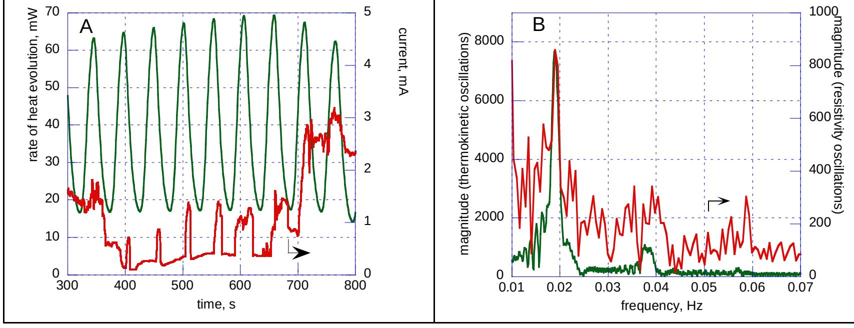


Figure 2 (A) Chronoamperometric measurement of current flow in Pd powder (red line) compared to thermokinetic oscillations (green line) in the sorption of D_2 in Pd, and (B) the corresponding power spectra. Note the excellent coinciding of peaks in both the Fourier transform curves at ca. 0.02 Hz.

Adsorption Mechanisms of Anisotropic Proteins under Controlled Transport Conditions

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

Immunoglobulin (IgG) adsorption on solid interfaces is the most relevant step in preparation of various immunoassays, immuno-biosensor, chromatographic immuno-affinity columns and biomaterials development. However, despite of the considerable experimental effort, the mechanisms of IgGs adsorption are not fully understood, mainly because of the lack of experimental methods providing the direct information about the adsorption kinetics under *in situ* conditions. Therefore, the goal of this work was to determine the adsorption of IgG on negatively charged polystyrene microparticles by using the dynamic light scattering (DLS), laser Doppler velocimetry (LDV) and AFM techniques. The dependence of the electrophoretic mobility of microparticles on the IgG concentration in the suspension was precisely measured for various ionic strengths and pH 3.5. The increase in the electrophoretic mobility with IgG concentration observed for all ionic strengths was quantitatively interpreted in terms of the 3D electrokinetic model. Typical results obtained for NaCl concentration of 0.01 M are presented in Fig. 1. On the other hand, the maximum coverage of IgG on microparticles was determined by applying the concentration depletion method based on AFM imaging of IgG monolayers adsorbed on mica. It was shown that IgG adsorption was irreversible increasing with ionic strength from 1.4 mg m^{-2} for 0.001 M NaCl to 2.0 mg m^{-2} for 0.15 M NaCl. The increase in the maximum coverage was interpreted in terms of reduced electrostatic repulsion among adsorbed molecules. This confirms that IgG adsorption at pH 3.5 is governed by electrostatic interactions and proceeds analogously to colloid particle deposition. Additionally, the stability and acid-base properties of the IgG monolayers on latex were determined in pH cycling experiments. The isoelectric point of latex supported IgG monolayers was 4.8. The results obtained in this work indicate that basic physicochemical characteristics of IgG can be acquired via electrophoretic mobility measurements using microgram quantities of the protein.

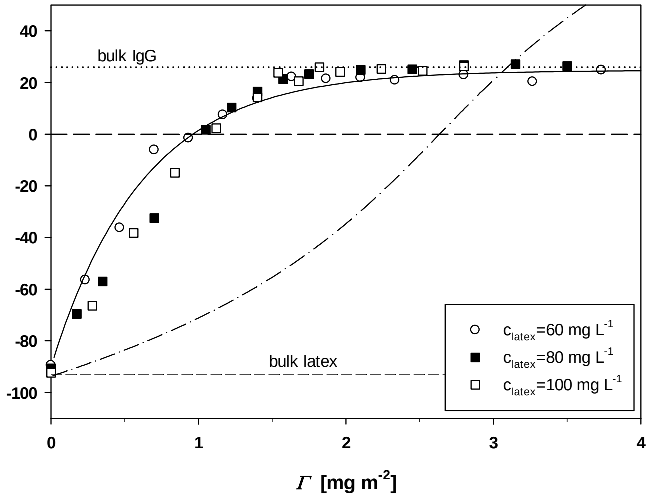
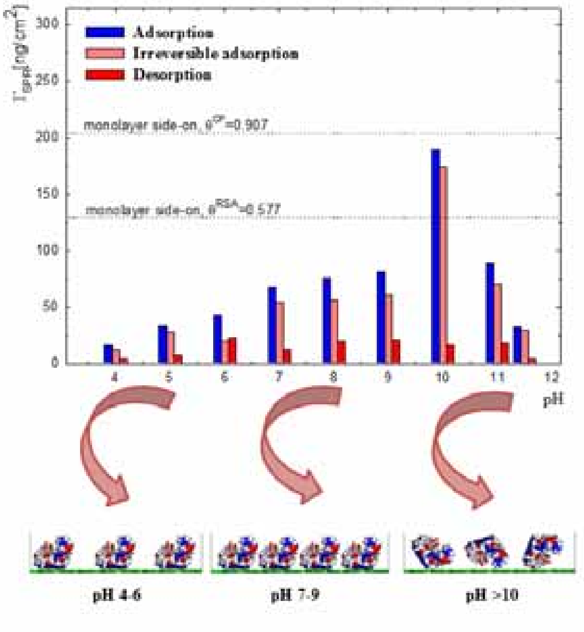


Figure 1. Zeta potential of microparticles ζ vs. the nominal coverage of IgG Γ [mg m^{-2}]. The points denote experimental results obtained for pH 3.5 and NaCl concentrations of 0.01 M. The solid line shows the results derived from the 3D electrokinetic model developed in this work. The dashed dotted line show the results calculated from the Gouy-Chapman (GC) 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)*

Hen Egg White Lysozyme (LSZ) is a widely used exemplar to study protein adsorption on surfaces and interfaces. We use fully atomistic Molecular Dynamics (MD) simulations, Multi-Parametric Surface Plasmon Resonance (MP-SPR), contact angle and zeta potential measurements to study LSZ adsorption at a silica surface. The simulations provide a detailed description of the adsorption mechanism and indicate that at pH7 the main adsorption driving force is electrostatics, supplemented by weaker hydrophobic forces. Moreover, they reveal the preferred orientation of the adsorbed protein and show that its structure is only slightly altered at the interface with the surface. This provides the basis for interpreting the experimental results, which indicate the surface adsorbs a close-packed monolayer at about pH10 where the surface has a large negative zeta potential and the LSZ is positively charged. At higher pH, the adsorption amount of the protein layer is greatly reduced due to the loss of charge on the protein. At lower pH, the smaller zeta potential of the surface leads to lower LSZ adsorption. These interpretations are complemented by the contact angle measurements that show how the hydrophobicity of the surface is greatest when the surface coverage is highest. The simulations provide details of the hydrophobic residues exposed to solution by the adsorbed LSZ, completing the picture of the protein layer structure[1-2].



[1] M. Ćwięka, K. Kubiak - Ossowska, P. Mulheran, B. Jachimska "Experimental and Theoretical Methods as a Tool for the Interpretation of Lysozyme Immobilization at a Silica Surface."- The FEBS Journal, Special Issue: FEBS, 2015, Vol 282,
[2] K. Kubiak–Ossowska, M. Ćwięka, A.Kaczyńska, B. Jachimska, P. Mulheran, "Lysozyme adsorption at a silica surface using simulation and experiment: effects of pH on protein layer structure.", Physical Chemistry Chemical Physics (PCCP), 2015,17,37,24070-77

Synthesis and Physicochemical Characterization of the Electrocatalysts Containing Non-noble (Fe, Mn) and Noble (Pd) Metals Deposited on Porous N-Doped Carbon Materials with Different Morphologies and Examination them in Oxygen Reduction Reaction

"Opus" research project NCN 2013/11/B/ST5/01417 [2014-2016]
(project leader: Aleksandra Pacuła PhD)

The electrocatalysts containing N-doped carbon materials with graphite-like structure and various grain morphology and porosity were prepared. The synthesis of the electrocatalysts consisted of heating of magnesium-iron-aluminum (Mg-Fe-Al) layered double hydroxides or magnesium-manganese-aluminum (Mg-Mn-Al) layered double hydroxides at temperatures of 600 or 700 ^{o}C for 30 min. (in the case of Mg-Fe-Al) or 180 min. (in the case of Mg-Mn-Al) in the flow of argon saturated with acetonitrile (CH_3CN) vapor acting as carbon and nitrogen source. Layered double hydroxides used in the synthesis contained various concentrations of transition metal (Fe or Mn) ions. For comparison, a series of the electrocatalysts derived from magnesium-aluminum (Mg-Al) layered double hydroxides free of transition metal ions were also prepared. As-prepared samples were treated with hydrochloric acid ($HCl:H_2O$ 2:1) in order to remove inorganic compounds such as metal (Mg, Al, Fe or Mn) oxides. The resulting acid-treated samples were applied for further studies.

Physicochemical properties of the electrocatalysts were characterized by means of X-ray diffraction (XRD) to describe their structure and phase composition; elemental analysis to estimate the bulk concentration of such elements as C, N, H; X-ray photoelectron spectroscopy (XPS) to estimate the surface concentration of such elements as C, N, O, Mg, Fe, Mn, Al, Cl and the state of oxidation; electron microscopy (SEM and EDS) to reveal morphology of the carbon materials and to detect metal particles (Mn, Fe) and evaluate their dimension and location and to estimate the surface composition (C, O, Mg, Mn, Fe, Al, Cl); low-temperature nitrogen sorption to measure specific surface area and to characterize porosity.

Electrocatalytic activity of the electrocatalysts for oxygen reduction reaction (ORR) was evaluated via cyclic voltammetry. Electrochemical experiments were conducted at room temperature (25 ± 1 ^{o}C) in aqueous solutions of potassium hydroxide (0.1 M KOH) or sulfuric acid (0.5 M H_2SO_4). Cyclic voltammetry was performed using electrochemical cell with a three-electrode configuration: a working electrode (stationary glassy carbon electrode coated with studied sample), a counter electrode (Pt wire) and a reference electrode ($Ag/AgCl/KCl_{sat}$).

The electrocatalysts prepared with the use of Mg-Fe-Al LDHs at 600 ^{o}C contained carbon deposit with plate-like morphology, whereas those obtained at 700 ^{o}C contained carbon nanotubes grown on iron nanoparticles. The extent of N-doping of carbonaceous component of the electrocatalysts was higher (ca. 5-10 wt %) for the samples prepared at lower temp. (600 ^{o}C) than that (ca. 2-3 wt %) for the samples prepared at higher temp. (700 ^{o}C). The electrocatalysts were active in ORR in both alkaline and acidic solutions.

The electrocatalysts prepared with the use of Mg-Mn-Al LDHs contained carbon deposit highly doped with nitrogen (ca. 7-8 wt %) with plate-like morphology. The electrocatalysts were not very active in ORR in alkaline solution and almost inactive in acidic solution. Specific surface area of the samples prepared at 600 ^{o}C (1185 and 1329 m^2 g^{-1} for C-$Mg_{2.6}Mn_{0.4}$Al-600 and C-$Mg_{2.8}Mn_{0.2}$Al-600, respectively) was higher than that of the samples prepared at 700 ^{o}C (929 and 936 m^2 g^{-1} for C-$Mg_{2.6}Mn_{0.4}$Al-700 and C-$Mg_{2.8}Mn_{0.2}$Al-700, respectively). The electrocatalysts derived from Mg-Mn-Al LDHs had high specific surface areas and therefore they will be used as supports for palladium (Pd) nanoparticles and then will be examined as ORR electrocatalysts.

Innovative Total Oxidation Catalysts Derived from Organosmectites Intercalated with Reverse Micelles Containing Oxide/hydroxide Nanostructures

"Opus" research project NCN 2013/09/B/ST5/00983 [2014-2017]
(project leader: Professor Ewa Serwicka-Bahranowska)

The project aims at design of a new class of active and thermally stable transition metal oxide combustion catalysts, as an alternative to widely used platinum group metal catalytic systems. The innovative approach to catalyst design consists in a combination of two synthetic procedures: one, involved the preparation of organoclays, and the other, consisting in manufacturing oxide nanoparticles via reverse micellar route.

Research concentrated on the development of procedure for the synthesis of microemulsions containing nanoparticles of manganese-aluminium hydrotalcite, to be used as precursors of oxide active phase. Synthetic smectite Laponite RD was used either in the sodium form (Na-L), or as an organoclay obtained by exchange of Na^+ with $(C_{16}H_{33})N(CH_3)_3^+$ cations (CTA-L). Composite catalyst precursors hydrotalcite/Laponite obtained from Na-L were prepared in aqueous medium, those obtained from CTA-L in isopropanol. Both were subsequently calcined at high temperature (600°C). The catalysts were denoted MnAl(rm)/Na-L(x)-600 and MnAl(rm)/CTA-L(x)-600, for aqueous and isopropanol route, respectively, where x=Mn/Si atomic ratio. Reference catalysts, with hydrotalcite component prepared in a conventional way, were also obtained. The materials were characterized with XRF, XRD, XPS, SEM, FTIR, H_2 TPR, and N_2 sorption in -196ºC, and tested in the catalytic combustion of toluene.

Results of the catalytic tests demonstrated that all studied catalysts are very active in the total oxidation of toluene. The materials prepared with the use of reverse micelles proved superior to the reference catalysts. Moreover, the composite catalysts synthesized in the organic environment are more active than their counterparts obtained in aqueous medium. The differences in activities may be assigned to the better dispersion of reverse micelles between the organoclay layers.

Results obtained in this work provide basis for the design of next generation of catalysts composed of oxide nanoparticles intercalated between the clay layers.

2-Oxoglutarate Dependent Oxygenases Catalyzing Atypical Oxidative Transformations - Structural and Mechanistic Studies

"Opus" research project NCN 2014/15/B/NZ1/03331 [2015-2017]
(project leader: Assoc. Professor Tomasz Borowski)

This research project focuses on three novel types of 2-oxoglutarate dependent dioxygenases whose structures and catalytic mechanisms are still unknown. They catalyze: oxidation of 2-oxoglutarate to ethylene, oxidative deamination (of kanamycin) and formation of an endoperoxide bridge (in the synthesis of a mycotoxin – verruculogen).

Within this project we will pursue a tightly integrated structural, biochemical/biophysical and computational studies on these ODDs with the purpose to: 1) unravel their 3D atomic structures, 2) shed new light on the reaction mechanisms, and 3) gain insights into factors determining reaction specificity.

The project started in September 2015. A production method for the enzyme synthetizing ethylene was worked out, catalytic activity of the enzyme was confirmed and crystallization experiments were initiated. An enzymatic activity test for any 2-oxoglutarate dependent dioxygenase was worked out and tested.

"Preludium" Research Projects of the National Science Centre

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

"Preludium" research project NCN 2012/07/N/ST5/00173 [2013-2015]

(PhD student: Tomasz Kruk MSc, supervisor: Professor Piotr Warszyński)

The aim of the project is the development of the scientific background functionalization method of polymer thin films by using the "layer-by-layer" deposition method in order to obtain coatings with specific properties. The functionalization of polymer films it will be obtained by the incorporation of nano - objects with specific desired properties (metallic, oxide, graphene oxide (GO), nanoparticles) in their structure, or by modifying the surface of such films. It will allow to obtain ultrathin films of selected properties.

The first task was devoted to the studies and optimization polyelectrolyte multilayers containing graphene oxide (GO). It was achieved through the incorporation of graphene oxide/graphene in the multilayers structure using “layer by layer (LbL)” method:

- polyelectrolyte (PE) / graphene oxide (GO^-),
- modification graphene oxide (GO^+) / polyelectrolyte (PE),
- modification graphene oxide (GO^+) / graphene oxide (GO^-).

The surface conductivity with the four point method was measured and it was noticed that using the proposed method it can obtain ultrathin conductive films on quartz and polyimide (PI) plates. Films containing the graphene oxide were subjected to modification which was carried out in situ in order to reduce graphene oxide in the structure of the film. The thermal reduction was conducted at different temperatures 150^0C, 180^0C and 250^0C. The surface conductivity of films depending on the number of layers. The resistivity of films containing (PE/rGO^-) decreases with the number of bilayers deposited and then the surface conductivity increases. Films formed of (rGO^+/PE) have a lower conductivity in comparison with the films (PE/rGO^-). On the other hand films consisting of (rGO^+/rGO^-) have higher conductivity in comparison with the films (PE/rGO^-) and (rGO^+/PE). Films (PE/GO^-) does not have conductive properties. The effect of temperature was visible to the initial number of layers (the higher the temperature, the greater the reduction of GO). From 5 bilayers weren’t significant difference in the conductivity of the surface measurements dependence of temperature.

The second aim of the task was the development a method of polyelectrolyte layers modified in order to eliminate non-specific binding. This objective achieved by immobilization of PEG (polyethylene glycol) on the film surface. We were going to synthesize the corresponding copolymers (polyelectrolytes grafted with PEG chains, such as PGA-g-PEG, PLL-g-PEG) in our laboratory. To create a layer of PEG on the surface of the films they covered with pegylated polyelectrolyte. The procedure for creating the external layer of pegylated was analogous to the creation of polyelectrolyte layers. Use copolymers of various chain length of PEG (Mw 1000, 2000, 5000) and varying degrees of grafting (10%, 30%, 50%) allowed obtaining films of different length and density of PEG chains on the surface. We verified efficiency of pegylated films for inhibition of adsorption of different proteins HSA and fibrinogen using quartz crystal microbalance (QCM) method. The studies showed that the most appropriate PEG to eliminate non-specific interactions is the chain length of 5000 MW and degrees of grafting ~ 30% and ~ 50%.

Electrokinetic Characteristics of Interaction between Recombinant HSA Monolayers and Ionic Ligands

"Preludium" research project NCN 2012/07/N/ST5/02219 [2013-2015]
(PhD student: Marta Kujda MSc, supervisor: Professor Zbigniew Adamczyk)

The goal of this work was to determine the mechanism of the adsorption of low molecular weight ligands, such as copper, zinc ions , tannic acid on albumin monolayers (HSA monomer and dimer dHSA) prepared on the mica surface.

In order to obtain quantitative data the non-invasive streaming potential method working under wet *in situ* conditions was applied. Studies of ligands binding process were conducted for protein monolayers with maximum coverage.

In these experiments, it was determined the following parameters: the adsorption equilibrium constant *K*a [cm], the maximum surface concentration of ligand $N^{*}_{L\infty}$ [cm^{-2}] and the binding energy $\Delta\phi_{m}$[kT]. The results showed the enhanced adsorption of copper ions on protein monolayers, compared to zinc ions. It was also indicated the weaker binding properties of the synthetic albumin dimer, in comparison to the albumin monomer (Fig.1).

In the experiments with low-molecular weight ligands, the preferential binding of tannic acid to the dimer monolayers was indicated. This situation can be explained due to the fact that the molecules of tannic acid, bind to the same regions of the protein what the most medicinal preparations. It was concluded that dHSA has better binding properties of the ligands in comparison to the monomer.

These results confirmed the effectiveness of the streaming potential method in the binding studies of the low-molecular weight ligands on the protein monolayers. The developed method could become alternative method of analysis the interactions in system: protein – ligand in comparison to the standard tests.

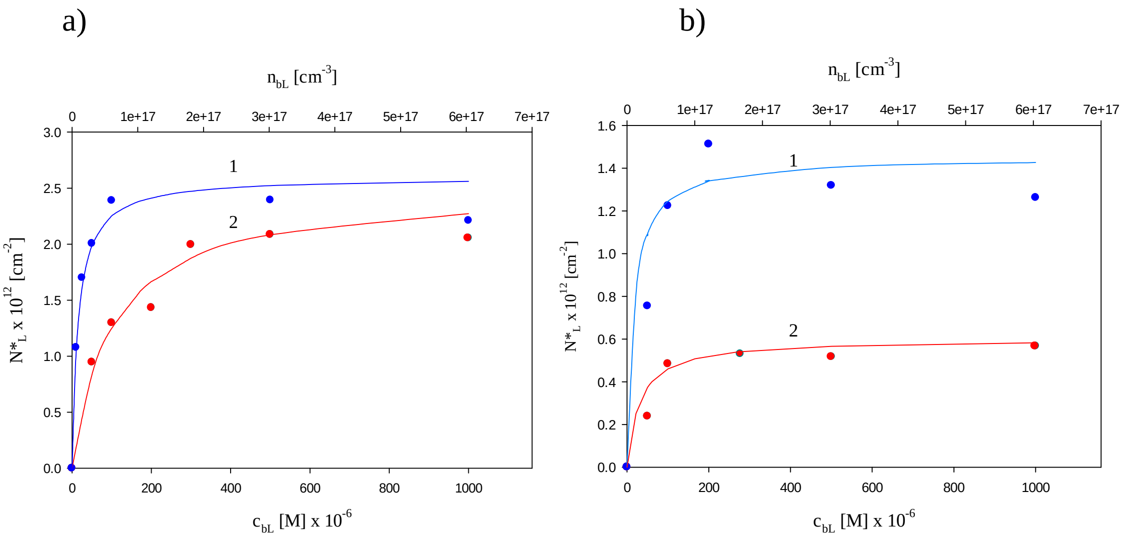


Figure 1. The binding isotherm of ions 1) Cu^{2+} (●), and 2), Zn^{2+} (●) on the protein monolayer: a) rHSA and b) dHSA presented as the dependence of ligand surface concentration [cm^{-2}] on the concentration of ions in a volume c_{bL} [M] (bottom axis) and n_{bL} [cm^{-3}] (top axis). The solid lines represent the Langmuir isotherm. The binding assays was carried out for the ionic strength of 10^{-2} M, pH 5.7.

Determining Mechanisms of Fibrinogen Adsorption on Colloids Particles

"Preludium" research project NCN 2013/09/N/ST4/00320 [2013-2015]
(PhD student: Paulina Żeliszewska MSc Eng, supervisor: Professor Zbigniew Adamczyk)

Fluorescent labeling of fibrinogen was performed by using the fluorescent dye. Next, the protein was purified and its concentration was determined by using spectrophotometer. Afterwards, characterization of labeled fibrinogen was performed. The diffusion coefficient (hydrodynamic diameter) of the labeled fibrinogen and the fluorescence intensity for various ionic strength and pH was determined and the stability was checked. The next stage of the research was investigated the fibrinogen adsorption kinetics on mica by using AFM microscopy shown in Figure 1. The points denote experimental results obtained by a direct AFM enumeration for ionic strength equal to 10^{-2} M, NaCl and pH 3.5 and the solid line shows exact theoretical results obtained using the RSA model.

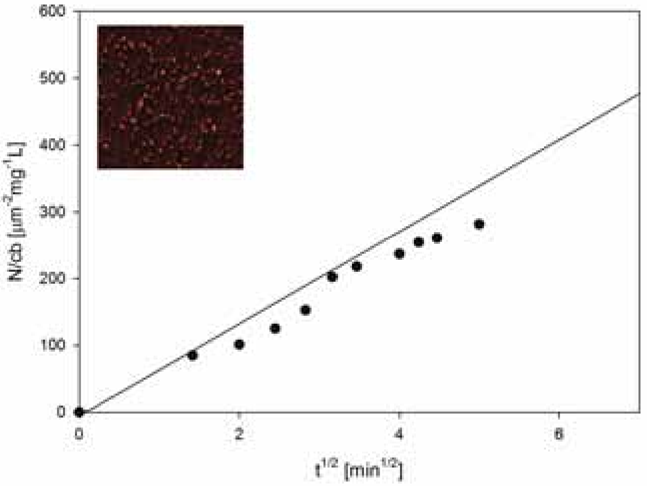


Figure 1. The dependence of the reduced surface concentration of fibrinogen on the square of adsorption time.

Afterward, the labeling fibrinogen adsorption on latex particles was determined. Adsorption of fibrinogen was studied by monitoring changes in the electrophoretic mobility (zeta potential) of latex particles induced by this process. Monolayers on latex were adsorbed from diluted bulk solutions at pH 3.5 and 7.4, ionic strength in the range of 10^{-3} to 0.15 M NaCl. Additionally, the dependence of the fluorescence intensity on the surface concentration was checked. The obtained results have essential significance enabling to develop an efficient method for studying globular protein adsorption at solid/ electrolyte interfaces.

Electronic Coupling of Nitric Oxide with Cobalt Centers in Various Coordination Environments: Impact of Electron Density Flow on Ligand Activation

"Preludium" research project NCN ST4 [2014-2016]
(PhD student: Adam Stępniewski MSc, supervisor: Professor Ewa Brocławik)

The aim of this research project was to explain by means of theoretical modeling the electronic factors determining catalytic activity of the cationic cobalt Co(II) center in the zeolite, with respect to nitric oxide, selected as the probe molecule. The task for 2015 was to determine the character of electron transfer between ammonia donor ligands and the Co-N-O core.

DFT modeling was performed for small cluster models constructed to mimic cobalt sites in zeolites, modified by co-adsorption of ammonia donor ligands. The systems with three or five NH_3 ligands in the cobalt coordination sphere were analyzed. The single aluminum tetrahedron (T1) was used to mimic zeolitic environment. The complex of Co(II) with five NH_3 ligands was considered unbound with the framework. Periodic calculations for solid-state models of chabasite confirmed the validity of small models used for cluster calculations with DFT and more exact, correlated wave-function methods.

The most interesting result was the analysis of many-configuration wave function in terms of resonance structures (corresponding to electromers with various charge-transfer characteristics) for cobalt complexes with the $\{Co(II)\text{-}NO\}^8$ core. Resolution of multi-configuration wave function (by means of localized active orbitals) into configurations corresponding to resonance structures $Co^{II}NO^0$, $Co^{III}NO^-$, $Co^{I}NO^+$, enabled quantitative interpretation of the NO activation In conclusion, singlet spin states for cobalt sites showed much higher red-shift (and activation) of NO sorbed on cobalt centers modified by pre-defined portion of ammonia than the triplet of the same system. Here, the electron transfer from the ammonia-modified Co(II) center to NO antibonding orbitals dominated charge transfer.

Very important theoretical finding was the indication of the role of spin polarization in electron transfer processes for three-component systems: Co(II) center – ammonia coordination sphere – NO ligand. This may have large significance for the mechanism of deNOx reaction on transition metal sites modified by donor ligands.

Mechanism of Irreversible Nanoparticles Adsorption on Colloids Particles

Research project: NCN
(project leader: MSc Marta Sadowska)

"Preludium" research project NCN 2013/11/N/ST4/00981 [2014-2016]
(PhD student: Marta Sadowska MSc, supervisor: Professor Zbigniew Adamczyk)

Nanoparticle monolayers formed at various interfaces are important for developing microcapsule systems based on the colloidosome concept. Also, such mono- and multilayers deposited at colloidal carriers play an essential role in the production of catalysts. For example hematite monolayers are used as catalysts in the Haber process. On the other hand, monolayers of proteins (enzymes) are exploited in enzymatic catalysis processes and in immunoassays. Given the deficit of systematic investigations devoted to nanoparticle deposition in this work extensive measurements of hematite nanoparticle deposition at planar interfaces and colloid carrier particles were performed. Precise electrokinetic and concentration depletion methods were applied combined with direct SEM and AFM aided enumeration of nanoparticles adsorbed at solid/electrolyte interfaces. The influence of the suspension ionic strength, pH and particle size on the mechanism of particle deposition and maximum coverages was systematically studied. Representative experiments obtained for hematite nanoparticles (of the size of 100 nm) at ionic strength of 10^{-2} M are shown in Figure 1. As can be observed, the experimental data are adequately reflected by the theoretical results derived from the electrokinetic model where the true three-dimensional electric charge distribution was quantitatively considered. It was also proven in an extensive series of experiments that the increase in the ionic strength induces a considerable increase in the maximum coverage of nanoparticles that was interpreter in terms of the decreased range of electrostatic repulsion. Therefore, for higher ionic strange one can form high density monolayers of nanoparticles at colloid carrier microparticles that has a major practical significance.

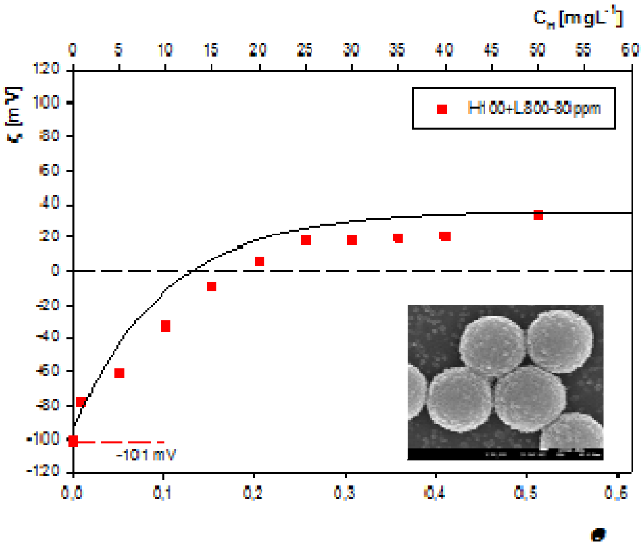


Figure 1. The dependencies of the zeta potential of L800 microparticles on the hematite nanoparticles coverage Θ for pH 5.5 and the ionic strength 10^{-2} M (points). The solid line shows the theoretical results derived from the 3D electrokinetic model. The inset shows the SEM micrograph of nanoparticle monolayer adsorbed at colloid microparticles.

"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, Austria, and Switzerland
(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 are the high resolution surface microscopies: scanning tunneling microscopy (STM) and the low energy electron microscopy (LEEM), which is also used in the project as a photoemission electron microscopy (PEEM) both with laboratory and synchrotron excitation sources.

The applied research methodology allows imaging of the surface structure (chemical, topographic and electronic) on micrometer and nanometer scale and also monitoring of the surface modifications induced by surface reactions. Currently the project is realized in cooperation with the Swiss Light Source (SLS).

One of the primary objectives of the model catalysis is to reduce a material gap between model catalysts and real industrial catalysts. An important step in realizing that goal is to extent the model studies on polycrystalline systems. The Austrian group has pioneered studies of catalytic reactions on polycrystalline platinum using PEEM. In polycrystalline Pt foils, monocrystalline grains with different orientations were identified based on different contrast in the PEEM images that is associated with different work functions. The present work was aimed at the direct determination of the polycrystalline grain orientation using LEEM and correlation of the crystallites orientation with the contrast obtained in the PEEM images. Due to the high work function of platinum, implementation of the PEEM measurements in the laboratory conditions requires the use of an appropriate light source. Methodology of the PEEM measurements using a xenon lamp with a laser ignition was developed. It was shown that the use of quartz optical elements resulted in enhanced imaging capabilities and allowed to image surfaces with the work function as high as 5.5 eV, which was sufficient for imaging grains of platinum with the (001), (110) and (111) orientations. Using the LEEM microscope a detailed analysis of the distribution of grain orientations in a clean Pt foil was performed. The foil was prepared according to the receipt which was applied for the monocrystalline Pt(111) substrates. For the atomically clean polycrystalline surface, the grains with sizes between several and several hundred microns were identified, with the majority of the grains exposing stepped surfaces. It was found that the grains that gave a uniform contrast in the PEEM images exposed the surfaces with the different degree of vicinality, and therefore there is no direct one-to-one correlation between the PEEM contrast and orientation of the grain. This means that the catalytic tests using polycrystalline samples require a microscopic diffraction method that allows for precise determination of the grain orientation.

The PEEM microscope which is designed to a synchrotron use was moved and installed at the National Synchrotron Radiation Center Solaris. The microscope was commissioned and the full functionality of the preparation and imaging chambers was demonstrated.

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

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

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

Molecular modeling of glucose mutarotation: results

We initiated a detailed computational investigation by using the molecular dynamics method, according to the QM/MM protocol, in order to study the mechanism of the mutarotation reaction that involves the glucose molecule.

The results of our study can be summarized as follows:

1. **The role of water.** The number of water molecules that directly contribute to the ring-opening reaction of hexopyranose molecules was determined. There can exist processes involving both one or two water molecules participating in the proton transfer(s). However, the dominating mechanism is that including only one water molecule (as proved for the case of β-glucose).
2. **Analysis of the subsequent steps of the ring-opening reaction.** According to the results, in the initial steps of the reaction, the water molecule (acting as the Brønsted base) detaches proton from the anomeric hydroxyl groups (at the C1 carbon atom). In the next step, there occurs a series of proton transfers, and the oxygen ring atom (O5) is protonated. This stage is the crucial one and initiates the breakage of the C1-O5 covalent bond. Starting from the protonation of O5, the postulated mechanism is nearly identical as that ascribed to the Brønsted acid-catalyzed mutarotation. We did not observe any significant differences between mechanisms corresponding to both considered anomers (i.e. to α and β glucose).
3. **Description of the dynamic aspects of the ring-opening reaction.** The results include the time characteristics of the process. The most time-consuming step is the spatial reorientation of water molecules that participate in the reaction. This is necessary for the proton transfer to occur.
4. **The conformational preferences of the aldehyde moiety.** In a series of additional simulations, we studied the influence of the dominating conformation of the aldehyde group of the acyclic hexopyranose molecules on the possible product of the ring-closing reaction (which is either α or β anomer). The calculated relative free energies are in agreement with the available experimental data estimating the relative population of α and β anomers (8 hexopyranoses of the D-series in aqueous solution). This leads to the conclusion that the conformational preferences of the aldehyde moiety play an important role in the ring-closing reaction and may determine the type of the reaction product.

Summarizing, the results of the project are connected with a detailed description of the ring-opening reaction of glucose and the conformational analysis of acyclic forms of all hexopyranoses of the D-series. In comparison to the existing results, our study was focused on recovering and analyzing the unbiased reaction path; the chosen computational protocols allow not to assume any reaction coordinate.

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. That results in a number 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 2015, we focused on the task of the project concerning the preparation of nanocapsules containing magnetic nanoparticles in the oil core of polyelectrolyte nanocapsules. The nanocapsules were synthesized by the method developed in our Institute i.e. direct encapsulation of emulsion droplets containing magnetite nanoparticles in the polyelectrolyte multilayer shell. Polyelectrolyte multilayer shell was prepared by the sequential adsorption of polyelectrolytes (layer by layer technique) saturation technique using biocompatible polyelectrolytes (Poly-L-lysine as the polycation and Poly-L-glutamic acid as the polyanion). The polyelectrolyte nanocapsules with encapsulated magnetic nanoparticles with the average size of 100 nm were synthesized. Figure 1 illustrates scheme of formation of nanocapsules.

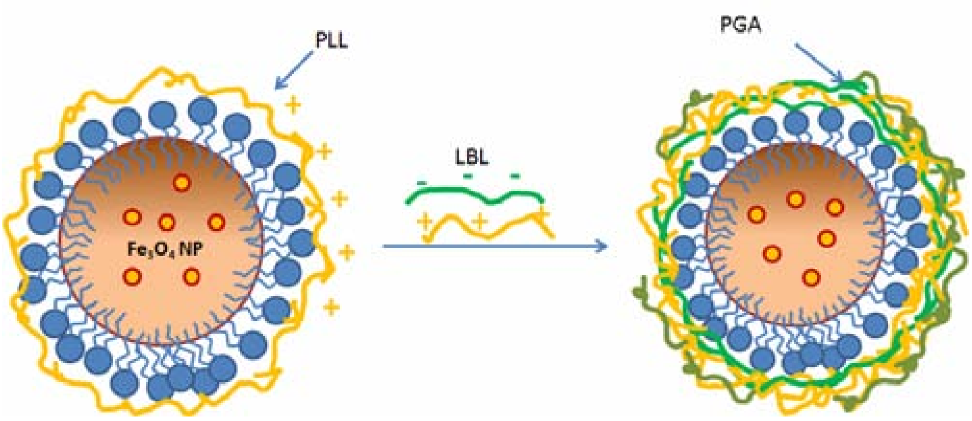


Figure 1. Formation of nanocapsules core with Fe_3O_4 nanoparticles and adsorption of subsequent layers of polyelectrolytes.

Theoretical Modeling of Influence of Liquid/Gas Interface Fluidity Variations on Kinetics of Bubble Collision with Liquid/Gas and Liquid/Solid Interfaces

"Iuventus Plus" research project MNiSW IP2014 053973 [2014-2016]
(project leader: Jan Zawała PhD)

The project aim is to describe theoretically (by means of Computational Fluid Dynamics – CFD) influence of variations in fluidity of the rising bubble surface (liquid/gas interface) as well as liquid/solid interface on kinetics of bubble collision with hydrophobic solid surfaces. This is important problem, because collision of a single air bubble with solid substrates is a fundamental step of many useful separation processes, for example froth flotation.

In the reported period geometry of the computational domain and was developed. It was a liquid column containing an air bubble of diameter 0.74 mm, described using cylindrical axi-symmetrical coordinate system. The parameters of the bubble motion (initial acceleration, shape deformations, local and terminal velocities), during its free rise due to the buoyant force in liquid column of various sizes were calculated. The obtained numerical data were compared with corresponding experimental results in order to check the calculations convergence and correctness. Moreover, variations of components of the total energy of the system (gravitational and surface energy, kinetic energy, rate of viscous dissipation of energy) during the bubble rise and collision with liquid/solid interface were calculated. In order to take into account the gradual decrease of the bubble surface fluidity (gradual immobilization) the simple theoretical model was elaborated and implemented into the numerical calculations. The model was based on proper variations in the liquid/gas interface viscosity. Higher viscosity meant higher degree of the bubble surface immobilization, i.e. mimicked higher adsorption coverage of the bubble surface by molecules of surface-active substance. The values of viscosity were properly adjusted to obtain similar bubble velocity changes as observed in experiments (from 100% of velocity in distilled water, when the bubble interface was fully mobile, to ca. 45% that velocity, when the bubble surface was fully immobilized). Additionally, the influence of degree of the bubble surface fluidity on kinetics of the bubble collision and attachment (three-phase contact formation) to the smooth hydrophobic solid surface was reproduced in the numerical simulations using the theoretical model elaborated. The obtained results corresponded very well with experimental data. In both cases it was found that increase in the bubble surface immobilization degree causes decrease in the bubble impact velocity, amplitude of consecutive collisions and degree of shape deformations (χ) (see Figure 1), due to increase of the drag, i.e. higher rate of dissipation of the kinetic energy.

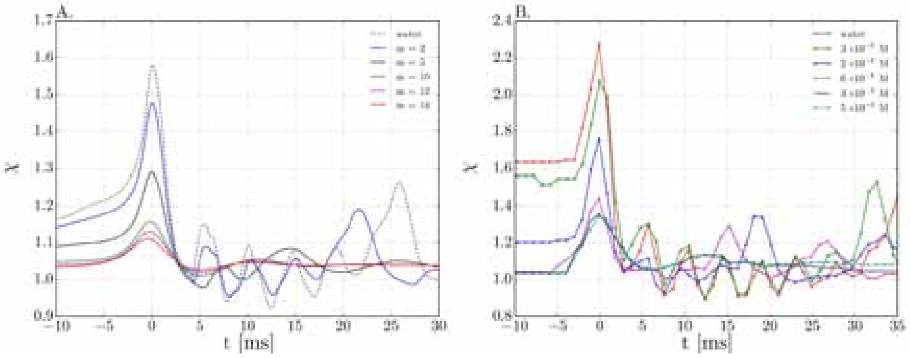


Figure 1. Variations in shape deformations of the bubble with different degree of interface immobilization, during its consecutive collisions with hydrophobic, smooth solid surface. (A) Numerical calculations, (B) experimental data.

Strategic Research Projects of the National Centre for Research and Development

NUCLEAR 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 NUCLEAR SP/J/7/170071/12 2012-2015]
(project leader: Professor Alicja Drelinkiewicz)

The aim of present work is to elucidate a role of experimental variables determining the activity of noble metals supported catalysts for the hydrogen and oxygen recombination reaction. 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 coated with Pt deposited onto alumina, known as "wash-coat" catalysts. They must be able to catalyze the conversion of hydrogen at room temperature and must be resistant to humidity because of its high level in the atmosphere of nuclear reactor.

The research work concentrated on experimental variables determining activity of Pd-Au catalysts supported on Al_2O_3 and SiO_2. The catalysts with various Pd/Au molar ratio (metal loading 2 wt %) were prepared by the reverse "water-in-oil" microemulsion method. This procedure allows preparing the catalysts of well controlled size of metal nanoparticles and controlled surface concentration of metal on the support surface.

The work deals with a role of the type of support (Al_2O_3, SiO_2) and the Au content represented by the Pd/Au molar ratio in activity and stability of catalysts in the reaction mixture consisting of humidity.

The following aspects were studied
a) preparation of catalysts using various supports
b) characterization of catalysts properties; textural (surface area, porosity; BET) and metal phase (size of metal particles, their distribution in support; XRD, XPS, SEM, TEM, HRTEM)
c) measurement of catalyst activity in the laboratory flow reactor using reaction mixture (0.5 % H_2 in air) saturated with water at temp. 25^0C
d) evaluation by microcalorimetric method the thermal effects during recombination reaction and the stability of catalysts
e) DFT calculations of electron interactions in the systems: water molecule – metal cluster $M_{2\text{-}26}$ (Pd, Pd-Au)

The results obtained by microcalorimetric measurements showed that the type of support as well as the composition of metal particles (Pd/Au) determined activity and deactivation of catalysts due to water formed in the catalytic reaction. Deactivation was the highest for alumina supported catalysts. The content of Au (Pd/Au molar ratio) determined the amount of heat evolved in recombination reaction and the stability/deactivation of catalysts. The best performance reflecting in relatively low thermal effect assisted by high stability displayed silica-supported Pd/Au catalyst of low Au content (10 mol % Au). The DFT calculation showed weaker interaction of water molecule with the Pd-Au clusters compared to that in the H_2O – Pd clusters.

Applied Research Programme Projects of the National Centre for Research and Development

HERIVERDE 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 aims at 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.

HERIe software has been developed for an assessment of risk of damage to cultural objects in given storage or display conditions. The software analyzes the impact – on a specific object - of one-year (or multiyear) relative humidity data measured in a given gallery or simulated for various climate-control scenarios. Such microclimatic data are decomposed into elementary variations (sinusoidal functions) using the Fourier transform. The elementary variations are used as the input into the finite element numerical simulation modeling the moisture adsorption and diffusion, and the resulting strain fields in the material. A complete strain history engendered in the investigated object by the microclimate of interest to a user is then obtained by superposition of the elementary strains. In the last step, a risk index, corresponding to the moisture-related strain determined, is calculated using relevant failure criteria derived from laboratory studies or condition surveys of collections. Finite element numerical simulations of heat and water vapour exchange between objects comprised in museum, library and archival collections and their environment were also used to assess the advantageous buffering effect of collections on microclimate fluctuations. The simulation results were coupled to modeling of indoor climate and energy consumption in buildings housing the heritage assets with the use of the WUFI®Plus software based on a transient balance of temperature and moisture.

In the present phase of the project, a HERIe module was developed which analyses damage risk for a gesso layer by moisture related strain of wooden panels of varying thickness, open through one or two faces to the water vapour diffusion. The module developed allows risk for panel paintings to be assessed, one of the most important categories of heritage objects vulnerable to fluctuations of humidity and temperature. In turn for libraries, a statistical bookshelf was created basing on measurements of book sizes and their numbers in storages of the National Library in Warsaw. Having such exemplary model book block allowed the effect of density and quantity of the library and archive materials on the microclimate to be analyzed. The calculations carried out for a typical library space with no climate control demonstrated that daily relative humidity fluctuations were reduced by about 5-10 % if the buffering effect of the collection was taken into account.

The two types of software are open tools with the constantly enlarged data base of the cultural heritage objects which can be analyzed. They will be continually refined tools for developing rational strategies of indoor microclimate management in museums, libraries and archives requires by a quantitative assessment of interrelation between the intensity of the hazard (climate fluctuations), the damage caused (cracks or deformation), and the cost of controlling the hazard.

"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: Assoc. Professor Maciej Szaleniec)

The aim of the project “Regioselective oxidation of cholesterol derivatives with a novel molybdoenzyme – 25-OH cholesterol dehydrogenase” is to develop a method for regioselective hydroxylation of cholesterol derivatives at C25 carbon atom with a novel molybdoenzyme (S25DH). During 2015 the research has been focused on ongoing development of S25DH overexpression system in *E. coli* (task 2), up-scaling of reaction (task 7) and development of methods for isolation and purification of the products from reaction mixture (task 8). Moreover, as a part of task 9 actions were undertaken for project results promotion and securing of IP rights.

Previous research on development of the overexpression system revealed problems with solubility of the α1 subunit of the enzyme and no expression of β subunit. The studies conducted as a part of task 2 during 2015 resulted in successful overproduction of all S25DH subunits, but unfortunately not all of them were soluble. Therefore, the genetic constructs of other α subunit isoenzymes were successfully designed , enabling overproduction of S25DH enzyme with different set of α subunits. It was assumed that successful production of α subunit would improve the solubility of whole S25DH enzyme. The cell extracts of *E. coli* transformed with S25DH genes were used as catalysts in hydroxylation of choles-4-en-3-on. For one of the α subunit isoenzyme the HPLC analyses showed the presence of the compound characterized by the same retention time as the product standard (purified product of hydroxylation by the native S25DH). Unfortunately, the obtained overexpression system of S25DH is not very efficient. In addition to work on S25DH enzyme, the overexpression system for AcmA from *S. denitrificancs* (i.e. 3-ketosteroid dehydrogenase) has been developed. Such enzyme was necessary for chemo-enzymatic synthesis of 25-hydroxycholesterol. Although the AcmA enzyme was successfully produced in *E.coli*, the obtained protein was insoluble and turned out to be inactive.

Within the scope of task 7 two synthetic methods have been developed: one-step synthesis of 25-hydroxy vitamin D (200 ml reactor scale that yielded 96 mg of the product isolated with 70% efficiency) and chemo-enzymatic method for production of 25-hydroxycholesterol (i.e. chemical oxidation of cholesterol to cholest-4-en-3-one followed by enzymatic hydroxylation and chemical reduction; the reactions yielded up to 70 mg of the product). In both cases the product isolation and purification method has been developed as a part of task 8 and the purified products were analyzed with HPLC-MS and NMR. The native AcmA enzyme was also tested as a catalyst for the first step of the chemo-enzymatic synthetic method (i.e. for oxidation of cholesterol to cholest-4-en-3-one).

Finally, the IP rights to developed methods were secured with two polish patent applications. The promotion of the project results was conducted by preparation of the technology offer, publication of promotion materials in Biotech Europe catalogue and presentation at the partnering events such as Life Science Open Space or BioEurope.

EC 7th Framework Programme Research Projects

NanoEIS Nanotechnology Education for Industry and Society

EC FP7-NMP-2012-CSA-6 NanoEIS 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. It constitutes 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 key area. Within the present project, the assessment of EU education in nanotechnology and teaching material development is undertaken, so that it corresponds to the European society and industry needs.

The nanotechnology curricula were analyzed at the level of secondary schools and European universities. Nanoindustry expectations were also assessed.

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. Full nanotechnology education is available at higher education level: at 1st, 2nd, and 3rd degree of higher studies.

A direct comparison of the industry expectations and universities offers shows a very substantial discrepancy. On he one hand, this raises the serious perspectives that highly trained students may not find suitable jobs while industry is looking in vain for urgently needed skills, in particular in health/safety, regulation, and environment/disposal/recycling. On the other, the investigated university courses emphasized classical, research-driven subjects such as characterization/metrology, nanoelectronics and nanostructures/composites.

In order to bring closer the employers' needs to the universities' offers, the new nanotechnology curriculum has been proposed. The proposed nanotechnology curriculum is designed for a typical Bologna scheme of education. It covers a module-based three year program of 1st degree (Bachelor), two year 2nd degree (Master), and four year 3rd degree (Doctoral) studies. It comprises not only the classical subjects taught at universities, but also the skills and knowledge anticipated by employers. The description of the proposed courses was supplemented with web-links to pages containing educational resources, source materials, and evaluation tests.

Finally, factors favoring smooth transition from academia to industry were evaluated. Our survey shows that direct involvement of industry in teaching is the single factor, which enables quick transition from the academic into the industrial sector. Small beneficial effects are found involving industry in curriculum or module development. Other efforts, like an industrial advisory panel (widely considered to be a best-practice element) have no detectable effect on inter-sectoral transition.

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. sdThe 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 third year of the project we continued on the development of methodology of formation of alumina capillary bridges using sol-gel approach. The necks were formed between alumina microparticles using aluminium isopropoxide and tertbutoxide as the alumina precursor. Then nanoparticles of the selected material with high thermal\electric conductance SiC, were suspended in the alumina precursor formation of necks were investigated. We found that addition of 10 wt% of PEI prevents necks from cracking during drying. Rectangular cavities were packed with microparticles with capillary bridges and filled with epoxy (provided by the project partner – LORD). The thermal conductivity of filled cavities were determined by IBM. Thermal conductivity was two times higher than for commercially available filling even without epoxy optimization. We expect that after optimization the conductivity will increase by 50%. We also worked on the selective hydrophobisation of microchips with aminothiols and fluorosilanes.

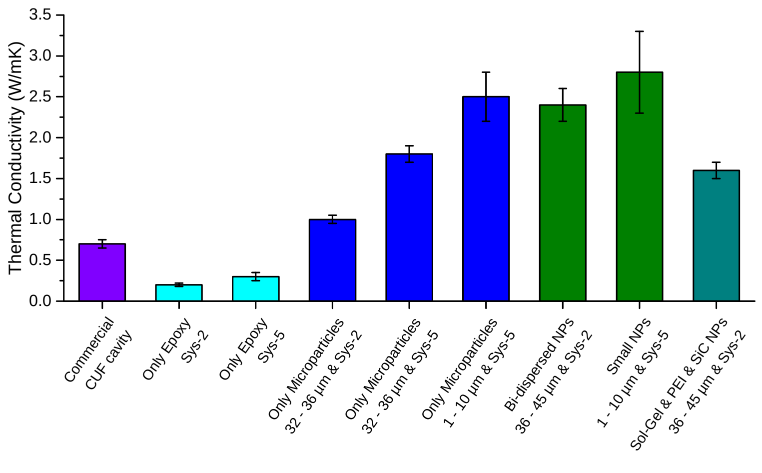


Figure 1. Comparison of thermal conductivity of cavities filled with various filling. Sys-5 – optimized epoxy, Sys-2 non-optimized epoxy.

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 2015 following events were organized including the Working Group meetings: WG2&5, “*Colloidal Interactions: Depletion Forces, Molecular Lubrication*”, Marcoule, France, WG1,6, “*Bubble and Drop Interfaces 2015*”, Golm, Germany. The annual conference of the Action took place during the ECIS 2015 Conference in Bordeaux, France. Training School “*Engineering: Fundamentals, Applications, and Analytical Methods”* was organized in London, UK and *ESC 2015* in Cracow, Poland. Additionally 15 STSMs were organized. The official WEB page of the Action can be found at the address: http://projects.um.edu.mt/cm1101/ .

ECOSTBio Explicit Control Over Spin-states in Technology and Biochemistry

EU COST Action CM1305 ECOSTBio [2012-2016]
(country coordinator: Professor Ewa Brocławik)

In the ECOSTBio Action a network of both experimental and theoretician research groups is created to tackle a diversity of chemical problems where spin is an important factor. This will be achieved by the joint creation of a SPINSTATE database of systems with known spin states and spin-related properties. The interactions of theorists and experimentalists will create a synergy, helping theoreticians to validate their models and experimentalists to improve the performances of novel materials with desired properties. Poland is represented by E. Brocławik, the National Coordinator.

The second scientific workshop and Management Committee meeting was held in Marseille (France), January 12-13, 2015. The third scientific workshop and Management Committee meeting took place Belgrade (Serbia), August 24-25, 2015. Two Short Term Scientific Missions (STSMs) were granted to the Institute of Catalysis, Polish Academy of Sciences: COST-STSM-CM1305-21775, supervisor: dr Lubomir Benco, Center for computational materials science, Vienna (Austria), Nov 2014 – Jan 2015 (mgr Adam Stępniewski) and COST-STSM-CM1305-21782, supervisor: prof. Tomas Bucko, Comenius University Bratislava (Slovakia), Feb 2015 – Apr 2015 (mgr Adam Stępniewski)

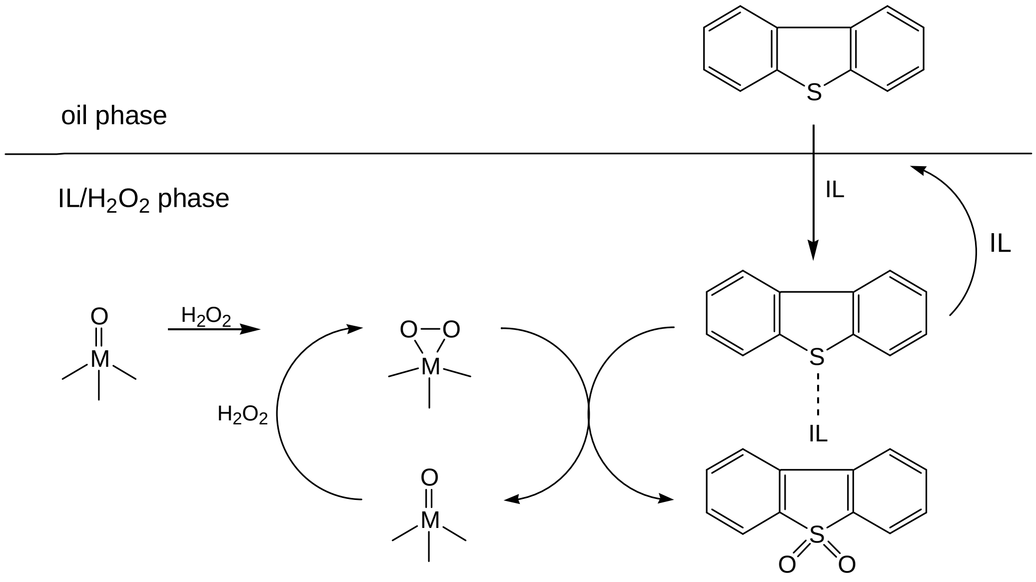
PoCheMoN Polyoxometalate Chemistry for Molecular Nanoscience

EU COST Action CM1203 PoCheMoN [2012 2016]
(representative: Professor Bogdan Sulikowski)

Oxidative desulphurization of paraffin hydrocarbons using ionic liquids

(Professor Bogdan Sulikowski, Janusz Nowicki DSc, Urszula Filek PhD)

In the period reported we have focused on the oxidative desulphurization of paraffin hydrocarbons. The early stage research was carried out as it is visualized in the Scheme below, with the use of amphiphilic ionic liquids:



The following ionic liquids were used for the process: [Rmim]HSO$_4$; Rmim]H$_2$PO$_4$, where R=C$_4$–C$_{12}$. As emulsifiers and co-catalysts some chosen ionic liquids were used. Phosphomolybdenum oxometallates and the POM precursors H$_2$WO$_4$ and H$_2$MoO$_4$ were used as the catalysts. Desulphurization level of the paraffin hydrocarbons was relatively low and did not exceed ca. 22.2 %.

SGI Smart and Green Interfaces - from Single Bubbles and Drops to Industrial, Environmental and Biomedical Applications

EU COST Action MP1106 SGI [2012-2016]
(country coordinator: Professor Kazimierz Małysa)

Research teams from various scientific institutions of 31 European countries are participating in activities of the COST Action MP1106 “Smart and green interfaces - from single bubbles and drops to industrial, environmental and biomedical applications (SGI)” project. The project is coordinated by professor Thodoris Karapantsios from Aristotle University of Thessaloniki, Greece, and professor Kazimierz Małysa from ICSC PAS is the Polish representative in the Management Committee of the COST MP1106, scheduled for the period: 11.05.2012 - 10.05.2016.

In 2015 the Management Committee Meeting of the COST Action MP1106 was held in Belgrade, Serbia on March 31 and professor Kazimierz Małysa attended the Meeting.

In 2015 there were 3 working groups meetings and conferences organized within the frame and with financial support of the COST Action MP1106, attended by scientists from the ICSC PAS.

Dr. Marcel Krzan, professor Kazimierz Małysa and dr. Jan Zawała attended the "Smart and Green Interfaces Conference – SGIC2015", March 30 – April 1, 2015, Belgrade, Serbia where they presented 2 oral and 2 poster contributions.

Dr. Marcel Krzan, Anna Niecikowska MSc and professor Kazimierz Małysa attended the 6th International Workshop on "Bubble and Drop Interfaces, July 06-10, 2015 Potsdam/Golm, Germany, where they presented 2 oral and 3 poster contributions.

Professor Kazimierz Małysa and dr. Jan Zawała attended the Meeting "Smart and green interfaces: Fundamentals and Diagnostics, Dotchi Exerowa Symposium", 29-31 October, 2015, Sofia, Bulgaria, where they presented 2 oral and 1 poster contributions.

Dr. Jan Zawała from our Institute applied and obtained financing from the COST P1106 project for the STSM visit in TIPs (Transfer, Interfaces & Processes) laboratory, Faculty of Applied Science Universite Libre de Bruxelles, planned for the period March 13-26, 2016.

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.

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

In 2015, at ICSC we focused on the preparation of polymeric nanoparticles containing hydrophobic neuroprotective agents (e.g. Polydatin, Closapine). PCL (polycaprolactone) nanoparticles were obtained from nanoemulsions by inversion-emulsification method. The nanoparticles containing neuroprotective drugs with an average size of 80 nm were obtained. Nanoparticles were also modified by the pegylation for biomedical application. Pegylated nanoparticles were formed from copolymer PEG-b-PCL. Figure 1 presents typical Cryo-SEM micrograph of PCL nanoparticles. They appeared to be non-toxic in the cell toxicity tests, and thus, suitable for encapsulation of neuroprotective components. The synthesized nanoparticles containing neuroprotective drugs were further tested by our consortium partners.

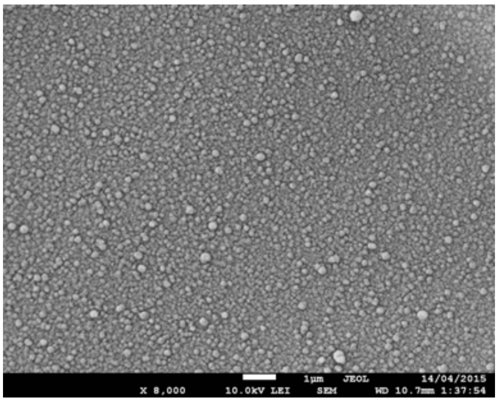


Figure 1. CryoSEM image of synthesized PCL nanoparticles.

FUNCLAY Synthesis and Functionality of Innovative Porous Clay Hybrid Nanostructures

The Polish-Norwegian Research Programme FUNCLAY project
210445/53/2013 [2013-2015]
(project leader: Małgorzata Zimowska PhD)

The aim of the project was functionalization of the PCH composite supports derived from the crystalline clay mineral and amorphous mesoporous silica. PCHs were prepared by the surfactant directed assembly of organosilica in the galleries of synthetic layered hydrous magnesium silicate Laponite. The obtained crystalline-amorphous composites were doped by a post-synthesis impregnation with tin (IV) chloride pentahydrate dissolved in water to give samples with Si/Sn = 10, 40 and 60 or in 2-propanol to give a sample with Si/Sn = 10. The effect of the porous clay heterostructure (PCH) doping with the tetravalent (Sn^{4+}) cations on the physicochemical and catalytic properties was investigated. In order to distinguish between the role of the clay component and that of the mesoporous silica, the clay-free mesoporous MMS silica doped with Sn (dissolved in water or in 2-propanol) were also prepared.

The influence of the PCH or mesoporous silica doping on the physicochemical properties (textural parameters, acidity) of the synthesized materials and on the catalytic activity was tested in Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone using a hydrogen peroxide as benign oxidant.

Impregnation of PCH composite with tin did not affect the character of nitrogen adsorption isotherm, but resulted in a slight decrease of BET specific surface area and the associated decrease of the total pore volume, most pronounced in the case of Sn-PCH-10 (from 667 m^2/g (PCH) to 515 m^2/g (Sn-PCH-10)). The downward shift of the isotherm after impregnation, with unchanged pore diameter maximum, suggested clogging of some of the PCH pores by Sn-species. Similar effect was observed for the Sn-doped MMS samples. With the increase of Si/Sn ratio a gradual segregation of Sn at the edges of PCH grains occurred (SEM analysis). In the sample with the highest tin content (Sn-PCH-10) XRD analysis revealed the presence of SnO_2 phase of up to ~100 nm particles dimention.

The structural changes of PCH composite were analyzed by FTIR spectroscopy and indicated location of part of tin cations into specific three dimensional amorphous silica sites of PCH component, despite the difference in size of Sn^{4+} (0.55 Å) and Si^{4+} (0.26 Å) cations. The ^{119}Sn Mössbauer spectroscopy confirmed about 30 % incorporation of the tetravalent (Sn^{4+}) cations in the PCH structure while the rest had parameters characteristic for SnO_2.

PCH composites showed high activity in cyclohexanone oxidation to ε-caprolactone with hydrogen peroxide. The addition of tin improved the catalytic properties of PCH. The best performance in terms of activity and yield of ε-caprolactone was observed for Sn-PCH-10.

Purely siliceous clay-free MMS support showed low conversion of cyclohexanone oxidation. Addition of tin increased the selectivity to ε-caprolactone, but the activity remained at a low level. It is apparent that the presence of the Laponite component of PCH composite is essential for obtaining high yield of ε-caprolactone. The effect is attributed to the presence of basic sites in the octahedral sheets of clay.

InLinePV In-line processing of n$^+$/p and p/p$^+$ junction systems for cheap photovoltaic module production.

The Polish-Norwegian Research Programme ID 199380 InLinePV(core) project 210445/53/2013 [2014-2016]
(coordinator: Professor Piotr Warszyński, principal investgator: Robert Socha PhD)

The price of photovoltaic modules limits utilization of this energy source in common daily use. The n+/p and p/p+ junction formation in separate steps creates additional costs that can be lowered when in-line process is applied. The project is focused on developing simpler, environmentally benign and cheaper methods for silicon doping to form necessary junctions.

The SINTEF Materials and Chemistry and Institute of Metallurgy and Materials Sciences Polish Academy of Sciences are the InlinePV project partners. The bilateral collaboration is aimed to achieve the exchange of know-how between the partners in scientific and technological areas of the project implementation leading to increase of the partners' capabilities.

The project partners collaborate on developing of new technology for formation of n+/p and p/p+ junction systems in silicon that are essential for photoelectric effect to occur. The phosphorus doping process is performed from the environmentally benign liquid sources instead of $POCl_3$ actually applied in industry that is toxic and difficult in use. The project activity resulted in development of phosphorus source that allows formation of adequate P distribution profile and efficiency comparable to the obtained from $POCl_3$ but with much lower costs of the process.

Additionally, the approaching of low silicon surface reflectivity is important for efficient light absorption leading to high performance of the photovoltaic cells. One of the ways to increase the light absorption in conventional silicon cells is texturization of the surface by chemical etching. The metal assisted etching (MAE) where the metal nanoparticle works as the local catalyst can be applied for this purpose. The single metal catalysts (Pd, Ag, Au) were tested in MAE process and compared with their bimetallic systems. The surface reflectance and surface composition after the etching process were adequate to the industrial requirements.

In order to improve efficiency of the produced PV cells, low dimensional structures with plasmonic properties and light converters were applied. In a laboratory scale, the systems with controllable absorbance and emission of the electromagnetic radiation in visible light range were obtained. The effort has been focused on proper particles dispersion and their adhesion to silicon cell surface.

Projects of EU Structural Funds Programmes

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. In the year 2015, 32 PhD students are studying in all partner institutions (IV/V year - 15 PhD students, V year - 17 PhD students), in ICSC PAS 8 PhD students (IV/V year - 3 PhD students, V year - 5 PhD students).

In the year 2015 11 PhD students publically defended the PhD thesis and received the PhD academic degree in chemical science in the field of chemistry: K. Kubiak (supervisor: professor Z. Adamczyk) - The stability of silver nanoparticles on boundary surfaces - AFM and QCM study; Ł. Kuterasiński (supervisor: professor M. Derewiński) - Nature of proton acidic centers in MFI type zeolites, isomorphic modified by boron; M. Gackowski (supervisor: professor M. Derewiński) - Silica monoliths with zeolite nanoparticles as a model flow microreactors; P. Batys (supervisor: assoc. professor P. Weroński) - Surface and transport properties of nanoparticle multilayers; A. Dziedzicka (supervisor: professor B. Sulikowski) - Modified zeolites as a catalyst for terpene transformation; Ż. Kalemba-Jaje (supervisor: professor A. Drelinkiewicz) - Transesterification of triglycerides with methanol in presence of solid polymer acid catalysts; A. Miłaczewska (supervisor: assoc. professor T. Borowski) - Research of structure and catalytic mechanism of activity of selected nonheme metalenzymes; P. Niemiec (supervisor: assoc. professor R. Tokarz-Sobieraj) - Theoretical description of modified heteropolyacids; M. Tatko (supervisor: assoc. professor P. Nowak) - New, highly conductive ionic conductors based on lantanide metal oxides for high-temperature solid oxide fuel cell; J. Dziedzic (supervisor: professor P. Warszyński) - Photocatalytic decomposition of organic compounds in water enhanced by encapsulated oxidants; K. Onik (supervisor professor M. Derewiński) - Hierarchic materials based on zeolites precursor as the basis of the modern catalytic systems;

Generally the all 17 PhD students, who realized individual PhD projects in ICSC PAS, finished the project, publically defended the PhD thesis and received the PhD academic degree in chemical science in the field of chemistry: - in the year 2014, M. Grzesiak-Nowak (supervisor: professor W. Łasocha) - Coordination polymers and metal-organic frameworks 'MOF' - materials for catalysis, crystal engineering; A. Szymańska (supervisor: professor W. Łasocha) - Polymetalates and peroxocomplexes as materials for applications in catalysis, medicine and industry; M. Krzak (supervisor: assoc. professor P. Nowak) - Anticorrosive composite epoxy coatings; M. Nosek (supervisor: assoc. professor P. Weroński) - Application of rotating disk electrode technique in colloidal thin films studies; A. Pajor-Świerzy (supervisor: professor P. Warszyński) - Electroactive multilayers films with nanoparticles;

- in the year 2013 M. Oćwieja (supervisor professor Z. Adamczyk) - Kinetics of silver particle adsorption on heterogeneous surfaces and morphology of silver monolayers.

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). In 2015 only finishing studies were conducted as the research schedule was planned to be finished by the end of 2014.

This studies encompassed a series of additional tests of chiral alcohols produced with PEDH as a catalyst by project industrial partner, TriMEN. The chiral chromatography was used to establish products purity, chirality and enantiomeric excess. Moreover an offer of catalyst was prepared for TriMEN that would avoid a need to obtain GMO allowance for a company, in order to decrease costs involved in implementation of PEDH based technology.

Unfortunately due to sudden change of priorities of TriMEN company and de facto suspension of its independent operations on the market of custom synthesis of chemical compounds the technology transfer the commercialization of PEDH was not successful. Therefore the aims at further development of plug flow reactor system were undertaken as well deployment of technological offer of production of range of chiral alcohols by ICSC PAS.

The development of the flow reactor based on monolithic silica support that was functionalized with linker groups and the enzyme was covalently immobilized. Moreover, the access to production plasmids o R-specific phenylethanol dehydrogenase and ethylbenzene dehydrogenase was secured .The transfection of E.coli with R-specific alcohol dehydrogenase allowed cheap production of the other enzyme, thus expanding the range of chiral isomers of alkylaromatic alcohols. The analysis of patent protection for both enzymes revealed that from the beginning of 2014 the (S)-specific enzyme is no longer protected by BASF patents, while (R)-specific enzyme is still protected in major European markets (e.g. UK, Germany, France) but not in Poland. Therefore the offer for production of chiral alcohols was presented on PODIO portal of Klaster Life-Science Kraków.

Finally the studies on enantioselectivity of EBDH was continued with recombinant enzyme characterized by native sequence as well as with 3 other mutants subjected to one amino acid mutation of the active site residues proposed in enantio-differentiation. The initial studies suggested that the native recombinant enzyme retains its enantioselectivity. However, the test were conducted for E.coli cell extracts which contain alcohol dehydrogenases, able to convert under conditions of activity assay (S)-1-fenylethanol to acetophenone. As a result the enantioselectivity of mutants could not be unequivocally determined,

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” was 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 was 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 was running since October 1, 2010. Its goal was 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 was 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.

The scientific employees of four partnership units took part in numerous specialist trainings concerning i.a. the latest trends and achievements in scientific research, operating scientific equipment, new research methods, modern methods of data analysis, etc.

PhD students were conducting research work in the appropriate partnership unit/s, receiving monthly fellowships, making purchases of materials and equipment necessary for their work. In addition, they were attending seminars according to the programme curriculum and participating in scientific conferences in Poland and abroad, where they presented the results of their research in the form of oral and poster presentations. The progress of the project was supervised by the Programme Board consisting of 8 members – two representatives from each partnership unit.

Moreover in the course of this project the following invited lecturers was organized in ICSC PAS in 2015:

- Jakub Antczak, MD (Jagiellonian University Medical College**) -** “*The use of electrophysiological tests in the diagnosis of diseases of the nervous system*”
- prof. Krzysztof Tokarski (Institute of Pharmacology PAS) - “*Electrophysiological methods used in brain studies in vitro*”
- prof. Konrad Szaciłowski (AGH University of Science and Technology) - *“Surface molecules. From elementary interactions to logic gates and artificial neurons”*

In the course of this project there were organized defenses of doctoral dissertations and the degree of doctor was conferred to 39 persons in the partnership units: 17 in chemical sciences, discipline chemistry (6 in ICSC PAS, 11 in FCh JU); 22 in medical science (9 in IF PAS, MC JU).

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)

The aim of the project was design, synthesis and study of the nanoscale structures arising in novel polymer polycation modified clays to be used as supports for immobilization and stabilization of metal nanoparticles in the confined interlayer space.

Organo-modified clay mineral samples were prepared by gradual delamination of the natural smectite - Jelszowy Potok (JP) or synthetic Laponite RD® (Lap), and subsequent introduction of the organic cationic species of polymer with high charge density (Polydiallyldimethylammonium chloride - p-DADMACl) containing 2% of $RuCl_3$. The stabilization of the introduced Ru^{3+} cations and p-DADMA species of cationic nature between anionic layers of clay mineral was assured through utilization of relatively strong electrostatic forces and the competitiveness in the interaction of cations with layers of mineral. Three weight ratios of clays and polymer JP/Lap:p-DADMACl (1:0.05; 1:0.25 and 1:3) were used for synthesis to investigate the interaction between clay, polycations and Ru species. The polymer-free Ru-JP and Ru-Lap were applied as a reference. The resulting organic derivatives containing Ru ions were reduced with $NaBH_4$ to obtain metallic particles distributed in the organo-clay supports.

The amount of p-DADMACl influenced the configuration and arrangement of p-DADMA polycations in the interlayer spaces of the clays. XRD analysis showed an increase of the d_{001} basal spacing in the p-DADMA-Jp_1:0.05 and p-DADMA-Lap1:0.05 samples (1.55 nm) compared to the natural clay mineral (1.25 nm) due to expansion of interlayer space, indicating intercalation of polycations between the layers of smectite. The introduction of the higher amount of the polycations to the clay mineral suspension (1: 0.25) resulted in a greater expansion of the interlayer spaces (1.63 nm). An addition of the large excess of p-DADMACl polymer to the clay mineral suspension (p-DADMA-Jp_1:3) did not result in the increase of interlayer distance of the obtained organic derivatives. This could indicate that there is a limit value of polymer amounts that no longer affects the configurations of polycations between the layers of the clay mineral.

SEM-EDS and XRF analysis confirmed the presence of Ru in the modified-clays structure and varied dispersion of the metallic particles in the resulting composite, depended on the p-DADMA content and consequently interlayer spaces of the clays.

The size, state of aggregation and stability of incorporated metallic Ru nanoparticles controlled by stabilizer content and its configuration between the clay layers were verified in the reaction of 2-butanone hydrogenation.

The research carried out is of great importance in applications of the environmentally friendly clay minerals to the catalytic reactions and also in the other areas of materials science, where optimizing of the synthesis conditions improves the physicochemical and catalytic properties of synthesized materials.