JERZY HABER INSTITUTEOF CATALYSIS
AND SURFACE CHEMISTRY
POLISH ACADEMY OF SCIENCES

DETAILED RESEARCH REPORT

year 2016

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 2016 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 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. „Activation of molecular dioxygen (3Σg) on W and Mo heteropolyacids of α-Keggin and α 1 and α 2 – Dawson structures modified with transition metal cation (TM=Cr3+, Fe2+, Mn2+, Co2+, Ni2+, Cu2+ i Zn2+) at the polyatom site" (Piotr Niemiec PhD, cooperation with Chemistry Department of the Jagiellonian Univeristy)
2. "Structural heterogenous oxide catalyst on ceramic foam support for combustion of volatile organic compounds" (Łukasz Mokrzycki PhD; cooperation with the Chemistry Department of the Jagiellonian University)
3. „Synthesis of ethyl acetate from bioethanol in a one-step oxidation reaction catalysed by palladium salts of heteropolyacids" (Urszula Filek PhD; cooperation with the Chemistry Department of the Jagiellonian University)

As during the time the projects were going on two leaders have left the Institute (Piotr Niemiec PhD and Łukasz Mokrzycki PhD), two next projects form the ranking list have received founding:

„Analysis of adsoprtion kinetics based on structure of the final adsorption monalayers" (Jakub Barbasz DSc; cooperation with the Institute of Physics of the Jagiellonian University)

„Studies on mechanisms of functionalization of surfaces of plazmonic nanoparticles with selected amino acids and mercaptoamines with the aim to broaden their usability in biological applications" (Magdalena Oćwieja PhD; cooperation with The Henryk Niewodniczański Institute of Nuclear Physics, PAS)

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. Prof. John Z. Larese, Department of Chemistry, The Univeristy of Tennessee, Knoxville (USA),
2. Prof. Wuge H. Briscoe, School of Chemistry, University of Bristol (UK),
3. Prof. Sam de Visser, Manchester Institute of Biotechnology and School of Chemical Engineering and Analytical Science (UK).

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

Catalytic processes using bio-resources

(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 project seeks to establish an effect of hydrogen bronzes expectedly formed within the hybrid systems of Pd nanoparticles dispersed in the MoO_3 matrix on its reactivity in hydrogen evolution from aqueous solutions of electrolyte and from alcohols (methanol, ethanol, isopropanol).

The work included synthesis of a range of Pd/MoO_3 catalysts with various content of Pd (0.5 – 4 %; (impregnated from $Pd(ac)_2aq$, reduced in H_2 at 250°C), characterized with methods including XRD, XPS, SEM (EDS), HRTEM. The tests for evolution of H_2 from alcohols (CH_3OH, C_2H_5OH, i-C_3H_7OH) have been carried out in flow microreactor, and the measurements performed with gas flow-through microcalorimeter in pulse mode. The evolution of hydrogen from aqueous H_2SO_4 solution has been investigated using CV method for systems of Pd/MoO_3 – conducting carbon Vulcan XC72(1/1 w/w).

The Pd particles of 6-8 nm in size observed in all catalysts aggregated gradually with the Pd content. Fig. 1 shows thermal effects of the reactions of methanol and isopropanol with the 2%Pd/MoO_3 and 0.5%Pd/MoO_3 at RT, compared to the pure MoO_3 matrix, which yielded only ca 5 kJ/mol, merely attributable to physical adsorption. For the 0.5%Pd/MoO_3, the pulses of isopropanol yielded the heat of 13 kJ/mol alcohol, slightly higher than that of 11 kJ/mol methanol. The difference was more pronounced in the 2%Pd/MoO_3, yielding 25 kJ/mol and 16 kJ/mol, respectively from i-C_3H_7OH and CH_3OH, comparable to the PdH_x formation (20 kJ/mol H).

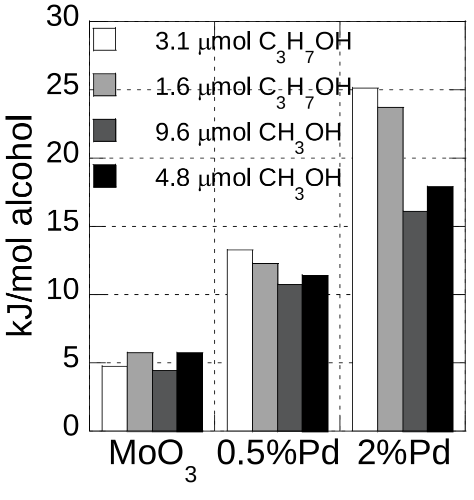


Fig. 1. The heats of alcohol - Pd/MoO_3

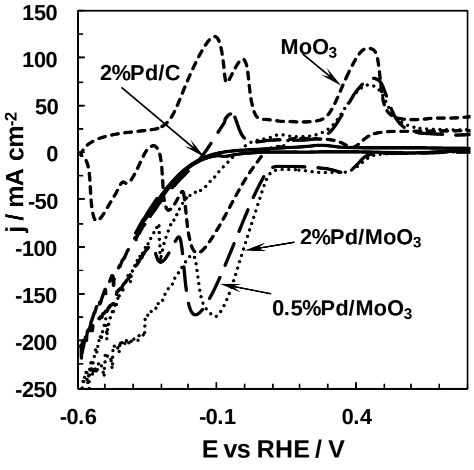


Fig. 2. Evolution of hydrogen on Pd/MoO_3.

In the catalytic processes of H_2 evolution from ethanol (200 – 550 °C), the MoO_3 and MoO_2 oxides were active only above 350°C. The H_2 evolution on the 2%Pd/MoO_3 started from 200°C, and its activity increased with temperature, beyond that of 2%Pd/MoO_2 or of the pure oxides. A significant enhancement of electrolytic H_2 evolution (electrolysis of water in fuel cells) due to the presence of MoO_3 has been manifested by comparing the activity of Pd/MoO_3 to that of Pd/C. The activity (potential, current density) depended on the content of Pd (0.5 – 2 weight % Pd). The CV method revealed, that the bronze formation hampered the H_2 evolution only in the 0.5%Pd/MoO_3. The effect decreased with Pd content, and the performance of the 2%Pd/MoO_3 was optimal, due to modifying effect of the MoO_3 matrix (observed in XPS) with a low degree of Pd aggregation. The obtained results may be used in designing electrodes for hydrogen fuel cells.

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

(Professor Wiesław Łasocha, Dariusz Mucha PhD, Barbara Bożek MSc)

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

Among the research conducted in 2016 worth of mentioning are:

- We conducted research on obtaining of new compounds from the group of peroxo- molybdates with protonated methylpyrydines.
- We investigated new compounds of molybdenum formed by reactions with amino-derivatives of naphthalene.
- We have studied the properties and catalytic activity of selected compounds of molybdenum (including transition metals) in the reactions of catalytic oxidation of cyclooctane with O_2.

Description of the most important results:

- We have obtained and investigated new peroxomolybdates of methylpyridine. As a result of the study was obtained 2 new peroxocompounds of the type of single and seven-nuclear peroxomolybdate clusters.
- We obtaied and investigated new octamolybdetes of 1-aminonaphthalene and 2-aminonaphthalene.

These compounds were subjects of structural and thermal stability studies. In these compounds there are isolated octamolybdate clusters surrounded by large organic cations. During the heat treatment, both the compounds exhibit thermal stability up to 150°C, and then undergo amorphization. In temperatures of approx. 400°C molybdenum oxide MoO_3 is produced. Both compounds crystallize in a triclinic system. In contrast to the compounds obtained from solutions acidified with HCl or CH_3COOH, the reactions carried out in aqueous solutions lead to a octamolybdates, wherein in addition to the organic cations there are neutral molecules of organic amines.

- We have tested catalytic activity and thermal stability of transition metal trimolybdates. Structural investigations of nickel trimolybdate after catalytic reaction were performed.

The use of the obtained results: A part of monophasic chemical compounds was used in the testing of catalytic activity in reactions of catalytic oxidation of hydrocarbons, such as cyclooctane and limonene, using air and O_2 gas. Transition metal polymolybdates proved to be active in the reactions of cyclooctane oxidation. The oxidation reactions using such catalysts produce as a results also suberic acid. By back titration method, its amount was estimated as 15-20% of obtained reaction products.

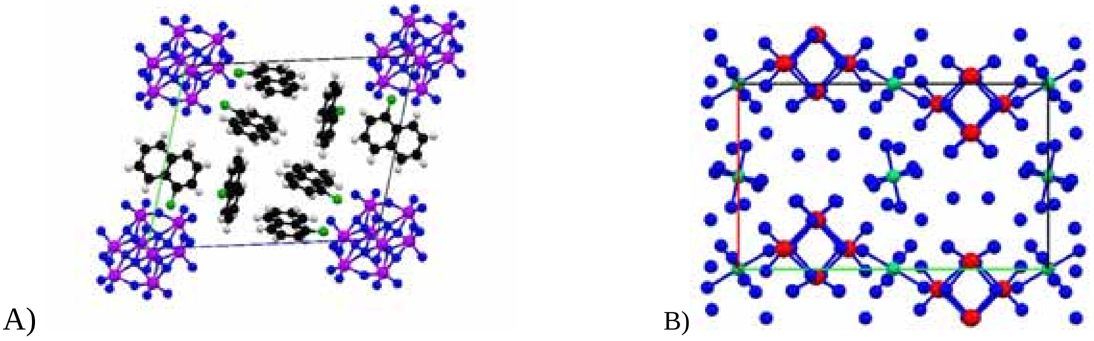

A) B)

Figure 1. Examples of new polioxomolybdates obtained in this study. A) unit cell of 1-aminonaphthalene β-octamolybdate, B) a structure of hydrated nickel trimolybdate. Colours: red, green, black, grey, blue and bluish represent: molybdenum, nitrogen, carbon, hydrogen, oxygen and nickel.

Catalytic oxide systems for production high value added products – components of fuels and plastics

(Dorota Rutkowska-Żbik DSc, Tadeusz Machej PhD, Michał Śliwa PhD, Katarzyna Samson PhD, Małgorzata Ruggiero-Mikołajczyk PhD, Łukasz Mokrzycki PhD, Wojciech Rojek MSc)

"Catalysis in the Protection of Natural Environment" group focuses its activities on the design of active and selective catalysts, which would enable to produce high value-added products from bio-mass. The aim of this year research task was to optimize the composition of mixed copper – silver catalysts deposited on oxide-type supports of varying reducibility and acid-base properties, and to study the influence of promoters (mostly Ru and Ce) on their catalytic activity in the hydrogenolysis of glicerol.

Mixed copper-silver catalysts with varying content of Cu and Ag (1, 2, 4, and 6 mmol of metal) per 1g of support (SiO_2, Al_2O_3, TiO_2, and MgO) were synthesised by two methods: wet impregnation and co-precipitation with NaOH. Next, the preliminary ranking of their catalytic activity in the hydrogenolysis of glycerol was established, and the influence of Ce and Ru as promoters was examined for the best performing catalysts. Samples containing 5% of Ru / Ce in 2mmolCu/MgO (2Cu/MgO), 4Cu/MgO, 2Cu/SiO_2, 4Cu/SiO_2 were obtained by wet impregnation and co-precipitation. All catalysts were preliminary characterised by the following physico-chemical methods: XRD for the phase compositions, BET for the specific surfaces, and H_2-TPR for the reducibility of the prepared samples. Next, the catalysts were tested in the hydrogenolysis of glycerol by mixing 2g of catalyst in 30 cm^3 50%vol. solution of glycerol in water in 100 cm^3 batch-type reactor in 200°C, t = 24h, pH_2 = 40atm, under mixing at a rate of 400 r.p.m. after pre-treatment consisting of purging of the sample by nitrogen, and pre-reduction in hydrogen atmosphere (200°C, t = 2h, pH_2 = 5atm, 100 r.p.m.). Glycerol conversion and selectivity to diols were monitored by HP GC with FID detector.

Our results indicate that the presence of silver does not ameliorate catalytic activity of the mixed metal catalysts. The best catalytic activity was found for samples containing 2 and 4 mmol Cu / 1g of support. Among the studied supports, catalysts with MgO showed the highest performance, but these samples were the most difficult for recycling. Catalysts deposited on SiO_2, although less active, lacked this disadvantage. Therefore the following catalysts were selected for further studies: 2Cu/MgO, 4Cu/MgO, 2Cu/SiO_2, 4Cu/SiO_2. The presence of promoters resulted in increasing of catalytic activity of the studied samples. The measured glycerol conversion reached 74–100% and 5-28%, with selectivity to 1,2-propanediol falling in the ranges 59-77% and 4-24% for samples with MgO and SiO_2, respectively. The yield to 1,3-propanediol reached 5-11% for catalysts based on MgO, whereas this product was not detected when the reaction was catalysed by samples with SiO_2. 2Cu/MgO with 5% Ru was found the most promising catalyst (100% conversion of glycerol, 77% selectivity to 1,2-propanediol).

The performed studies aimed at the optimization of the composition and the properties of the catalyst, which will be selective towards valuable products of glicerol conversion, which are diols: 1,2-propanediol and 1,3-propanediol. These compounds are used as monomers in the production of numerous polymers incl. polyesters, polyethers, and polyurethanes.

Hydrogenation of acetol in the presence of metallic catalysts supported on micro- and mesoporous carriers

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

The aim of the research was to investigate the possibility of recycling of heterogeneous ruthenium catalysts supported on SBA-15 mesoporous silica in the hydrogenation of acetol to 1,2-propanediol (Fig. 1). 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.

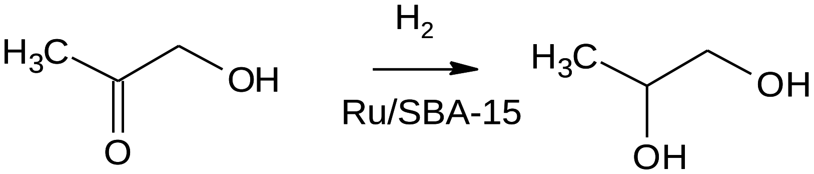


Figure 1. Scheme of acetol hydrogenation

Tests were carried out over an SBA-15 supported catalyst, containing 2 wt.% ruthenium (2 wt.% Ru/SBA-15), and a reference sample, containing 2 wt.% ruthenium supported on high surface area silica (2 wt.% Ru/SiO_2). The test reaction was carried out under mild conditions of pressure and temperature (1 bar H_2 and room temperature); water was used as solvent. 1,2-propanediol was the only reaction product. In the first catalytic run the 2 wt.% Ru/SBA-15 catalyst reached 95% acetol conversion within 4 h. Recovered and reused lost some activity, and the conversion fell to 60%. However, when the recovered catalyst was subjected to re-reducing treatment with $NaBH_4$ solution prior to the second run, the original high catalytic activity was restored. Initial acetol conversion over the reference catalyst was 36%. The reused catalyst gave only 11% conversion and its performance remained poor even after re-reducing treatment with $NaBH_4$ solution.

XPS study showed that the catalysts deactivation resulted from the partial reoxidation of ruthenium surface coupled with chemisorption of the oxidation products. For the 2 wt.% Ru/SBA-15 catalyst, both effects could be reversed by re-reduction with $NaBH_4$ solution. Such a treatment had no positive outcome in the case of the 2 wt.% Ru/SiO_2 reference. Results of TPR analysis indicated that the difference between the two catalysts could be related to the much poorer reducibility of the ruthenium active phase in 2 wt.% Ru/SiO_2 sample.

The obtained results are the starting point for development of a recyclable heterogeneous catalyst for liquid phase hydrogenation, exhibiting high catalytic activity under mild conditions of pressure and temperature.

Heteropolycompounds 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)

Research aimed at synthesis and characterization of physico-chemical and catalytic properties of cobalt salts of $H_3PMo_{12}O_{40}$ (H_3PMo) i $H_3PW_{12}O_{40}$ (H_3PW) heteropolyacids. Salts with different degree of Co substitution were referred to as $H_{3-2x}Co_xPMo$ and $H_{3-2x}Co_xPW$, where x=0.5, 1, 1.5. The synthesized materials were employed as catalysts in the Baeyer-Villiger oxidation of cylohexanone to ε-caprolactone with molecular oxygen in the presence of sacrificial aldehyde (Fig. 1). ε-caprolactone is a substrate for the synthesis of biodegradable polymer for medical applications.

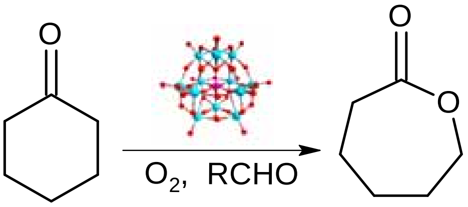


Figure 1. Oxidation of cyclohexane to caprolactone

Synthesized materials were analyzed with FTIR, UV-Vis, thermal analysis DSC and cyclic voltammetry. All studied heteropolycompounds showed catalytic activity in oxidation of cyclohexanone. The unsubstituted H_3PMo was more active than the unsubstituted H_3PW. Insertion of Co in cationic positions improved the catalytic properties, and all tungstophosphate salts were more active than their molybdophasphate counterparts. In both series the salts containing one cobalt cation per Keggin unit were the most active ones. For the $H_{3-2x}Co_xPMo$ system the following order of catalytic activity was observed:

$$HCoPMo > Co_{1.5}PMo > H_2Co_{0.5}PMo > H_3PMo$$

Catalytic activity of $H_{3-2x}Co_xPW$ compounds changed in the following manner:

$$HCoPW > H_2Co_{0.5}PW > Co_{1.5}PW > H_3PW$$

The HCoPW catalyst was most active of all synthesized heteropolycompounds. The data indicate that both the redox and the acid properties of the catalysts are factors influencing their catalytic performance.

Obtained results form basis for undertaking a detailed study on the role of the acid and the redox function of heteropolycatalysts in oxidation of cylohexanone to ε-caprolactone with molecular oxygen.

Selective hydrogenation of benzene on metal catalysts

(Professor Ewa Serwicka-Bahranowska, Jan Połtowicz PhD, Katarzyna Pamin PhD, Dorota Duraczyńska PhD, Alicja Michalik-Zym PhD, Małgorzata Zimowska PhD mgr inż. Bogna D. Napruszewska MSc)

Research aimed at determining the activity and selectivity of a series of supported ruthenium catalysts in reaction of liquid phase benzene hydrogenation. The reaction involves two consecutive steps, and yields cyclohexane via an intermediate formation of cyclohexene (Fig. 1). Over majority of typical metal catalysts the reaction leads to the formation of cyclohexane. However, it has been shown that the use of ruthenium black catalyst allows one to enhance selectivity to the cyclohexene intermediate, which is the more desired product. In this work the influence of different supports and supporting procedures on the catalytic performance of the active ruthenium phase were studied.

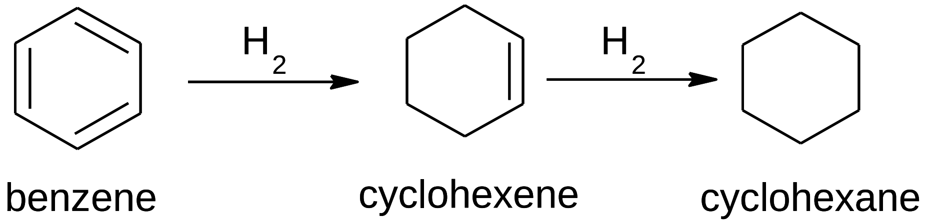


Figure 1. Scheme of benzene hydrogenation

Hydrogenation of benzene was carried out in a 1000 ml titanium reactor, under 50 bar pressure, at temperature 150°C. The studied catalysts, each containing approximately 2 wt% of ruthenium, included Ru/SBA-15, obtained by impregnation of mesoporous SBA-15 silica, Ru/SBA-15(AEPTS) obtained by grafting ruthenium on SBA-15 functionalized with aminoethylaminopropyltriethoxylsilane (AEAPTS), and Ru/PDDA-mt prepared by cation exchange with organic derivative of montmorillonite obtained by intercalation of clay with poly(-diallyl dimethyl ammonium) cations (PDDA). In all cases an aqueous solution of $RuCl_3$ was used as the ruthenium-containing reagent. Catalytic experiments with hydrogenation of benzene showed that the yield of cyclohexene depended strongly on the type of the catalyst and changed in the order Ru/SBA-15 > Ru/PDDA-mt > Ru/SBA-15(AEPTS). Results of SEM and TEM analysis suggest that the degree of Ru dispersion may play a decisive role in determining the catalytic properties of investigated materials. In Ru/SBA-15 catalysts the size of Ru nanoparticles is 5-8 nm, in Ru/PDDA-mt they are not bigger than 2-3 nm, and in Ru/SBA-15(AEPTS) the grafted ruthenium species are too small to be detected by TEM analysis.

These results are the basis for further work aimed at optimization of the metal component dispersion.

Photocatalytic activity of layered mineral/transition metal oxide composites

(Professor Ewa Serwicka-Bahranowska, Professor Piotr Warszyński, Professor Paweł Nowak, Grzegorz Mordarski PhD, Alicja Michalik-Zym PhD, dr Elżbieta Bielańska PhD)

The study aimed at synthesis, physico-chemical characterization and comparison of the photocatalytic properties of TiO_2/montmorillonite composites doped with transition metal ions.

TiO_2-montmorillonite composites were synthesized from sodium form of montmorillonite, using the so-called pillaring procedure, in which the interlayer Na^+ cations are exchanged for large titanium oligocations. After calcination at 450°C the Ti oligocations transform into nanoclusters of TiO_2 (pillars), which bond permanently the neighboring layers. The resulting composite, referred to as Ti-PILC, was doped with 1 wt.% of chromium (Cr-Ti-PILC), iron (Fe-Ti-PILC), or palladium (Pd-Ti-PILC), by means of impregnation with solutions of appropriate salts followed by calcination. The resulting materials were characterized with XRD, XRF, SEM, Raman spectroscopy and N_2 adsorption/desorption. Synthesized composites were tested in the photocatalytic degradation of methyl orange, a model organic substance, upon illumination with UV and artificial solar light (ASL).

The Ti-PILC composite was characterized by a relatively well ordered structure, with interlayer spacing of ca. 2.5 nm and specific surface area of 379 m^2/g. Doping had no significant impact on the textural parameters of Ti-PILC matrix. TiO_2 nanoparticles displayed the structure of anatase. Investigation of photocatalytic decomposition of methyl orange demonstrated that upon 4 h illumination with UV light concentration of the colorant fell to ca. 20% of the initial value (Fig. 1). Experiments with Cr-Ti-PILC and Fe-Ti-PILC samples showed that doping with chromium and iron almost completely destroys photocatalytic properties of the composites. In contrast, in the case of Pd-Ti-PILC, a rapid decomposition of methyl orange was observed even before the start of the illumination and, upon switching the UV source on, an almost complete decoloration of the solution occurred within 2 h.

The obtained results form basis for further work on the photocatalytic properties of clays pillared with transition metal oxides.

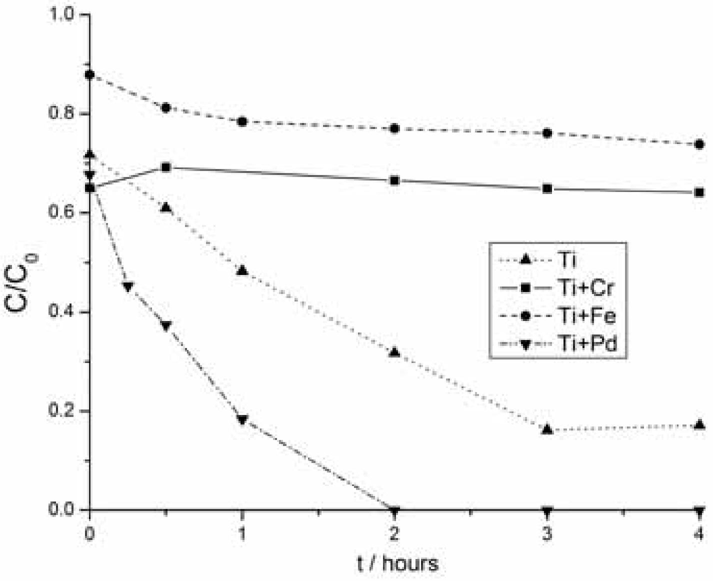


Figure 1. Photocatalytic decomposition of methyl orange over Ti-PILC and Me-Ti-PILC (Me=Cr,Fe,Pd) composites. Initial concentration of methyl orange $1x10^{-5}$ mol·dm^{-3}, concentration of the photocatalyst suspension 1000 mg·dm^{-3}. Intensity of UV irradiation 48.8 mW·cm^{-2} (Xenon lamp).

New composite cathode materials for high temperature fuel cells

(Michał Mosiałek DSc, Grzegorz Mordarski PhD, Professor Paweł Nowak, Aneta Krawczyk MSc, Elżbieta Bielańska PhD)

Differences in thermal expansion coefficients (TECs) of different components of a solid oxide fuel cell (SOFC) may lead to the appearance of mechanical tensions during the temperature changes and result in poor thermal shock stability of the cell. It limits significantly the choice of the materials for the construction of SOFCs, what is especially important in the case of the cathode, because the main energetic losses in SOFC are caused by the high overpotential of the cathodic reaction. Recently that issue becomes more and more important due to the tendency of lowering the operating temperature of the SOFCs. Unfortunately, the known cathode materials with high catalytic activity in the oxygen reduction reaction (ORR) and sufficiently high electric conductivity reveal also high TEC, much higher than electrolyte materials appropriate for this temperature range. The goal of this work was to develop the cathode materials with high catalytic activity in ORR and showing TEC comparable to the electrolyte materials presently used in the construction of SOFCs for the work in the intermediate temperature range.

The research was conducted in two directions. In the first one two different materials were either mixed to form a composite, or arranged in spatially distributed layers. $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) with moderate catalytic activity in ORR, but high electric conductivity and relative low TEC as well as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) characterized by the high catalytic activity in ORR, but low electrical conductivity and high TEC were applied. The second method relied on preparing a matrix of the cathode by sintering $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ cathode material, which is characterized by the low catalytic activity in the ORR and moderate electric conductivity but TEC very similar to TEC of the electrolyte. That matrix was activated by the deposition of an active phase on the internal surface of the matrix by infiltration of the solutions of a catalytically active phase in the matrix and sintering. In both cases the samaria-doped ceria (SDC) was used as the electrolyte. Obtained cathodic half-cells were tested by electrochemical impedance spectroscopy in the temperature range 500-700 °C and the oxygen partial pressure range 0.001-1.0.

The composite cathodes obtained by mixing LSCF and BSCF powders in 1:1 wt. ratio then screen-printing and sintering reveal the lowest polarization resistance among first series of cathodes. These cathodes reveal much better thermal shock stability than BSCF cathode. The obtained cathode material revealed also the lowest activation energy of the polarization resistance (see Table 1). Cathode materials obtained by the second method (incorporation of the second active cathode material into LSF structure) did not reveal enough good properties.

Table 1.

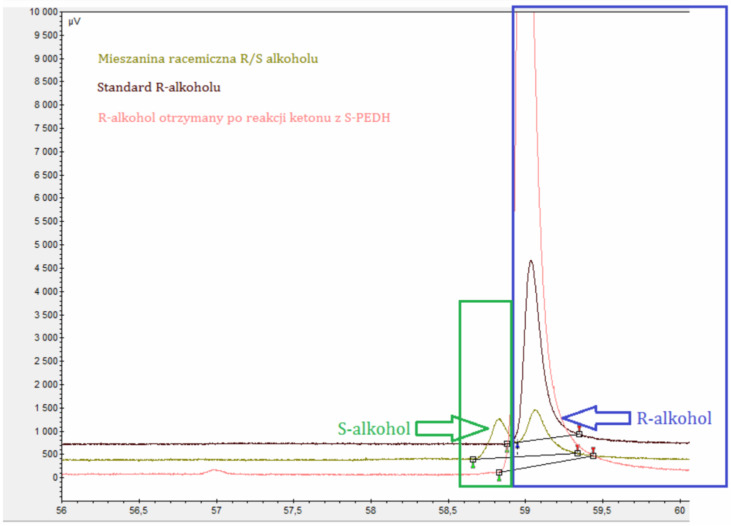
Polarization resistance Ω cm^2	Temperature	LSCF	BSCF	LSCF+BSCF
	700 °C	2.1	14	0.46
	600 °C	18	76	2.8
Activation energy in the range 600-700 °C / kJ mol^{-1}		72	51	33.5

Described LSCF-BSCF composite cathode material can be used in SOFCs.

Enzymatic redox processes

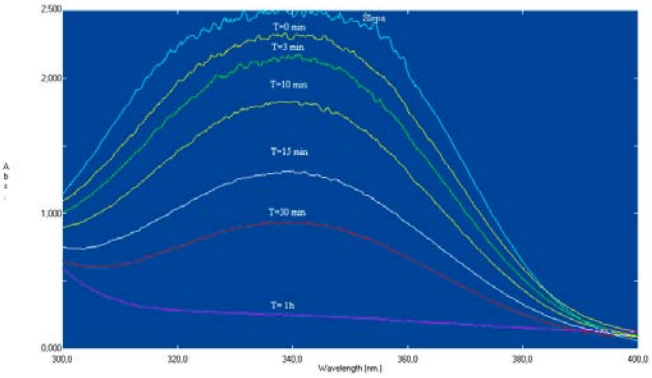
(Maciej Guzik PhD, Assoc. Professor Maciej Szaleniec, Assoc. Professor Tomasz Borowski)

Research topic covers issues related to the oxidation and reduction reactions of compounds of bacterial origin in order to change their optical configuration. The motivation for conducting this research is a fact that a change in the optical configuration may enhance biological properties of these compounds. The parental compounds are derived from bacterial polyesters after their depolymerisation and represent a class of hydroxyacids with absolute R optical configuration of the hydroxyl group. The project aim was to employ NADH-dependent dehydrogenases for converting the R-alcohols first to oxo-compounds and then to analogue S-alcohols.



The biopolymer was obtained via bacterial fermentation with *Pseudomonas putida* strain. It was subsequently depolymerised to obtain a mixture of monomers that contained specified proportions of aliphatic hydroxyacids. Several trails were undertaken in order to obtain oxo-compounds via enzymatic reactions that employed NADH-dependent phenylethanol dehydrogenase (S-PEDH). Despite numerous efforts to obtain oxo-compounds via this route, we were not able to achieve our goal. Therefore the enzymatic approach was changed to a chemical oxidation process (Dess-Martin reagent). Having the oxo-compound the reverse reaction with S-PEDH was verified and the R-alcohol was obtained. This was verified with aim of gas chromatography equipped with a chiral column (Scheme 1). In order to obtain an S-alcohol we have employed an analogue enzyme (NADH-dependent phenylethanol dehydrogenase (R-PEDH)). It was possible to obtain S-alcohol when the oxo-compound and R-PEDH were used in the enzymatic process.

A simple chemo-enzymatic process for reverting optical configuration of hydroxyacids has been developed.



The future steps will include further process optimisation in order to achieve reasonable reactor reaction conditions.

Physics and Chemistry of Surfaces and Nanostructures – Experiment and Theory

Physical and chemical properties of heteropolycompounds and their catalytic activity in conversion of alcohols. DFT calculations vs. experiment

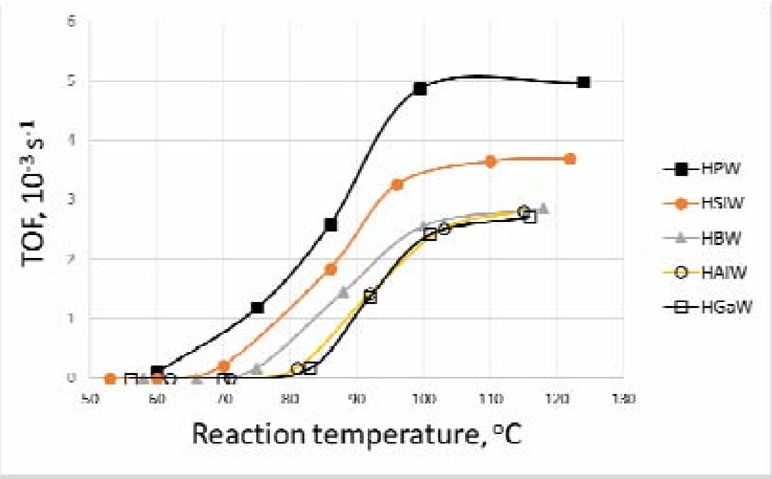
(Professor Małgorzata Witko, Assoc. Professor Renata Tokarz-Sobieraj, Robert Gryboś PhD, Urszula Filek PhD, Anna Micek-Ilnicka DSc)

The main goal of experimental and theoretical studies was description of electronic structure as well as physical, chemical and catalytic properties of heteropolycompounds, possessing the Keggin anion structure, with selected group 13-15 elements (P, Si, B, Al, Ga,) as central cations.

Following the literature, three heteropolyacids, with the Keggin anion structure $[XW_{12}O_{40}]^{5-}$, and different central cations (group 13 elements: B, Al, Ga) were synthesized. Their physico-chemical and catalytic properties were compared with properties of commercially available $H_3PW_{12}O_{40}$ (HPW) and $H_4SiW_{12}O_{40}$ (HSiW) heteropolyacids. All compounds have tungsten as addenda atoms. Results of XRD measurements of the obtained samples are typical for Keggin anions. Thermal stability, established by derivatography, was as follows: 434 ^{o}C $H_5BW_{12}O_{40}$ (HBW), 474 ^{o}C $H_5AlW_{12}O_{40}$ (HAlW) and 440 ^{o}C $H_5GaW_{12}O_{40}$ (HGaW). IR spectra of solid heteropolycompounds show structural stretching vibrations characteristic to Keggin anions at the following frequencies for $[BW_{12}O_{40}]^{5-}$: 1002, 959, 917, 807 cm^{-1}, for $[AlW_{12}O_{40}]^{5-}$: 967, 907, 798, 758 cm^{-1} and for $[GaW_{12}O_{40}]^{5-}$: 967, 900, 762, 734 cm^{-1}. For all compounds, in parallel to experimental studies, quantum-chemical simulations were carried out. Calculations were done using the DFT method, employing both the cluster geometrical model (Keggin anion with/without H^+) and the periodic model (optimization of the crystal unit cell).

For each system, parameters of the electronic structure (i.e. population analysis of the active centres, character of the frontier orbitals, DOS) were obtained. Theoretical IR spectra were compared to experiment. Position of the frontier orbitals was used as a measure of redox properties, resulting in the following sequence: P (-4.33) < Si (-3.95) < Ga (-3.61) < Al (-3.59) < B (-3.53). Acidic properties were approximated by energies of creation of H^+ cations from $H_5O_2^+$ and/or OH^- groups (created on different oxygen centres).

Catalytic properties were tested in a reaction of conversion of ethyl and isopropyl alcohol, in a gas phase, in temperature ranges 70-290 ^{o}C and 50-130 ^{o}C, respectively. Sample weights were 0.1 g, reagent flow was 35 ml/min, WHSV - 1,9 h^{-1}. Ethylene, diethyl ether and propylene, di-isopropyl ether were the products of these reactions.



Dependence of TOF on the reaction temperature on heteropolyacids (figure) with different central cations allowed for setting the following sequence of catalytic activity: HPW>HSiW>HBW>HGaW≥HAlW, which corresponds well with theoretical predictions.

Determination of catalytic properties of $H_5BW_{12}O_{40}$, $H_5AlW_{12}O_{40}$ and $H_5GaW_{12}O_{40}$ contributes to the fundamental knowledge about chemistry of heteropolyacids

Materials with variable porous structures: synthesis, physicochemical and catalytic properties, spectroscopic and quantum-chemicals studies

(Professor Ewa Brocławik, Professor Bogdan Sulikowski)

Quantum chemical modeling was aimed at the characterization of the acidity of OH groups in modified USY zeolites to supplement IR experiment. The other task was to model donor properties of ammonia-modified Co(II) sites in zeolites; here the dependence of the shift of NO stretching frequencies upon Co(II) spin state, the number of ammonia co-ligands and zeolite type was the main goal. 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.

Stretching frequencies of NO probe interacting with ammonia-modified Co(II) sites in Chabasite were calculated for realistic periodic models of CHA zeolite. Periodic DFT methods and ab-initio Molecular Dynamics were invoked. In addition, the shift upon CO probe of stretching frequencies of acidic OH groups in modified USY zeolite were calculated for cluster and periodic models. Starting from NaY, a series of samples was prepared by applying various methods of modification: ion exchange with ammonium ions, calcination at broad range of temperatures and extraction with HCl solutions. Some samples were also modified by solid-state ion exchange of additional 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. Experiments aimed at generation of secondary mesopore system were also performed. Physicochemical characteristics of modified Y zeolites were correlated with the catalytic properties in isomerization of α-pinene.

Quantum chemical modeling successfully widened the interpretation of IR spectra of NO probe for donor properties of ammonia-modified Co(II) sites; here, the dependence on the zeolite type was also addressed. Preliminary results for the shift of OH stretching frequencies upon the interaction with CO probe correlated well with the experiment and indicated the preference of The C-end bonding over O-end bonding for CO. Solid-state NMR studies of 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 aluminium sites can be clearly resolved. Finally, the subtle changes in aluminium content in the pristine and dealuminated mesolite samples were successfully monitored.

The use of periodic models and ab-initio molecular dynamics opened new window for theoretical interpretation of the dependence of the properties of active sites in zeolites upon the framework type.

Structural, electron and dynamics properties of surface and nanostructures studied with microscopic and spectroscopic techniques in the ultra-high vacuum conditions

(Professor Józef Korecki, Assoc. Professor Nika Spiridis, Jacek Gurgul DSc, Robert Socha PhD, Dorota Wilgocka-Ślęzak PhD, Piotr Mazalski PhD, Ewa Madej PhD, Kinga Freindl PhD, Barbara Wolanin MSc Joanna Wojas MSc, Natalia Kwiatek MSc)

The aim of this study was to grow epitaxial heterostructures and nanostructures with specific physicochemical properties. The research was focused on both structural aspects as well as on electronic and magnetic properties. In particular, engineering of the magnetic anisotropy was carried out by selection of a proper composition of the heterostructures that resulted in favorable relationships between the surface or/and interface anisotropy and the volume anisotropy. In the studied systems, reorientation of the spontaneous magnetization (so called spin reorientation transition – SRT) occurs both in-plane and between an in-plane and out-of-plane directions. The SRT's were observed in metallic two- and multi-layer systems, as well as in metal-oxide heterostructures. The latter systems were also studied in view of their structural and electronic properties, beneficial in applications as model catalysts and their polycrystalline counterparts.

The magnetic anisotropy was studied in epitaxial Co/Fe(110) bilayers deposited on a W(110) substrate. In this system the in-plane SRT was observed for a metastable bcc-Co phase. The magnetic surface anisotropy in the Co/Fe(110) bilayers exhibited a strong non-monotonous dependence on Co coverage in the Co thickness range from a submonolayer to 2 nm. Magneto-optical studies revealed a sharp maximum of the magnetic surface anisotropy, 2.44mJ/m^2, at a Co thickness of 0.5 nm. This giant interfacial magnetic anisotropy allowed a small fraction of a Co monolayer to reorient the magnetization of the bulk-like Fe film. We conclude that 1 ML and 2 ML bcc Co(110) exhibited in-plane magnetic anisotropy with a [1-10] easy axis.

Another SRT type was observed in ultrathin Fe layers in the MgO(001)/Cr/Fe/MgO epitaxial system, in which an optimized post-preparation treatment induced SRT from an in-plane to the normal direction, in the Fe layers thinner than 1 nm. The influence of the interface atomic structure on the SRT was studied using conversion electron Mössbauer spectroscopy. It was found that the SRT is caused by the segregation of Cr atoms to Fe/MgO interface.

In Fe/MgO/Fe and MgO/Fe/FeO systems the magnetic properties resulting from dipole and indirect exchange interactions were studied. For the Fe/MgO/Fe tri-layers, being the archetype of the magnetoresistive tunnel junction, the antiferromagnetic interlayer exchange coupling (IEC) was detected for the MgO spacers as thin as single atomic layers. The IEC was substantially modified by the nanostructurization of the tunnel junctions, and a dependence of the dipole coupling on the size of junction was determined. In view of the important role of the chemical structure at the Fe/MgO interface on the magnetic properties, a detailed study of the interfacial FeO formation was carried out.

The atomic and electronic structure of the metal-oxide interface was studied during nucleation and initial growth of Fe on a (1x1) rutile-TiO_2(110) surface as a function of coverage and annealing temperature using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The deposition of 0.03 ML - 0.3 ML of Fe resulted in the growth of one-, two- and three-dimensional iron clusters. Surface annealing at 373 K and 473 K resulted in a moderate sintering of the Fe clusters, whereas annealing at higher temperatures led to Fe incorporation into the substrate. The analysis of the Fe 2p core excitations showed that even after room temperature processes, iron was partially oxidized at the iron-oxide interface.

Using low energy electron microscopy the different structures of oxygen chemisorbed on the Fe(110) surface were verified and their structural domain patterns were described.

Studies of the influence of microscopic and physicochemical parameters on the ability to control the properties of systems with biomedical importance

(Professor Tomasz Pańczyk, Assoc. ProfessorWojciech 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 to control the phenomena occurring in systems with biomedical importance. The studies were devoted to the design of a system, based on the structure of carbon nanotubes, which in neutral (physiological pH) is able to lock drug molecules but at the acidic pH of tumor microenvironment it selectively releases the drug molecules to the bulk. Moreover, we also focused on the influence of the vicinity type of pyranose residue (monomer, alkylated monomer, residue in a chain, etc.) on the elasticity of this residue and on the determination of the degree of hydration of PAMAM dendrimers on the silica surface. Understanding the dendrimer-solid support interaction is of great importance for dendrimer-based drug delivery system designing.

The above aims have been achieved by the molecular dynamics analysis of the co-adsorption of drug molecules and various dyes molecules on the surface and in the inner cavity of carbon nanotubes. We studied the mechanism of changes of the adsorbed phase structure as a function of pH and determined the free energy barriers against the desorption of drug and dyes molecules. By applying a series of metadynamics-based simulations, the ring-inversion free energies were determined for all aldohexoses of the D series, as well as for the corresponding derivatives (alkylated monomers and homodi- or trimers). The kinetics of dendrimer deposition and the maximum surface coverage on the silica surface were determined using the quartz crystal microbalance with dissipation monitoring (QCM-D) and multi-parametric surface plasmon resonance (MP-SPR) methods: the kinetics depends on the ionic strength and pH of solutions.

The most essential results coming from the performed studies were following: we showed that the creation of a drug carrier which is able to selectively release the drug molecules within the acidic microenvironment of tumor tissue is possible. The key factor is the application of suitably chosen dye molecule which forms the co-adsorbed phase in the carbon nanotube interior. Among many probed dyes molecules only two have revealed the requested properties. Further, it was shown that hexopyranose functionalization may have a diverse effect on the ring rigidity: alkylation may lead to both systematic decrease (α anomers) and increase (β anomers) of the ring flexibility. Conversely, glycosylation influences the ring-inversion properties in a non-systematic fashion, showing decorrelation of the ring-inversion free energies with those corresponding to monomers. The comparison of QCM-D and MP-SPR allowed us to state that the dendrimer film contains approximately 70% water. These results indicate that 6th generation PAMAM dendrimers form very hydrated films on silica surfaces. In this case the number of water molecules associated per dendrimer molecule varied from 10 450 to 9 200. The hydration of dendrimer films seems to be a crucial aspect of their implementation. This data confirmed that dendrimers are very promising candidates for many biological applications.

The systems composed of carbon nanotubes/dyes/drug or PAMAM dendrimers reveal useful properties as drug delivery systems. They offer ability of triggering drug release in response to the pH change. Practical realization of such functional composite systems needs, however, further studies. Conformational rearrangements involving the hexopyranose ring are essential for carbohydrate-protein interactions and require consideration when applying the computational methodologies aimed at predicting the 3D carbohydrate structure.

Nanostructures of Soft Matter

Topology and electrokinetic properties of protein monolayers on the solid substrate/electrolyte interfaces. Determining conformations of blood serum proteins by streaming potential measurements and nanoparticle and polymeric microparticle deposition

(Professor Zbigniew Adamczyk, Jakub Barbasz DSc, Marta Kujda PhD, Aneta Michna PhD, Maria Morga PhD, Małgorzata Nattich-Rak PhD, Monika Wasilewska PhD)

Streaming potential measurements and controlled deposition of nano- and microparticles was applied in order to characterize human serum albumin (HSA) monolayers on mica. 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 acquired by *in situ* streaming potential measurements. In this way the mean-field zeta potential of monolayers was determined. 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 for various ionic strength and pHs. It was confirmed that for higher ionic strength, the microparticle coverage abruptly increases with HSA monolayer density. In this way, a unique functional relationship between the particle coverage and the HSA surface concentration was formulated. Based on this relationship, a robust method for quantitatively determining the coverage of albumin under *in situ* conditions for the range inaccessible to conventional methods can be developed. It was also concluded that these 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.

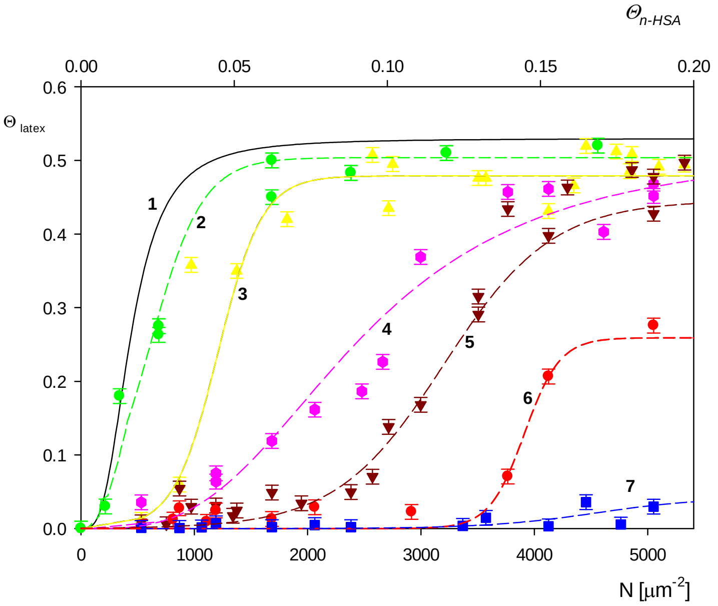


Figure 1. The microparticle coverage vs. the HSA surface concentration N_a (lower horizontal axis) or the normalized coverage (upper horizontal axis) for various ionic strengths (HSA monolayer adsorption was carried out at pH 3.5, and microparticle deposition at pH 5.5, bulk latex concentration 0.5% adsorption time 24 hours). The solid line 1 shows the limiting theoretical results derived from the fluctuation theory for microparticle deposition at surfaces having a positive charge. The points denote the experimental results obtained by AFM and optical microscopy for: (●), 0.15 M; (●), 5×10^{-2} M; (●), 4×10^{-2} M; (●) 3×10^{-2} M, (●), 2×10^{-2} M (●)10^{-2} M.. The dashed lines shows the interpolations of experimental data.

Determination of mechanisms of synthesis, structure, and transport parameters of supported colloidal particle multilayers

(Assoc. Professor Paweł Weroński, Jakub Barbasz DSc, Piotr Batys PhD)

Multilayer adsorption of colloidal particle at solid-liquid interface leads to a spontaneous formation of porous thin film that has a significant effect on ion transport from the bulk solution to the adsorption surface. The main aim of our research was in-depth analysis of transport properties of several specific spherical particle multilayers synthesized in layer-by-layer process. We also planned to address two specific research questions. First, can we use colloidal particle multilayers to model the concentration profile of chemical species at the solid-liquid interface? Second, how accurate is our simplified theoretical approach? To address the second question, we planned to compare our theoretical and experimental results.

We used a simple diffusion cell to form colloidal particle multilayers. We produced the films according to the layer-by-layer protocol, using positively and negatively charged, monodisperse, polystyrene latex particles of the diameter 800 nm. We adsorbed the multilayers on the polished surface of gold disk electrodes. During the adsorption experiments, we maintained a relatively high electrolyte concentration. That let us limit the range of particle-particle electrostatic interaction to a short distance. Next, using cyclic voltammetry and the technique of rotating disk electrode, we quantitatively evaluated transport properties of each multilayer through the determination of the equivalent thickness of stagnant solution layer. After electrochemical measurements, we dried and weighed the films. That let us calculate the mean surface coverage of single layer. Knowing this parameter, we created virtual counterparts of our experimental multilayers. For that, we used a computer program based on the extender model of random sequential adsorption. For each of the virtual multilayers, we then calculated a few parameters and functions such as the mean film thickness, equivalent thickness of stagnant solution layer, spatial distribution of porosity, tortuosity, and diffusivity, as well as the concentration profile of ions diffusing through the film. Finally, from the theoretically calculated diffusivity distribution and experimentally determined equivalent thickness of stagnant solution layer, we also found the mean thickness of the films studied in our experiments.

Results of our research suggest that the spatial distribution of porosity, tortuosity, and diffusivity of spherical particle multilayers exhibit characteristic oscillations dependent on the particle surface coverage and decaying with the increase of distance from the collector. In spite of that, the calculated profile of ion concentration in multilayer is practically linear. This result may seem somewhat counterintuitive. However, this is a consequence of relatively high porosity of the films formed of monodisperse spherical particles. Our finding suggests that concentration profiles in non-uniform porous films can be, in many cases, accurately described using simplified theoretical models. Moreover, to obtain a non-linear concentration profile we need to use polydisperse or multimodal particles that form much less porous structures. Discrepancies between the experimentally and theoretically determined film thickness are small and do not exceed 2%. The good agreement between our theoretical and experimental results supports the validity of our theoretical model.

Results of the research can be useful for the production of functional nanomaterials such as membranes, heterogeneous catalysts, anti-reflective surfaces, or optical elements. The observed essential effect of adsorbed particle polydispersity on multilayer transport parameters suggests that this relationship deserves a closer investigation.

Influence of kinetic energy on kinetics of bubble coalescence at free surface of pure liquids

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

The aim of the research task was to determine an influence of kinetic energy associated with the bubble motion on the bubble coalescence time at surfaces of pure liquids. This is an important problem, encountered in many important processes, where dynamic collisions between liquid/gas interfaces are occurring (phase separations, foam formation, etc.), because probability and kinetics of coalescence play important role in the processes outcome and effectiveness. Investigations, focused on fundamental phenomena determining the stability of liquid films under dynamic conditions, aimed at evaluation of the most important factors influencing probability and number of bounces of single gas bubbles at liquid/gas interface before the coalescence. Unique experimental set-up was build and used to monitor the dynamic phenomena occurring during the bubbles collisions with liquid/gas interfaces being at rest (stagnant) or vibrating with precisely controlled acceleration (frequency and amplitude).

To determine factors influencing the outcome of the bubble collisions with liquid/gas interfaces, the experiments and numerical simulations were performed for liquids of different physicochemical properties (distilled water, silicone oils). Experiments were aimed at determination of the probability of bouncing and numbers of bounces before rupture of the bubbles of various radii (R_b ranging from 0.31-0.87 mm) at liquid/gas interfaces being at rest or oscillating. The coalescence times (t_c), i.e. the time spans between the bubble first collision to the moment of its rupture (coalescence), were determined. Moreover, values of threshold acceleration, related to the liquid/gas interface oscillations, needed to prolong the bubble lifetime (t_c) at the liquid surface were determined, as well.

It was found that the t_c values, which were strongly affected by number of the bubble bounces prior to its rupture at liquid/gas interface, can be significantly prolonged from several dozens of milliseconds, at stagnant surfaces, to several hundreds of milliseconds in the case of vibrating (with controlled frequency) liquid/gas interfaces. This effect is a consequence of re-supplying, by induced oscillations of the liquid/gas interface, the kinetic energy dissipated during the bubble motion and collisions with liquid/gas interface. It caused that deformation of the bouncing bubble during each subsequent collision, which was decreasing at stagnant surface, was practically constant at vibrating liquid/gas interface (see Fig. 1). Constant degree of the bubble shape deformation means that the radius of the liquid film formed during the bubble collisions was also constant and was too large to reach so-called critical thickness of rupture during the collision time. It is worthy to add here that preliminary studies carried out for solid/liquid interface revealed that this effect seems to be universal. Spectacular prolongation of the bubble lifetime was observed even in the case of the bubble collisions with vibrating solid surface of high hydrophobicity.

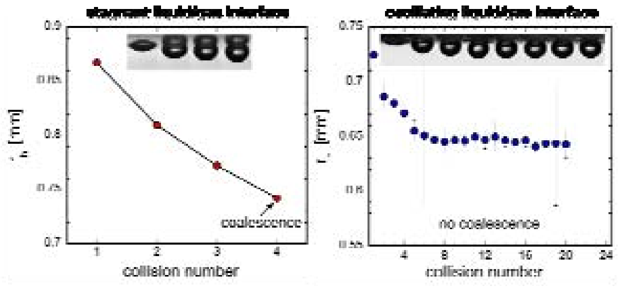


Figure 1. Radius of the bubble (horizontal) during its collisions with stagnant and vibrating liquid/gas interface.

Functional multilayer polyelectrolyte films

(Professor Piotr Warszyński and his team)

The main goal of this task was to develop the scientific methodology for the controlled production of functional multilayer thin films containing various polyelectrolytes, hydrophobic nanoparticles and lipids.

As a part of the research the effect of selected polyelectrolytes used in the form of multilayer cushion for supported lipid bilayers on the formation and properties of obtained bilayers consisting of synthetic phospholipids was determined. Additionally, fluorescent, hydrophobic nanoparticles of sizes in the range of 2.7nm to 5.4nm were embedded into lipid bilayers getting the model nanocomposite films containing substrates of different hydrophobicity. The studies included the characteristics of wettability of the selected polyelectrolyte films by means of the contact angle measured by direct image analysis of the profile of sessile drops. The obtained results were used for the surface free energy (SFE) determination according to Owen's model. The liposome adsorption and the lipid bilayer formation on a surface of polyelectrolyte multilayers were monitored by the quartz crystal microbalance. The incorporation of selected nanoparticles into the lipid bilayer was detected by the emission spectra in the range of 350-500 nm by using the spectrofluorimeter for both: suspensions of liposomes with nanoparticles as well as for supported lipid bilayers containing nanoparticles, deposited on polyelectrolyte films.

One of the most important achievements was the development of the impact of polyelectrolyte films on the formation of supported lipid bilayer on their surface, which allows controlling the fusion of liposomes and the structure of the resulting bilayers in relation to the type of polyion pair used. Another achievement was to develop a method of the formation of functional multilayers with components of varying hydrophobicity. It gives a possibility to incorporate the hydrophobic nanoparticles into hydrophilic films to obtain functional nanocomposites. The formation of polyelectrolyte-lipid films containing nanoparticles inside the alkyl part of lipid bilayer was optimized. It has been shown that the particles in the range of 2.7 to 5.4 nm can be embedded into the bilayers of studied phospholipids. Moreover, the amount of incorporated nanoparticles present in the supported lipid bilayer is large enough to be detected using fluorimetry, which confirms the application potential of studied nanocomposite films.

The results of the work will be used in the development of manufacturing technology of biocompatible and bioactive coatings with controlled permeability. Lipid-polyelectrolyte films can be applied for the construction of biocompatible microcapsules with controlled physicochemical properties used as carriers for hydrophilic or hydrophobic active substances. The ability of the incorporation of additional components as nanoparticles into the structure of microcapsule coating allows achieving the desired functionality, e.g., the use of fluorescent or magnetic particles make possible the applying of such nanocomposite ad theranostic carriers.

Physics and Chemistry in Cultural Heritage Protection

Modelling environmental conditions and energy consumption in buildings preserving cultural heritage assets

(Professor Roman Kozłowski, Leszek Krzemień PhD, Marcin Strojecki PhD)

This research aims at estimating the buffering impact of hygroscopic cultural heritage objects on the indoor microclimate of buildings, in which they are preserved. Different types of buildings of libraries, archives and museums are analysed, each of which is characterized by specific, important for the microclimate control features. These encompass tightness of the building shell characterized by the air exchange rate between indoors and outdoors as well as the usage pattern, in particular the indoor heating strategy. The influence of the collections on the energy consumption in these buildings, depending on the assumed microclimate control scenarios, is assessed as well.

The buffering impact of wooden objects preserved in museum storages was investigated in detail. The research work was divided into two steps in which different numerical simulation tools were used. In the first step, a computer model of water vapour diffusion and adsorption by wooden objects was prepared in the COMSOL Multiphysics software. The modelled objects had a rectangular cuboidal form reproducing wooden sculptures whose surfaces are parallel to the tree trunk axis. Various dimensions of sculptures were taken into account based on statistics of objects kept in storages of the Old Master Department of the National Museum in Krakow housed in the Erazm Ciołek Palace. The rectangular cuboids of 200x250x600, 250x300x1200, 250x450x1450 mm^3 imitated small, medium and large sculptures, respectively. In the modelling, varying coverage of sculptures with paint layers or gilding, impermeable to water vapour, were taken into account. The simulated dynamic changes of the water content were fitted to these measured experimentally for wooden imitations of the sculptures in the form of hollowed-out cylinders, by modifying the water vapour diffusion coefficient in wood. Since WUFI®Plus software, used in the second step of the work to model microclimate and energy consumption in buildings, is able to simulate only one-dimensional heat and moisture transport processes, the cuboidal sculpture models were reduced to the case of one-dimensional water vapour uptake through only one surface, by modifying the object geometry and adjusting again the water vapour diffusion coefficient of wood.

Such one-dimensional model was implemented into WUFI®Plus to simulate microclimate and to assess energy consumption in buildings. Detailed analysis of the impact of large paper collections, kept in the library stores, on the energy consumption was the next research task accomplished in the research period. The energy consumption calculations were carried out for several climate control scenarios based on international museum standards. The calculations have demonstrated that energy necessary to humidify and dehumidify air in the buildings is reduced by at least 21%, for a typical storage space filled in 16% by the paper objects, when compared to an empty room.

The numerical simulation tools developed provide practical information to a broadly-defined conservation community, which allows better strategies for the collection care to be developed. Identifying real indoor microclimate in institutions preserving cultural heritage assets allows advantageous buffering impact of collections on microclimate fluctuations to be assessed on one hand, and the possible preventive measures in case of risks to collections due to excessive water vapour and heat flows to be devised, on the other.

"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: 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, in the next stage of the studies the most promising architectures have been analyzed in terms of the influence of the mutual interactions between the carriers and modulation of the stability of the encapsulated drug molecules. Those mutual interactions or interactions with large macromolecules present in physiological fluid are highly important. We still focused on the pH change from physiological 7.4 to acidic one occurring in tumor tissue as a triggering factor for drug release.

Two types of systems were studied: (i) doublets of carbon nanotubes covalently linked to gold nanoparticles functionalized by hydrazone bonds containing chain molecules and (ii) systems of carbon nanotubes functionalized by biocompatible polymers and targeting factor (folic acid). These systems utilize the effect of blocking of drug molecules by some dyes molecules revealing pK_a values in the range 5 – 7.

The obtained results suggest that blocking of carbon nanotubes by functionalized gold nanoparticles leads to even more promising results. We found that the presence of mutual interactions between carbon nanotubes facilitates the unblocking of carbon nanotube at acidic pH. A spontaneous dissociation of carbons nanotubes and gold nanoparticles has been observed. We, however, found that enhancing the systems sizes leads to stronger and stronger biding of gold nanoparticles to the carbon nanotube and the risk of total blocking of gold nanoparticle becomes very likely for larger systems. That problem has been carefully analyzed and we pointed out how to limit these strong dispersion interactions in the case of actual systems. The most effective approach seems to be the application of different diameters of carbon nanotubes and gold nanoparticles. The calculation results concerning the influence of the functionalization of the carbon nanotube by biocompatible polymer, lead to the conclusion that the presence of polymer layer prevents nanotubes from agglomeration in aqueous media. The presence of polymer layer strongly affects the behavior of drug and dye mixture co-adsorbed in the inner space of the nanotube. The results suggest that the system state is additionally stabilized at the neutral pH. At acidic pH we still observe a spontaneous release of dyes from the nanotube but the drug molecules (doxorubicin) become totally blocked in the nanotube interior by the polymer chains localized at the nanotube tips. Thus, the presence of that polymer layer renders application of that system as pH controlled drug carrier impossible. That problem has been carefully analyzed and possible ways of its workaround in actual applications were provided.

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 endosomes. 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]
(project leader: 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 alkaloids. Structures of these proteins are not known, as are the detailed mechanisms of their catalytic reactions.

In the experimental studies we have tested various conditions of protein expression and optimized protein crystallization conditions. In computational studies we have continued quantum-chemical investigations on factors determining regioselectivity of the reaction and conducted molecular dynamics simulations for enzyme-substrate complexes. Catalytic activity tests have been done for a purified protein with the use of HPLC method and their results confirmed measurable enzymatic activity of the protein.

Expression conditions have been optimized for each of the studied proteins, purification procedures have been determined, as well as, preliminary crystallization conditions.

Obtained results should enable us to obtain good quality crystals and hence crystal structures, which will be used in computational studies for the whole family of the proteins and design of mutations potentially altering substrate specificity of the studied enzymes.

Molecular mechanics force field for structure, dynamics and conformation of carbohydrates involving furanoses

"Sonata Bis" research project NCN 2015/18/E/ST4/00234 [2016-2020]
(project leader: Assoc. Professor Wojciech Płaziński)

Parametrization of the GROMOS force field at the level of tetrahydrofuran molecule

The aim of the study was to develop the parameters to simulate the tetrahydrofuarn (THF) molecule within the united-atoms force field GROMOS. THF molecule includes a saturated five-membered ring containing four carbon atoms and one oxygen atom, which is a characteristic motif of the all furanose molecules. Moreover, unlike pyranose rings, the furanose ring (including THF) has a high degree of flexibility, fairly well characterized by experimental studies (NMR).

Based on the quantum-mechanical calculations, we determined the energy profiles corresponding to changes of the values of individual torsion angles in the ring of THF as well as of the full pseudorotation of the above ring. The next step was adjusting the parameters of the classical force field and validating them by a series of molecular dynamics simulations in the presence of explicit solvent (chloroform, acetonitrile and water). The results were then compared with the literature experimental data (i.e. the vicinal proton-proton NMR coupling constants). We employed both the classic Karplus equation (with the Haasnoota-Altona corrections) and the Wu-Cremer equation (derived for THF). Independently of the solvent, the differences between the experiment and the simulation were not greater than 1 Hz, indicating a very high quality of derived parameters and allowing to use them in further stages of parametrization procedure (hydroxylated and alkylated THF).

"Sonata" Research Projects of the National Science Centre

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

"Sonata" research project NCN 2011/01/D/ST5/04917 [2011-2016]
(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 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 barriers, such as a high cost of energy production and low durability. The aim of the project was to perform investigations of electrocatalysts for the cathodic oxygen reduction reaction (ORR) in fuel cell. It was planned to use Pd, Pt and PdPt nanoparticles as the metal phase. As the support material, hybrid composite composed of conducting polymer – polypyrrole (PPY) and heteropolyacids (HPAs) was applied. In the previous stages of the project, PPY supported PdPt catalysts were investigated. Due to the application of bimetalic system instead of commonly used platinum, a cost of production could be reduced. Moreover, an improvement of catalyst resistance to poisoning by carbon monoxide could be expected.

Studies undertaken in 2016 involved modification of palladium and palladium-platinum catalysts with Keggin, $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and Dawson type HPA, $H_6P_2W_{18}O_{62}$. Polypirol-heteropolyacid, PPY-HPA nanocomposites (prepared in the previous stage of the project by pirol polymerization in the presence of HPAs) were used. PPY-$H_3PMo_{12}O_{40}$ composite was used to synthesize Pd/PPY-$H_3PMo_{12}O_{40}$ catalyst. The materials were characterized by BET, XRD, XPS, FTIR and TEM methods. Pd/PPY-$H_3PMo_{12}O_{40}$ nanohybrid composite ensured both, electron and proton transfer. In addition, electronic properties of Pd nanoparticles were modified as a result of strong electronic interactions with conducting polymer, PPY. This led to the enhanced activity of Pd/PPY-$H_3PMo_{12}O_{40}$ compared with Pd/PPY. Electrocatalytic activity of the prepared materials towards ORR was investigated in 0.5 M H_2SO_4 using rotating ring disc electrode voltammetry. The half-wave potential, $E_{1/2}$ was shifted to higher values. An increase of current density was also observed. Moreover, the amount of undesired H_2O_2 intermediate was lower by ca. 50 % compared with Pd/PPY.

In the last stage of the project, PdPt nanoparticles (with the optimal Pd:Pt atomic ratio of 50:50, estimated in previous studies) were deposited in the matrix of the hybrid composites, PPY-$H_3PMo_{12}O_{40}$, PPY-$H_3PW_{12}O_{40}$ and PPY-$H_6P_2W_{18}O_{62}$. An increase in activity towards ORR was observed only for $Pd_{50}Pt_{50}$/PPY-$H_3PMo_{12}O_{40}$ compared with $Pd_{50}Pt_{50}$/PPY without heteropolyacid. The $E_{1/2}$ was shifted to higher values by ca. 10 mV. The amount of the produced H_2O_2 was preserved and the current density was slightly lowered. The results are consistent with studies for the $Pd_{50}Pt_{50}$/PPY catalyst modified by HPAs introduction to the catalyst suspension (studies undertaken in 2015). Among three tested heteropolyacids, $H_3PMo_{12}O_{40}$ was shown to be the most effective. A role of $H_3PMo_{12}O_{40}$ is related to its properties, such as electronic structure of Keggin anion (associated with molybdenum presence), fast charge transfer dynamic and acidic properties. Additionally, XPS analysis showed that electronic interactions between $H_3PMo_{12}O_{40}$ and metal particles could facilitate the electrode process and affect the activation of PdPt nanoparticles in ORR.

Although conducted studies were fundamental, they could contribute to a better understanding of factors responsible for catalysts activity in ORR. Consequently, it could be expected that the obtained results would influence activity studies of other electrocatalytic reactions, for example electrooxidation of formic acid, methanol or ethanol.

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 formulation 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 2016, we were focused on the preparation and modification of nanocapsules containing hydrophobic anticancer agents for passive and active targeting to the tumor. Nanocapsules were obtained by method developed previously in our lab, i.e., by direct encapsulation of emulsion droplets in the biocompatible polyelectrolyte multilayer shells. The nanocapsules containing anticancer drugs with an average size of 100 nm were obtained and further modified by pegylation. Pegylated polyelectrolytes PLL-g-PEG and PLL-g-PEG-BIOTIN were used. Targeting ligand (antibody anti_CEA) was immobilized by streptavidin bridge to the PEG-BIOTIN chain. The results show that our pegylated nanocontainers can be further considered as a promising drug delivery system for passive and active targeting of anticancer drugs.

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 the 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* and belongs to so-called 'EBDH-like' family (EBDH – ethylbenzene dehydrogenase).

In order to obtain S25DH for experimental purposes a large scale *S. denitrificans* cultivation was conducted at the facility of the scientific partner in Poznan. 486 g of fresh cell mass were obtained from the 100 L fermentation.

Preparative purification of heterotrimeric (αβγ) S25DH was conducted according to the previously established protocol which consisted of three chromatographic steps. However the amino acid sequence analysis of purified S25DH revealed the contamination of α subunit by at least four other S25DH-like isoforms. Further enzyme purifications were performed using different fraction of *S. denitrificans* proteins: i) membrane proteins fraction, ii) fraction containing both membrane and soluble proteins, iii) fraction containing only soluble proteins in order to identify relative abundance of α isoforms. Purified S25DH α subunits after SDS-PAGE separation were sent to a partner in AGH in Krakow for further qualitative and quantitative sequencing using ESI/MS/MS.

In a parallel project the S25DH overexpression system was established which enabled production and reconstitution of recombinant S25DH containing either α subunit or S25DH-like containing α2. Such recombinant enzymes were tested in the reaction with cholest-4-en-3-one as a substrate. LC/MS analysis confirmed presence of 25-hydroxyproduct in case of both proteins. Such result indicates that not only S25DH but also at least one of S25DH-like isoforms is able to catalyze hydroxylation at C25 of 3-ketosterols.

Based on the purified S25DH preliminary tests of reaction kinetics were conducted using stooped-flow and isothermal calorimetry (ITC) . In stopped-flow experiment the oxidized S25DH was mixed with a substrate without a reoxidant which allowed observation of the reduction rate of various redox centers in the enzyme. However, due to the residual presence of re-oxidant agent ($[Fe(Cp)_2]BF_4$) tests were ambiguous and therefore will be repeated. This time re-oxidant agent present in S25DH after purification will be removed by dialysis or SEC. In the ITC experiments the heat of cholest-4-en-3-one hydroxylation was determined. This time the major problem was to high heat generated during the mixing of 2–methoxyethanol with aqueous reaction medium.

Based on the homology model of αS25DH other models of S25DH-like α subunits were prepared. Structural differences in active site and binding pocket between different isoforms were determined. Similar comparison was prepared for αS25DH and αEBDH (reference structure). For selected models of αS25DH in a complex with cholest-4-en-3-one, using QM and QM:MM models, alternative reaction pathways were calculated: i) homolytic activation of C-H bond with a radical intermediate, ii) heterolytic cleavage of the C-H bond with a transient carbocation intermediate. The former pathway turned out to be more probable. This result was confirmed by convergence of experimentally determined kinetic isotope effect (KIE) for 25,26,26,26-[2H]-cholesterol and theoretically calculated iKIE obtained from cluster model calculations.

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 collisions 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.

In the reported period the interrelation between influence of the bubble radius (R_b), surface tension and values of threshold acceleration related to oscillations of the liquid/gas interface on the probability of prolongation of the bubble lifetime was investigated. The experiments were carried out in pure water and silicone oil of known physicochemical properties for 7 different diameters of the capillary orifices, used for bubbles generation. Due to the differences in surface tensions of water and oil, for identical capillaries sizes the range of the R_b for water was equal to 0.51-0.87 mm, while for oil equal to 0.310.60 mm.

It was found that minimum (threshold) acceleration of the oscillating liquid/gas interface, needed for prolongation of the bubble lifetime is directly related to bubble radius and surface tension of liquid phase. Independently on kind of the liquid, values of the threshold acceleration in a function of oscillation frequency was increasing with the R_b decrease. Moreover, comparing the acceleration values for the bubbles of similar sizes for different liquids, it was found that threshold acceleration needed for the bubble lifetime prolongation are significantly smaller for the liquid of smaller surface tension. The results obtained are additional proof of correctness of the hypothesis about crucial role of bubble deformation, determining size of the liquid film, in probability of bouncing from liquid/gas interface and prolongation of its lifetime. The bubble ability to be deformed depends on its internal pressure (Laplace - Δp). Higher the Δp, higher the threshold acceleration needed to prolong the bubble lifetime (the velocity of collision of the bubble with liquid/gas interface has to be larger) to assure deformation and proper (large enough) radius of the liquid film. The Laplace pressure is smaller for larger R_b. Moreover the Δp decreases with decreasing liquid surface tension. Analysis of calculated values of the Δp and results of the bubble deformation (calculated and obtained in numerical simulations) are additional and rather strong proof for correctness of the postulated mechanism of the bubble bouncing from liquid/gas interface.

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

"Sonata" research project NCN 2014/13/D/ST4/01846 [2015-2018]
(Project leader: Monika Wasilewska PhD)

Immunoassays are powerful bioanalytical systems which utilize the sensitivity and specificity of the antibody-antigen interactions in order to detect and quantify the amount of a specific analyte present in a sample. Antibodies are widely used in immunoassays to detect and quantify antigen. The most commonly used antibodies are immunoglobulins G (IgG). They are used mainly for preparation of solid-phase immunoassays, medical diagnostic tests, biosensors, etc.

The main goal of this study was to determine the mechanisms of monoclonal IgG (anti-fibrinogen) adsorption on polystyrene microspheres by applying the *in situ* LDV electrophoretic mobility measurements supplemented by the atomic force microscopy (AFM) determination of the maximum coverage of the protein. The acid-base properties of the IgG monolayers were also determined in pH cycling experiments. Experimental data were quantitatively interpreted in terms of the general electrokinetic model. Extensive experiments using the above techniques were also performed with the aim of quantitatively evaluating human serum albumin adsorption on IgG monolayers.

It was determined that IgG adsorption on microparticles was irreversible and that the monolayers were stable against pH cycling between 3.5 and 10.

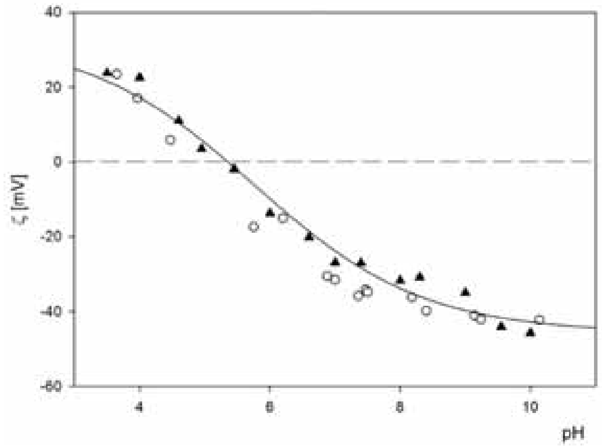


Figure 1. The dependence of the zeta potential of the IgG monolayer on microparticles on pH cycling starting from 3.5 to 10 and back to 3.5 (three cycles for each curve were made for a fixed ionic strength 10^{-2} M). The points denote experimental results obtained from the LDV electrophoretic mobility measurements, (○) the monolayer adsorbed at pH 7.4, the coverage 2.1 mg m^{-2}, (▲) the monolayer adsorbed at pH 3.5, the coverage 2.1 mg m^{-2}. The solid lines are interpolations of experimental data.

The maximum coverage of IgG varied between 2.1 and 3.4 mg m^{-2} depending on ionic strength that suggested the head-on adsorption mechanism where the Fab (antigen binding) fragments of the molecule are directed to the microparticle surface. It was confirmed that the adsorption of human serum albumin on IgG monolayers was negligible at pH 7.4 that is consistent with a basic physical mechanisms, i.e., molecule transport governed by diffusion of the protein monomer.

Obtained results have an essential significance for efficiently performing the variety of immunological assays where the immunolatexes are applied.

"Opus" Research Projects of the National Science Centre

Structure and Function of Acireductone Dioxygenases – Experimental and Computational Studies

"Opus" research project NCN NZ1 04999 [2012-2016]
(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 and NO. Crystals of ARD enzymes were obtained and their structures were solved. Moreover, reaction mechanisms of the enzyme and two synthetic inorganic complexes catalyzing model reactions for ARD were scrutinized with DFT methods. In addition, the synthesis route to the stable and convenient to store form of ARD substrate was worked out and the substrate was characterized with spectroscopy (IR, Raman, UV-vis, NMR) and crystallography methods.

In the last year, we did a QM/MM (ONIOM) study on the reaction mechanisms of Fe-ARD and Ni-ARD. Comparison of the results obtained for these two forms of the enzyme allowed us to formulate a hypothesis that rationalizes dependence of the reaction specificity on the identity of the metal ion bound in the active site.

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 was to clarify the relationship between the properties of the catalyst system and its operation based on the reaction of dimethyl ether synthesis (DME) from H_2 / CO_2 mixture. Work on this project was completed in January 2016 year.

The major scientific achievements obtained in the framework of this project are following:

1. It was shown what is the effect of the ZrO_2 phase composition responsible for the copper dispersion, on methanol yield, and hence dimethyl ether yield (DME). Research carried out during the project showed that the tetragonal ZrO_2 phase has positive effect on the formation rate of CH_3OH/DME.
2. The mechanism of the tetragonal ZrO2 phase effect was explained. It is shown that in the case of the tetragonal phase of ZrO_2 copper surface ions (Cu^{+1}) are stabilized by oxygen vacancies. It has been also shown using a quantum chemical method DFT that, for this phase of ZrO_2 system Cu^{+1} – oxygen vacancy is more stable than the case of monoclinic phase ZrO_2.
3. It was shown, what is the metallic promoters (Cr, Mn, Ga, Ag) influence on the DME yield for montmorillonite K10 impregnated both HPMo and HPW acid function.
4. Negative water steam impact on DME yield has been proven.
5. It was shown that the NaOH precipitation method gives the catalysts where both the BET surface area and copper surface area leads to the highest yield of DME. In the case of hybrid catalysts metallic components, DME yield depends in a complex way from these both surfaces i.e. BET surface and copper surface area.
6. Acidity studies by NH_3 - TPD and in situ IR studies showed that the high concentration of acid sites with an average strength leads to easier dehydration of methanol and this is ensured by HPW heteropolyacid.

On the basis of described above scientific results, received within this project realization, the highly efficient catalysts in high pressure dimethyl ether synthesis from H_2/CO_2 mixture will be synthezied.

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 was the synthesis of novel layered materials with unique hierarchical structure of pores. The main cognitive aim of the project was 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 were expecting that such new layered and hierarchic structures will serve as viable catalysts in the transformations of organic molecules in the liquid phase.

The two series of specimens containing micro- and macropores were obtained and studied: (i) the suspensions of nanoparticles with the size of ca. 5 nm; and (ii) the layered, amorphous materials prepared from nanoparticles. The syntheses of suspensions of protozeolitic nanoclusters were carried out at low temperatures (≤50ºC), and the Si/Al ratios were changed from 12 to 70. The suspensions obtained were stable in time (NMR, DLS) and monodispersed (ca. 5 nm). After lyophilisation the samples were amorphous (XRD). It was shown that the nanoclusters are formed only if the organic template (TPAOH) was used. The specific character of the nanoclusters was evidenced by TG and DSC. The nanoclusters revealed partially ordered porous structure and the presence of strong acid sites. Moreover, their amount followed the aluminium content. The increase of a structural ordering with the decrease of aluminium content was also observed.

By applying solid-state nuclear magnetic resonance (NMR) several experiments were made, shedding new light onto the synthesis of zeolitic nanoclusters at low temperatures (below 50^{o}C). ^{29}Si MAS NMR spectra of the lyophilised suspensions of nanoparticles showed the presence of typical zeolite signals, assigned to various Si(0-2Al) and Si(1-2OH) environments. In the as-prepared and lyophilised samples *tetrahedral* aluminium was evidenced by NMR only.

The layered materials containing aluminium exhibited strong proton acidity, similar to that revealed by the standard zeolites. Thus, such materials were studied in the two processes requiring acid sites, isomerization of aminal and isomerization of α-pinene. These two reactions were studied under mild conditions, at low temperatures and atmospheric pressure. Very good catalytic results were obtained. The conversion of α-pinene over mesoporous materials (Si/Al = 12 and 40) was much higher in comparison with the amorphous aluminosilicate (SA), standard ZSM-5 zeolite (MFI) and alumina (Al_2O_3). Such an effect can be ascribed to better and faster access of substrates to the active sites via mesopores. To conclude, the initial reaction rate of α-pinene was a function of aluminium. The initial reaction rate obtained over the mesoporous hierarchic materials was from 1.79 to 4.83 mmol α-pinene/g_{cat} x min. These data are comparable with or higher than those documented earlier for the modified ferrierite catalysts at 90^{o}C [R. Rachwalik, Z. Olejniczak, J. Jiao, J. Huang, M. Hunger, B. Sulikowski, *J. Catal.* **252**, 161-170 (2007)].

One scientist obtained the title of *professor within chemical sciences,* and four persons have successfully finished their PhD studies, due to investigations performed, *inter alia,* within this project.

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 (task completed) Catalytic studies involved optimization of hydrogenation reaction conditions for 8 prochiral ketones (acetophenone, acetol, methyl ethyl ketone, cyclohexyl methyl ketone, ethyl phenyl ketone, methylacetopnenone (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.

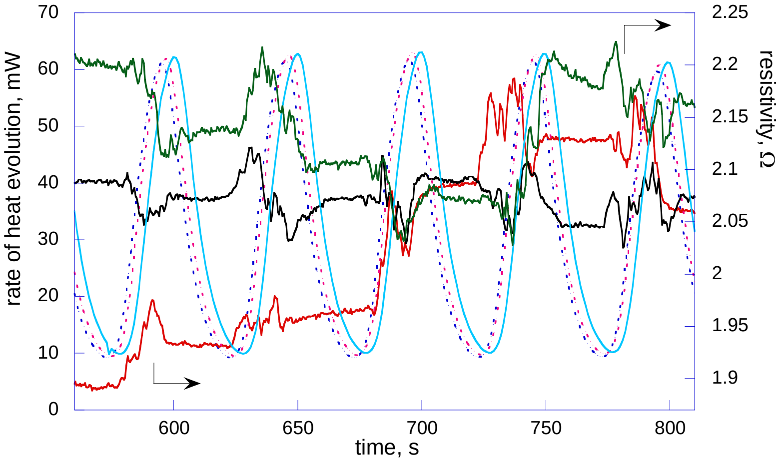


Figure 1. Mathematical (deterministic) chaos in resistivity of Pd powder (solid red, green and black lines) accompanying thermokinetic oscillations (solid blue and dotted lines) in sorption of D_2 in Pd in three separate sorptions at 75 °C. It can be seen the Pd resistivity either climbs or drops with 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.

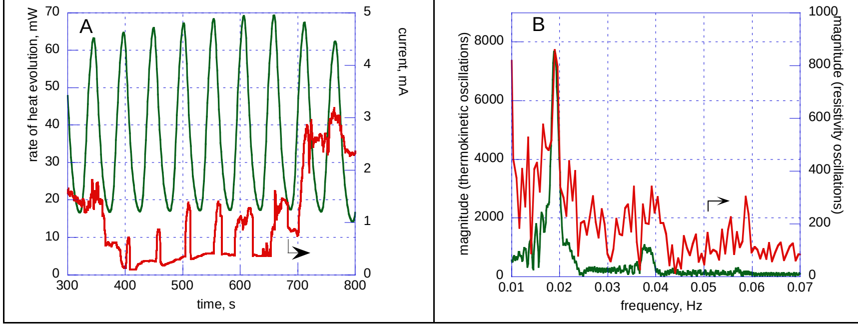


Figure 2 (A) Chronoamperometric measurement of current flow in Pd powder (red line) compared to thermokinetic oscillations (green line) in the sorption of D_2 in Pd, and (B) the corresponding power spectra. Note the excellent coinciding of peaks in both the Fourier transform curves at ca. 0.02 Hz.

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 using the dynamic light scattering (DLS), micro-electrophoretic measurements aided by laser Doppler velocimetry (LDV) and AFM. 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. An abrupt increase in the electrophoretic mobility of microparticles with IgG concentration was observed for all ionic strengths that was quantitatively interpreted in terms of the 3D electrokinetic model. Additionally, 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. Additionally, the stability and acid-base properties of the IgG monolayers on latex were determined in pH cycling experiments. The isoelectric point of IgG monolayers on microparticles was equal to 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.

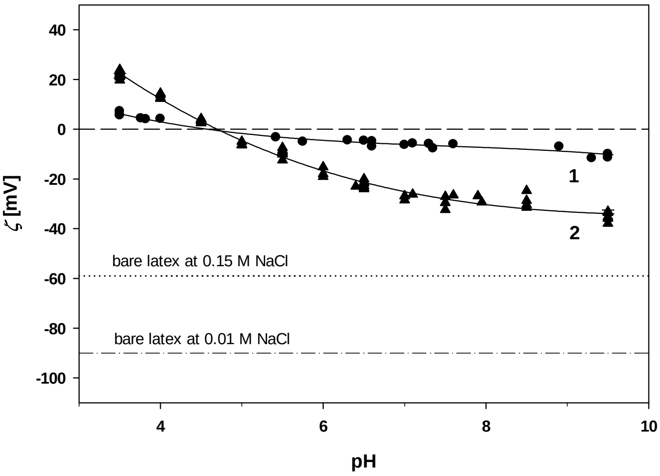


Figure 1. The dependence of the zeta potential of the IgG monolayers (adsorbed on microparticles) on pH cycling starting from pH equal to 3.5 to 9.5 and back to 3.5 (three cycles for each conditions were preformed). The solid lines are interpolations of experimental data. Curve 1 presents the results obtained for 0.15 M NaCl, protein coverage Γ = 2 mg m^{-2} (circles), curve 2: 0.01 M, NaCl, protein coverage Γ = 1.8 mg m^{-2} (triangles).

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)*

How does a negatively charged protein spontaneously attach itself to a negatively charged inorganic surface? In recent years there has been a lot of interest in the adsorption of proteins to inorganic materials, since this provides a means to developing new technologies such as drug delivery systems, diagnostics, and antibacterial coatings.

Details of BSA adsorption on silica surface is revealed by fully atomistic Molecular Dynamics (MD) simulations (0.5μs) and supported by steered MD (SMD) as well as Dynamic Light Scattering (DLS), Multi-Parametric Surface Plasmon Resonance (MP-SPR) contact angle and zeta potential experiments. Experimental and theoretical methods are comprehensive to each other and used together lead to a wider understanding of the mechanism of BSA adsorption and protein orientation on the surface. Basing on MD results we provide the list of most important residues for BSA adsorption at SiO_2, the details of the adsorption process, analysis of the driving forces and the mechanism of BSA mobility on the SiO_2 surface, while SMD provides energy barriers for diffusion and desorption.

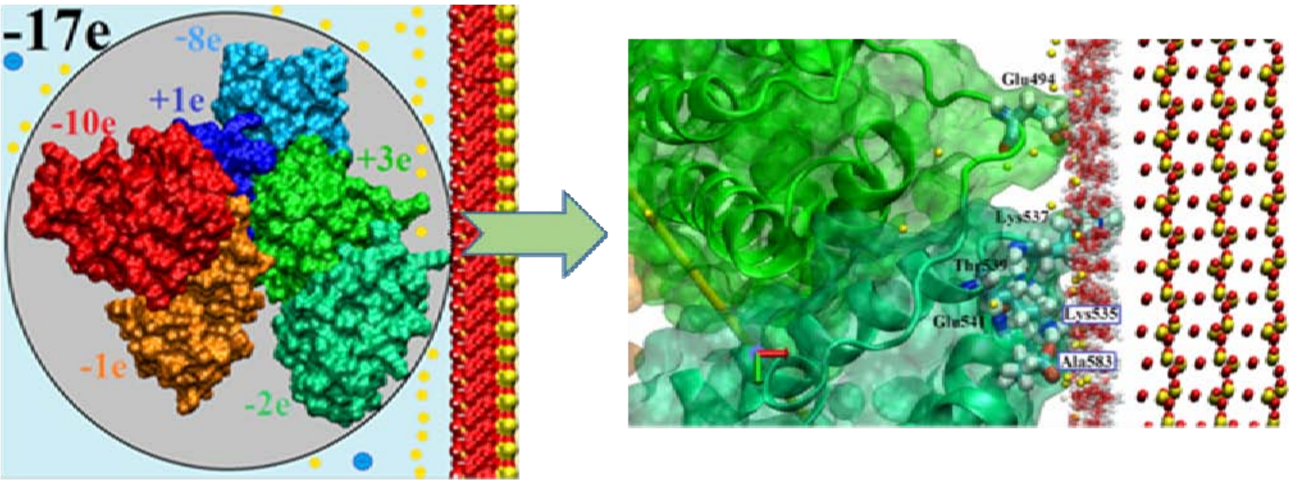


Figure 1. Snapshots illustrating the BSA adsorption on SiO_2, close-up view of the key residues.

B.Jachimska, K.Tokarczyk, M.Łapczyńska, A.Puciul-Malinowska, S.Zapotoczny, Colloids Surf. A, 489 (2016) 163-172
K.Kubiak-Ossowska, B.Jachimska, P.Mulheran, J. Phys. Chem. B, 120 (2016) 10463-10468

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 [2014-2017]
(project leader: Aleksandra Pacuła PhD)

The electrocatalysts containing N-doped carbon materials with graphite-like structure and various grain morphologies (plate-like or tubular) were prepared. The synthesis of the electrocatalysts consisted of heating of magnesium-iron-aluminum (MgFeAl) layered double hydroxides at temperatures of 600 or 700 ^{o}C for 30 or 180 min. in the flow of argon saturated with acetonitrile (CH_3CN) vapour acting as carbon and nitrogen source. Layered double hydroxides used in the synthesis contained various concentrations of iron ions ($Mg_{4.8}Fe_{0.6}Al$ or $Mg_{3.7}Fe_{0.2}Al$). For comparison, a series of the electrocatalysts derived from magnesium-aluminum (Mg_3Al) 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 or Fe) oxides. The resulting acid-treated samples were applied for further studies. The obtained samples were denoted as: C-$Mg_{4.8}Fe_{0.6}$Al-600-30, C-$Mg_{4.8}Fe_{0.6}$Al-700-30, C-$Mg_{4.8}Fe_{0.6}$Al-600-180, C-$Mg_{4.8}Fe_{0.6}$Al-700-180, C-$Mg_{3.7}Fe_{0.2}$Al-600-30, C-$Mg_{3.7}Fe_{0.2}$Al-700-30, C-$Mg_{3.7}Fe_{0.2}$Al-600-180, C-$Mg_{3.7}Fe_{0.2}$Al-700-180, C-Mg_3Al-700-30 and C-Mg_3Al-700-180.

Physicochemical properties of the electrocatalysts were characterized by means of X-ray diffraction (XRD), elemental analysis, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Mössbauer spectroscopy and electron microscopy (SEM and EDS).

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). Cyclic voltammetry was performed using electrochemical cell with a three-electrode configuration: a working electrode (rotating glassy carbon electrode coated with studied sample), a counter electrode (Pt wire) and a reference electrode ($Ag/AgCl/KCl_{sat}$).

The electrocatalysts were active in ORR in alkaline solution. The electrocatalysts prepared at higher temperature (700 ^{o}C), under shorter heating (30 min.), using precursor of higher Fe content ($Mg_{4.8}Fe_{0.6}Al$) appeared to be more active in ORR. The oxygen reduction reaction proceeded via 2- and/or 4-electron pathway in the presence of the electrocatalysts. The estimated number of electrons involved in ORR was 3 for C-$Mg_{4.8}Fe_{0.6}$Al-700-30, C-Mg_3Al-700-30, C-Mg_3Al-700-180.

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, involving the preparation of organoclays, and the other, consisting in manufacturing oxide nanoparticles via inverse micellar route.

Research concentrated on determination of the effect of calcination temperature on the performance of catalysts prepared from microemulsion of Mn-Al hydrotalcite as a precursor of the 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 hydrotalcite/Laponite catalyst precursors obtained from Na-L were prepared in aqueous medium, those obtained from CTA-L in isopropanol. 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 catalysts prepared in aqueous conditions displayed higher activity after calcination at 450^{o}C, as compared to calcination at 600^{o}C. In contrast, the catalytic activity of samples synthesized in the organic environment increased after calcination at higher temperature. Moreover, independently of the calcination temperature, the catalysts prepared in the organic medium were more active than their counterparts obtained in aqueous system.

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).

In experimental studies we have optimized procedures of protein production for two oxygenases, conducted stability studies for proteins in various buffers, tested a wide array of crystallization conditions and, as a result, we have obtained first crystals, which have been used in preliminary diffraction experiments. Moreover, catalytic activity of one of the proteins has been confirmed. In computational studies we have done docking experiments for one enzyme-substrate pair and conducted molecular dynamics simulations for resulting complexes.

We have identified conditions in which two proteins are stable and crystalize. A model for enzyme-substrate complex has been obtained.

The above results should enable us to optimize crystallization conditions and ultimately obtain and solve crystal structure. The structure, in turn, will be used in computational studies on the mechanism of the catalytic reaction.

Theranostic nanocarriers for MRI imaging

"Opus" research project NCN 2015/17/B/ST5/02808[2016-2019]
(project leader: Professor Piotr Warszyński)

Nanotechnology is an multidisciplinary research field involving chemistry, physics, material science, biology, and medicine. In particular, the nanotechnology is currently offering various exciting possibilities in biomedical fields, and this application is referred to as ‘nanomedicine’. It is the field of research with huge expectations for the development of personalized medicine based on the application of nanoparticles (NPs) as nanoscale materials interact effectively with biological systems. In particular, the simultaneous use of nanodiagnostics in vivo imaging and nanotherapeutics for drug delivery may allow overcoming many intractable health challenges. Theranostics is a promising field that combines therapeutic and diagnostic capabilities into a single multifunctional platform. This concept is highly relevant to agents that target molecular biomarkers of disease and is expected to contribute to personalized medicine. The majority of the imaging and therapeutic compounds are based on gadolinium complexes, iron oxide nanoparticles, gold nanoparticles or quantum dots combined with anticancer drugs. The main drawbacks of these kinds of small-sized molecules are their not sufficiently long blood circulating times, their cytotoxicity, poor biodistribution, etc. For that reason, it is extremely important, to involve nanotechnology tools, and develop new strategies for simultaneous diagnosis and treatment systems. The most promising approach is based on incorporation of imaging species (e.g. gadolinium ions, iron oxide nanoparticles) into polymeric micro or nanocarriers loaded with therapeutic agents.

The main project objective is to develop the scientific background for a completely new strategy for theranostics by applying biodegradable and biocompatible nanocarriers that are able deliver the therapeutic components to the site of its action, image a diseased tissue and monitor the delivery without simultaneously imposing side effects. The use of theranostic nanocapsules may be the ideal solution for future personalized therapy e.g. for cancer treatment.

In 2016 we were focused on synthesis of theranostic nanogels based on the physical crosslinking of polymers. The nanogel capsules were obtained by emulsification method and technique based on reverse emulsion template. Nanogels were formed by physical crosslinking of alginate by gadolinium ions (MRI contrast). The average size of synthesized nanoparticles was about 110 nm and the batch concentration was 10^{10} particles/ml. The morphology of nanogeles was visualized by Cryo-Scanning Electron Microscopy. Surface of nanogels particles was modified by the Layer-by-Layer (LbL) technique using natural polyelectrolytes. The cytotoxicity of non-modified and LbL modified nanogels was evaluated by the cellular viability quantification and cell death assessments using MTT and LDH biochemical tests, respectively. We encapsulated the model compound - fluorescent dye (Rhodamine b) in nanogels networks and proved the possibility of GdNG visualization by MRI.

A new generation of hierarchical Y and omega zeolite catalysts: advanced IR and NMR studies and molecular modeling

"Opus" research project NCN 2015/17/B/ST5/00023 [2016-2020]
(project leader: Professor Ewa Brocławik)

The preparation of hierarchical zeolites containing additional system of mesopores. Desilication of zeolites in alkaline solutions was found to be the most effective and non-expensive way of producing of mesopores in zeolites. Most of studies concerned on zeolite desilication was performed for ZSM-5 using most commonly NaOH as the desilicating agent. Here, desilication of commercial zeolite FAU with the Si/Al ratio of 30, obtained by dealumination of typical zeolite Y, was performed. Variable parameters of desilication were: the kind of desilication agent (NaOH, tetrabutylammonium hydroxide (TBAOH), or a mixture of NaOH/TBAOH), temperature of process, and post desilication treatment - calcination in air or at vacuum.

Desilicated zeolites were the subject of characterization studies. The status of Si and Al were followed with MAS NMR and XPS. The pore structure was studied by N_2 adsorption, and the acidity was determined by IR spectroscopy. The concentration of both Bronsted and Lewis sites was examined by quantitative experiments of pyridine adsorption, whereas the nature of Lewis sites and the acid strength of Si-OH-Al groups was studied by low temperature CO sorption. The heterogeneity of Si-OH-Al groups was also analyzed. The accessibility of sites to bulky reactants was studied by quantitative IR studies of bulky probe molecules: 2,6 ditertbutyl pyridine. The effect of the desilication of zeolites as well as modification of their structural and acidic properties on catalytic activity was studied in the isomerization of α-pinene.

Si-OH_1-Al groups in parent zeolite FAU-30 were found to be homogeneous and very strongly acidic. They were more acidic than hydroxyls in HMOR and HZSM-5 which are known as strongly acidic zeolites. The treatment of FAU-30 with diluted NaOH at mild conditions (room temperature) caused a decrease of the Si/Al ratio to ca. 10, a complete destruction of zeolite structure and loss of acidity. On contrary, the treatment with TBAOH resulted in only small Si extraction and slight increase of Si/Al. Furthermore, desilication with NaOH/TBAOH preserved zeolite structure and microporosity, but distinctly increased the volume of mesopores of diameter ca. 3 nm. Si/Al decreased to ca. 18. XPS showed the same ability of Si in surface zone and inside the bulk to extraction. Desilication with NaOH/TBAOH did not decrease neither the concentration nor the acid strength of SiOH-Al. However, it produced some Lewis acid sites being extraframework Al species. Moreover, calcination of desilicated zeolites transformed some tetrahedral Al to extraframework octahedral species. Catalytic activity in the α-pinene isomerization increased distinctly upon desilication due to the production of mesopores, the increase of accessibility and preserving of very high strength of acid sites.

Hierarchical zeolites generated by mild desilication (after former dealumination) should show much better catalytic activity than traditional zeolites due to both high acidity and better accessibility of active sites for reagents – we hope to establish a general procedure for synthesis of such materials.

Nanoparticle monolayers of controlled heterogeneity and structure as efficient antifoulong substrates

"Opus" research project NCN 2015/07/B/ST5/00847 [2016-2019]
(*project leader: Professor Zbigniew Adamczyk*)

Deposition mechanism of gold nanoparticles on poly(allylamine chloride) (PAH)-modified silica and mica was investigated by the quartz crystal microbalance (QCM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and streaming potential measurements (SP). The influence of the suspension concentration, ionic strengths and pH was studied. It was shown that the particle deposition was irreversible that enabled to precisely determine the maximum coverage of monolayers that systematically increased with ionic strength. The experimental results were quantitatively interpreted in terms of the random sequential adsorption (RSA) model where the bulk and surface transfer steps are considered in a rigorous way. The results obtained by QCM were exploited as reference data for interpreting the streaming potential (SP) measurements of gold nanoparticle monolayer formation at PAH-modified mica. In these experiments the coverage of particles was determined via SEM and AFM imaging of monolayers. This allowed to quantitatively interpret the zeta potential vs. particle coverage dependencies derived from SP measurements in terms of the general electrokinetic model without using adjustable parameters (see Fig. 1). In this way, a functional dependence was specified for calculating the nanoparticle coverage *in situ.* Additionally, by using the SP measurements, thorough electrokinetic characteristics of gold nanoparticle monolayers were acquired. They comprised the dependence of the monolayer zeta potential on ionic strength (for a fixed pH) and the acid-base characteristics of monolayers, derived in pH cycling experiments carried out at fixed ionic strength. It was concluded that these results enable to develop a reproducible method for preparing gold nanoparticle monolayers of controlled coverage and fully characterized electrokinetic properties with potential application as protein adsorption platform.

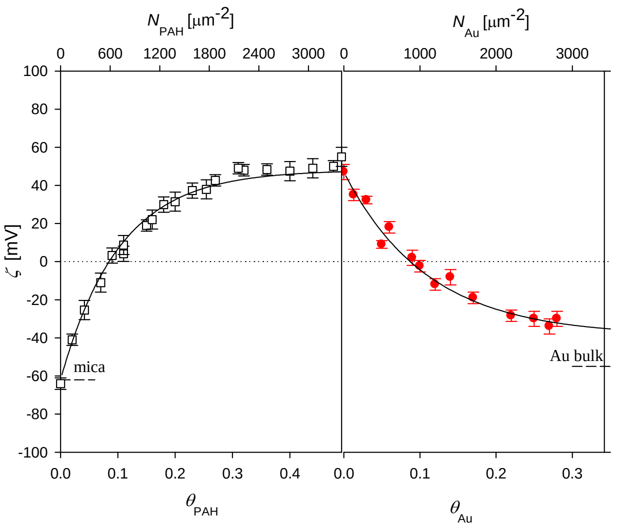


Figure 1. The dependence of the zeta potential of mica ζ on the coverage of gold nanoparticles on PAH monolayers derived from streaming potential measurements. Particle deposition was carried out for pH 5.7, I = 1x10^{-2} M NaCl. The square points denote experimental results for PAH and the circle points denote the results obtained for the gold nanoparticles. The solid lines denote exact theoretical results calculated from the 3D electrokinetic model.

"Preludium" Research Projects of the National Science Centre

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

"Preludium" research project NCN 2013/11/N/ST4/00984 [2014-2016]
(PhD student: Adam Stępniewski MSc, supervisor: Professor Ewa Brocławik)

All tasks listed in the project plan were successfully completed. Therefore, the main goal of the grant was achieved: we described the electronic factors essential for catalytic activity of cobalt centers in various atomic environments. This constituted a challenge for the project because of complicated electronic structure of the studied systems, containing only one NO molecule and then modified by coadsorption of NH_3 molecules. Active sites were represented by small models based on the single aluminium tetrahedron. Their properties were verified by larger clusters cut from chabazite framework. The comparison of cluster geometries with those derived from periodic modeling was helpful. The result of our research was the electron density distribution along the Co-NO bond. We identified the form of the ligand with NO^-, NO^+ and NO^0. The weights of the resonance structures $Co^{III}NO^-$, $Co^{I}NO^+$, $Co^{II}NO^0$ enabled us to understand the NO activation/deactivation for all studied systems. The electron density transfers resulted in the formation of Co-NO bond were useful for comparison purpose between two centers. In this case, the interpretation of charge flow channels was clear only for complex with three NH_3 ligands and for that with five NH_3 ligands, the latter interacting non covalently with zeolitic framework (both complexes were in the singlet state, the system with five NH_3 ligands exhibited lower ability to activate NO). Using the analysis of electron density transfers we successfully described the influence of NH_3 molecules on the donation (transfer of electron density from NO to cation Co^{2+}) and backdonation (transfer of electron density from cation Co^{2+} to NO). Spin state may close or open the specific channels, playing important role in the weakening of N-O bond. On the basis of calculations for the selected clusters being the part of chabazite or ferrierite structure we indicated that the framework can support the backdonation. The success of this project was also the reinterpretation of experimental IR spectra with DFT calculations for small models. The cooperation between theory and experiment allowed us to assign the models to IR bands registered for centers Co(II). We concluded that various form of active site may coexist in reality Their presence in zeolite may be modified by such factors like a zeolite type, experimental conditions. In order to determine the ground state of the active sites we applied the high-level correlated quantum chemical methods. Our results have a contribution to the discussion on the applicability of these methods

Mechanism of Irreversible Nanoparticles Adsorption on Colloids Particles

"Preludium" research project NCN 2013/11/N/ST4/00981 [2014-2016]

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

The major goal of this project was to develop a quantitative description of nanoparticle deposition mechanisms on polymer microparticles. The first stage of the research was the synthesis and a thorough characterization of hematite nanoparticles of various size, then the characterization of polystyrene microparticles. In a next step, the electrophoretic mobility of polystyrene microparticles coated with nanoparticles was measured. The last step was to determine the maximum coverage of hematite nanoparticles on the surface of polystyrene microparticles in order to determine the limits of applicability of the 3D electrokinetic model.

The maximum coverage of hematite nanoparticles monolayers was determined via electrophoretic mobility measurements and theoretical calculations (Table 1).

Table 1. The SEM micrographs of hematite nanoparticle adsorbed at colloid microparticles and the maximum coverage of the hematite nanoparticles on the microparticles.

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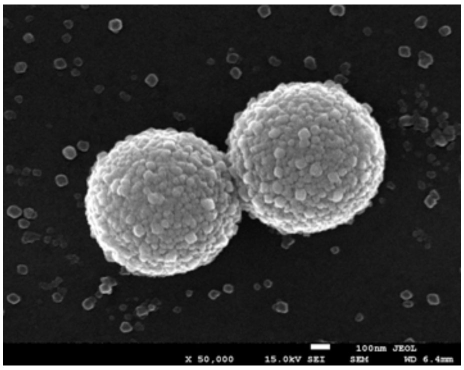
<tr><td rowspan="10">
</td><td rowspan="2">I [M]</td><td rowspan="2">$\kappa\, d_H/2$</td><td colspan="2">Maximum coverage of hematite nanoparticles</td></tr>
<tr><td>Electrophoretic mobility</td><td>Theoretical modeling</td></tr>
<tr><td colspan="4">HE29</td></tr>
<tr><td>10^{-4}</td><td>0,5</td><td>0,30±0,10</td><td>RSA model not apply</td></tr>
<tr><td>10^{-3}</td><td>1,5</td><td>0,30±0,10</td><td>0,15</td></tr>
<tr><td>10^{-2}</td><td>4,8</td><td>0,40±0,10</td><td>0,31</td></tr>
<tr><td colspan="4">HE86</td></tr>
<tr><td>10^{-4}</td><td>1,4</td><td>0,30±0,10</td><td>0,19</td></tr>
<tr><td>10^{-3}</td><td>4,6</td><td>0,35±0,10</td><td>0,31</td></tr>
<tr><td>10^{-2}</td><td>14</td><td>0,50±0,10</td><td>0,50</td></tr>
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As can be noticed, the increase in the ionic strength induces a considerable increase in the coverage of hematite nanoparticles. This is due to a reduced range of electrostatic repulsive forces among the nanoparticles. It was also observed that for low ionic strength the maximum coverage are much larger than those of the theoretical, predictions derived from the RSA model. An important part of this work was determining the range of validity of the 3D electrokinetic model, previously used for planar interface. In this model, the electrostatic and hydrodynamic flow fields around deposited particles are evaluated by using the multipole expansion method. Our measurements confirmed that the 3D electrokinetic model is applicable for curved interfaces that have an essential significance for basic science. The results has also exploited for a quantitative interpretation of adsorption phenomena of globular proteins on colloidal carrier particles that is essential for the effective conduct of immunoassays. The research also has practical significance for the effective conduct of immunoassays and enzyme reaction in bioreactors.

Polyelectrolyte-lipids films with incorporation hydrophobic nanoparticles

"Preludium" research project NCN 2015/19/N/ST4/00917 [2016-2017]
(PhD Student: Magdalena Włodek MSc, supervisor: Professor Piotr Warszyński)

The main goal of the project is to develop scientific background for the method of formation of hydrophilic polyelectrolyte – lipid films with embedded hydrophobic nanoparticles in order to obtain structures with desired functionalities, combining substrates of highly different hydrophobicity.

In our research done so far, quantum dots were inserted directly into the hydrophobic part of lipid bilayer, during its preparation as lipid vesicles. Liposomes were formed in the presence of suspensions of nanoparticles by drying a mixture of hydrophobic particles and phospholipids in chloroform, thus obtaining a QD-lipid film which was then hydrated, sonicated and subsequently extruded in two series, each of 15 times through polycarbonate membranes with nominally 200nm pores (first series) and 100nm (second one) to obtain the final vesicle-QD hybrid dispersion. As the result of this procedure, hydrophobic nanoparticles (commercial suspensions of CdS quantum dots with size: 2.7nm, 3.8nm, 4.9 nm or 5.4 nm) were located in the hydrophobic region of the liposomes. Obviously each suspension contains QD of one particular size. The presence of quantum dots within liposomes' structure was proved by the fluorescence experiments. First the suspensions of non-modified QD in toluene were studied to find the fluorescence of the selected QDs (Figure 1(a)). Next, the fluorescence emission spectra of QDs incorporated into lipid bilayer of liposomes in buffer solution were collected (Figure 1(b)). As a background – spectrum of liposomes without quantum dots was subtracted from each spectrum of liposomes- QD suspension. One can see that incorporation of QD into lipid bilayer of selected liposomes was successful, leading to the formation of hybrid (lipid-QD) materials. Moreover, the location of the hydrophobic quantum dots in liposomes was identified additionally by the cryo-TEM measurements.

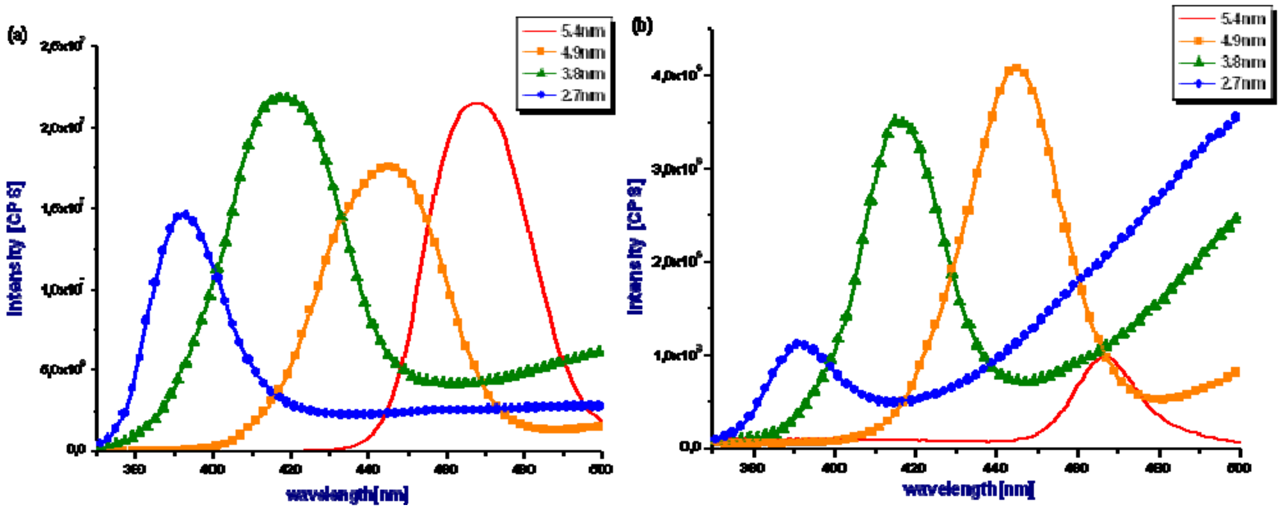

Figure 1. Emission spectra of quantum dots (a) in toluene and (b) POPC:POPE vesicles with QD (suspension).

"Fuga" Research Projects of the National Science Centre

High resolution analysis of the spatial properties of structured magnetic nanostructures

"Fuga" research project NCN 2015/16/S/ST3/00450 [2015-2018]
(Project leader: Piotr Mazalski PhD, supervisor: Assoc. Progessor: Nika Spiridis)

In the frame of project, Tridyn simulations were performed to follow the ion distributions in cobalt nanostructures irradiated by Ga^+ ions. The cobalt nanostructures with different combination of buffer and cap layers – platinum and/or gold were simulated. The simulations allow to: (i) follow changes of the atomic chemical profiles in the nanostructures irradiated with different ion fluences, (ii) investigate layer mixing during irradiation, (iii) optimize thickness of the cap layer (Pt or Au) to allow penetration of the Ga ions to the Co layer, (iv) define the Ga^+ ion beam fluence, which will be used in real experiment, (v) investigate the efficiency of the etching process during the irradiation.. Four different types of nanostructures: Al_2O_3/Pt/Co/Pt, Al_2O_3/Pt/Co/Au, Al_2O_3/Pt/Au/Co/Pt, Al_2O_3/Pt/Au/Co/Au were deposited using molecular beam epitaxy. In this nanostructures two different types of the cobalt layers were prepared: a cobalt wedge, with thickness d_{Co}= 0-5 nm or a flat cobalt layer, with a well-defined thickness d_{Co}= 3 nm. The nanostructures were irradiated by Ga^+ ions with energy 30 keV in two different forms – as a fluence gradient or with a well-defined ion fluence. Preliminary magnetooptical studies showed significant influence of the buffer and cap layers on magnetic properties of the nanostructures. Depending on the buffer and cap layer, as a function of the cobalt thickness and ion fluence, the following changes were observed: (i) two regions with perpendicular magnetic anisotropy (**PMA**) for Pt/Co/Pt, (ii) one region with **PMA** for Pt/Co/Au, (iii) one region with **PMA** for Au/Co/Pt, but for different values of cobalt thickness and ion fluence as compared to Pt/Co/Au, (iv) two regions with enhanced magnetic anisotropy for Au/Co/Au but without **PMA**. The observed differences are probably related with different types of changes induced at the cobalt interfaces and possible alloy and/or stress formation. Performed simulations were not conclusive concerning the alloy formation in the irradiated nanostructures, therefore the chemical structure was studied using X-ray photoelectron spectroscopy (XPS). The measured XPS spectra revealed differences in the chemical composition, but detailed quantitative analysis is necessary (in progress). Additionally, a work related to implementation and tests of the PEEM and XAS microscope at the Solaris synchrotron was also performed.

Effect of electromagnetic radiation in the infrared range on protein-surface interactions

"Fuga" research project NCN 2015/16/S/ST4/00465 [2015-2018]
(project leader: Magdalena Kowacz PhD, Supervisor: Professor Piotr Warszyński)

Protein-surface interactions are of great importance for protein biological functions (e.g. cell adhesion) or bio-engineering applications (e.g. compatibility of implants). Ability to control interactions of biomacromolecules with solid surfaces is therefore a way to tune biological and bio-inspired processes. Infrared (IR) light has been recently shown to promote hydration of hydrophilic interfaces including surfaces of proteins. Propensity of the solute to separate from the aqueous solvent and partition to an interface is determined by relative balance between solute-solvent affinity (hydration) and solute-surface affinity (e.g. specific interactions or hydrophobic attraction). Adhesion to the solid is also connected with (at least partial) dehydration of the protein and/or solid interface. The aim of this project is to explore possibility to affect protein-surface interactions with the use of a remote physical trigger - the IR electromagnetic radiation – by means of manipulation of hydration of the solute and the surface.

First step toward understanding of protein-water-surface interplay under the influence of electromagnetic radiation was exploration of protein partitioning to silica nanoparticles. Adsorption of proteins to nanoscale objects defines the effective properties of both, the solid and the adsorbed proteins forming particle’s corona. Our study revealed that IR can promote hydration of polar protein residues and dehydration of its hydrophobic compartments. This has important consequences for short–range (hydrophobic) and relatively long-range (dipole-like or water mediated) protein-protein interactions. Due to these effects IR light was shown to modulate interactions of protein-decorated nanoparticles. Aggregation of nanoparticles in solution (determined by mutual attraction of protein coronas) may have important implications for their biological fate as size of the aggregates will decide on their ability to cross biological barriers (like entering the cell). Furthermore, IR-enhanced hydration may have implications for protein biological functions. It has been recognized that protein physiological activity is inherently bound to its ability to induce structuring of adjacent water layers and that functional motions of proteins are associated with breaking and subsequent restoration of this water structure. On the other hand, protein ability to fold (for many proteins necessary to perform their function) is recognized to depend on entropy gain on dehydration of hydrophobic compartments. Therefore, our results suggest that IR radiation can be potentially explored as a new tool to fine-tune bio-inspired processes. Apart from biological implications and potential bioengineering applications, effect of IR light can be considered non-negligible environmental factor able to modulate interactions of surface-adsorbed biopolymers (in soil or surface waters) and thus their fate in the environment.

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

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.

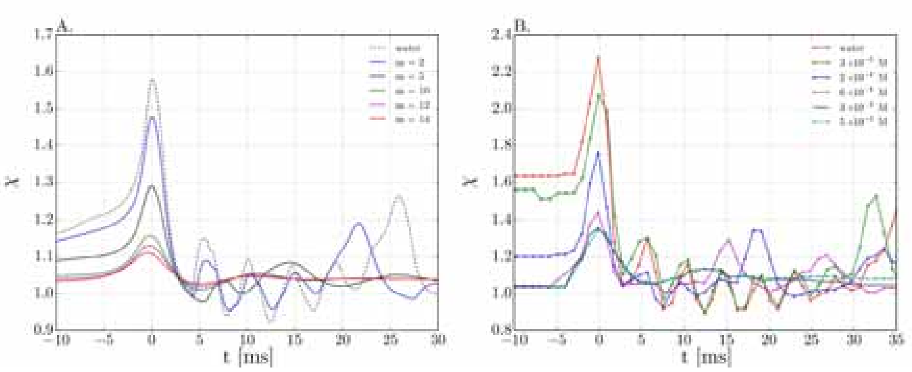

Figure 1. Variations in shape deformations of the bubble with different degree of interface immobilization, during its consecutive collisions with hydrophobic, smooth solid surface. (A) Numerical calculations, (B) experimental data.

Determination of the influence of surface properties of silver nanoparticles on their cytotoxic activity towards the human cells of immune system and the cells of connective tissues

"Iuventus Plus" research project MNiSW IP2015055974 [2016-2019]
(project leader: Magdalena Oćwieja PhD)

Recent literature reports have indicated that the mechanisms of silver nanoparticle activity are strictly related with the release of silver ions from the nanoparticle surfaces. On the other hand, it is well known that the activity of colloidal silver is directly or indirectly tuned by the stabilizing agent molecules which, depending on their chemical structure, can screen or enhance the activity of nanoparticles. In order to determine the mechanisms of biological activity of nanosilver, the influence of surface charge, chemical structure of stabilizing layers and the oxidation state of nanoparticles on the processes of their uptake, accumulation and biodegradation in prokaryotic as well as eukaryotic cells should be determined. Taking into account the potential application of silver nanoparticles in medicine, it is especially important to define the impact of surface properties of silver nanoparticles on their cytotoxic activity towards the human cells of immune system and towards the cells of connective tissue. This issue is also a main goal of the project.

The development of preparation methods of silver nanoparticles characterized by similar size distribution and various surface properties was a main task of the experimental works intended for the realization in 2016. The silver nanoparticles were obtained with the use of a chemical reduction method based on the reduction of silver ions by sodium borohydride. Then, the nanoparticles were modified using trisodium citrate or cysteamine hydrochloride in the ligand-exchange process.

The morphology and size distribution of silver nanoparticles were determined using the micrographs obtained from transmission electron microscopy (TEM) whereas the stability of the suspensions, under controlled conditions of pH and ionic strengths, was studied with the use of dynamic light scattering techniques (DSL). The measurements of electrophoretic mobility allowed to determine the surface properties of nanoparticles (zeta potential, charge density, number of uncompensated charges). The chemical structure and conformation of stabilizing agent molecules adsorbed on the nanoparticle surfaces were determined from the spectra acquired from surface-enhanced Raman spectroscopy (SERS). Atomic absorption spectrometry (AAS) was applied in order to find the kinetics of silver ion release from the nanoparticle surfaces under stable conditions of temperature, oxygen concentration, pH and ionic strength.

Finally, three methods of preparation of spherical silver nanoparticles, of an average size of 10 nm and various surface properties, were developed. The nanoparticles stabilized by citrate anions exhibited the most negative value of zeta potential (ζ = - 55±2 mV for pH 7.4, I=0.01 M). Moreover, these nanoparticles were resistant to an oxidative dissolution process. In turn, the unmodified nanoparticles, obtained with the use sodium borohydride, also showed a negative surface charge (ζ = - 32±2 mV for pH 7.4, I=0.01 M) however, they were more prone to dissolution than citrate-stabilized nanoparticles. On the other hand, the profiles of silver ion release from unmodified nanoparticles and positively charged (ζ = + 47±2 mV for pH 7.4, I=0.01 M) cysteamine-stabilized nanoparticles were comparable.

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
[2013-2017]
(project leader: Professor Roman Kozłowski)

The principal outcome of the project has been HERIe - a web-based decision-supporting tool based on quantitative assessment of risk of climate-induced physical damage to wooden heritage objects (available at herie.mnk.pl). The software analyses 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. A complete strain versus time history engendered in the investigated object by the microclimate of interest is obtained, as well as a risk index using relevant failure criteria.

Failure criteria used so far in assessing the risk of damage were derived from laboratory studies of mechanical properties of wood and gesso – the materials building up the painted wood structure. In the present phase of the project, crack propagation induced by strains experienced by the restrained wooden elements were used as an alternative measure of the risk of damage. The information on a relationship between the crack propagation and strain in cracked wooden panels was derived from earlier on-site monitoring of wooden objects displayed in museums using the acoustic emission method based on recording sound waves during fracture processes in materials (Fig. 1). Further insight into the strain-crack propagation relationship was provided by studies which compared the present preservation state of the historical furniture and the state recorded on archival photographs.

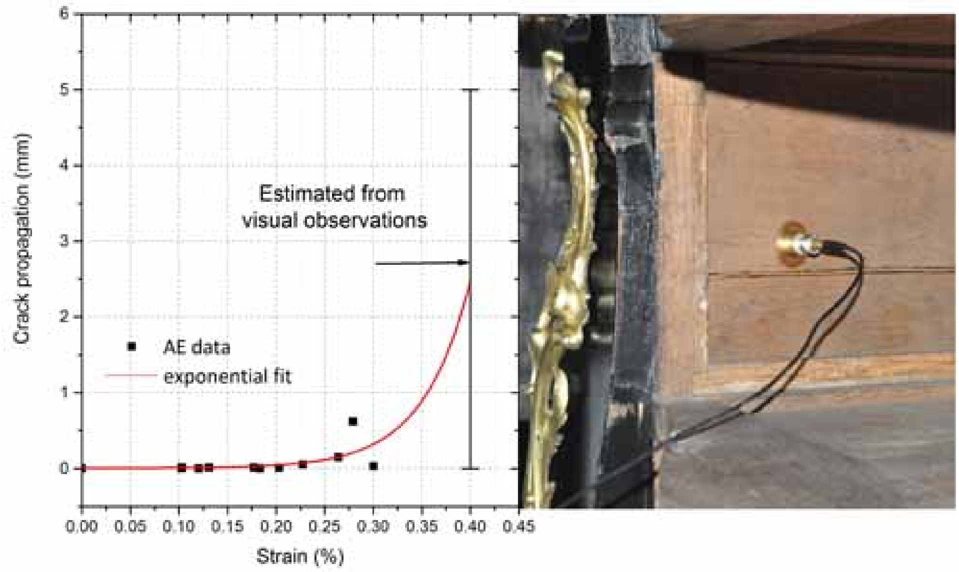

Figure 1. Crack propagation as a function of shrinkage strain experienced by wooden elements in furniture (left). The data for small strains were obtained from the acoustic emission monitoring using sensors located close to the tips of the existing cracks (right).

All strain-time histories experienced by the restrained wood are combinations of many simple swelling-shrinkage cycles of varying ranges. The HERIe software uses modified rainflow counting method to obtain simple strain cycles to which then the crack growth magnitude is ascribed. In this way, the risk index is formulated in a way which is easy to interpret and use, as damage progress in response to a particular microclimate fluctuation.

The HERIe software is an open tool - with the research progress, it will become platform of data gathering over an extended time period. The algorithms used by the software will be refined with the growing understanding of the damage mechanisms, as well as the data base of the cultural heritage objects analyzed will be enlarged.

"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 [2012-2016]
(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 the last 3 months of the project we focused on 3 tasks: task 7 - upscaling of biosynthesis, task 8 - development of the method for product isolation and purification task 9 - technical description of the invention and promotion of the project's results.

The up-scaling of the developed process was demonstrated in the semi-technical reactor system that comprised of 1 L glass reactor fitted with temperature and pH control with mechanical mixing. As a catalyst the S25DH enzymatic preparation obtained from *S. denitrificans* bacteria was used for hydroxylation of vitamin $_{D3}$ to calcifediol. The total volume of the reaction mixture was 0.7 L and it comprised of 2-methoxyetanol, propylated cyclodextrine, $K_3(Fe[CN]_6)$ as a reoxidant, K_2HPO_4/KH_2PO_4 as a buffer. The 3-day reaction enabled 90% conversion of the substrate.

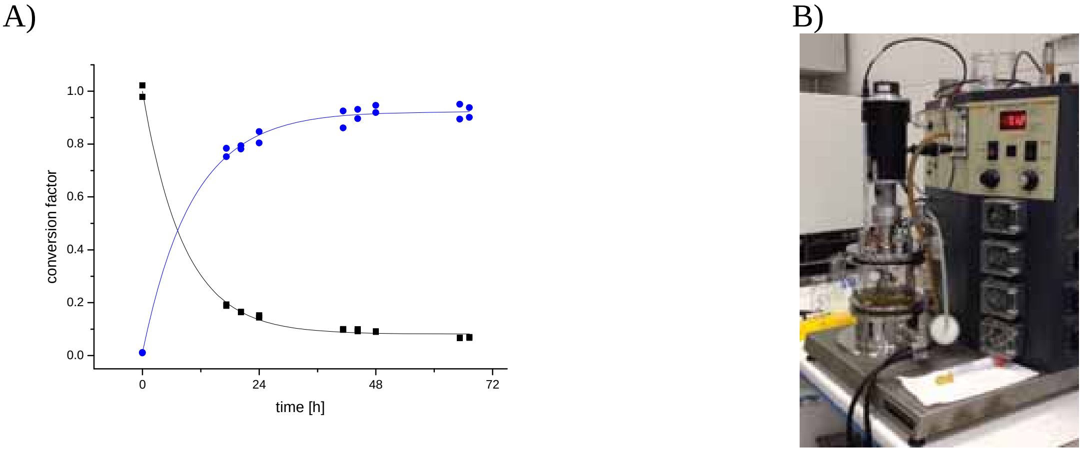

Figure 1. A) Progress curve of cholefalciferol (black line) hydroxylation to calcyfediol (blue line), B) pilot semi-technical reactor instalation used in the syntesis equiped mechanical mixer, thermostat and pH control.

The extraction and purification method was developed within task 8. Calcyfediol was isolated with liquid-liquid extraction and purified with preparative chromatography in normal phase on a silica column. The obtain product was tested by external laboratory for impurities and conformity with pharmacopeia requirement and positively passed the examination.

The analogical synthesis aiming at production of the 25-hydroxycholesterol from cholesterol was conducted at the smaller scale (350 ml) in the bottle with magnetic stirring. However, due to overheating of the reaction vessel by the stirrer the catalyst quickly deactivated which resulted with unsatisfactory reaction yields.

Finally within task 9 the cooperation with industrial partner was initiated. The details of the implementation procedures and legal agreements have been arranged and the implementation was initiated at the end of 2016. Moreover, the promotion of the project results was conducted. The technological offers were deposited in pharmalicese.com and tto.lifescience.pl technology platforms. The promotion articles were also published in Biotechnologia.pl both in paper and electronic version. Finally the paper with most of the results was published in Applied Microbiology and Biotechnology.

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.

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. Four Working Groups have been established in the Action plan: WG1 - SPINSTATE database, WG2 - Enzymatic spin states, WG3 - Spin crossover and WG4 - Biomimetic spin states.

In the year 2016 two meetings took place: Fourth scientific workshop in Prague, April 13-15, 2016 and Fifth scientific workshop in Kraków, September 8-9, 2016.The workshop in Kraków has been organized by the Institute of Catalysis PAS and by the Faculty of Chemistry, Jagiellonian University, the main organizers were: Prof. Ewa Brocławik and Dr. Tomasz Borowski (Polish Academy of Sciences), Dr. Mariusz Radoń (Jagiellonian University). 55 participants from all countries contributing to this COST action took part in the meeting.

One Short Term Scientific Mission has been awarded to the Institute of Catalysis: dr Mariusz Gackowski spent 3 months in Stuttgart in the group of prof. Hunger, the topic was devoted to Nuclear Magnetic Resonance spectroscopy and included training and establishment of common research.

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 last period, within studies on application of heteropolyacids and their precursors in the process of oxidative desulphurization of hydrocarbon-based fuels using hydrophobic liquids, the following tasks were carried out:

- Studies on the oxidative desulphurization of hydrocarbon-based fuels using hydrophobic liquids and some chosen precursors of heteropolyacids (molybdic acid, tungsten acid and polytungstic acid). Investigations on application of heteropolyacids precursors in the process of oxidative (dibenzothiophene) led to the conclusion that the highest effectivity (i.e., the degree of desulphurization) was possible to achieve using the following catalytic systems: (i) C_8mim]OTf/molybdic acid; (ii) C_8mim]NTf_2/molybdic acid (> 95 % of desulphurization); and also (iii) [bmim]HSO_4/molybdic acid (> 75% of desulphurization). However, the efforts made so far in order to transfer these results into the process of thiophene removal remained largely unsuccessful.
- Synthesis of new ionic liquids with the POM anions ([Rmim]$H_5PMo_9V_3O_{10}$) and preliminary experiments in their applications to the process of oxidative desulphurization of hydrocarbon-based fuels were carried out. Synthesis of ionic liquids of the [Rmim]$H_5PMo_9V_3O_{10}$ type proved to be however unsuccessful. It was shown that during dehydration of these liquids, which is essential for their stability and further use as catalysts, the partial decomposition of the ionic liquids took place.

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 Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences together with the research teams from various scientific institutions of 31 European countries were participating in activities of the COST Action MP1106 “Smart and green interfaces - from single bubbles and drops to industrial, environmental and biomedical applications (SGI)” within the period: 11.05.2012 – 10.05.2016.The project was coordinated by prof. Thodoris Karapantsios from Aristotle University of Thessaloniki, Greece and prof. K. Małysa from ICSC PAS was the polish representative in the Management Committee of the COST Action MP1106,

Last meeting of the Management Committee of the COST Action MP1106 was held in Athens, Greece on May 4th 2016, during the Conference "Smart & Green Interfaces", coupled with annual meeting of the COST MP1106 working groups, which took place in Athens on May 4-6, 2016. Scientists from the ICSC PAS (3 persons) participated in the Conference and presented the following contributions:

1. J. Zawala, P.B. Kowalczuk, D. Kosior, J. Drzymala, K. Malysa, "A Correlation Between Kinetics of Bubble Attachment to Solids and Flotation Efficiency", (oral)
2. M. Krzan, "Influence of bubble wake development on bubble motion in surfactant solutions", (oral)
3. A. Wiertel, J. Zawala, K. Malysa, "Kinetics of bubble coalescence at surfaces of different fluids – influence of external disturbances and size of the liquid films formed", (poster)
4. M. Krzan, E.Jarek, H. Petkova, E. Santini, V. Ungalanthan, M. Lofti, A. Javadi, E. Mileva, P. Warszynski, R. Todorov, F. Ravera, L. Liggieri, R. Miller, D. Exerowa, "Biodegradable aqueous foams based on xantan and gellan gums", (poster)
5. M. Krzan, "Influence of n-alcanol chain length on local and terminal velocities of rising bubbles", (poster)

Dr. Jan Zawala from our Institute applied and obtained financing from the COST P1106 project for the STSM and spent 2 weeks (13.03 - 26.03.2016) visit in TIPs (Transfer, Interfaces & Processes) laboratory, Faculty of Applied Science Universite Libre de Bruxelles. The purpose of the two weeks Short Term Scientific Mission in the TIPs laboratory under the supervision of Prof. Benoit Scheid was to elaborate the principles of a model describing drainage of foam films formed at a liquid/gas interface by a colliding bubble.

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 2016, at ICSC we were focused on the preparation and modification of nanocapsules containing macromolecular neuroprotective substance. Nanocapsules core were obtained by complexation of Catalase with oppositely charged polyelectrolyte. Such macromolecular complexes were further encapsulated in the polyelectrolyte multilayer shells. The polyelectrolyte multilayer shell was constructed by sequential adsorption of polyelectrolytes (layer-by-layer) method. 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. Additionally we developed algorithms for the evaluation of the kinetics of release of active compounds from nanocapsules with polymeric shells.

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 or boron doping process is performed from the environmentally benign liquid sources instead of $POCl_3$ or BBr_3, actually applied in industry, which are toxic and difficult in use. The project activity resulted in development of phosphorus and boron sources that allows formation of adequate P or B distribution profiles and the cell efficiency comparable to the obtained from $POCl_3$ or BBr_3 but with much lower costs of the process. Additionally, the obtained surface glasses containing phosphorus or boron showed ability to be removed/etched from the silicon surface much efficiently than the already applied ones that is important for industrial application.

Other International Research Projects

Immobilization of metal nanoparticles on organo-modified layered silicates.

Research project under Polish-Slovak Scientific and Technological Cooperation [2016-2018]
(project leaders: Małgorzata Zimowska PhD, Helena Pálková PhD)

The aim of the project was immobilization and stabilization of ruthenium metal nanoparticles on the polymer modified clay mineral supports to be active in the reaction of 2-butanone hydrogenation.

Organo-modified clay mineral samples were prepared by delamination of the natural smectite - Jelszowy Potok (JP) in distilled water and subsequent introduction of the organic cationic species of polymer with high charge density (Polydiallyldimethylammonium chloride - PDDA) with an average molecular weight of 400 000-500 000. Two weight ratios of clay and polymer were used for synthesis of organo-modified layered silicates (JP-PDDA_1:0.05 and JP-PDDA_1:0.25) to be further applied as a supports for Ru species.

Immobilization and stabilization of the introduced Ru^{3+} cations between anionic layers of clay mineral on the synthesised composites varying with JP-PDDA ratio was assured through 3 different proposed in this study novel approaches. In the first approach, directly introduced to the organic JP-PDDA composites Ru^{3+} cations were reduced with $NaBH_4$ to obtain metallic particles distributed in the organo-clay supports. In the second case the reduced Ru-PDDA domains were intercalated into the interlayer space of JP. In the third approach prior to the reduction Ru-PDDA domains were anchored between the layers of clay mineral JP. The polymer-free Ru-JP, containing the same 2 % of Ru in respect to JP, was applied as a reference.

The amount of PDDA influenced the configuration and arrangement of PDDA polycations in the interlayer spaces of the clay minerals. XRD analysis showed an increase of the d_{001} basal spacing in the JP-PDDA_1:0.05 sample (1.45 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 (1.55 nm).

Introduction of Ru cations, followed by reduction with $NaBH_4$, resulted in materials whose interlayer spacing differed both from that characteristic of the organoclay counterparts without metallic ruthenium and from the one observed in metallic Ru-containing unmodified clay mineral.

While all Ru-JP-PDDA_1: 0.05 composites exhibited slight increase of d_{001} basal spacing without exceeding the value 1.5 nm of interlayer space, Ru-JP-PDDA_1: 0.25 samples were characterized by a shift of d_{001} to 1.86 nm.

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

Composites with a smaller amount of PDDA (JP-PDDA_1: 0.05) contained about 1.56 % Ru, while in nanostructures with higher content of PDDA (JP-PDDA_1: 0.25) the amounts of Ru were lower and equal 1.32-1.39 %.

TEM analyses indicated that the size and state of aggregation of incorporated metallic Ru nanoparticles was depended on the method of immobilization and influenced the activity of synthesized composites in the reaction of 2-butanone hydrogenation.

The highest 82 % conversion of 2-butanone to butanol showed the catalyst with the highest size of Ru clusters (approx. 5 nm) obtained by the reduction of the Ru-PDDA prior to intercalation. Other catalysts with smaller crystallites of Ru (2-3 nm) showed catalytic activity in the range of 5-30%.

Our studies revealed that the size of crystallites and their susceptibility to reoxidation is crucial for their use in the hydrogenation reaction of 2-butanone.