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DETAILED RESEARCH REPORT

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Contents

Statutory Research

Catalytic Materials and Processes for Sustainable Development

Catalytic Processes Using Bio-Resources.
The Pd-Ir catalysts for the conversion of carbonyl compounds

(Professor Alicja Drelinkiewicz, Erwin Lalik PhD, Robert Kosydar PhD, Aleksandra Pacuła PhD, Tomasz Szumełda PhD)

The aim of studies was to determine reactivity of bimetallic PdIr catalysts in the hydrogenation of carbonyl compounds, such as cinnamaldehyde (CAL) and bio-reagent furfural (FU).

The research included the preparation of catalysts by a reverse water-in-oil microemulsion (w/o) method (Triton X 114, cycloheksane, $NaBH_4$ reducing agent) using mesoporous supports SiO_2 (Davisil grade 634, surface area of 291 m^2/g, porosity 0.85 cm^3/g), carbon black (Vulcan XC72 Cabot, 228 m^2/g, 1.77 cm^3/g). The bimetallic catalysts consisting of the 2wt%Pd and 1.3wt% Ir ($Pd_{74}Ir_{26}$) were prepared using precursor solutions (aqueous solutions of $PdCl_2$ i $IrCl_3$) of growing concentration: 0.013, 0.02, 0.04, 0.08, 0.14 i 0.2 M. The monometallic 2%Pd and 2%Ir catalysts as well as the bimetallic catalyst of lower Ir content, $Pd_{85}Ir_{15}$ (2%Pd) were also synthesized using 0.02 M precursor solution. The catalysts were characterized by BET, XRD, XPS, SEM, HRTEM techniques. The surface properties of metallic particles (fraction of Ir and Pd) were evaluated by CV (0.5 M H_2SO_4) measurements.

Results. The nearly monodisperse metallic particles of size within very narrow range 2.5-6 nm (SEM, TEM) appeared in all the catalysts. Regardless of the preparation conditions and Ir content, average size of the PdIr nanoparticles was almost close 4 - 4.5 nm (XRD, TEM), similar to that of Ir (4.2 nm) but below that of Pd (6.2 nm). The preservation of fcc crystalline Pd structure assisted by a small shift of the XRD reflexes to higher angles proved the formation of PdIr "alloy structures". The results of EDS and STEM techniques showed the particles of $Pd_{74}Ir_{26}$ i $Pd_{85}Ir_{15}$ nominal compositions, being in accordance with the intended ones. The CV measurements showed the Pd/Ir molar ratios at the particles surface 4.9 - 3.4 exceeded the nominal one Pd/Ir = 2.85. This indicates the Pd and Ir components segregation resulting in the outer surface enriched in Pd. With growing concentration of precursor solution the surface fraction of Ir gradually increased (from 0.05 to 0.23 corresponding to Pd/Ir = 19 and 3.4) revealing a slowly decreasing metal segregation. The modification of Pd electron properties in the PdIr surface was confirmed by the XPS spectra (a shift of Pd binding energy) as well as definitively weaker interaction with hydrogen (lower potential of of hydrogen desorption in the CV experiments) and lower heat of hydrogen sorption determined by calorimetric measurements.

The catalytic experiments showed that the activity of bimetallic catalysts in the hydrogenation of cinnamaldehyde (CAL) and furfural (FU) was determined by the Pd/Ir surface composition. In the hydrogenation of CAL (toluene, 25^0C, p atm) only the catalysts prepared using the precursor solution of low concentration e.g. with outer surface distinctly enriched in Pd displayed higher activity than that of Pd. The highest activity, ca. 2-times higher compared to Pd exhibited the PdIr catalyst with the surface Pd/Ir = 5.7 (prepared using 0.02 M precursor solution). All the bimetallic PdIr catalysts characterized by higher selectivity to unsaturated alcohol than that of Pd, the highest (ca. 3-times higher compared to Pd) displayed the most active catalysts characterizing by the Pd/Ir = 5.7 surface molar ratio.

In the hydrogenation of bio-reagent, furfural ((isopropanol, 35^0C, 6 bar) the activity of PdIr decreased with growing surface fraction of Ir, whereas all the catalysts displayed similar selectivity to furfuryl alcohol (ca. 60 %), much higher compared to Pd (40 %). Simultaneously, gradually increased selectivity to furan ring hydrogenation while the reactivity to isopropyl acetal, a product of side reaction between furfural and solvent decreased. Further growth in activity and selectivity to unsaturated alcohol (furfuryl alcohol) was achieved over the catalyst with lower nominal Ir content ($Pd_{85}Ir_{15}$) and the surface much more enriched in Pd (Pd/Ir = 8, CV, XPS), most probably because of better dispersed Ir.

The obtained results could be utilized to design the bimetallic PdIr catalysts of much higher activity and selectivity to unsaturated alcohol compared to monometallic Pd.

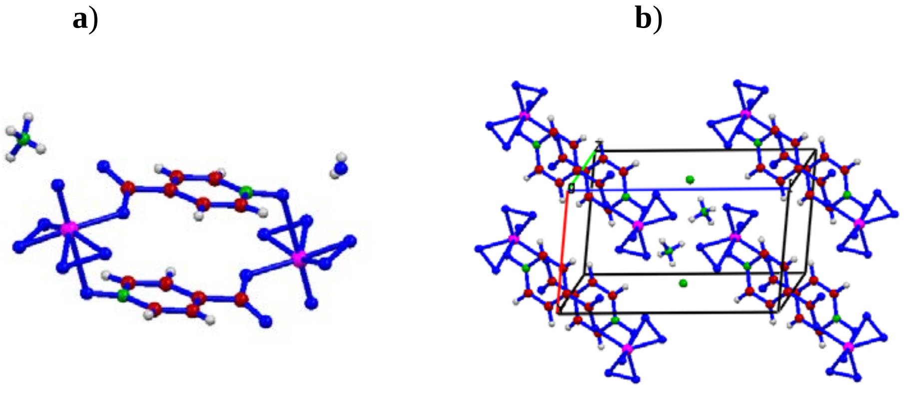
New peroxo- and polyoxo- compounds of Mo (VI), W (VI) and V (V). Synthesis, structural studies and applications in oxidation processes

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

The conducted recently research concerned the synthesis and structural studies of new peroxido compounds of Mo and W. The main results obtained in the last period can be briefly summarized as:

1. Due to the observation that the investigated peroxidomolybdates of nicotinic acid often contain N-oxide groups (as building blocks), a series of syntheses were carried out in which N-oxides of nicotinic acid derivatives were used as the substrate. It has been found that such syntheses are more reproducible, more efficient and much shorter.
2. A series of syntheses of new peroxido compounds of Mo and W, were carried out with the isonicotinic acid N-oxide (**N-iso**). So far, it has been possible to isolate new, pure phases of ammonium, potassium and sodium compounds with molybdenum (**1,2,3**) and potassium salt with tungsten (4).
3. The refinement of the crystal structure of ammonium (1) and potassium (2) salt of aqua-oxo-diperoxo- (**N-iso**) -molybdenum (VI) was completed. The ammonium salt was examined by X-ray single crystal methods, salt (2) by powder diffraction methods, studies of the crystal structure of compound (4) are in the final stage of implementation.
4. A number of attempts have been made to obtain new polymolybdates of complex aniline derivatives. The obtained compounds are at the stage of powder diffraction investigations.
5. For selected compounds, tests of catalytic oxidation of cyclic hydrocarbons (carried out at IKiFP PAN) and epoxidation of cyclooctane (University of Aveiro, Portugal) have been performed. Selected materials were tested in the IF PAN as part of pharmacological investigations.

The following Figure shows the asymmetric unit (a), and the projection of structure (b) of triclinic hydrated ammonium salt 'oxo-diperoxo- (**N-iso**) -molybdenum (VI) (1), Spheres with magenta, brown, blue and green colors indicate Mo, C, O and N atoms, small gray spheres represents H atoms.


a) **b**)

Crystallografic data:

(**a**) Chemical formula C6 H8 Mo N2 O9 .SG P-1, a 6.5619(3), b 7.1063(3), c 12.0469(4)Å,
α 91.517(3), β 96.093(3), γ 104.610(4)°, vol. = 539.694 Å^3, Z=2

(**b**) Chemical formula C6 H8 Mo K N O9 .SG P 2_1/n, a 9.2483, b 19.549, c 6.9661 Å, β 111.32 °, vol.= 1173.24 Å^3, Z=4

Catalytic Oxide Systems for Production High Value Added Products – Components of Fuels and Plastics

Studies of Nature and Characters of Active Sites in System Cu-FAU31 as Catalysts for Furfural to Furan Hydrogenation

(Associate Professor Dorota Rutkowska-Żbik, Michał Śliwa PhD, Katarzyna Samson PhD,
Małgorzata Ruggiero-Mikołajczyk PhD, Łukasz Kuterasiński PhD, Wojciech Rojek MSc,
Jerzy Podobiński MSc)

The aim of the statutory research was to 1) synthetize copper-based catalysts, in which Cu phase is introduced into zeolitic matrix and to test them in furfural hydrogenation process in the gas phase and 2) to define which of the active centres present in the obtained materials (redox-type or Brønsted acid type) are responsible for their activity.

Two series of catalysts of varying content of copper (1, 2, 5 %mas) were synthetized on the following zeolites: beta (BEA) and faujasite (FAU). The obtained samples were characterised with the following physic-chemical methods:: XRD, IR in the presence of probe molecules (ammonia, carbon oxide), low-temperature nitrogen sorption, H_2-TPR, NMR, SEM. The catalytic tests in furfural hydrogenation were done using gas flow reactor under atmospheric pressure in temperatures 300° and 400°C. The selectivities to the desired furfural hydrogenation products (2-metylfuran (2-MF) and furan) as well as by-products (methane, ethane, and butane) were measured.

The conversion of furfural over Cu containing BEA samples reached 100%, but the selectivities to the desired products were very low (selectivity to furan was 2% at 300° and 400°C; selectivity to 2-methylfuran was 10% and 0%, respectively - for systems containing 2 %mas Cu). In case of samples containing 2 %mas of Cu introduced into FAU the conversions were much lower (53% and 56% at temperatures 300° and 400°C, respectively), with selectivities to furan 75% and 100% as well as 25% and 0% to 2-methylfuran, respectively. The catalysts based on FAU zeolite were selecter for further studies.

Table. Results of catalytic tests for faujasite (FAU) and faujasite with blocked acidic centres (NaFAU) with and without copper redox active phase (S – selectivity, Y – yield).

Sample	**Conversion [%]**		**S_{Furan} [%]**		**$S_{2\text{-}MF}$ [%]**		**Y_{Furan} [%]**		**$Y_{2\text{-}MF}$ [%]**	
	300 ºC	**400 ºC**	**300 ºC**	**400 ºC**	**300 ºC**	**400 ºC**	**300 ºC**	**400 ºC**	**300 ºC**	**400 ºC**
FAU	24	56	100	100	0	0	24	56	0	0
Cu$_2$FAU	53	55	75	100	25	0	40	55	13	0
NaFAU	0	0	0	0	0	0	0	0	0	0
Cu$_2$NaFAU	27	22	50	81	50	19	14	18	14	4

As the next step, the samples with blocked acid centres were obtained (denoted further as NaFAU) and their catalytic activity was tested – see Table for the results. The performed experiments allowed to propose the relation between the type of acid centres (redox-type, Brønsted acid type) and the type of products (2-metylfuran and furan) obtained in the studied reaction. It was found that the production of 2-methylfuran is determined by the presence of the redox-type centres, whose activity is higher at 300ºC, while the acid centres are responsible for furan production. The latter become more active at 400ºC.

New Catalytic Materials for „Green Chemistry" Processes

Hydrotalcite Systems as Catalysts for Baeyer-Villiger Oxidation

*(Professor Ewa Serwicka-Bahranowska, Roman Dula PhD, Dorota Duraczyńska PhD,
Robert Karcz PhD, Alicja Michalik PhD, Bogna D. Napruszewska MSc,
Joanna Kryściak-Czerwenka PhD, Katarzyna Pamin PhD, Jan Połtowicz PhD,
Małgorzata Zimowska PhD)*

Investigations encompassed design and synthesis of heterogeneous catalysts, based on synthetic magnesium-aluminium hydrotalcites and heteropolycompounds, for mild oxidation reactions in the liquid phase. Part of research concerned compositional modification of the layered silicate kanemite.

Studies of hydrotalcite catalysts of Mg/Al ratio in the 1.93 - 6.63 range demonstrated that along with the increase of the Mg content, the interlayer divalent carbonate anions become gradually replaced with monovalent bucarbonate an/or nitrate anions. The observation contradicts the generally accepted view that the hydrotalcite-like structures have greater affinities for multivalent anions compared with monovalent ones. It is argued that in materials with low degree of Al for Mg substitution, hence larger distance between the charge generating sites, compensation by monovalent anions enhances Coulombic interactions within the hydrotalcite-like structure. Magnesium-aluminium hydrotalcites have been used as catalysts for the oxidation of cyclohexanone to ε-caprolactone, using H_2O_2 as an oxidant. Reaction was carried out at 70°C. It has been shown that the catalytic activity increases as the crystal size of the hydrotalcite diminishes. Catalyst crystallinity may be controlled by an appropriate choice of the synthesis conditions, or by mechanical comminution. In particular, grinding in a planetary mill has been shown to significantly enhance the hydrotalcite catalytic activity. Optimum effect depends on the time of treatment. Short grinding results in a decrease of the crystal size and an increase of surface hydrophilicity. Both effects are beneficial for catalysis. Prolonged grinding causes surface hydrophobization, which is unfavorable for H_2O_2 adsorption and impairs catalytic properties.

Investigation of heteropolycompounds concentrated on W- or Mo-Keggin type of heteropolyacids, with protons substituted to a different degree with cobalt, manganese, or iron. The general formula of the samples was $H_{3-2n}M_nPX_{12}O_{40}$, where n = 0,5, 1, or 1,5, M = Co, Mn, Fe, and X = Mo or W. The materials were used as catalysts in the liquid-phase oxidation of cyclohexanone to ε-caprolactonein the oxygen-aldehyde system, at 40°C. For both the tungsten and the molybdenum based series, the optimum degree of substitution, from the catalytic point of view, corresponded to the replacement of two protons with a cation of transition metal. This pointed to the importance of the catalyst bifunctionality and participation of both the acid and the redox function in the catalytic transformation. Best performance was obtained for the tungstophosphoric acid partially substituted with cobalt. The proposed reaction mechanism identified participation of heteropoly compounds in three steps of the investigated reaction: oxidation of aldehyde to peracid (redox function), activation of carbonyl group (Lewis acidity), and decomposition of the Criegee adduct to ε-caprolactone (Brønsted acidity).

Modification of kanemite composition, consisting in replacement of interlayer sodium cations with other monovalent cations, was carried out by means of ion exchange. Characterization of the resulting materials with XRD, SEM/EDS, and FTIR showed that the structural order in the silicate depends on the nature of the introduced cation.

Equivalent Electrical Circuit of the Magnesium Electrode Corroding in Indifferent Electrolyte Solutions

(Michał Mosiałek DSc, Professor Paweł Nowak, Grzegorz Mordarski PhD)

Magnesium alloys found practical applications relatively recently in comparison to other metals, therefore their properties are not very well known. The susceptibility of magnesium alloys to corrosion is one of the most important reasons that limits their usage. Therefore, a quick and accurate method of evaluating the corrosion resistance of magnesium alloys is needed. Electrochemical impedance spectroscopy (EIS) is one of the methods of choice, and fitting equation describing the adequate equivalent electrical circuit (EEC) to the measured data is the most commonly used procedure of interpretation of the results obtained using EIS. The development of such EEC was the subject of our research. First of all, we examined the corrosion of magnesium itself, because in all alloys and composites containing magnesium, the most sensitive to corrosion component is magnesium. We also examined corrosion of some magnesium alloys: AZ91, WE43, ZRE1, and QE22.

The main problem in the study of magnesium corrosion is the susceptibility of magnesium to corrosion, which results in very rapid changes in the surface properties of the tested sample, which in turns implies quick changes in the corrosion process rate. Most of the investigations were carried out at a reduced temperature (2 °C), in solutions with low concentration of inorganic salt (0.5% NaCl) additionally saturated with magnesium hydroxide in order to slow down corrosion process. The presence of magnesium hydroxide stabilizes pH at relatively high level and decreases the corrosion rate as a result of the $Mg(OH)_2$ layer precipitation on the corroding surface. Besides, such conditions are similar to the conditions under which magnesium alloys corrode during the operation of means of transport in winter. In such conditions, magnesium alloys are exposed to the contact with NaCl solutions formed as a result of using this substance to remove ice from the road surface. The rotating disk electrode method was used in order to define hydrodynamic conditions in the solution. The tests were carried out in a typical electrochemical cell, in a three-electrode setup, in solutions deoxidized by bubbling argon or hydrogen.

The extremely strong impact of agitation on the kinetics of the magnesium corrosion process was observed. Impedance spectra of pure magnesium electrode measured on a stationary electrode and an electrode rotating at low angular velocity are shown in Figure1. As can be seen, the movement of the electrode causes a dramatic change of the spectra parameters, although the shape of the spectrum remains unchanged. Both spectra shown in Figure1 could be fitted using EEC presented below the spectra. The behavior of corroding magnesium electrode was well described with the parameters obtained with this EEC. We observed similar effects in the measurements carried out using the linear polarization method, as well as in measurements of stationary corrosion potentials. The presented investigations results in very important conclusions concerning the methodology of evaluation of magnesium susceptibility to corrosion by electrochemical methods. Namely, in such measurements, it is necessary to use strictly defined and repeatable hydrodynamic conditions. The analysis of scientific and scientific-technical literature on the corrosion of magnesium and its alloys shows that this problem has been neglected so far.

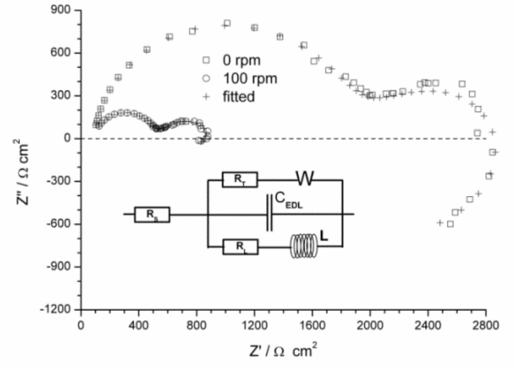


Figure 1. Impedance spectra of stationary Mg electrode an the electroderotating with 100 rpm rate electrodes in deaerated 0.5% NaCl solution saturated with $Mg(OH)_2$ measured in 2 mHz – 10 kHz frequency range.

Enzymatic Processes - Basic and Applied Research.

Characteristics of Native and Immobilized (R)-1-Phenylethanol Dehydrogenase

(Professor Tomasz Borowski, Associate Professor Maciej Szaleniec, Maciej Guzik PhD, Agnieszka Wojtkiewicz PhD, Mateusz Tataruch PhD)

The purpose of our basic research pursued with computational methods is to obtain insights into mechanisms of enzymatic reactions of selected proteins. Recently-reported structures of benzylsuccinate synthase (BSS) allowed us to study, by means of MD simulation, the dynamic behaviour of known BSS substrates and derivatives that are not converted by the enzyme. Based on the analysis of the active site structure and results of comparative sequence analysis of BSS analogues, mutations of crucial residues were introduced into the BSS model enabling penetration of the m-xylene into the active site. Moreover, a QM:MM modelling was conducted to study the reaction pathway, elucidating the mechanism of the radical transportation from Gly828 through Cys492 to toluene. We were also able to re-examine the previously described QM-based mechanistic model with full information on the substrate-enzyme interaction enabled by multiscale QM:MM modelling.

With the use of MD simulations we study dynamical behaviour of active sites in various forms of superoxide dismutases that bind iron or manganese. The long-term goal of these studies is to obtain insights into factors determining which transition metal ion is used by these enzymes.

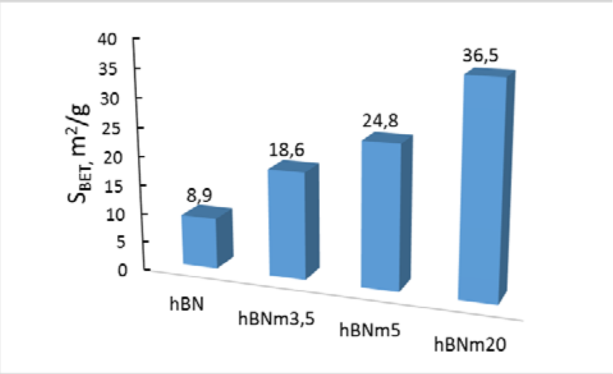
The applied research was aimed at optimization of the immobilization process for (R)-1-phenylethanol dehydrogenase (R-PEDH) on silica supports. R-PEDH is a bacterial enzyme found in denitrifying bacteria *Aromatoleum aromaticum* (gen. Azoarcus) and belongs to the short-chain dehydrogenase/reductase family (SDRs). Enzymes from the SDR family catalyze oxidation of alkohols to ketones and usually turn over many different alternative substrates. R-PEDH catalyzes the NAD^+-dependent stereospecific oxidation of (*R*)-1-phenylethanol to acetophenone and industrially useful NADH-dependent reverse reactions - reduction of acetophenone to (*R*)-1-phenylethanol. High stereospecificity and availability of an overexpression system for the R-PEDH makes it a powerful tool for production of chiral alcohols.

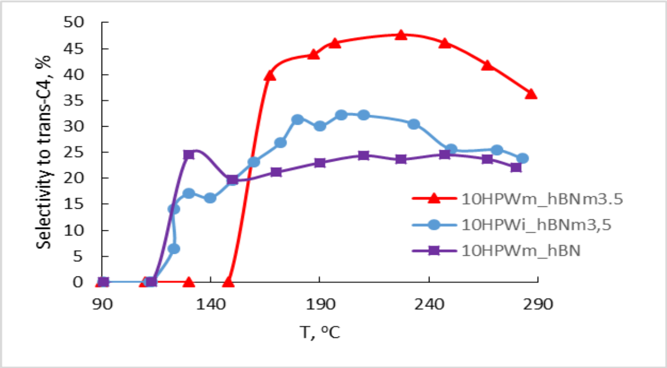
Immobilization studies were preceded by bacterial culture and enzyme isolation using Strep-Tag affinity chromatography. R-PEDH was immobilized on silica spheres (Matspheres®) provided by the Canadian company MATERIUM Innovations. The reference carrier was crystalline microcellulose. Silica spheres were tested in two variants: the Matspheres®-OH and Matspheres®-NH_2. Immobilization of the enzyme was carried out by covalent binding. For carriers with amino and hydroxyl groups, glutaraldehyde and divinyl sulfone were used as the binding agent respectively. Enzymatic activity was measured by UV-vis spectrophotometry and HPLC methods using ACF as a model substrate. It was shown that only the enzyme immobilized on a silica support with amino groups (Metaspheres®-NH2) possesses the catalytic activity. The optimal concentration of isopropanol (10%) was determined for reaction in the NADH co-substrate recovery regime. R-PEDH immobilized on Metaspheres®-NH_2 was tested in a batch reactor. The studies showed a 35-fold higher operational stability of immobilized R-PEDH (35 days) compared to a homogeneous enzyme (24 h).

Dehydration of Alcohols on the Modified Heteropolyacids

(Professor Małgorzata Witko, Associate Professor Renata Tokarz-Sobieraj,
Anna Micek-Ilnicka DSc, Urszula Filek PhD, Natalia Ogrodowicz MSc)

Heteropolyacids (HPA) are polyoxometalates having very high acidity. The dehydration of primary alcohols on HPAs leads to the formation of the unsaturated hydrocarbons and ethers due to the existence of acidic Brönsted centers. The aim of the investigation was a synthesis of active catalysts for the n-butyl alcohol dehydration in the gas phase. Dodecatungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW) was supported on selected materials characterized by high specific surface area i.e. titanium dioxide (TiO_2), hexagonal boron nitride (hBN) and montmorillonite (K-10). Two of these supports, TiO_2 and K-10, had intrinsically high specific surfaces, namely: 183 and 250 m^2/g, respectively. The surface of commercial hBN (S_{BET}), in turn, was initially 9 m^2/g, but it was eventually increased to 37 m^2/g by grinding of the material in a ball mill for up to 20 hours (figure). So modified samples were denoted "*hBNmhours*", where *mhours* means the period of grinding in hours.





The following techniques were used to support the active phase (heteropolyacid) on the support:

- impregnating of the support with HPA solution in alcohol (ethanol)
- ball milling of support suspension in ethanol with heteropolyacid for 3.5 hours.

The physicochemical characterization of catalysts was carried out using XRD, FT-IR, SEM, TG/DSC, BET, TPD of ammonia techniques. The catalytic activity of supported heteropolyacids was measured by the catalytic system containing a flow microreactor connected *on-line* with gas chromatograph. A care has been taken so that the amounts of catalysts in each experiments always corresponded to $3 \cdot 10^{-5}$ mol H^+, what allows to compare the acid properties of catalysts.

The n-butanol conversion was carried out within the temperature range of 90-290 °C, at the alcohol partial pressure of 3 kPa. The catalytic activity of supported materials were compared to the unsupported HPW. The highest conversion of alcohol (100% w 190 °C) and the yield of di-n-butyl ether (DNBE) was achieved for the HPW/K10 catalyst, whereas for the unsupported heteropolyacid, the maximal conversion was 58% at 110 °C. The hBN-supported catalysts reached the same level n-butanol conversion, independent of technique of their preparation. Eventually, the sequence of n-butanol conversion was found to be:HPW/K-10 > HPW/TiO_2 > HPW > HPW/hBN.
it is worthy to mention that the synthesis method of HPW/hBN catalysts turned out to affect significantly their selectivity. Thus the catalyst HPWm-hBNm3.5 showed the highest selectivity to trans-2-butene (figure). On the other hand, the selectivity to cis-2-butene was higher than selectivity to trans-2-butene for others HPW/hBN catalysts. In turn, the highest selectivity to di-n-butyl ether DNBE was reached for HPWi-hBNm3.5 (65% at 110 °C), whereas for others catalysts this selectivity equals 20 %.

Physics and Chemistry of Surfaces and Nanostructures – Experiment and Theory

Studies of Physicochemical Properties of Novel Zeolite Materials by Solid-State Nuclear Magnetic Resonance Spectroscopy

(Professor Bogdan Sulikowski, Mariusz Gackowski PhD)

In the period reported we have carried out studies aimed at desilication of zeolite Y. A pristine sample was previously modified by dealumination. To achieve this goal, the parent dealuminated material with enhanced Si/Al ratio was treated with alkali solutions of different inorganic and organic agents. The status of aluminium and silicon in samples was studied by NMR and thus local environments of the nuclei were obtained. For aluminium, 1D spectra were recorded. Optimization of 2D experiments allowed acquisition of multi-quantum NMR spectra. By applying ^{27}Al 3MQ Magic-Angle-Spinning NMR, different alumina oxides and some hierarchical zeolite samples were studied.

Optically clear sols can be used for synthesis not only zeolites but also amorphous aluminosilicates under mild conditions. Therefore, the composition and behaviour of such sols are of utmost importance. It was of interest to shed some light on the synthesis of aluminosilicate sols and to follow changes taking place in sols in prolonged time, from few hours to nearly 300 days, by using ^{29}Si and ^{27}Al NMR. We developed a method for studying simultaneously sols containing *small aluminosilicate molecules* and *larger nanoclusters* formed from them. Finally, mesoporous layered aluminosilicates prepared from sols were studied extensively by silicon and aluminium solid-state MAS NMR.

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

Magnetic Anisotropy in Epitaxial Layers of 3d Metals: Influence of Neighboring Layer

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

The research task was aimed at optimization of the catalytic and spintronic functionality of model nanostructures of transition metals and their oxides. Both surface nanostructures obtained by molecular beam epitaxy and bulk materials active in chemical reactions at the gas/solid interfaces were studied.

The magnetic anisotropy was engineered in epitaxial layers and multilayers of 3d metals and their oxides. The research in this class of materials was performed for systems containing several tens of nanometer thick Fe(110) films grown on a W(110) single crystal, the magnetization of which is switchable in the plane by the layer thickness, temperature, and first of all by the proximity of another layer. A single and double reorientation of spontaneous magnetization in the epitaxial Au/Co/Fe(110) three-layers was observed. This type of behavior is due to the strongly nonmonotonic dependence of the magnetic anisotropy of the Co layer as a function of thickness. In the Co/Fe(110) system, the cobalt layers were epitaxially stabilized in the BCC structure. The effect of a strong dependence of magnetic anisotropy on the sublayer thickness was accompanied by a modification of the magnetic properties by gas adsorption. In the CoO/Fe(110) system, which exhibits the effect of the exchange bias due to the interaction of an antiferromagnet (CoO) and a ferromagnet (Fe), based on experimental magneto-optic Kerr effect and X-ray magnetic circular dichroism data and computer simulations, it was shown that the ferromagnetic layer with a strong uniaxial magnetic anisotropy determines the orientation of the spins in the adjacent antiferromagnetic layer, and is able to cause their rotation.

In metallic multilayer systems, containing epitaxial layers of the FeRh alloy, the temperature phase transition antiferromagnet-ferromagnet in FeRh was studied for its role for modifications of the magnetic properties in neighboring ferromagnetic layers. A spintronic application of this novel approach to magnetic recording was proposed.

The nucleation, growth and temperature stability of Au-Fe bimetallic nanoparticles on a (110) oriented single crystal of TiO_2 (rutile), which were formed for sub-monolayer iron and gold coverages as a result of Au deposition on the surface with preadsorbed Fe, was analyzed as a function of metal doses and temperature. It has been found that for small Fe coverages, iron and gold nucleate independently and monometallic nanoparticles are formed. At higher coatings, Fe nanoparticles are nucleation centers for gold, and the Au-Fe bimetallic particles exhibit significant temperature stability up to approximately 700 K.

The second group of research tasks was related to the analysis of the surface composition and electronic states in different catalytic, photovoltaic, photo- electrochemical systems.

Significant efforts were devoted to the maintenance, calibration and measurements at the PEEM/XAS beamline at the National Synchrotron Radiation Center "Solaris". The end stations were made available to external users, both as a result of the general call for proposals and as part of the CERIC/ERIC consortium. Ten external user experiments were carried out at the PEEM end station, fully operated by ICSC PAS, and seven experiments at the XAS end station, to operation of which our Institute significantly contributes.

Molecules with biological Importance in Reference to their Interaction with a Surface and Refining their Theoretical Description

(Professor Tomasz Pańczyk, Associate Profesor Wojciech Płaziński, Agnieszka Brzyska PhD, Paweł Wolski PhD)

Molecules with biological importance deserve a particular research attention because they take part in various processes occurring in living organisms. Therefore, molecules belonging to the class of DNA/RNA fragments, proteins, oligo and poli saccharides or other molecules with confirmed or predicted pharmacological activity are extensively studied using various theoretical/computational tools. The aim of the studies was thus a careful analysis of the mentioned systems using more and more accurate and reliable methods. So far, the studies were mainly focused on getting fundamental insights into the properties of the studied systems and refining their theoretical description.

The studies were carried out for the following class of systems with biological importance: drugs carriers based on the structure of carbon nanotubes modified by magnetic nanoparticles and functionalized with folic acid and poly ethylene glycol molecules, and with doxorubicin or carmustine drugs molecules. The second system was the fragment of a telomeric DNA and the focus was on the analysis of formation/unfolding of secondary structures of the i-motif type as a function of pH. The results allow us to propose a design of a drug carrier with promising properties and with the chemical structure simple to engineer using well known chemical processes. The results concerning the telomeric DNA allow us to recognize the factors which are responsible for thermodynamic stability of the secondary DNA structures. This knowledge is necessary in further studies concerning the selective stabilization of those structures due to interactions with the nanostructured objects like carbon nanotubes.

Another part of the studies concerned elucidating the mechanism of interactions between selected heavy metal ions and chromatographic stationary phase containing *Spinacia oleracea L.* extract. The investigation included modeling of measured adsorption isotherms and quantum-mechanical calculations oriented at determining the mechanism and energetic characteristic of metal ion binding by particular elements of *Spinacia oleracea L.* extract. The results (binding stoichiometry and energy as well as adsorption capacity) suggest that immobilized molecules of chlorophyll a are responsible for metal chelation process whereas the 1:1 binding stoichiometry results from complexation with porphyrin rings. The affinities of the investigated bivalent metal cations for the sorbent are in the order: Pb(II) > Cu(II) > Ni(II) > Zn(II) ≈ Cd(II) ≈ Co(II) according to both quantum-chemical calculations and experimental measurements.

In addition, for various molecular systems (saccharides, spiropyrans, furan derivatives) the theoretical studies of the structural/conformational changes caused by the external stretching forces were carried out. It was a simulation of the classic AFM experiment. These studies mainly concerned molecules used as mechanosensors (mechanohores) and potentially self-repairing materials. Such substances can be used, for example, in the development of artificial muscle. The result was a theoretical description of the chemical reactions mechanisms induced by external forces.

Nanostructures of Soft Matter

Topology of Protein Monolayers at the Solid/Electrolyte Interfaces and Mechanisms of Their Interactions with Ionic and Macromolecular Ligands.

Mechanisms of Albumin Monolayesrts Formation on Heterogeneous Surfaces

(Professor Zbigniew Adamczyk, Jakub Barbasz DSc, Aneta Michna PhD, Maria Morga PhD, Małgorzata Nattich-Rak PhD, Magdalena Oćwieja PhD, Marta Sadowska PhD)

Serum albumin (HSA) binds many endogenic and egzogenic ligands, controls their concentration and facilitates their efficient transport to various tissues. In addition to the important physiological role, HSA is often used for drug delivery and for medical device coating (hemodializer membranes and peacemakers, orthopedic titanium implants, catheters) which prevents adhesion of other proteins, platelets and bacteria. Albumin monolayers are exploited as biosensors for a quantitative detections of various ions such as Cd^{2+}, Ni^{2+}, Zn^{2+}. Adsorption kinetics of human serum albumin (HSA) at a gold substrate was studied using the quartz microbalance (QCM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy. Measurements were performed at pH 3. for various bulk suspension concentrations and ionic strengths. The QCM experimental data were compared with the dry coverage of HSA derived from AFM and from the solution of the mass transfer equation acquired using a hybrid random sequential adsorption model. In this way, the water factor and the dynamic hydration function for HSA monolayers were quantitatively evaluated as a function of dry coverage for various ionic strengths. A comparison of these results with those obtained for a silica sensor (see Fig. 1) confirmed that the QCM kinetic measurements are sensitive to the roughness of the sensor characterized in terms of the *rms* parameter. For the more rough gold sensor (*rms* = 2.5 nm, average surface feature size 6 nm) the QCM mass transfer rate constant was 2.6 times lower than for the silica sensor characterized by *rms* = 0.86 nm. This gives for the gold sensor the apparent water factor equal to one and zero hydration function. Moreover, the hydration function increased for larger HSA coverage and was dependent on ionic strength in contrast to the silica substrate. This unexpected behavior was interpreted in terms of the buoyancy effect where the HSA molecules adsorbing in cavities existing at rough surfaces replace the stagnant (hydrodynamically coupled) water. Hence, these results confirm that the sensor roughness of the size comparable with protein molecule dimensions exerts a decisive influence on their adsorption kinetic derived from QCM measurements.

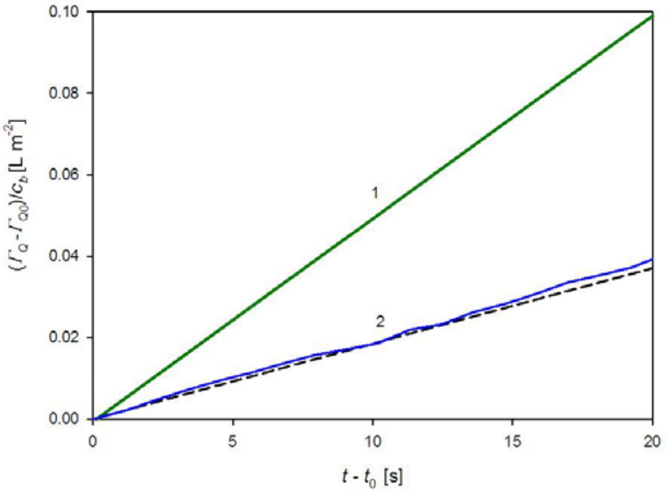


Figure 1. Dependence of the normalized HSA coverage at QCM sensors on the normalized adsorption time *t* averaged from a few runs performed at various bulk suspension concentrations (1 to 10 mg L^{-1}); pH 3.5, 0.15 M NaCl, flow rate $2.5x10^{-3}$ cm^3 s^{-1}. 1 – silica sensor, 2 – Au sensor. The dashed line shows the dry mass calculated from the convective diffusion theory.

Determination of Mechanisms of Synthesis, Structure, and Transport Parameters of Supported Colloidal Particle Multilayers

(Associate Professor Paweł Weroński, Karolina Pałka MSc)

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. That allows for using colloidal particle multilayers as functional nanomaterials such as membranes or heterogeneous catalysts. A simple and effective method of synthesis of colloidal particle multilayers is the “layer by layer” technique. So far, theoretical studies of multilayers dealt with systems of spherical particles with alternating surface charge and identical diameters. The assumption of constant size of all particles forming the multilayer is, however, a strong limitation that can essentially influence the applicability of derived results in real-world experiments.

The main aim of our research was to generalize the theoretical model of synthesis of spherical particle multilayer for bimodal systems where the diameters of particles of even and odd layers are different. For that, we developed generalized numerical algorithms and computer codes. Next, we used them to produce virtual multilayers of bimodal particles of the size ratio 2:1 and various single-layer surface coverages. We also conducted numerical analysis of various important functions and parameters describing the structure and transport properties of the multilayers. These are the multilayer thickness as a function of layer number and single-layer surface coverage, specific surface area and particle volume fraction as functions of distance from the substrate surface and single-layer coverage, power spectral density of outer surface roughness, and two-dimensional correlation functions.

Our results let us formulate a number of interesting conclusions. The important parameter determining the multilayer properties is the single-layer surface coverage. All the investigated parameters are sigmoid functions of single-layer surface coverage that suggests the existence of two different particle-adsorption regimes. Functions such as the multilayer specific surface area and particle volume fraction exhibit decaying oscillations with the amplitude decreasing with the increase of distance from the adsorption surface. Compared to monomodal particle multilayers, the oscillation decay is slower and therefore the oscillations are relatively long ranged. Therefore, the bimodal particle multilayers are characterized by enhanced layer-ordering, especially at large surface coverages. Application of bimodal particles results in the increase of specific surface area and decrease of particle volume fraction of multilayer.

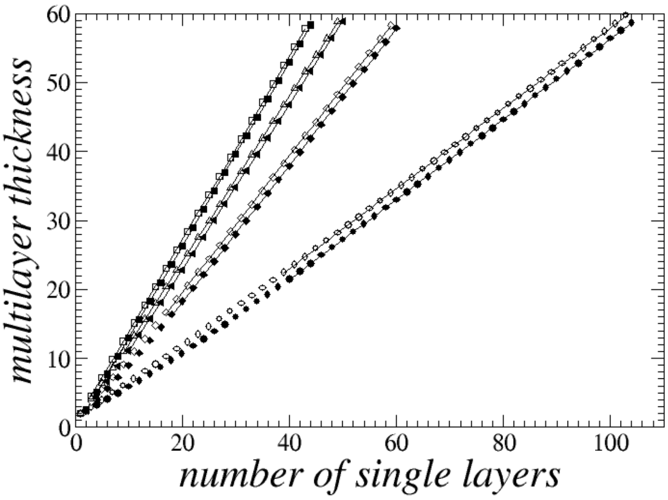


Figure. 1. Thickness of bimodal particle multilayer, normalized by the large particle radius, as a function of single-layer number, calculated for the coverage 0.1 (circles), 0.2 (diamonds), 0.3 (triangles), and 0.4 (squares).

Influence of Initial Adsorption Coverage on Kinetics of Dynamic Adsorption Layer Formation

(Associate Professor Jan Zawała, Dominik Kosior PhD, Agata Wiertel-Pochopień MSc, Anna Niecikowska PhD)

The statutory task was aimed to investigate influence of initial adsorption coverage at detaching bubble on kinetics of formation of dynamic adsorption layer – DAL. Different stages of the DAL formation at the air bubble rising in various surfactant solutions were monitored by tracking the bubble local velocity and shape deformation variations as a function of distance from a bubble formation point (capillary orifice).

In order to control the initial adsorption coverage at the surface of motionless bubble, a single bubble generator, allowing precise control over the bubble detachment frequency, was elaborated. In addition, so-called “bubble trap”, based on programmable stepper motor and a glass dome placed just above the capillary orifice, was developed. The moment of trap closure and opening (full dome rotation around its own axis) was synchronized with the moment of a single bubble generation. By software-controlled adjustment of time of the bubble residue inside the trap, time available for adsorption of surface-active molecules at the bubble (liquid/gas) surface (initial adsorption coverage) could be controlled. The values of initial adsorption coverage over the detaching bubble were calculated on the basis of equilibrium parameters of Frumkin adsorption isotherms, obtained for the studied surfactants, used for numerical derivation of Word-Tordai equation (diffusion limited adsorption model). The DAL formation kinetics at the rising bubble surface was tracked for surfactants of different adsorption kinetics. It was found that for all studied substances the time (distance covered) needed for full establishment of the DAL architecture at gas/liquid interface and its full immobilization was decreasing with initial adsorption coverage increase (see Fig. 1). Similarly, value of the bubble maximum velocity and distance of bubble deceleration, before velocity plateau was decreasing with the initial adsorption coverage (time of bubble residue inside the trap) increase. Identical trend was found for values of the bubble deformation ratio. In addition, it was found that the deformation ratio of the bubbles detaching from the capillary orifice with completely different initial adsorption coverage and reaching similar velocity at different distances from formation point, was identical. This means that the structure of the DAL at their surface was identical, as well.

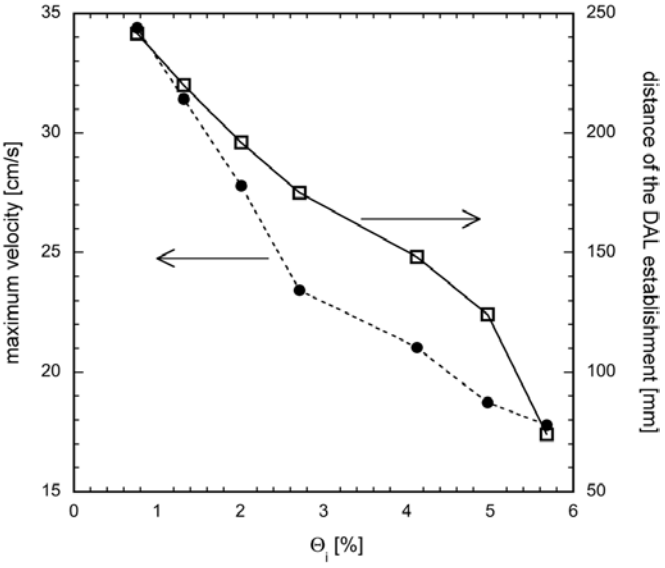


Figure. 1. Maximum velocity of the rising bubble and distance needed for full establishment of the DAL structure and bubble Surface immobilization as a function of initial adsorption coverage of the liquid/gas interface

Functional Polyelectrolyte Multilayers Films.
Antibacterial and Antiadhesive Mutlilayrered Nanocomposite Films

(Professor Piotr Warszyński, Marta Kolasińska-Sojka PhD, Tomasz Kruk PhD)

The main goal of the task was to optimize the methodology of producing multilayer films and coatings of nanocapsules with controlled physicochemical properties and specific functionalities. One of the task was to determine the effect of metal oxide nanoparticles on the formation and antibacterial properties of polyelectrolyte films. The investigated systems were obtained by sequential adsorption from aqueous solutions, "layer by layer" (LbL).

Microbiological tests of polyelectrolyte films with copper nanoparticles have been carried out using the fluorescent dyeing method. In these studies, the antibacterial and anti-adhesive activity of films $(PDADMAC/CuNPs)_n$ was evaluated. The substrate (silicon) and polyelectrolyte films of type $(PDADMAC/PSS)_n$ were used as reference materials. The structure and properties of the films with nano-objects were investigated using spectroscopic and microscopic methods: spectroscopic ellipsometry, UV-Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), optical and fluorescence microscopy. In addition, the build-up of polyelectrolyte films was followed by means of quartz crystal microbalance with dissipation monitoring (QCM-D). The stability of the suspension, the size of the nanoparticles and other materials were determined by dynamic light scattering (DLS).

The first aim of the work was to produce stable copper nanoparticles, exhibiting biocidal properties. In the next step, the nanoparticles were embedded in the polyelectrolyte film structure to produce films with antibacterial and antifungal properties, which were verified on the number of bacterial strains and fungi. The studies of microbial activity for polymer films with nanoparticles were performed in the collaboration with an external laboratory at the Faculty of Chemistry of Jagiellonian University and Warsaw Medical University.

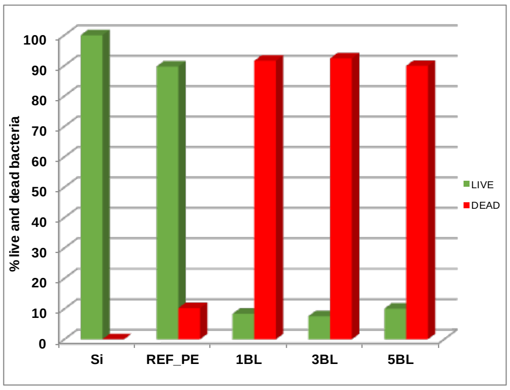


Figure 1. The viability of S. aureus after 6h of incubation with the CuNPs-containing coatings.

As depicted in Fig. 1, after 6h of incubation of the prepared samples, the number of living cells exceed 90% for the reference ones, i.e., silicon wafers bare and coated with (PDADMAC/PSS) films, whereas all the samples containing CuNPs showed antibacterial properties, with the significant decrease in viability of bacteria. Independently on the number of layers, less than 5% of the microorganisms remain alive. Thus, even one bilayer film was sufficient to exhibit antibacterial action.

Properties of Degradable Surfactants as Emulsifiers/Nanoemulsion Stabilizers

(Professor Piotr Warszyński, Ewelina Jarek PhD, Marzena Noworyta Eng)

The main objective of the research is the determination of adsorption properties of degradable surfactants: esterquats and/or amidequats. They contains in the molecular structure ester or amide bond that can undergo hydrolysis. Thus, those surfactant can be used as pH-sensitive emulsifiers or emulsion stabilizers.

We determined surface tension isotherms of for amidoquat type surfactants:

- C_{10}EATMBr [2-(decanolylamino)ethyl]trimethylammonium bromide,
- C_{10}MTMBr (*N*-decylcarbamoylmethyl)trimethylammonium bromide,
- C_{12}PATMBr [3-(dodecanolylamino)propyl]trimethylammonium bromide
- C_{12}ETMBr (*N*-dodecylcarbamoylethyl)trimethylammonium bromide,

the surface active quaternary ammonium compounds, in which the hydrophobic part of the moieties (C10 and C12 alkyl chains) are linked to the charged head group via amide bonds R-CO-NH- or R-NH-CO- oriented in the opposite direction. The surface tension isotherms were measured in various pH conditions and concentration of NaCl. We found significant differences in surface activity of amidoquat depending on the orientation of amide bond. However, in contrast to esterquat surfactants results cast doubts that those differences were resulting from the surfactant hydrolysis. The DFT calculations confirmed that the evaluated free energy barrier for basic hydrolysis is much higher that for esterquats. We proposed diferent mechanism for the explanation of the observed differences in surface activity – formation of complexes with hydroxide anion via hydrogen bond. The results of DFT computatation performed to support that hypothesis confirmed possibility of such a mechanism of surface activity diferences.

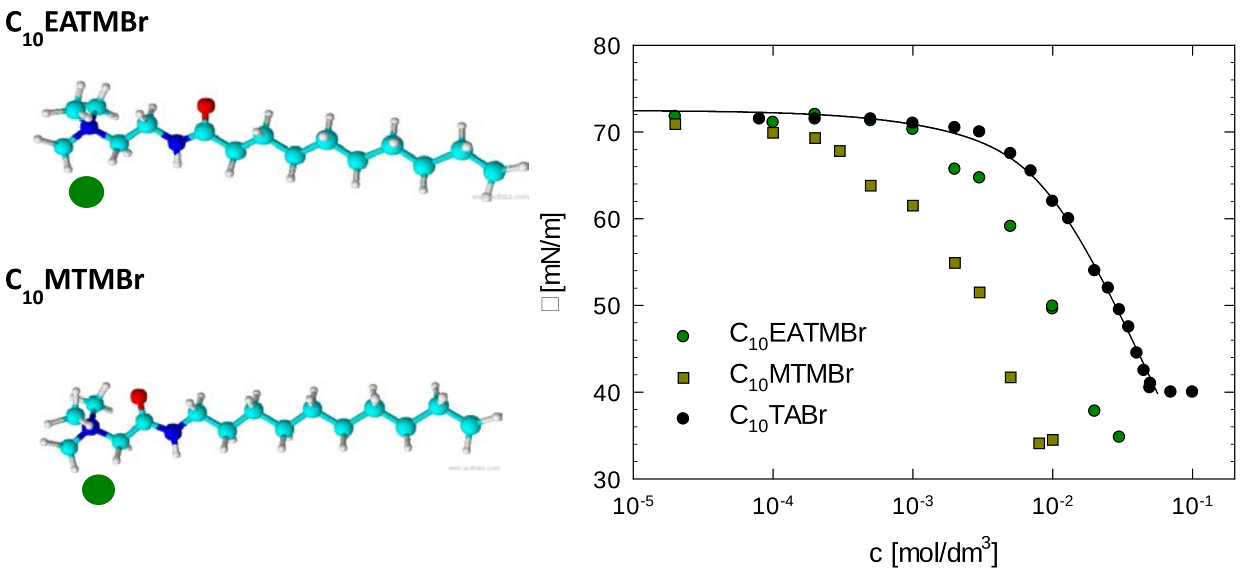
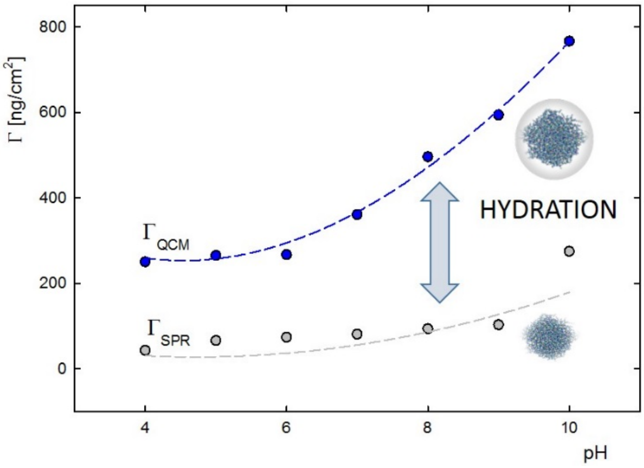


Figure 1. Minimized structures and surface tension isotherms for amidoquat surfactants.

Physicochemical Properties of Functional Nanocarriers Based on Dendrimer Systems

(Associate Proessor Barbara Jachimska, Martyna Jucha MSc, Paulina Komorek MSc, Agnieszka Siemek MSc)

The primary research goal was to create a scientific basis for understanding the mechanism of creating nanocarriers based on the structure of a dendrimer molecule that potentially allows immobilization of the therapeutic agent in a multilayer polymer coating, or inside the structure of the molecule. The dendrimer molecule, therefore, can simultaneously play a dual role in the delivery or release of the active substance.



Adsorption studies of poly (amidoamine) dendrimers (PAMAM) on model surfaces carried out with atomic force microscopy (AFM), quartz microbalance (QCM) and surface plasmon resonance (SPR) allowed to correlate the degree of ionization of dendrimers with dendrimer monolayer properties and to determine the degree of hydration PAMAM type dendrimer structures.

These measurements indicate the critical role of pH and ionic strength on the conformation of the dendrimer molecule structure caused by the change of ionization degree of amino groups. These properties can be an important aspect of the application of these polymers as potential drug carriers. The release of drugs can be controlled by changing the conformation of the molecule by external factors such as the pH or ionic strength of the solution. Understanding the mechanism of forming dendrimer complexes with selected ligands is a key issue allowing them to determine their application potential in the field of their functioning as drug carriers.

The conducted research issue leads to the development of a methodology for obtaining stable hybrid structures that can be used as functional biomedical materials.

Physics and Chemistry in Cultural Heritage Protection

Quantitative Assessment of Risk to Heritage Objects Due to Microclimatic Conditions in the Environment

(Professor Roman Kozłowski, Associate Professor Łukasz Bratasz, Leszek Krzemień PhD, Arkadiusz Kupczak PhD, Marcin Strojecki PhD)

Fields of local strains induced by the impact of ambient humidity variations were analysed at the level of yearly growth ring structures in wood using in-plane digital speckle pattern interferometry. The investigations were carried out for the key wood species used in the past as artistic materials. In softwoods, the dimensional change of latewood in a growth ring was even one order of magnitude larger that of earlywood. This leads to a marked profile of moisture related dimensional change (the swelling profile) in wood's structure. The swelling profile is less pronounced in hardwoods such as poplar, walnut, oak, and lime widely used in the past in Europe to produce supports for panel paintings. The reduced profile manifests not only in smaller variations in the local strain values but in the diffused anatomical limits between early- and latewood.

Further, the strain fields in the pictorial layers laid on various wood supports - investigated previously – were measured. A considerable smoothing of the moisture related strain profile across the decorated surface was evident when compared to the bare wood. The experimental results obtained were complemented by the numerical modelling of strain using the finite element analysis, which – in addition - allowed the elastic energy release rate, the result of crack propagation and formation of new surface in the material, to be determined at various locations on the surface, and spots of likely crack initiations in the pictorial layer to be identified. It was found that the maxima of the energy release rate coincided with the transition zones between earlywood and latewood, therefore, these zones are the most energetically favourable area for a crack to develop. The modelling results were confirmed by experimental observations of crack growth in the pictorial layers on wood.

A methodology to model dynamic processes of water vapour adsorption/desorption and diffusion in wooden objects of considerable dimensions as well as strain/stress distributions across these objects was developed. As the water vapour diffusion in the wood structure is not instantaneous, the outer parts of massive wooden elements shrink or swell more quickly than the interior in response to changes of ambient relative humidity. The uneven dimensional response between the exterior zone and the core of the element leads to stress. It has been demonstrated that the energy release rate for cracks o varying length propagating in the radial direction is the optimum parameter to be used in the assessment of physical damage risk for such objects. The risk criterion based on the wood's fracture toughness perpendicular to the fibre was proposed. Crack propagation was proposed as the index of damage which transforms the energy release rate into the macroscopic magnitude of damage.

Measurements of acoustic emission were carried out for cylindrical wood specimens during a controlled temperature change corresponding to the thermal eradication of wood destroying insects, applied in the conservation practice. The measurements aimed at establishing if a typical change in the microclimatic parameters which is applied during such process leads to any level of damage in bulky wooden objects. Specimens of seasoned wood and of wood experiencing uncontrolled microclimatic variations in the past in the laboratory, imitating historical wood, were investigated. No measurable damage of the specimens was identified.

"Sonata Bis" Research Projects of the National Science Centre

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: Professor Tomasz Borowski)

Within this project we pursue a tightly integrated structural, biochemical and computational studies on two groups of 2-oxoglutarate dependent dioxygenases (ODD) involved in biosynthesis of alkaloids. Structures of these proteins are not known, as are the detailed mechanisms of their catalytic reactions.

One of the proteins was produced in a truncated form, without 33 N-terminal amino acids, for the purpose to obtain a more compact variant of the protein with lower conformational flexibility (without disordered loop regions). This involved molecular biology procedures to obtain a plasmid with an appropriately truncated gene, expression of E. coli cells on a minimum medium and purification of the protein in quantities sufficient for crystallization trials. As a result good diffracting crystals were obtained. X-ray diffraction experiments were conducted for native and truncated forms at DESY III and BESY II synchrotrons, structural models were solved for protein complexes with Ni, co-substrate, inhibitor and substrate, the best at ca. 1.2 A resolution. Microscale thermophoresis (MST) experiments were conducted to estimate binding constants for substrates, inhibitor and co-substrate. For another protein, crystallization trials with substrate were continued and attempts were made to assess the stoichiometry of the protein-ligand interactions by means of MST and ITC methods. For two other proteins, nano differential scanning fluometry (nanoDSF) measurements were done to assess protein stability at various buffers. Moreover, MST experiments were conducted within an attempt to characterize ligand binding parameters. Crystallization trials were continued with manual and automatic setups with the use of over a dozen different commercially available screens. These experiments were done in cooperation with BIOCEV (Prague) and MCB (Kraków).

Within computational studies the reaction mechanism of the AsqJ enzyme was scrutinized with the purpose to identify factors determining reaction specificity of ODD enzymes. Obtained insights will be used to devise mutants with altered specificity.

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: Associate Professor Wojciech Płaziński)

Validation of the GROMOS force field for furanoses and re-interpretation of conformational equilibria in furanose rings

The aim of this step of the research study was to extensively investigate and interpret the conformational equilibria present in furanose monosacharides. This was achieved by performing, analyzing and interpreting the molecular simulations performed at the two separate levels of accuracy: (i) QM/MM molecular dynamics (MD) simulations carried out for model furanose mononers; (ii) classical MD simulations, carried out within the recently developed GROMOS force field for a wide set of furanose monosaccharides.

The QM/MM MD simulations showed that the conformational properties of five-membered furanoside rings are highly dependent on the environment of the considered molecule (i.e. vacuum *vs*. aqueous solvent). The presence of solvent induces a charge flux that involves atoms creating furanose ring. Such charge reassignment results in a systematic alteration in the free energies of ring-distortion by ~3-7 kJ/mol, depending on the system; namely, the conformational equilibrium is shifted toward the $^3T_2$ and $^2T_3$ ring shapes (i.e. North and South hemispheres of the pseudorotation itinerary) disfavoring those corresponding to the ^OE and E_O geometries (East and West). This effect is supposed to be present in all furanose-containing molecular systems and contributes to the wide applicability of the two-state model approximately describing the pseudorotational equilibrium in five-membered rings.

Regarding the results obtained from the classical MD simulations, we found that the conformational equilibrium in the furanose rings often deviates from the two-state model, assuming the north *vs.* south division of the pseudorotation itinerary. These deviations are not limited to the compounds exhibiting *arabino*-like topology of the substituents. Moreover, the two-state model is rather poorly applicable for the elastic rings exhibiting non-negligible conformer populations at the east and/or west regions even if those regions correspond to the expected free energy barrier (e.g. oxolane). Contrary to pyranoses, in the case of furanoses, the O-methylation at the anomeric carbon atom does not lead to any significant alterations in the ring-distortion properties. Finally, the trends in population of the staggered conformers of both the lactol and hydroxymethyl groups reflect the findings reported earlier for pyranoses.

"Sonata" Research Projects of the National Science Centre

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

"Sonata" research project NCN 2014/13/D/ST4/01846 [2016-2019]
(project leader: Monika Wasilewska PhD)

Immunoassays are important application areas of proteins immobilized on solid substrates. Common adsorbed proteins are immunoglobulins G (IgG) or their active fragments, which specifically bind to its antigen with high affinity. Although immobilized antibodies play a critical role in immunoassays, the mechanisms of the immobilization processes are poorly understood. Little in situ research has been done on how IgG adsorb on immobilized proteins monolayers. There is a lack of systematic investigations of the relationship between the immobilization conditions and resulting protein coverage, local distribution, and orientation of this adsorbed protein and their bioactivity.

In 2018 we were focused on: (●) Streaming potential studies of fibrinogen (HPF) covered silica substrate, (●) Streaming potential, OWLS and QCM measurements of the HPF/IgG monolayers and bilayers formation on silica sensor (IgG adsorption onto fibrinogen monolayers and vice versa) (●) Examination of the structure, and stability of adsorbed protein bilayers onto solid/liquid interface via streaming potential, OWLS, QCD, and AFM imaging.

The obtained data have been provided us with vital information about the HPF/IgG monolayers and bilayer formation and their behavior. The results of the work will be used in the formulation of the mechanism of the protein bilayer formation on the solid substrates, and in the formulation of an efficient method for detection of trace amounts of proteins (immunoglobulins) for the development sensitive immunoassays.

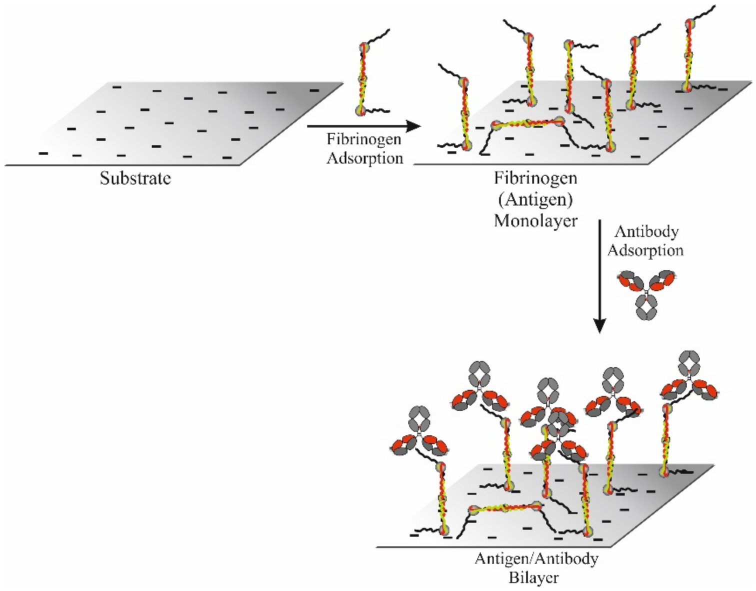


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Figure 1. A scheme of HPF /IgG bilayer formation

Lipase-Mediated Biosynthesis of Novel Lactose Esters. Physicochemical and Anticancer Studies

"Sonata" research project NCN 2015/17/D/ST4/00514 [2016-2019]
(project leader: Maciej Guzik PhD)

Stage 1 cont.: Precursors preparation for biocatalytic synthesis of sugar esters

The whole process of obtaining bacterial PHA was improved by applying additional polymer purification protocol after fermentation in bioreactor. The method is based on filtration and separation of the polymer on activated charcoal column. That procedure allowed to obtain extra pure substrates and materials for future synthesis. During preparations of precursors for further biocatalytic reactions with a sugar several issues occurred with purification and hydrolysis of modified monomers of 3-hydroxynonanoic acid methyl ester. Especially it was difficult to achieve higher efficiencies of reactions which block 3-OH groups of PHN monomers. In that situation another type of reaction was proposed: the substrate was derevatised with fluorsulphonyl-2,2,2-trifluoropropane. Analysis confirmed the desired pure product was successfully obtained.

Stage 2 cont.: Biocatalysis- Screening of various reaction media and effect of lipase immobilization

In order to increase the efficiency of lactose tranestrification reaction by our model substrate which is methyl ester of nonanoic acid reactors with other sugars (which build the disaccharide): glucose and galactose were set. The reactions were catalysed by previously selected immobilized lipases (*Themomyces lanuginosa* - TL-IM, *Candida antarctica* lipase B - CALB). In this time a method of extraction the reagents from batch reactors was optimized (by using solution of MeOH 50%/ 50% H2O or pyridine). Then separation and identification of quantitative and qualitative methods using HPLC-MS (with triple quadrupole), GC and GC-MS were upgraded. The mentioned analysis confirmed a presence of expected sugar fatty acid esters after 24h of the reaction and revealed drop in the substrate concentrations giving 42% and 37,6% glucose conversion for reactors with TL-IM and CALB, respectively, after 24h (reaction medium 2-methyl-2-butanol, 2M2B).

To verify whether it is possible to widen reaction media spectrum we set up reactors with: DMF, DMSO, acetone, toluene, pyridine, system 2M2B 80%/20% pyridine, tert- buthanol beside already examined 2M2B and system of 2M2B 80%/20% DMSO. Combinations of all sugars: lactose, glucose, galactose were tested. The experiments confirmed that 2M2B is the best reaction medium but additionally revealed that pyridine and system 2M2B 80%/20% pyridine are also reliable media for conducting biocatalysis. That happened because these solvents improve solubility of the sugar and the sugar fatty acid ester also making them easier to extract from whole reactors.

Continuing a cooperation with Eucodis Bioscience GmbH(Austria) the best working towards fluorinated PHN monomers lipase EL70 was applied. In that case the homogenous enzyme was immobilized on modified mesoporous silica supports (Materium, Canada). The lipase was covalently attached to the supports by crosslinking their –OH groups with divinyl sulphone or -NH2 groups with glutaraldehyde. All these operations gained efficiency of glucose transesterification to its nonanoic acid ester to 88,5% and 98,4% of conversion for Spheres-OH and Spheres-NH2 respectively.

Formation Mechanisms and Functionality of Nanoparticle Multilayers with Incorporated Biomolecules

"Sonata" research project NCN 2015/17/D/ST4/00569 [2016-2019]
(project leader: Maria Morga PhD)

The research goals of the SONATA project realized in 2018 included: (i) revealing the electrokinetic properties of silicon Si/SiO_2 wafers at solid/liquid interfaces of electrolytes of mono- and bivalent cations and the dependence of the zeta potential of the silicon surface on pH and ionic strength of the solution; (ii) determining the physicochemical properties such as: the intrinsic viscosity, molar mass, geometrical cross section area, molecule volume and extended chain diameter of the molecules of PLL (poly-*L*-lisine) using viscosity measurements in diluted solutions of aqueous suspensions, dynamic light scattering (DLS), microelectrophoresis and molecular dynamics modeling; (iii) development of an efficient procedure of obtaining macrocation monolayers of strictly defined electokinetic properties on mica/electrolyte and Si/SiO_2/electrolyte interfaces; (iv) determining the mechanisms of the polypeptide adsorption on the solid substrates under *in situ* conditions using the streaming potential method as well as determining the stability of obtained layers on ionic strength and pH of an electrolyte.

Since it is assumed that electrokinetic properties affect the formation and stability of macrocation monolayers, it is especially important to find correlation between physicochemical properties of polypeptide monolayers and electrolyte solutions. Therefore, in the course of the research, using the RSA modeling and the 3D electrokinetic model, the correlation between the coverage of obtained polypeptide monolayers and their zeta potentials was found. Precise modeling of RSA adsorption kinetics for linear polypeptides was possible due to the earlier development of methods allowing to determine the basic physicochemical parameters of macromolecules by means of experiments supported by modeling with molecular dynamics.

During the research, the molecule density equal to 1.6×10^3 kg m^{-3}, the chain diameter equal to 0.92 nm, and the monomer length equal to 0.33 nm were determined for the first time. The latter value allows to calculate the extended (contour) length of the molecule of arbitrary molar mass. Good agreement between experiments and theoretical results, indicates that the MD modeling can serve as a prediction tool of the polyelectrolyte properties in bulk solution.

Knowing the adsorption kinetics of the polypeptide at the solid/liquid interfaces, a number of research was carried out using the streaming potential method to determine the dependence of surface zeta potential on the coverage of the macromolecule monolayers.

It is also worth underlying that as a result of the research the physicochemical basis for determining the molar mass of macromolecules, in particular linear polyelectrolytes with high degree of elongation and relatively large surface charge, is the subject of the patent application: "Method for determining the molar mass of linear polyelectrolytes, especially polylysine." (Polish Patent Application P.426566 (2018).

Besides for significance in basic sciences, the studies provide a basis for developing a robust method of preparing multilayer materials with well-controlled surface properties and electrokinetic characteristics. This is important from the point of view of biomedical applications allowing to investigate protein adsorption at interfaces in a controlled manner.

Bio Oligo/Polysaccharides under the External Forces

"Sonata" research project NCN 2015/19/D/ST4/01979 [2016-2019]
(project leader: Agnieszka Brzyska PhD)

Nigeran (called also as mycodextran), produced intracellularly by *Aspergillus niger* and *Penicillium crustosum*, is an unbranched polysaccharide made of α-D-glucopyranose units alternatively connected by (1→3) and (1→4) glycosidic linkages. We have examined theoretically the possible enforced conformational transitions in the nigeran oligosaccharides (up to heptasccharide) to gain additional insight into the structural role played in this polymer. In order to simulate such structural changes we used the Enforced Geometry Optimization (EGO) method. Two types of monomeric: A (with the terminal glycosidic atoms in the position 1 and 3) and B (with the terminal glycosidic atoms in the position 1 and 4), dimeric: AB and BA (see Figure 1), trimeric: ABA and BAB etc. up to heptameric: ABABABA and BABABAB forms were considered here. The external stretching forces were applied to the two terminal glyosidic oxygen atoms of the glucopyranose ring in the mycodextran oligosaccharide chains. The modes of the force action are shown also in Figure1.

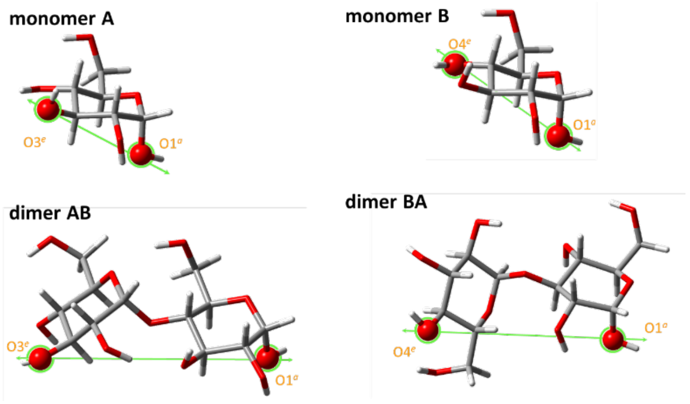


Figure 1 The stretching force action modes with the featured terminal glycosidic oxygen atoms (e-equatorial, a-axial position) for monomeric and dimeric systems.

The results provide new insight into the mechanism of the conformational transitions in such oligosaccharides. The complex responses to the external forces can be related to the different glycosidic bond types in the examined structures. Moreover, the type of the conformational conversion can also depend on the pyranose ring position in the oligosaccharide chain.

Influence of ZrO_2 Crystallographic Structure on Activity of Cu/ZrO_2 and Cu/ZrO_2-ZnO Catalysts Doped with Ga, Mn, Ni in Low Temperature Steam Reforming of Bio-Ethanol

"Sonata" research project NCN 2016/23/D/ST4/02492 [2017-2020]
(project leader: Michał Śliwa PhD)

CuO/ZrO_2 catalysts were synthesized via co-precipitation method using Na_2CO_3 as precipitating agent. Content of CuO and ZrO2, aging time and calcination temperature of catalysts precursors were varied. The catalyst were characterized by means of N2 adsorption, temperature programmed reduction (H_2-TPR), N_2O dissociative chemisorption, X-ray diffraction (XRD) and CO_2 temperature programmed desorption (CO_2-TPD).

For catalysts calcined at 300 ^oC and 350 ^oC, only CuO phase is visible. The increase in calcination temperature of the catalyst to 550 ^oC results in appearance of diffraction peaks of $2\theta = 35.5^o, 50.9^o$ and 60.7^o ascribed to tetragonal ZrO_2 (t-ZrO_2). With the increased temperature of calcination the increase in the CuO crystal size is observed which is due to sintering. For non-aged catalysts, which were calcined at 300 ^oC and 350 ^oC, the increase in the ZrO_2 content has only minor influence on CuO crystal size.

For CO_2-TPD runs, all catalysts show broad desorption profile ranging from RT – 400 ^oC. In the case of catalysts calcined at 300 ^oC and 350 ^oC, the signal coming from CO_2 desorption is overlapping with signal assigned to CO_2 which is released due to malachite phase decomposition in temperature range above 300 ^oC. In order to have better insight in the desorption process, TPD profiles have been deconvoluted. The observed peak maxima were assigned accordingly to the areas related with CO_2 desorption from weak (50 ^oC – 150 ^oC), medium (150 ^oC – 240 ^oC) and strong (>240 ^oC) basic sites. The quantitative analysis of deconvoluted TPD profile shows that aged catalysts possess the lowest concentration of surface basic sites. Additionally, the highest contribution of weak basic sits is observed for these catalyst.

The value for CuO crystal sizes based on Rietvield refinement are much lower than P_{Cu} for all synthesized catalysts. This means that during reduction at 250 ^oC priori to introduction N_2O pulses, the Cu particles sinter. Especially, surface Cu particles are more prone to agglomerate and sinter due to low Hüttig temperature of copper. The presence of small CuO crystallites in the catalyst leads to lower value of P_{Cu} and higher copper dispersion (D_{Cu}). On the other hand for aged catalysts, the increase of CuO crystal size with temperature of calcination does not result in decrease value of P_{Cu} and D_{Cu} whereas loss of BET specific surface area for these catalysts is pronounced. In this case, the surface Cu particles mobility is hindered. The observed surface copper stabilization can be due to ZrO_2 phase transformation from tetragonal to monoclinic which occurs in the subsurface region.

For all catalysts, the reduction stoichiometry (Cu/H_2) is slightly above one, meaning that all CuO is reduced to metallic copper during TPR. The maximum reduction rate (T_{max}) occurs at lower temperature for all catalysts then for standard CuO (T_{max} = 338 ^oC) resulting from copper-zirconia interaction. Based on the broad shape of TPR profile, one can say that at least two copper species are present in the obtained catalysts.

It has been found that metallic copper dispersion (D_{Cu}) does not depend on calcination temperature for samples which were aged for 1 h. On the other hand, for non-aged catalysts the decrease in D_{Cu} is observed with higher temperature of calcination. The temperature corresponding to maximum reduction rate (T_{max}) decreases for samples with higher D_{Cu}. The contribution of weak basic site is the highest for catalysts which were aged whereas for non-aged catalysts mainly medium basic site dominate on the surface.

"Opus" Research Projects
of the National Science Centre

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

"Opus" research project NCN 2014/15/B/NZ1/03331 [2015-2018]
(project leader: 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 (EFE), oxidative deamination of kanamycin (KanJ) and formation of an endoperoxide bridge (in the synthesis of a mycotoxin – verruculogen; FtmF).

Within the last year, experimental studies covered optimization of crystallization conditions for the KanJ protein as well as optimization of protein production protocol for homologous EFE enzymes showing different enzymatic activity. Studies were done in cooperation with the prof. Wladek Minor group at the University of Virginia.

An expression protocol was successfully optimized for the EFE homologue from *Penicillium chrysogenum* and now a soluble fraction of the protein is achievable; the next step will be optimization of the purification protocol. Initial studies were also done for another homologue – from *Penicillium Digitatum* species. New constructs were designed and prepared based on the pMCSG9 plasmid.

In the case of KanJ the difficult and time consuming stage was the one connected with growing crystals that would allow for solving the structure. The structure was finally solved thanks to soaking the crystals with iodine salts. Six further structures were solved with: nickel ion, 2-oxoglutarate, kanamycin, neamine, amikacin and ribostamycin. ITC measurements were conducted to estimate binding constants and protein-ligand stoichiometry. Activity tests were performed for three antibiotics: kanamycin B, ribostamycin and neamine with the use of HPLC/MS method. In the preparatory steps, the activity tests were run for various conditions differing in buffer concentration, pH and Fe^{2+} concentration. Computational studies on the catalytic mechanism of KanJ were continued for various protonation forms of the substrate. A manuscript of a publication dedicated to structural and biochemical characterization of KanJ was prepared.

For FtmF computational studies were continued and a manuscript of a publication was prepared. Based on results of docking, MD simulations and quantum-chemical calculations an alternative binding pose for the substrate within the FtmF active site was suggested and the role played by ascorbate for product selectivity was elucidated.

Theranostic Nanocarriers for MRI Imaging

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

Neurodegenerative diseases (e.g. Alzheimer's, Parkinson), psychiatric disease (e.g. schizophrenia), cancer, bacterial infection and many others are still a challenge for medicine. One of the major drawbacks of current conventional therapies is lack selectivity of preparations, since administered drugs are more or less equally distributed within the body. This results in many of the negative side effects due to the impact of the drug in the whole body, also on the healthy part of it. It seems reasonable to find the route of controlled delivery of therapeutic, which would result in an action of the active substance only in strictly defined, pathologically changed place in the body. The solution of this problem is the drug targeting, i.e., delivery of the therapeutic component selectively and simultaneously monitoring its distribution. The term "theranostic" is defined as a material that combines the modalities of therapy and diagnostic imaging. Thus, theranostics deliver therapeutic drugs and diagnostic imaging agents at the same time within one dose. The ultimate goal of the theranostics is to gain the ability to image and monitor the diseased tissue, delivery kinetics, and drug efficacy with the long-term hope of gaining the ability to tune the therapy and dose with heretofore unattainable control.

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 to 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 2018 we were focused on the synthesis of theranostic polyelectrolyte nanocarriers containing Gadolinium as MRI contrast agent. The nanocarriers were synthesized by the sequential adsorption of charged nanoobjects (layer by layer technique) on nanoemulsion droplets. For the preparation of theranostic nanocarriers we used biocompatible polyelectrolytes: Poly L-lysine as the polycation and Poly Glutamic acid as the polyanion) and Gadolinium labeled Poly L-lysine as MRI contrast. The size of obtained theranostic nanocarriers was in the required range of 100-200 nm. Synthesized nanocapsules could be visualized by MRI. We concluded that the Gd complexes containing nanocarriers exhibit beneficial T_1 relaxation properties, while enhancement of T_2 relaxivity was not observed.

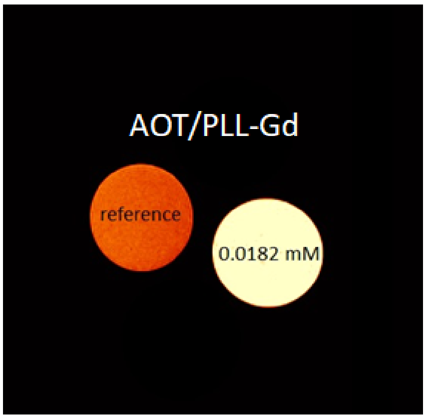


Figure. MRI of theranostic polyelectrolyte nanocapsules in gel phantom.

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 mesoporesvis desilication in alkaline solutions, found the most effective and non-expensive way of producing of mesopores in zeolites. Most of existing attempts concerning zeolite desilication was performed for ZSM-5 using NaOH as the desilicating agent; here desilication of commercial zeolites with the Si/Al ratio of 30, obtained by dealumination of typical zeolites Y and mazzite, 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-Al groups in dealuminated zeolites FAU and mazzite were found more acidic than hydroxyls in HMOR and HZSM-5 which are known as strongly acidic zeolites. The treatment of dealuminated FAU and mazzite 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. However, 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. Very strongly acidity of obtained Si-OH-Al groups was evidenced in low temperature IR studies of CO sorption. Huge red-shift of stretching OH frequency caused by the interaction with CO probe was registered which can be taken as the measure of the acid strength, higher than in other zeolites. Catalytic activity in the α-pinene isomerization also increased distinctly upon desilication due to the production of mesopores, the increase of accessibility and preserving very high strength of acid sites. We have also obtained very good, nearly quantitative agreement between the experimental OH frequency red-shift upon CO adsorption in dealuminated zeolite Y and the values computed by extracting anharmonic OH frequencies from ab initio molecular dynamics simulation performed for the realistic zeolite models and at experimental temperature. Quantum chemical modeling performed for periodic models not only confirmed that Brønsted sites in dealuminated mazzite belong to strongest acid sites from among known zeolites, but also for the first time determined their location in mazzite at 12-T position in the wide channel.

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 positively charged gold nanoparticles at silica/silicon substrates was investigated scanning electron microscopy (SEM), and atomic force microscopy (AFM). The gold nanoparticles were synthesized in a chemical reduction method using sodium borohydride as reducing agent. Cysteamine hydrochloride was applied to generate a positive surface charge of nanoparticles. The stability of nanoparticle suspensions under controlled pH and ionic strength was determined by dynamic light scattering (DLS). The electrophoretic mobility measurements showed that the zeta potential of nanoparticles decreased with ionic strength and pH from 56 mV at pH 4.2 and I=10^{-4} M to 22 mV at pH 8.3 and I=3×10^{-3} M. The surface enhanced Raman spectroscopy (SERS) confirmed chemisorption of cysteamine on nanoparticles and the contribution of amine moieties in the generation of nanoparticle charge. The gold nanoparticle monolayers of a coverage determined by SEM and AFM were deposited on silicon/silica wafers under diffusion-controlled transport. The topology of the substrate and the nanoparticle monolayers (see Fig. 1) comprising the root mean square (*rms*) parameter was also quantitatively determined as a function of the particle coverage. For the bare wafer the surface *rms* was equal to 0.15 nm and systematically increased with the nanoparticle coverage. These results were adequately interpreted in terms of a general theoretical model developed for surface covered by features of arbitrary shape. Additionally, the stability and electrokinetic characteristics (zeta potential vs. pH) of the monolayers were acquired using streaming potential measurements. It was shown that the inversion of the negative zeta potential of the bare substrate (overcharging) occurs at the nanoparticle coverage equal to 0.15, whereas for larger coverages positive zeta potential values were asymptotically attained. Additionally, the desorption kinetics investigated by the streaming potential method confirmed the stability of the gold particle monolayers for a broad range of ionic strength and pHs. It was argued that these results enable to develop efficient methods of gold sensor preparation exhibiting well-controlled surface roughness and electrostatic charge comprising both negative and positive values.

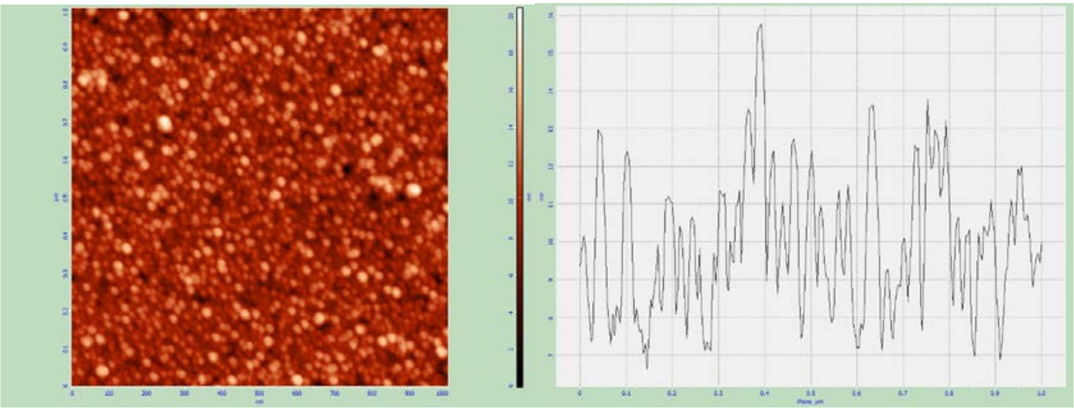


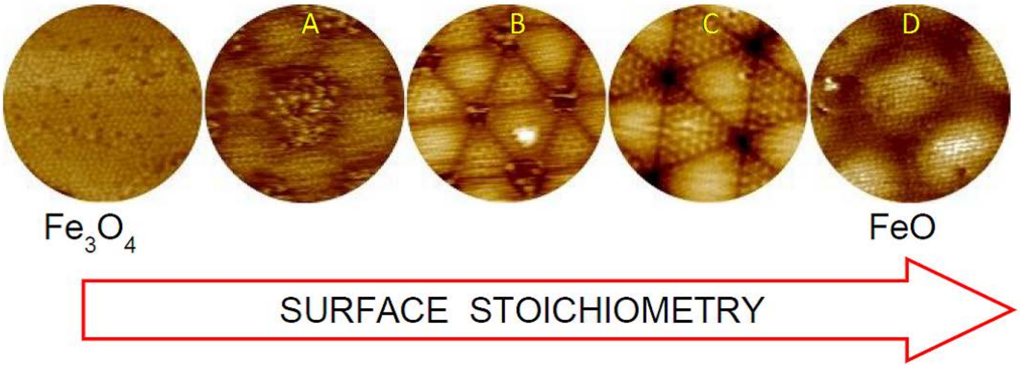
Figure 1. The Au nanoparticle monolayer (particle size 9.5 nm) on the silicon/silica wafer derived from AFM imaging, surface concentration of particles N = 1800 μm^{-2}, the coverage θ = 0.13. The right hand side shows a local profile of the interface for this particle coverage.

Magnetic Nanoparticles on Periodic Iron Oxide Templates: Control of Magnetism Using Particle Substrate Interaction and External Electric Field

"Opus" research project NCN 2016/21/B/ST3/00861 [2017-2020]
(project leader: Associate Professor Nika Spiridis)

The surfaces of iron oxides, magnetite (Fe_3O_4) and hematite (alpha-Fe_2O_3), with a specific orientation, exhibit periodic modulations of the surface structure that are termed in the literature as the biphase supestructures. In the project, these superstructures are used as templates for the self-organized growth of the magnetic nanoparticle assemblies.

Investigations of epitaxial magnetite films on a Pt (111) singe crystal allowed us to order the observed superstructures according to the degree of surface reduction and to give a simple explanation and atomic models of different biphase superstructures (A, B, C and D) on the Fe_3O_4(111) surface, at it is shown in the atomically resolved STM images .



On the magnetite surface with the B-type superstructure, gold and cobalt nanostructures were grown at room temperature. It was found that both metals nucleate at the specific sites of the superstructure. The surface density of the Au nanoparticles increases with the amount of gold and reaches a maximum corresponding to one nanoparticle per a unit cell of the superstructure. The resulting assembly of nanoparticles is characterized by a hexagonal order with a superstructure periodicity of 5.5 nm. In the case of cobalt, a higher density of nanoparticles was observed and a lack the of hexagonal order, therefore, in the further studies, gold was used as a precursor providing an ordered nucleation of Co.

In parallel to the thin film systems on the single crystalline Pt(111) substrate, we started to develop a growth method of epitaxial iron oxides on low-cost and easy-to-use oxide substrates, such as MgO(111) and Al_2O_3(0001), using a platinum buffer layer. These systems are more practical and effective for *ex situ* analysis.

A 50 nm thick Pt film on Al_2O_3 (0001) was prepared *ex situ* by ion sputtering, and then its surface was cleaned with a treatment applied for surfaces of Pt single crystals. Low Energy Electron Microscopy (LEEM) studies showed that Pt film exhibits a (111) texture, with crystallite sizes of about 150 nm. However, at the nanometer scale the surface showed a monocrystalline quality, as confirmed by scanning tunnel microscopy (STM). Platinum deposited under ultra high vacuum on MgO (111) formed a continuous epitaxial layer of orientation (111), which is characterized by a large number of screw dislocations.

Development of Modern Generation Technology of Stable Biological Surface Film for Various Bio-Medical Applications (Antibacterial or Regeneration Properties)

"Opus" research project NCN 2016/21/B/ST8/02107 [2017-2020]
(project leader: Marcel Krzan PhD)

During the project, we want to develop technology for generation and application of stable thin films of surface formulated from mixtures of hypoallergenic, non-toxic biological polymers, mainly biosurfactants (proteins, polysaccharides, glycolipids and phospholipids). The scientific goal of the project is to investigate the competitive adsorption processes occurring in multi-component solutions, where the main substrates are various surface-active bio-polymers. During the project, we want to investigate which of the available biopolymer formulations have sufficient surface activity to be used in cosmetic products. We want to determine the minimum described above necessary to carry out wetting or to create the surface effect of surfactant concentrations. To achieve this effect, we plan detailed research on the tested solutions of biopolymers. We want to set the above-described minimum concentrations necessary to carry out wetting or to create a surface surfactant concentration effect. To achieve this effect, we plan detailed research on the tested solutions and mixtures of biopolymers.

During the second year of the project, many compositions of biological mixtures of polymers with high surface activity, foamability and promising biological activity (bacteriostatic properties) were developed. New green surfactants and natural nanoparticles have been introduced into the project. Their surface activities were analysed based on measurements of local velocities and deformations of gas bubbles, measurements of foam fractions stability, dynamic surface activity measurements and surface dilational elasticity measurements. The methodology for measuring the adsorption kinetics of bio-surfactants and surfactants on the surface of a free gas bubble was also developed using innovative surfactants whose surface activity is induced using ultraviolet light.

The obtained results were presented during national and international scientific conferences 61st Polish Chemical Society conference, Krakow, Poland, International Conference on Catalysis and Surface Chemistry, Krakow, Poland, Eufoam 2018, Liege, Belgium, and 17th Food Colloids Conference, 2018, Univ. Of Leeds, UK (10 presentations, 5 oral and 5 posters). They were also used to prepare publications, including one chapter in the book (published in 2018) and three publications in ISI / JCR journals (to be submitted in December/January 2018/2019).

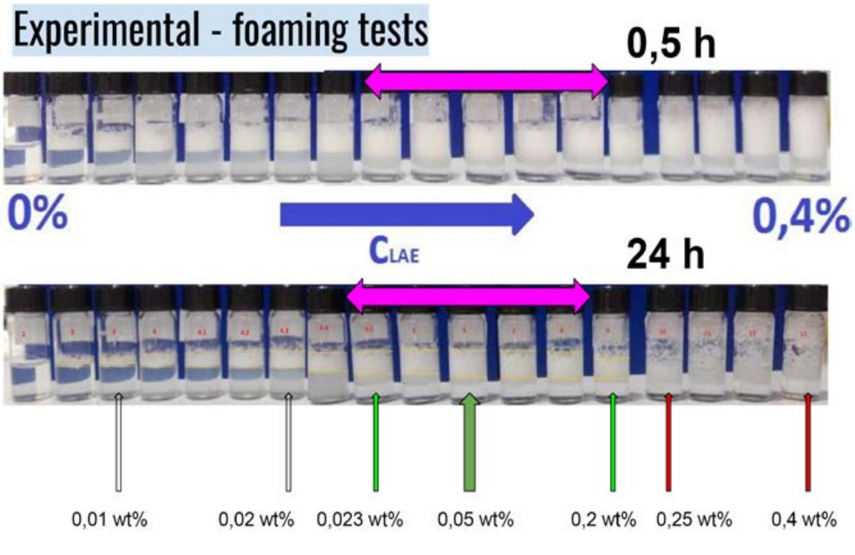


Figure 1. Foam stability variations in foams generated from solutions of green surfactant, LAE – lauroyl ethyl arginate according to crystalline cellulose nanoparticles concentrations

The Mechanism of Regioselective Oxidative Dehydrogenation of 3-Ketosteroids Catalyzed by Δ^1-Cholest-4-en-3-one Dehydrogenase from *Sterolibacterium denitrificans*

"Opus" research project NCN 2016/21/B/ST4/03798 [2017-2020]
(project leader: Associate Professor Maciej Szaleniec)

The aim of the project is to evaluate the reaction mechanism of steroids dehydrogenation catalyzed by Δ^1-cholest-4-en-3-one dehydrogenase (AcmB). The enzyme is produced by denitrifying bacterium, *Sterolibecterium denitrificans,* and belongs to the FAD-dependent 3-ketosteroid dehydrogenases. It catalyzed the oxidative dehydrogenation od 3-ketosteroids that leads to formation of a double bond between C1 and C2 atoms of a steroid ring A. The project focuses on elucidation of the enzyme's structure together with characterization of its catalytic properties. Furthermore the theoretical calculations are applied for study of the reaction mechanism.

In the first stage of the study the full biochemical characterization of the enzyme was conducted. We determined the dependence between the reaction velocity and temperature and pH. In particular, we demonstrated that the pH optimum of the reaction depends on the type of electron acceptor e.g., for dichloroindophenol, the pH optimum was 6.5, while for phenazine methosulfate it was 8.0. The measurements of denaturation temperature confirmed enzyme stability in a broad range of pH (6.5-8.0). Finally, a high enzyme activity at pH 6.5 was confirmed for 1,4-benzoquinone, 1,2-naphtoquinone or vitamin K_3 as the enzyme re-oxidants.

A spontaneous enzyme aggregation was studied in detail. We confirmed that AcmB aggregates regardless of the presence of reducing agent (2-mercaptoethanol), pH or ionic strength. On the other hand the incubation in the presence of 0.02–0.1% of non-ionic detergent, Tween 20, led to a partial AcmB de-aggregation with simultaneous preservation on the enzyme activity. A partial de-aggregation was achieved by a high enzyme dilution in the reaction buffer. The level of aggregation and the type of aggregates were visualized by atomic force microscopy. Additional theoretical calculations allowed to speculate that AcmB purified by in a standard procedure and diluted in the reaction buffer to concentration of 0.2 µg/ml contains low-aggregated mono-, di- and trimeric forms (5, 11 and 12% of protein concentration). Remaining 72% were other, bigger aggregates. Combined experimental and theoretical studied of the surface of AcmB homology model allowed to speculate that hydrophobic interactions are most probable factors responsible for the protein aggregation, while a native form of the AcmB is a monomer.

Directed side mutagenesis was applied to elucidate the reaction mechanism. Essential role in the catalysis was confirmed for Tyr363 and Tyr118. Mutagenesis of Tyr467 and Tyr115 had a negative impact on the reaction activity, indicating that those residues may be involved in proton transfer after a substrate dehydrogenation.

Experimental studies were supported by theoretical QM calculation with a cluster morel derived from KstD1 from *Rhodococcus erythropolis*. KstD1 is the best characterized family member and the closest relative to AcmB. Calculations confirmed the postulated in the literature reaction mechanism of 3-ketosteroid dehydrogenase from *R. erythropolis*. The most probable mechanism of steroid dehydrogenation by KstD1 proceeds with a proton abstraction from C2 of substrate by a tyrosyl anion, followed by a carbocation transition state stabilized by a keto-enoyl tautomerization. In the next step a hydride transfer from C1 to the flavin occurs and is associated with a second transition state characterized by the highest energy barrier.

Theoretical and Experimental Studies on the Mechanism of Oxidative Dehydrogenation (ODH) of Light Alkanes over Vanadium-containing Hierarchical Zeolite Materials

"Opus" research project NCN 2016/23/B/ST4/02854 [2017-2020]
(project leader: Associate Professor Dorota Rutkowska-Żbik)

The aim of this work is to gain understanding in the nature of the V species introduced in V-containing zeolite materials with hierarchical micro- and mesoporous structure (mostly derived from BEA zeolite) responsible for their catalytic activity in the oxidative dehydrogenation (ODH) of light alkanes into light alkenes and to determine the mechanism of the ODH process.

Two series of vanadium catalysts were obtained, with the amount of vanadium changing in the range 0.5 – 7 %mas: series I was obtained using two-step post-synthesis method, consisting of the de-alumination of the parent BEA zeolite, followed by the introduction of vanadium into the formed vacant sites (samples denoted as VxSiBEA) at pH = 7; series II (denoted further as VxHAlBEA) was obtained by impregnation of BEA zeolite (Si:Al = 17) with ammonia metawanadate at pH = 7; series III was obtained using two-step post-synthesis method, from partially de-aluminated BEA (samples denoted as VxHAlSiBEA(pH=2.6)) at pH = 2.6; series IV was obtained using two-step post-synthesis method, from partially de-aluminated BEA (samples denoted as VxHAlSiBEA(pH=7)) at pH =7. The physico-chemical characterization of obtained samples was started in order to verify their chemical composition and qualitative description of the vanadium active centres. The XRD diffractograms are similar and do not contain peaks derived from other crystallographic phases than BEA. Vanadium ions are well dispersed. Introduction of V results in slight expansion of BEA structure and suggests that vanadium is incorporated into BEA structure. XRF analysis confirms the amount of V introduced into zeolite structures in all samples based on SiBEA, on contrary in all samples based on HAlBEA the nominal content is higher that found by XRF. The obtained materials exhibit specific surface area of 400-600m^2/g depending on the type of support and amount of introduced vanadium. In order to study the speciation of vanadium, the obtained samples were examined with UV-VIS spectroscopy. Depending on the synthesis method, the samples exhibit peaks at 270 and 340 nm, characteristic for tetrahedral V atoms. At higher vanadium loadings (ca. 5%), there appear peaks at 430 nm typical for octahedral vanadium atoms. The observation was further confirmed with ^{51}V NMR.

Additionally, the DFT method (BP/def2-TZVP) was used to describe geometry and electronic structure of BEA zeolite substituted with vanadium atoms placed in all inequivalent T-sites and in exchange positions. The quantum-chemical calculations aimed at the determination of electronic and geometry structure of the proposed sites and their properties were initiated. The following forms of vanadium ions were considered: $–(Si\text{-}O)_3\text{-}V{=}O$ i $–(Si\text{-}O)_4\text{-}V\text{-}OH$.

The Influence of Counterions on the Formation and Functionality of Polyelectrolyte Membranes

"Opus" research project NCN 2016/23/B/ST8/03128 [2017-2020]
(project leader: Marta Kolasińska-Sojka PhD)

The scientific goal of the project is to describe the influence of ions from the Hofmeister series on the formation and properties of polyelectrolyte multilayers, because the mechanism of interactions of counterions from the lyotropic series on the resulting polyelectrolyte films is not known yet. Systematic studies of surface properties and permeability of selected polyelectrolyte systems formed in the presence of counterions from the lyotropic series, towards certain electroactive probes, will help to understand the mechanism responsible for buildup of such structures and thus, it will enable the design of materials with precisely defined properties. This will be extremely important in the production of selective membranes, biomaterials or nanocontainers.

In the conducted studies, multilayer films were deposited by the sequential adsorption technique (layer by layer, LbL) of polyions from their solutions. This year's research in the project involved a comparison of the effects of monovalent cations: Li^+, Na^+, K^+ on the formation and structure of multilayer polyelectrolyte films, as well as the multilayers permeability for selected electroactive probes. Using a quartz crystal microbalance, the kinetics and effectiveness of the polyelectrolyte films deposition process were carried out for: PAH/PSS and PDADMAC/PSS in the presence of indifferent electrolyte: LiCl, NaCl, KCl in three various ionic strengths: $I = 0.015M$, $I = 0.15M$ and $I = 1.5$ M. By direct analysis of the profile of sessile drop, the wettability and surface energy of the resulting polyelectrolyte films were examined in relation to the electrolyte used during deposition.

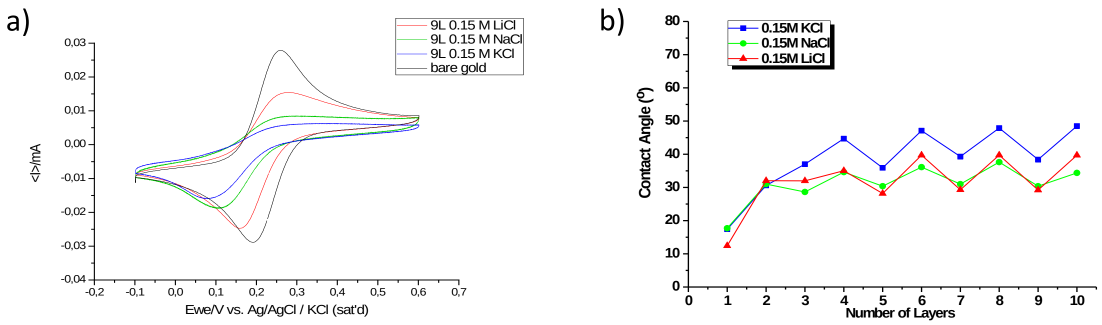


Figure 1. (a) Voltammograms for electrodes modified with 9-layer PDADMAC/PSS films obtained from 0.15M solutions of LiCl, NaCl or KCl; registered for equimolar mixture of potassium hexacyanoferrate (II) and (III); (b) water contact angle on surface of PDADMAC/PSS series of films having 1 to 10 layers.

It has been observed that the permeability of polyelectrolyte films to an equimolar mixture of potassium hexacyanoferrates (II) and (III) is consistent with the Hofmeister classification. Among the studied cations, the lowest-hydrated potassium formed films of the highest density, which are least permeable to the used electroactive probe. The measured water contact angles on the surface of series of PDADMAC/PSS films having 1- to 10-layers deposited in the presence of analogous salt solutions showed the highest hydrophobicity of films deposited from polyions solutions in KCl.

The influence of ionic strength on the thickness of the obtained films was also confirmed - the thickness of multilayers increases along with the increase of the ionic strength, and this effect is much more pronounced for the PDADMAC/PSS system comparing to PAH/PSS because of the PDADMAC structure. Wettability studies confirmed the more hydrophobic nature of positively terminated films.

Dendrimers as a Platform for Designing Biologically Active Carrier

"Opus" research project NCN 2016/23/B/ST5/02788 [2017-2020]
(project leader: Associate Professor Barbara Jachimska)

Experimental research so far confirms that dendrimers, due to their specific physical and chemical properties resulting mainly from their structure, have high application potential. It is particularly interesting to use these systems as drug carriers for molecular targeted therapy. Nanoparticles entering biological systems are almost always covered with biofluids. Thus, to develop selective delivery of nanocarriers to particular compartments of the body, it is crucial to understand phenomena involved in conformational changes and the displacement of proteins at the interface. Protein coatings on the surface of nanoparticles often modulate their biological responses as they undergo conformational changes and dynamic exchange with other proteins. The first stage of the research was related to the interaction of plasma proteins with the dendrimer surface and included the characterization of the structure of the protein shell. At this stage, it was essential to determine the stability of the complexes formed and changes in the native structure of the adsorbed proteins at the interface. The research was conducted in a multifaceted way by determining a number of physicochemical properties of the system using complementary measurement techniques. Changes in the secondary structure of the protein were monitored using circular dichroism (CD) and compared to the crystallographic structure available in Data Bank. Changes in size, charge and stability of the complex were determined, among others, by measurements of dynamic light scattering (DLS), capillary electrophoresis, UV-vis spectroscopy, gel electrophoresis. The key conditions for creating the complex were determined (critical environmental conditions, critical protein concentrations relative to the carrier) allowing both to optimize the system and to obtain significant correlations between physicochemical properties that determine the stability of the system under examination. Simultaneously, conformational changes of proteins analyzed using complementary techniques such as surface plasmon resonance (SPR) and quartz crystal microbalance (QCM-D). SPR is a suitable tool to follow kinetic studies of protein adsorption and desorption from the surfaces of functional materials and allows to determine the association and dissociation constant for the dendrimer/protein complex.

In Search of Effective and Environmental Friendly Frothers and Emulsifiers – Quantitative Description of Thin Liquid Film Stability in Solutions of „Green” Surfactants

"Opus" research project NCN 2017/25/B/ST8/01247 [2018-2021]
(project leader: Associate Professor Jan Zawała)

The presented research project is aimed to investigate potential application of bio-surfactants (proteins, lipids derivatives, natural polyelectrolytes) as new, effective and environmental friendly stabilizers of foam and emulsion films under dynamic conditions. Scientific tasks planned within the project framework are planned to be performed according to the new methodology and by use of the new experimental set-up which elaboration is one of the scientific tasks of the project. The new experimental set-up should allow quantitative description of kinetics of drainage of single symmetrical liquid films (foam and emulsion), formed at the liquid/gas and liquid/liquid interfaces by the colliding bubbles and /or droplets in solutions of biodegradable and environmental-friendly surfactants.

In the reported period the single bubble/droplet generator was elaborated, allowing control over the moment of formation of single bubble/droplet at capillary/needle orifice. Precise control over the single bubble/droplet formation is necessary tool for quantitative determination of kinetics of drainage of liquid films under dynamic conditions. The main elements of this automatic apparatus were two peristaltic micro-pumps connected to the pressure sensor and pressure stabilizer as well as two glass pressure cells. All electronic parts of the generator were controlled and synchronized by elaborated software, implemented to the Raspberry Pi PC with Unix operating system. Single bubble/droplet formation algorithm was based on software-controlled pressure inside the system. In the case of bubbles generation, a single bubble formation could be induced by inducing pressure impulse of adjustable magnitude, controlled by two synchronized pumps. Droplet generation was realized by control over the flow rate of oil and water phases in specially designed cell, in which the needle was sealed inside a narrow glass tube. The droplet detachment was induced by inducing water phase flow impulse, creating shear force of adjustable magnitude. It was found that new generator elaborated allow formation of bubbles/droplets of reproducible size in quite wide range of diameters.

In addition, to control the initial adsorption coverage over the immobilized bubble interface, so-called bubble trap was developed. The bubble trap was based on programmable stepper motor and glass dome located just above the capillary orifice. The moment of trap closure and opening (full dome rotation around its own axis) was synchronized with the moment of a single bubble generation. By software-controlled adjustment of time of the bubble residue inside the trap, time available for adsorption of surface-active molecules at the bubble (liquid/gas) surface (initial adsorption coverage) could be controlled. It was found that profiles of the bubble rising velocities as well as bubble terminal velocity strongly depends on initial adsorption coverage over the liquid/gas interface.

pH Stimuli Responsive Surfactants and Copolymers for Nanovehicles Formation

"Opus" research project NCN 2017/25/B/ST4/02450 [2018-2021]
(project leader: Professor Piotr Warszyński)

The main project objective, realized by the consortium of two research groups from Jerzy Haber Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences and from Wrocław University of Science and Technology, Faculty of Chemistry, is to develop scientific background of a novel strategy of formation of pH sensitive nanostructures: thin films or nanocapsules. Using newly-synthesized amphoteric surfactants with hydrophobic chains of different lengths, mixed with polyelectrolytes and/or amphiphilic polyelectrolytes with hydrophobic groups grafted on the polyelectrolytes backbone by pH-labile linker, we will construct nanostructures which decomposition can be trigger by change of pH. Application of this type of components will allow to obtain nanostructured thin films with controlled hydrophobicity, or antimicrobial properties sensitive for changes of environment. We synthesized and characterized by using spectroscopic method following amphoteric surfactants:
[(3- alkanoyilomethyoamine)propyl] dimethylammonium acetate (s1),
[(3- alkanoyilomethyoamine)propyl] dimethylammonium 2-hydroxypropanesulfonates with different length of hydrophobic chains: C_{10}, C_{12}, C_{14} or C_{16} (respectively s2, s3, s4, s5) where hydrocarbon chains are linked with amide groups via carbon of this group and
[(3-alkylmetyloamino)-3-oxopropyl] dimethylammonium 2 hydroxypropane sulfonates where hydrocarbon chains (lengths: C10, C12, C14 or C16) are connected by nitrogen atoms of amide group with the rest molecular backbone of respective s6, s7, s8 or s9 compounds. Molecular structures of these compounds are presented in figure 1. We synthesized amphiphilic polyelectrolytes on the basis on polyethylenimine (PEI) and poly(4-styrenesulfonic-co-maleic acid) (PSS/MA) with hydrocarbon chains (C12 or C16) linked by pH-sensitive, amide group. Obtained degree of hydrophobization is 15% or 40%. Using the pendant drop shape analysis method, we also determined adsorption kinetics (dynamic surface tensions) of surfactants s1 to s5 at various pH and ionic strength. The most sensitive on pH is the surfactant s5. (Fig. 1).

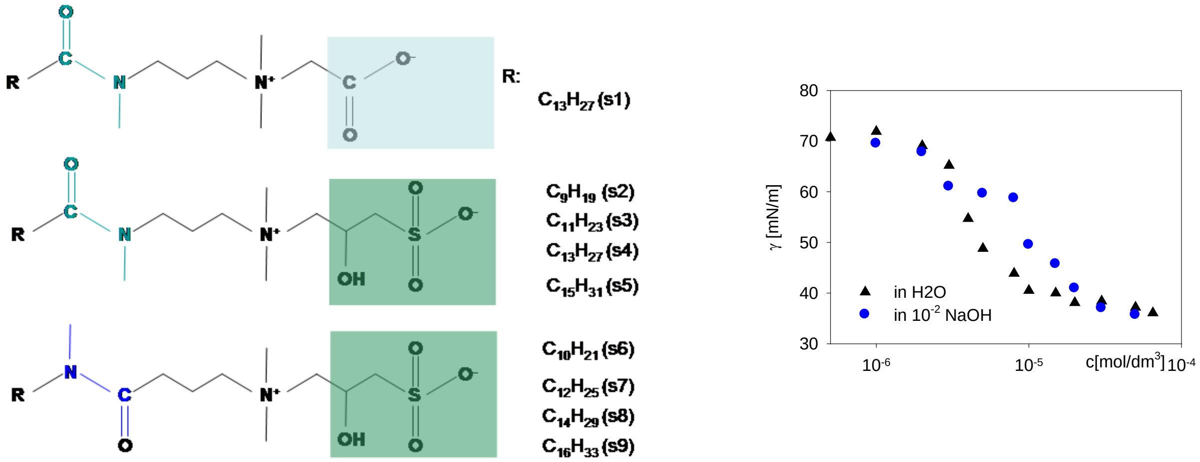


Fig.1 Molecular structures of newly- synthesized surfactants and surface tension dependency on concentration of surfactant - [(3- hexadecanoilomethyoamine)propyl] dimethylammonium 2-hydroxypropanesulfonate (s5).

Studies of the Interactions of Carbon Nanotubes with Telomeric DNA by Means of the Molecular Dynamics Simulations

"Opus" research project NCN 2017/27/B/ST4/00108 [2018-2021]
(project leader: Professor Tomasz Pańczyk)

Proliferation of cancer cells involves a few various pathways. One of them is infinite proliferative capacity being an effect of telomeres and telomerase dysfunction. Human telomeres are composed of G-rich and C-rich duplex with a single-stranded 3′-overhang; the G-rich strand can form a four-stranded G-quadruplex structure, and its complementary C-rich strand may adopt intercalated i-motif structures. Formation of i-motif within C-rich strand of telomere has been observed at reduced pH. In vitro studies suggest that formation of the i-motif can indirectly facilitate formation of G-quadruplex and this leads to inhibition of telomerase activity. This, in turn, stops the infinite proliferation of cancer cells. Carboxylated single-walled carbon nanotubes (CNT) have been found as a unique moiety which can selectively stabilize human telomeric i-motif structure by binding to the 5'- end major groove under physiological conditions. However, the biological relevance of i-motif structure has not been fully understood though it was demonstrated that stabilization of i-motif DNA by carboxylated CNT can inhibit telomerase activity both in vitro and in vivo.

Thus, in the first stage of the studies the molecular topology of the system i-motif – carbon nanotube was considered in order to veryfy and optimize the simulation setup. Two types of carbon nanotubes (10,0) and (20,0) differing in chirality were analyzed and they were additionally covalently functionalized. Missing parameters of the force field were determined using quantum chemical calculations and also partical charges on atoms forming functional groups were determined. These computations were done using the RESP ESP charge derive program available on the web page of the RED server maintained by the RED developers. The functional groups used for functionalization of carbon nanotube were amines and groups containing guanine residues – the complementary base to cytosines forming the i-motif. The molecular topology of the i-motif structure was derived using pdb file 1EL2.

The obtained results are currently the starting point for further studies focused on the analysis of DNA fragments containing sequences rich in cytosine or guanine. They are interesting either as isolated fragments due to ability of changing their spatial structures due to pH change or due to their interaction with nanostructured objects like carbon nanotubes.

Biopolymers as Templates for Preparation of Nanostructured Hydrotalcite-Like Materials and their Calcined Mixed Oxides Derivatives for Catalytic Applications

"Opus" research project NCN 2017/27/B/ST5/01834 [2018-2021]
(project leader: Professor Ewa Serwicka-Bahranowska)

The project sets the frame for fundamental research into designing nanostructural hydrotalcite-like compounds (Htlc) and their calcined mixed oxides derivatives with aid of commonly available, cheap and environmentally friendly natural biopolymers (e.g., starch, gelatin), used in the capacity of sacrificial soft biotemplates. The approach represents an alternative to the use of the more expensive, more complex and less green procedures based on synthetic templating agents (e.g., surfactants, block copolymers). The novel materials will be designed for application as catalysts in two types of environmentally friendly processes: a) liquid phase Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone, monomer for biodegradable polymer (nanostructured Htlc of basic character) and b) abatement of volatile organic compounds (calcined derivatives of transition metal-containing nanostructured Htlc precursors).

In the first months of project implementation investigations concentrated on the comparative study of Mg-Al Htlc materials synthesized in the standard conditions and in the presence of a biopolymer, using different precipitating agents. The synthesized materials were characterized with XRD, SEM/TEM, FTIR, and N_2 adsorption/desorption at 77 K. The studies confirmed that the proposed strategy of synthesizing Htlcs with aid of a sacrificial biotemplate is an efficient means to manufacture nanostructured materials. Fig. 1, showing SEM images of Mg_3Al-Ht(st) prepared in a standard manner and Mg_3Al-Ht(bio), synthesized in the presence of biotemplate, recorded for the uncoated specimens, reveals that although both materials are characterized by plate-like morphology, the lateral dimensions of individual platy particles in Mg_3Al-Ht(st) are in the range 300-350 nm, while those in Mg_3Al-Ht(bio) are of order of magnitude lower, i.e. 30-40 nm). Catalytic tests of cyclohexanone oxidation to ε-caprolactone demonstrated that biotemplate-directed synthesis of Htlc, although far from being optimized, is beneficial for the catalytic properties, as Mg_3Al-Ht(bio) yields ca. 50% more lactone than the Mg_3Al-Ht(st) sample. Results will serve as the basis for further studies.

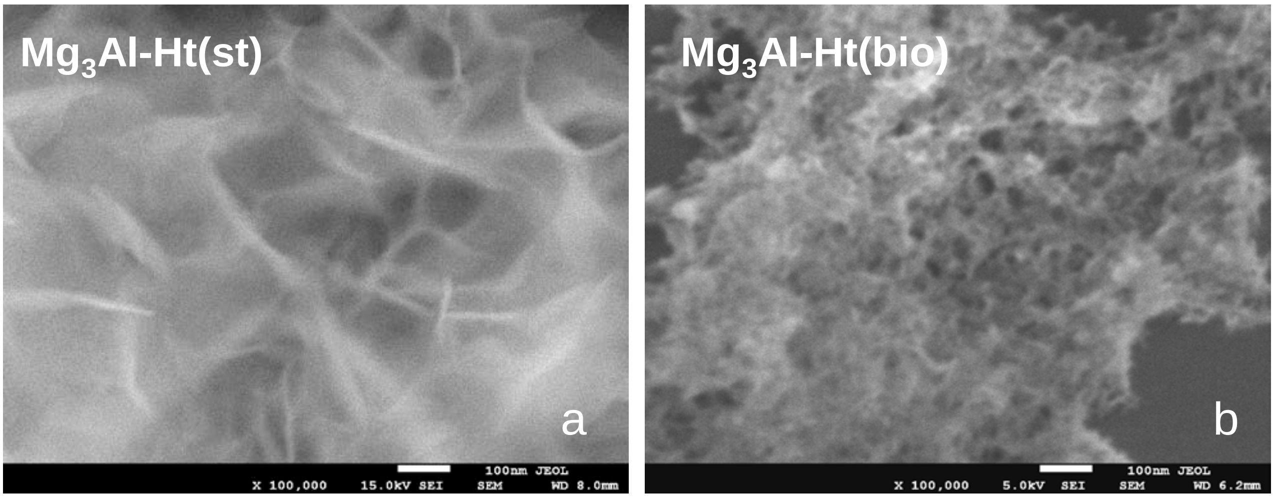


Figure 1. SEM images of Mg_3Al-Ht(st) and Mg_3Al-Ht(bio) (uncoated powders deposited on copper grid).

"Preludium" Research Projects of the National Science Centre

Synthesis of Theranostic Biopolymer-Based Nanoparticles

"Preludium" research project NCN 2016/23/N/ST5/02783 [2017-2019]
(PhD student: Marta Szczęch MSc, supervisor: Professor Piotr Warszyński)

Hybrid (multifunctional) nanoparticles (HNPs) are a very promising group of nanosystems with a great biomedical application, especially in nanomedicine. One of the types of these nanosystems are theranostic nanoparticles that allow to delivering of both therapeutic and imaging agents in the same dose. This multifunctional aspect is a huge advantage of the HPNs but there are also some obstacles that limited its using in clinical trials e.g. ineffective delivery of the hybrid nanosystems to the specific part of the body, low content of imaging agents or limited biodistribution.

The aim of the “PRELUDIUM” project is to develop the scientific background of the synthesis methodology of biocompatible and biodegradable hybrid nanoparticles for hydrophobic substances, optimization of magnetic compounds concentration, characterization of the HNPs physicochemical properties, functionalization of their surface properties and finally, evaluation of primary biological tests.

In 2018 we were focused on the preparation and analysis of biopolymer nanoparticles (NPs), polycaprolactone – PCL, with superparamagnetic iron oxide nanoparticles (SPIONs) as MRI contrast active agent, that was incorporated into PCL NPs. For the preparation of PCL NPs, we used methods based on nanoemulsion template, while for the functionalization of obtained nanocarriers we used Layer-by-Layer (LbL) technique. The MRI agent was incorporated into the PCL NPs in two ways: 1) by incorporation into the NPs solid core and 2) by incorporation into the polyelectrolytes shall using the LbL technique. The synthesized NPs were characterized by size/size distribution (DLS), zeta potential (LDE), visualization (Cryo-SEM) and stability measurements (DLS). Using T2 and T1 NMR relaxation measurements and relaxation time-weighted images with 9.4T preclinical MRI scanner we demonstrated that the synthesized nanocarriers can be detected due to a locally altered contrast in the MR image. The results provide the basis and can be further considered as a promising theranostic delivery system.

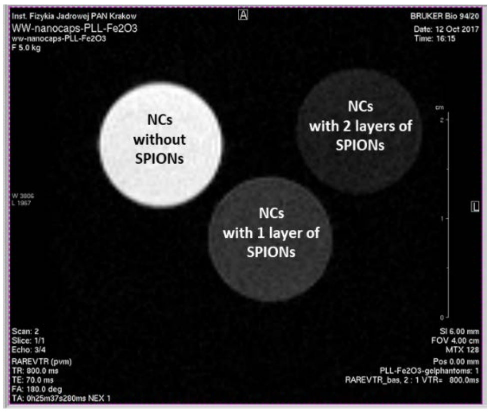


Figure 1. The MRI analysis of PCL NPs modified by the different layer of SPIONs.

Functional Hybrid Nanomaterials Based on poly(Amidoamine) PAMAM Dendrimers

"Preludium" research project NCN 2016/23/N/ST4/02532 [2017-2019]
(PhD student: Karolina Tokarczyk MSc, supervisor: Associate Professor Barbara Jachimska)

The success of novel therapeutic strategies relies strongly on the development of a reliable active agent delivery mechanism. In this research project, we addressed the question of how G4 PAMAM dendrimers form complexes with a therapeutic agent, 5-fluorouracil (5-FU) and interact with bovine serum albumin (BSA) as a model plasma protein.

The analytical techniques, such as: UV-Vis spectrophotometry, dynamic light scattering, electrophoretic mobility, Fourier-transform infrared spectroscopy (FTIR) were used for physicochemical characterization of the system in bulk solution. Multi-parametric surface plasmon resonance (MP-SPR) and quartz crystal microbalance with dissipation monitoring (QCM-D) delivered information about the properties of the formed complexes at solid/liquid interface on a model biocompatible Si/SiO2 surface.

The G4 PAMAM dendrimer surface charge was analyzed and showed that the dendrimer zeta potential depends strongly on pH. The IEP was found at pH 10.4. The G4 PAMAM-FU complexes were prepared at different molar ratios from 1:1 to 1:50 and the optimum conditions for drug-dendrimer complexation were determined. The results show that ~70% of the 5-FU was loaded onto the G4 PAMAM dendrimers with higher capacity at pH 7.4, which are physiological conditions in comparison to acidic conditions. Drug molecules complexed within dendrimer macromolecules reduce their surface charge. It has been demonstrated that physicochemical properties of the nanocarrier such as surface charge and hydrophobicity affect the amount and conformation of proteins that adsorb onto the nanoparticle surface. Altogether our results reveal that protein aggregates upon contact with dendrimers and their complexes. The electrostatic and hydrophobic forces drive the adsorption of biomolecules to the drug carrier surface. Proteins significantly reduce dendrimer surface charge, which changes from 61 mV to 16.9 mV.

It is critical to characterize not only the interactions of therapeutic agents with a nanocarrier but also with proteins and other biomolecules present in physiological fluids. This new understanding of dendrimers as nanocarriers and their interactions with plasma proteins delivers new insight into the interaction mechanism when the nanoparticles enter physiological fluids. Expanding knowledge of the interaction between dendrimers with active agents and plasma proteins will contribute to further, more advanced research on PAMAM dendrimers, especially as intelligent pharmacophores nanocarriers.

Effect of Controlled Adsorption Time on Kinetics of Three-Phase Contact Formation at Solid Surfaces with Different Hydrophobicity

"Preludium" research project NCN 2017/27/N/ST4/01187 [2018-2020]

(PhD student: Agata Wiertel-Pochopień MSc, supervisor: Associate Professor Jan Zawała)

The goal of this project is to determine the effect of controlled adsorption time of surface-active substances (SAS) at an air bubble (gas/liquid) interface on kinetics of its attachment and three-phase contact (TPC – gas/liquid/solid) formation at a solid surface of different hydrophobicity. In this project an unique experimental set-up which contains an automatic programmable bubble generator with a bubble "trap" is being developed. Thanks to the specially design trap the bubble can be "captured" motionless for any (precisely adjusted) time, selected on the basis of adsorption kinetics of the SAS studied. During the time of bubble residue inside the trap the gas/liquid interface can be saturated by the SAS molecules in a desired degree. As a result, the initial adsorption coverage upon the bubble release can be precisely controlled.

Experiments on kinetics of the three-phase contact formation on quartz surface in cetyltrimethylammonium bromide (CTAB) solutions were carried out using different values of adsorption time. For three chosen pairs of CTAB concentrations, the conditions of the experiments were selected in such a way to ensure constant value of the bubble adsorption coverage despite different CTAB concentration. The table shows values of chosen CTAB concentrations (c_{CTAB}), adsorption times (t_{ads}) and initial adsorption coverage at interface gas/liquid (θ), which were calculate on the basis of Ward-Tordai equation. Figure presents dependence of time of the three-phase contact formation (t_{TPC}) on initial adsorption coverage. As seen, value of the t_{TPC} is practically constant for the same initial adsorption coverage, despite different CTAB concentration.

Studies show that by using a trap (controlled time of adsorption) it is possible to control a degree of adsorption coverage at the gas/liquid interface for different concentrations of solution of the same SAS, which has a profound influence on times of the three-phase contact formation at a slightly hydrophobic solid surface.

Table 1. Adsorption time needed to attained constant adsorption coverage for different CTAB concentration pairs

	c_{CTAB} [mol/dm^3]	t_{ads} [s]	θ [%]
pair 1	$1\text{x}10^{-7}$	1.6	0.034
	$5\text{x}10^{-8}$	50.1	
pair 2	$2\text{x}10^{-7}$	1.6	0.068
	$1\text{x}10^{-7}$	50.1	
pair 3	$1\text{x}10^{-6}$	1.6	0.34
	$5\text{x}10^{-7}$	50.1	

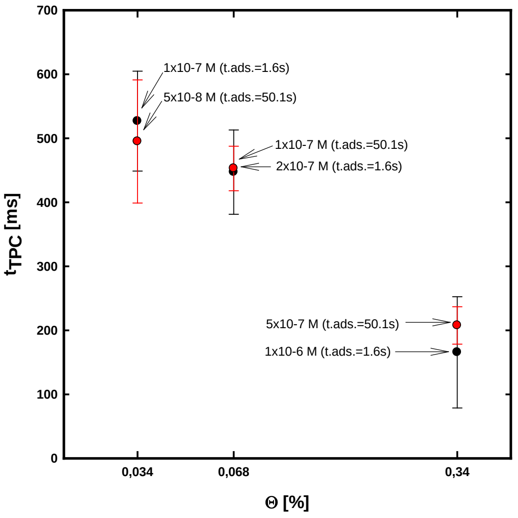


Figure 1. Dependence of t_{TPC} on θ

Tungsten-Containing Aldehyde Oxidoreductase from *Aromatoleum aromaticum* - Study of Catalytic Reaction Mechanism

"Preludium" research project NCN 2017/27/N/ST4/02676 [2018-2020]

(PhD student: Agnieszka Winiarska MSc, supervisor: Associate Professor Maciej Szaleniec)

Tungsten-containing aldehyde oxidoreductase (AOR) is an enzyme derived from bacteria *Aromatoleum aromaticum* which in anaerobic conditions is capable of denitrifying degradation of number of organic compounds including environmental pollutants e.g. phenols, aromatic hydrocarbons (toluene, ethylbenzene), aromatic alcohols (e.g. benzyl alcohol) and alkyl and aromatic amino acids. AOR catalyzes oxidation reaction of aldehydes to corresponding carboxylic acids, and previous studies of the AOR_{Aa} lead to hypothesis that it is employed in removal of toxic aldehyde by-products accumulating during the fermentative degradation of various compounds.

The research planned in the project aims to provide knowledge about the structure of the active enzyme center and its reactivity, which will enable to determine the mechanism of AOR_{Aa} reaction.

As part of the project, preliminary studies of the kinetics of oxidation reactions of aldehydes to carboxylic acids catalyzed by AOR_{Aa} have been made. The enzyme showed a very broad substrate spectrum, catalyzing the oxidation reaction for many aldehydes, both aromatic and aliphatic. The highest specific activity was observed for the reaction with benzaldehyde, phenylacetaldehyde and acetaldehyde using benzyl viologen (BV) as the electron acceptor. For the phenylacetaldehyde oxidation reaction, the dependence of the reaction rate on the pH of the buffer was determined, showing the optimum at pH 8.0 (Tris-HCl buffer, for BV and NAD^+ as electron acceptors).

"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: Associate Professor Nika Spiridis)

In the frame of the project, we have continued studies of ultrathin cobalt layers surrounded by different combination of ultrathin nonmagnetic layers, such as: 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. Thickness of the Co layer was d_{Co} = 3 nm, which corresponds to magnetization orientation in the layer plane. Ion irradiations with different ion fluences were performed in the form of adjacent stripes (with millimeter width) for samples representing each combination of layers. Depending on the ion fluence and the type of the buffer/cap layer it was possible to induce perpendicular magnetic anisotropy in the irradiated region. Magnetooptical spectroscopy measurements were performed for selected irradiated stripes (Charles University in Prague). The measured spectra allowed us to propose the model of the internal layers/sublayers structure (including their chemical composition and thickness) in the sample before and after irradiation. Magnetooptical spectral dependencies, simulated based on the proposed model of the layers, were in a good agreement with the experimental data. Additionally, the layer thicknesses estimated from this studies agree with values obtained from previous XRR studies. At the final stage of the project also positron annihilation studies on selected irradiated stripes were performed (Helmholtz-Zentrum Dresden-Rossendorf). Analysis of these results showed that gold layers used as cap or/and buffer layers generate after irradiation much more structural defect density than platinum layers.

Irradiations using a focused ion beam (FIB) were also performed on Al_2O_3/Pt/Co/Pt with a cobalt layer thickness d_{Co}= 3nm, corresponding to magnetization in the sample plane. The irradiation was performed in the form of micrometer size squares – each with a different ion fluence. However, an unconventional path of the ion beam was used – the ion beam was swept in a spiral like manner, from the center to the border of the irradiated region. Magnetooptical studies revealed local modification of the magnetic properties and the appearance of perpendicular magnetic anisotropy (PMA) for selected ion fluence. Interestingly, it was observed that the magnetization orientation depends on the sense of the ion beam sweep. It means that inside areas irradiated with selected fluence it is possible to create four individual subareas with inclined magnetization. Generally, obtained results show that using FIB irradiation it is possible to create a matrix of micrometer sized regions with PMA (even with a different internal orientation of magnetization inside of a single region) embedded in an in-plane oriented surrounding.

Additionally, PEEM studies were performed at Elettra sinchrotrone in Trieste. These studies allow to visualize magnetic domain structure in regions irradiated with a selected ion fluence – the size of domains was below the lateral resolution of the magnetooptical microscope.

The obtained results will be used in the prepared publication (a part of the results have already been used in papers sent for review).

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)

Interaction of proteins with solid surfaces is a process of fundamental biological importance as well as foundation for many bioengineering applications.

Protein-surface interaction is a first step in a cascade of signaling events leading to cell adhesion. The latter plays a key role in regulation of such processes as growth, differentiation and cell migration. There is growing body of evidence suggesting that abnormalities in cell adhesion are very important factor determining invasiveness of tumor cells. Then, today's exposure to nanoparticulate matter (purposely generated for use in medicine or coming from environmental pollution) calls for the recognition of its interaction with biological systems, where protein-surface interactions are of key importance.

In the field of biomaterial engineering, the process of protein adsorption is requirements for proper vascularization of artificial tissues. On the other hand, for implants having direct contact with blood stream, protein adhesion can have adverse effects. In analytical chemistry protein adsorption can significantly affect sensor performance. Therefore, there is a need in recognition of the mechanisms regulating protein-surface interactions, ability to control them and to design surfaces of desired properties. The aim of this project was to investigate the ability of a remote physical trigger – electromagnetic radiation in the infrared range – to affect protein-surface interactions from the perspective of the impact of IR on hydration properties. IR is a part of natural solar radiation in its non-ionizing range. It causes no chemical reactions to occur, yet it makes bonds to vibrate. And this very subtle influence was shown in our studies to affect for example the way proteins aggregate in solution or interact with the surface (non-specific aggregation is recognized to be involved in development of neurological diseases, while surface adhesion defines e.g. biocompatibility of implants or cell adhesion). Infrared light can protect proteins from loss of their native structure (which decides of their functionality) in contact with the solid surface. This effect depends on the ability of infrared light to promote enhanced hydration of polar functional groups of proteins. Hydrated groups then act as a kind of lubricant in contact with the surface. On the other hand IR light decreases water affinity of non-polar protein compartments, thus stimulating native protein fold and preservation of biologically active structure. Changes in protein interfacial characteristics in response to IF determine not only protein conformation and its interaction with the surface. They define also mutual interaction of nanoparticles with adsorbed layer of proteins (and size of such aggregates can decide about their ability to cross biological barriers). Furthermore, enzymatic activity of proteins also responds to IR stimuli thanks to the ability of the latter to promote mutual alignment of water molecules. Those effective water wires can then conduct protons, the process involved in enzymatic performance.

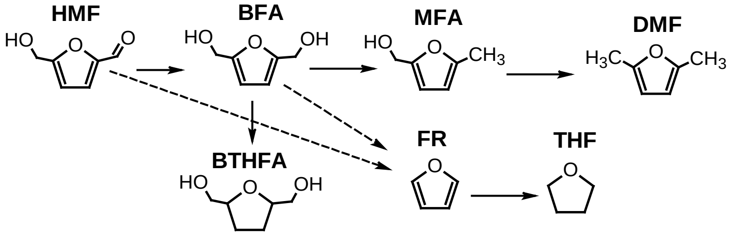
Our studies suggest that exposure to IR light (purposely generated or as part of natural solar radiation) can potentially affect protein-based biological processes. Furthermore, IR can find applications as a remote physical trigger to control bioengineering processes.

"Miniatura" Research Projects of the National Science Centre

The Role of Hydrogen Molybdenum and Tungsten Bronzes in Hydrogenation of Bioreagent 5-Hydroxymethylfurfural over Pd/MoO_3 and Pd/WO_3 Catalysts

"Miniatura" research project NCN 2017/01/X/ST4/00731 [2017-2018]
(project leader: Robert Kosydar PhD)

World reserves of non-renewable crude oil are limited. Therefore the replacement by sustainable sources of fuel and chemicals is highly needed. The dehydration of saccharides from biomass-derived cellulose produces 5-(hydroxymethyl)furfural (HMF). It is so called *platform molecule* with multifunctional structure. The selective hydrogenation of HMF is a key reaction in its upgrading to valuable products. The aldehyde group –CHO can be reduced to –C–OH giving 5-(hydroxymethyl)furfuryl alcohol (BFA – important in polymer industry). The alcohol group –C–OH can be deoxygenated producing methyl –CH_3 group leading to 5-methylfurfuryl alcohol (MFA) which can be further reacted to 2,5-dimethylfuran (DMF – biofuel/fuel additive). The functional groups may be removed by decarbonylation leading to furan (FR). Furan ring can be also saturated by C=C bond hydrogenation producing appropriate saturated compounds (like BTHFA, THF – important solvent).



In our experiments the Pd/*c*-WO_3 and Pd/SiO_2 catalysts exhibited the highest activity. However Pd/SiO_2 started to deactivate at HMF conversion above 50%. Pd/*m*-WO_3 and Pd/MoO_3 were much less active.

Among all the tested catalysts, Pd/MoO_3 was the most selective to BFA product, showing the highest ability of aldehyde group reduction. In turn, Pd/*m*-WO_3 catalyst had the highest ability to furan ring saturation (producing BTHFA, THF). The reference Pd/SiO_2 catalyst produced large amount of furan (FR). The reactivity of Pd/*c*-WO_3 catalyst was different as 5-methylfurfuryl alcohol (MFA) and biofuel 2,5-dimethylfuran (DMF) were dominating. As DMF was formed from MFA in consecutive reaction large amounts of DMF were obtained above 40% of HMF conversion. All these data proved an interaction of palladium with the support as the selectivity was remarkably different than observed for Pd/SiO_2.

It must be pointed out that during the HMF hydrogenation over all the Pd-free supports when bronze structures were not formed, no activity was observed under studied conditions. Additionally the hydrogenation reactions over a mixture of catalyst and appropriate support were applied. In the case of Pd/*m*-WO_3 + WO_3 as well as Pd/MoO_3 + MoO_3 the increase of selectivity towards decarbonylation to furan and decrease in selectivity of furan ring hydrogenation was observed. It proved that the support itself was converted into hydrogen bronze structure which participated in HMF hydrogenation reaction as well. Even when Pd/SiO_2 + MoO_3 was applied in the reaction, the different selectivity was noticed suggesting that hydrogen (H) activated on Pd migrated from Pd/SiO_2 grains to MoO_3 support forming bronze which was active in the reaction as well.

Stabilization of the Catalytic Activity of 1-(*R*)-Phenylethanol Dehydrogenase by Immobilization on Polylysine

"Miniatura" research project NCN 2017/01/X/ST5/00735 [2017-2018]
(project leader: Mateusz Tataruch PhD)

1-(*R*)-phenylethanol dehydrogenase (*R*-PEDH) is a bacterial enzyme used in biotechnological processes for the synthesis of enantiomerically pure aromatic alcohols. Due to the high application potential of *R*-PEDH, the project aims to broaden current knowledge about the stabilization of enzyme activity by preparation of conjugates between α-poly-D-lysine (PL) and *R*-PEDH.

Covalent immobilization of enzymes on synthetic polymers is well known and intensively studied topic. However, commonly applied methods that use bifunctional linkers, such as glutaraldehyde, very often result in uncontrolled cross-linking of enzymes and lead to its activity reduction. The solution to this problem can be a new linking system to form enzyme-polymer conjugates using aromatic aldehyde and hydrazine moieties. In this case, polymer and the enzymes were first modified via free amino groups with the linking reagents succinimidyl 4-formyl benzoate (S-4FB) and succinimidyl 6-hydrazinonicotinamid acetone hydrazone (S-HyNic), respectively and then conjugate them in a second step. This approach allows obtaining a stable covalent bis-aryl hydrazone bond (BAH). During the conjugation reaction these linkers can only react with each other but not with themselves and not with other functional groups present in the polymer or enzyme. In a result only the desired conjugate will be formed.

The state of knowledge regarding *R*-PEDH covers only 3 publications. Up to date, the subject of this enzyme immobilization is not described in the scientific literature.

The main goal of this project was to create an *R*-PEDH-polylysine (PL) conjugates using BAH bond formation. The first stage of the research was the cultivation of a bacterial *E. coli* strain transformed with the gene responsible for the enzyme expression. Next, *R*-PEDH isolation via affinity chromatography (Strep-Tag) was performed. In this stage 60 ml of *R*-PEDH solution was obtained. The enzyme concentration and its specific activity were 0.7 – 2.0 mg/ml and 5-10 U/mg respectively. In the next stage, the synthesis of S-HyNic and S-4FB compounds was carried out. NMR analysis confirmed the structure of the synthesized linkers. In the main part of the project, modification of polylysine and enzyme by S-HyNic and S-4FB linkers was performed. Due to the presence of modifying groups, the enzyme was immobilized on the polymer via UV-Vis quantifiable BAH bond formation.

Research carried out under the project has set the direction for further optimization of the *R*-PEDH immobilization process on polylysine. The low degree of substitution of the biocatalyst by S-4FB and the usage of polylysine of higher molecular weight are the factors determining the higher activity of the *R*-PEDH-BAH-PL complex. However, the obtained results clearly show that *R*-PEDH is not an enzyme resistant to this type of functionalization. During functionalizing of the enzyme with the S-4FB molecule, and also after its immobilization, the biocatalyst loses catalytic activity. Three days after functionalization, *R*-PEDH-4FB complex showed only 10% of the initial activity, whereas for the non-functionalized biocatalyst the value was 85%.

Hydrotalcite-Like Heterogeneous Catalysts for Baeyer-Villiger Type Oxidation of Steroids to Corresponding Lactones with Hydrogen Peroxide

"Miniatura" research project NCN 2018/02/X/ST4/01605 [2018-2019]
(project leader: Robert Karcz PhD)

Steroid substrates and initial reaction parameters were chosen on the basis of literature research. Reagents for synthesis of hydrotalcite catalysts and catalytic experiments were purchased, along with compressed gases required for gas chromatography. On the basis of reaction parameters, the standard solutions of epiandrosterone were prepared, and analyzed using GC with flame ionization detector (FID). During this step method for analysis of steroids was optimized.

Optimization of analysis method was followed by studies of influence of reaction temperature on conversion of epiandrosterone (Figure 1).

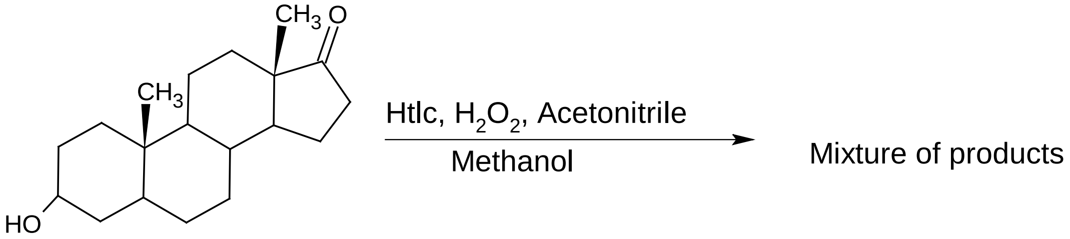


Figure 1. Scheme of epiandrosterone conversion reaction in the presence of hydrotalcite catalyst.

The reaction was carried out over a typical Mg_3AlCO_3 hydrotalcite (Htlc), prepared by co-precipitation at constant pH. Material was characterized by XRD (Figure 2) and applied as catalyst for oxidation of epiandrosterone in range of temperatures 40-60 °C. Samples were withdrawn from reaction mixture at the beginning of the reaction (before catalyst introduction) and after 3 and 24 hours of reaction. CG analysis revealed that epiandrosterone conversion occurred, and three new peaks resulting from products were present.

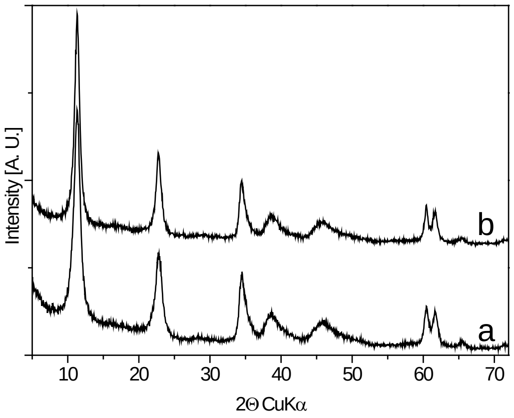


Figure 2. PXRD pattern of prepared catalyst (a) and reference material (b).

GC-MS analysis was used for identification of the reaction products. Results of analysis will be compared with HPLC to verify GC-FID method.

Searching of Novel bBcterial Ketosteroid Dehydrogenases for Oxidative Dehydrogenation of Steroids

"Miniatura" research project NCN 2018/02/X/ST4/01963 [2018-2019]
(project leader: Agnieszka M. Wojtkiewicz PhD)

The aim of the project is the identification of a physiological role for potential FAD-dependent 3-ketosteroid dehydrogenases (KstD) from two strains: *Sterolibacterium denitrificans* Chol-1S (two genes) and *Pseudomonas putida* KT2440 (three genes). In particular the project will help to answer following questions: i) is the expression of mentioned genes leading to catalysts with KstD activity; ii) are active enzymes regioselective in the direction of Δ^1 or Δ^4 products; iii) are substrates of the reaction only non-branched four-ring steroids as androstendione or branched at C17 as cholestenone or 3-ketopetromyzonole or two- or five-ring systems as well; iv) are functional catalysts differ in pH optimum or in the preference of an electron acceptor.

In the first stage of studies the necessary materials for the project were bought: components for genome DNA isolation from bacterial strains and for latter genes visualization. Oligonucleotides used as primes for genes isolation from genomic DNA were designed and ordered (for two sequences from *S. denitrificans* (SMB21450, SMB25049) and three from *P. putida* (Pp_2607, Pp_2600, Pp_2605). Amplification of mentioned genes was confirmed by horizontal electrophoresis. For each gene a product of 1.7 kbp was obtained. Amplified genes were isolated for further construct preparation and bacteria transformation.

In the next step genes will be transferred to *E. coli* DH5α, while bacteria will be cultivated for enzyme isolation. Obtaining of functional enzymes will lead to answer for above questions.

In parallel, using theoretical approaches, the analysis of five studied sequences was prepared. The sequences were aligned to the sequence of KstD1 from *Rhodoccocus erythropolis*. KstD1 is the closest homologue with crystallographic structure. After alignment the conserved amino acid residues were identified as present or absent in five studied sequences. Such alignment confirmed, that at least three sequences poses conserved residues and may be functional enzymes with KstD activity (Table 1).

Table 1. Identification of presence (+) or absence (-) of conserved amino acid residues that takes part in the reaction after sequence alignment with KstD1 z *R. erythropolis*. Residue numbers are from known ketosteroid dehydrogenase from *S. denitrificans*, AcmB. In brackets is presented the replacement of conserved residue was presented.

Protein	Y363	Y118	Y536	Y467	Y115	G540
KstD1	+	+	+	- (F)	- (F)	+
AcmB	+	+	+	+	+	+
SMB21450	+	+	+	+	+	+
SMB25049	+	+	+	+	+	+
Pp_2607	+	+	+	+	- (S)	+
Pp_2600	+	- (M)	+	- (Q)	- (I)	+
Pp_2605	+	- (M)	+	- (Q)	- (M)	+

"Beethoven" Research Projects of the National Science Centre

Domain Wall Dynamics and Magnetic Texture Behavior in Magnetic Films with Dzyaloshinskii-Moriya Interaction

"Beethoven" research project NCN 2016/23/G/ST3/04196 [2018-2021]
(project leader: Piotr Mazalski PhD)

In the frame of project ultrathin magnetic layers, in which the Dzyaloshinskii-Moriya interaction (DMI) is expected, were grown using molecular beam epitaxy. For example, cobalt wedge layers were deposited on a platinum buffer layer. The cobalt layers were capped by gold and magnesium oxide layer, half by half – MgO/Pt/Co/Au&MgO. Preliminary magnetooptical studies revealed a strong influence of the cap layer on magnetic properties of the Co layer. Unfortunately, due to an irreproducibility of the layer growth and some problem in optical measuremnts, it was not possible to unambiguously confirm the presence of DMI in the created samples. Presently, new layer sequences also with alternative ferromagnetic sublayers are under preparation.

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

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)

Some literature evidences indicate that biological activity of silver nanoparticles can be model by specific organic and inorganic molecules acting also as stabilizers. Taking into account this issue, the aim of realized research was to determine the impact of sodium hexametaphosphate on the cytotoxicity of two types of silver nanoparticles towards histiocytic lymphoma (U-937) and human promyelocytic (HL-60) cell lines.

The nanoparticles were synthesized in a chemical reduction method using sodium borohydride and trisodium citrate or sodium phosphinate and sodium hexametaphosphate. It is worth mentioning that the nanoparticles obtained with the use of well-known sodium citrate were a reference system. Both types of the nanoparticles were characterized using various experimental techniques such as transmission electron microscopy (TEM), dynamic light scattering (DLS), microelectrophoresis and surface enhanced Raman spectroscopy (SERS).

The cellular response on the nanoparticle treatment was also broadly investigated. The cell viability after does-dependent nanoparticle treatment was determined using MTT and LDH assays. Moreover, the membrane integrity was assessed in MDA tests. The effect of silver ions, delivered in the form of silver nitrate, on the cell viability was also tested in separate experiments in order to compare them with the outcome coming from the nanoparticles. The cytotoxicity of stabilizing agents and their mixtures with silver ions and the nanoparticles of various concentrations was also assessed in order to detect possible interactions occurring in investigated systems.

Both types of silver nanoparticles was characterized by spherical shape and an average size of 10±4 nm. Independently on the types of stabilizing agents, the nanoparticles exhibited negative zeta potential decreasing with increase of ionic strength and decrease of pH. The results of studies revealed that independently on the type of tumoral cells, citrate-stabilized silver nanoparticles were less toxic than hexametaphosphate-stabilized nanoparticles although they exhibited a similar ion release profile. The impact of hexametaphosphate-stabilized nanoparticles on the viability of tumoral cells was much higher than this observed for silver ions of the same weight concentration. Aqueous solutions of phosphate salts, used in the same concentrations as during the nanoparticle synthesis, did not cause the disruption of the cells. However, the addition of sodium hexametaphosphate to the citrate-stabilized nanoparticles increased LDH secretion and MDA content in the cells in comparison to the previous results. It was also determined that sodium hexametaphosphate enhanced the cytotoxicity of silver nanoparticles as well as silver ions of the same weight concentration. Nevertheless, the cellular response on the nanoparticle treatment was dependent on silver dose and individual features of the tumoral cells.

Based on these findings the meachanism of biological activity of the systems of silver-sodium hexametaphosphate was proposed. It assumes that sodium hexametaphosphate facilitates the penetration of nanoparticles into the cells. Hence in the presence of sodium hexametaphosphate the doses of silver nanoparticles and ions causing total deactivation of the tumoral cells was significantly lower than in the case of the citrate-stabilized nanoparticles.

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

New Functionalised Polymers for Biomedical Applications

"Leader" programme research project NCBiR 0090/L-7/2015 [2017-2019]
(project leader: Maciej Guzik PhD)

Reactions were carried out to modify the polymer - polyhydroxyoctanoate (PHO) with drugs leading to the functionalised materials. For this purpose, a two-stage reaction was carried out, in which the first one consists in obtaining cyclic oligomers, whereas the second one is a biocatalytic modification reaction in which screening tests were carried out to determine which solvent is the most promising in this reaction. The obtained oligomers were modified with three drugs: anti-inflammatory (diclofenac), steroid (betamethasone) and antibiotic (oxytetracycline). The course of the reaction was monitored using: LC-MS.

Soft foams were prepared using a porogen leaching technique. Foams were obtained from 2 different porogen fractions - glucose, <90 μm and 90-300 μm. A protocol was developed in which the time needed for evaporation of the solvent, foam aging and subsequent rinsing of foams in distilled water were determined. During the flushing, the glucose level was monitored using a glucometer. At the same time, two parallel series of foams with and without fluorescein were made (to enable imaging of foams in confocal microscopy). In cooperation with the Faculty of Materials Science and Ceramics of the AGH University of Science and Technology, Β-TCP / PHO composites were obtained using the immersion method which consisted of dipping ceramic pellets in prepared polymer solutions. Materials were visualized using scanning electron microscopy (SEM), both before and after incubation in a solution simulating body fluids (SBF). Pre-incubation studies have shown that the polymer does not completely cover the ceramic grains and is not compatible with the ceramic material (the polymer detaches itself from the surface). Incubation in SBF showed the formation of an apatite layer on the surface of the material, a feature that promises the later use of prepared composites in bone tissue regeneration processes. In addition, their compressive strength as well as wettability and surface energy have been determined.

Pilot studies were conducted to determine the degree of bacterial adhesion to the surface (polystyrene (PS), PHO). The research included the analysis of 4 reference strains in terms of the amount of biomass produced depending on the selection of the inoculum charge and the type and supplementation used for the medium. Two gram-positive strains were selected: *S. epidermidis* ATCC 35984 (RP62A) and *S. epidermidis* 12228 and 2 gram-negative strains: *E. coli* ATCC 25922, *P. fluorescens* PCL 1701. In further stages of the research, these strains will serve as models in biofilm analysis using microscopic imaging. The Crystal Violet (CV) method was applied, which allowed to determine the conditions allowing to obtain a strong, well-developed biofilm with large biomass for each of the tested bacterial strains. Studies have shown that the density of inoculum and adequate nutrient supplementation affect the size of the produced bacterial biomass.

Nanoindentation tests of PHO films, which were created by dissolving the polymer in various solvents, were performed. The results showed that Young's modulus is close to the values obtained during AFM studies. The high modulus of elasticity and hardness gives hope for the use of material in applications where load transfer is necessary. Fluorescence imaging and confocal cytoskeleton architectures of cells grown on media made from PHO were performed. There were clearly visible cell edges with highly polymerized actin and coarse actin filaments running throughout the cell body and directly above the nucleus. A protocol for the staining of mouse embryonic fibroblasts (MEF 3T3) was developed to visualize the structure of intermediate filaments. They are an extremely important intracellular element because they are responsible, inter alia, for adhesion, which is closely related to the type of substrate on which cells are located.

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

Development of methodology of Synthesis and Stabilization of Metal Nanoparticles for Conductive Materials

"Homing" research project FNP Homing/2017-3/28 [2017-2019]
(project leader: Anna Pajor-Świerzy PhD)

In recent years, conductive inks and pastes composed of metal nanoparticles (NPs) have attracted much attention because of their potential application in the field of electronic industry. Silver NPs, due to their high conductivity and oxidation stability, have been the most commonly used so far for the fabrication of electronic circuits and devices. Although Ag NPs have obvious advantages, their high price limits their application on a large industrial scale. Among the metals, which can be used as a replacement of silver are tin and nickel, due to their much lower cost and good electrical conductivity. However, Sn and Ni NPs are easily oxidized in air, resulting in poor conductivity. As a suitable option to overcome the high cost of Ag and to prevent the spontaneous oxidation of Sn and Ni, Sn-Ag and Ni-Ag core-shell particles can be synthesized and investigated.

The general objective of the "Homing" project is a development of the methodology of synthesis of nanoparticles stable against aggregation and oxidation, which can be used as a functional component of low-cost, conductive pastes or inks for printing process on glass and plastic substrates. The using of nickel and tin nanoparticles will reduce the cost of producing conductive nanomaterials. However, the disadvantage of the mentioned nanoparticles is their fast oxidation process in an atmospheric environment, therefore the important aim of the project is to create a protective layer on their surface in the form of silver, which will result in core-shell nanoparticles (where core - Ni or Sn, shell - Ag). The obtained nanoparticles will be used as a functional component of conductive pastes and inks that will be applied in the printing process (screen printing, inkjet printing) on glass or plastic substrates.

During the research carried out in 2018, two simple and fast methods of a synthesis of core@shell (Ni@Ag) nanoparticles were developed. The synthesis of nickel cores was based on the reduction of Ni ions by sodium borohydride as a reducing agent, while the formation of the silver coating was based on the transmetalation reaction, which involves the reduction of silver ions on the surface of the nickel nanoparticles. In the first method of synthesis of Ni@Ag nanoparticles an excess of $NaBH_4$ was used. To avoid the formation of Ag nanoparticles during the transmetallation process, the obtained Ni NPs was washed. In the second method, a deficiency of the reducing agent was used, therefore the process of washing Ni NPs was not required. The obtained nanoparticles have a suitable size, 70 nm according to the first and 250 nm for the second method of synthesis, for the production of conductive materials such as pastes or inks. The synthesis method, which was performed in the deficiency of $NaBH_4$, was more efficient and allowed to obtain a dispersion of Ni@Ag nanoparticles with a higher percentage of metallic nickel, which is required for the fabrication of conductive circuits. In addition, the obtained Ni@Ag NPs were characterized by long-term (6 months) stability against aggregation and oxidation processes, therefore they are a promising material for the production of electronic devices.

Exchange of PhD Students and Academic Staff Programme Projects of the Polish National Agency for Academic Exchange

International Scholarship Exchange of PhD Candidates and Academic Staff

Project NAWA PPI/PRO/2018/1/00006/U/001 PROM [2018-2019]
(project coordinator: Professor Tomasz Borowski)

The purpose of this project is to improve competencies of PhD students and research staff from Poland and from abroad, by their active participation in scientific conferences, schools, workshops and research internships related to their PhD programs. Within the project the following short term educational activities will be supported:

1. active participation in a scientific conference abroad (e.g. presenting a poster or giving a flash talk);
2. participation in a workshop, training or a summer/winter school (either as an attendee or as a tutor/lecturer);
3. completing a research internship.

The project started on 1st October 2018. In 2018 an agreement with NAWA was signed, regulations and other documents relevant for two competitions for scholarships for PhD students at ICSC PAS were prepared, these two competitions have been announced and opened. Preparations of two schools, addressed primarily to PhD students and which will take place in ICSC PAS in March and July 2019 have started.

EU COST Actions

ECOSTBio Explicit Control Over Spin-states in Technology and Biochemistry

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

The action CM1305 ECOSTBio, a part of the EU project „European Cooperation in Science and Technology" (coordinated by University of Groningen, the Netherlands), closed April 30, 2018. European funds were used in aim is to construct a network of both experimental and theoretician research groups to tackle a diversity of chemical problems where spin is an important factor. This has been 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 created a synergy, helping theoreticians to validate their models and experimentalists to improve the performances of novel materials with desired properties. The Spin State Database has been set in Girona (https://iochem.udg.edu:8443/).

The project effected in 237 published papers, in consecutive years: 2018 - **60,** 2017 - **61,** 2016 - **60**, 2015 - **41,** 2014 – **15,** accordingly (Institute of Catalysis PAS contributed with **8** papers).

In the year 2018 the summarizing and closing scientific meetings took place: eight scientific workshop in Berlin, April 9-11, 2018. Prof. E. Broclawik and Tomasz Borowski participated in the meetings as the Polish representatives to the Management Committee for CM-1305, and Ms Zuzanna Wojdyła who presented her achievements within STSM scientific stages.

NEUBIAS A New Network of European Bioimage Analyst to Advance Life Science Imaging

EC COST Action CA15124 NEUBIAS [2016-2020]
(investigator: Marcel Krzan PhD)

This Action is a program for establishing a network of BioImage Analysts, in order to maximize the impact of advances in imaging technology on the Life-Sciences, and to boost the productivity of bioimaging-based research projects in Europe. The Action aims to provide a stronger identity to image analysts by organising a new type of meeting fostering interactions between all stakeholders including: Life scientists, image analysts, microscopists, developers and the private sector. It will collaborate with European Imaging research infrastructures to set up best practice guidelines for image analysis. The Action created an interactive database for BioImage analysis tools and workflows with annotated image sample datasets, to help matching practical needs in scientific problems with software solutions. It will also implement a benchmarking platform for these tools. To increase the overall level of image analysis expertise in the science, the Action proposed a novel training program with three levels of courses, releasing of open textbooks, and offering of a short-term scientific missions program to foster collaborations, image analysis technology access, and knowledge transfer for scientists and specialists lacking these means.

As a member of the COST CA15124 (I am not a member of the Management Committee) in the second year of the action, I continued collaboration online with other COST action participants. I worked online with other associates in the action of scientists creating new algorithms to facilitate and accelerate research work using automated image analysis. The results of the research - obtained more easily and with much greater precision thanks to the new software have already been presented during scientific conferences. Thanks for the project were added in the case of all conference presentations (if the research material was prepared using the new software): 61st Polish Chemical Society conference, Krakow, Poland, International Conference on Catalysis and Surface Chemistry, Krakow, Poland, Eufoam 2018, Liege, Belgium, and 17th Food Colloids Conference, 2018, Univ. Of Leeds, UK. (7 conference presentations) and in the chapter published in 2018 in the scientific book. M.Krzan, A.Kulawik-Pióro, B.Tyliszczak „Foams stabilized by particles" chapter 15 in book "Foam Films and Foams: Fundamentals and Application" (D.Exerowa, G.Gochev, D.Platikanov, L.Liggieri and R.Miller (Eds.), book in series of "Progress in colloids and Interfacial Science" in preparation, 2018, ISBN 9781466587724, pp. 279-294.

Projects of the Norwegian Research Council

Sustainable Management of Heritage Buildings in a Long-Term Perspective

Norwegian Research Council research project 274749 SyMBoL (2018-2021)
(*project leader: Marcin Strojecki PhD*)

The SyMBoL project aims to advance the understanding of physical decay of artistic materials in heritage wooden buildings through an extensive laboratory study of accumulation of climate-induced physical damage in wooden specimens mimicking original elements. The lab study will be complemented by direct tracing of fracturing intensity in original wooden objects in the Ringebu and Kvernes stave churches using the non-destructive acoustic emission technique. In turn, mechanical and moisture properties of naturally aged polychrome layers on wood will be characterized using micro/nano-indentation methods. The outcomes will be correlated with the numerical simulation of the dynamic processes of water vapour uptake/release and the related strains and internal stresses.

The second objective is to use this knowledge to develop science-based indoor climate management plans for the sustainable use of the churches, maintaining adequate comfort for visitors while minimizing the degradation risk.

The results will be beneficial for local authorities, conservators, and decision makers to understand hazards, to prioritize conservation treatments for painted wood structure, and to be effective in planning indoor climate management. Last but not least, the results will be beneficial also for the general public as an effective cultural heritage management will guarantee a safer preservation of historic buildings and their content and will promise an higher comfort for visitors while minimizing the energy consumption.

Projects of EU Structural Funds Programmes

Cross-institutional PhD Studies „Interdisciplinarity for Innovative Medicine” InterDokMed

EU Structural Funds project NCBiR PO WER ŚSD InterDokMed [2017-2022]
(project leader: Assoc. Prof. Renata Tokarz-Sobieraj)

The Interdisciplinary PhD Project is implemented as part of the Operational Program Knowledge, Education and Development for 2014-2020, action 3.2 Doctoral studies, Axis III Higher education for the economy and development. The aim of the project is to increase the quality and effectiveness of education at doctoral studies, through the development of an extended program, its implementation and implementation, as part of InterDokMed's Interdisciplinary for Innovative Medicine.

The project is implemented by a consortium of five scientific units with at least A category and KNOW status. The project coordinator is the Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences and partners: Maj Institute of Pharmacology Polish Academy of Sciences, The Henryk Niewodniczański Institute of Nuclear Physics Polish Academy of Sciences, Faculty of Chemistry, Jagiellonian University and Faculty of Medicine, Jagiellonian University Collegium Medicum. The choice of implementing units guarantees the implementation of interdisciplinarity through the implementation of scientific research covering more than one area of knowledge (exact sciences / medical sciences), more than one field (chemical / physical / medical sciences) and several scientific disciplines (physics, chemistry, pharmacology, medicine).

As a result of recruitment (two dates - September 2017 and February 2018), 50 PhD students.

In 2018, the implementation of the scientific program began, which includes 4-year (8 semesters) education in the exact and biomedical sciences profile. In 2018, the doctoral students carried out classes in English, statistics course and field lectures, covering all fields of science represented by partner units: "Chemistry in a pill", "Physics in a pill", "Civilization diseases" and "Pharmacology of civilization diseases". On 22-24 June 2018, stationary workshops on translational sciences were organized for PhD students. As part of the workshop, 13 specialists from partner units presented 22 h lectures on the border of natural and medical sciences. The form of classes and the accumulation of various topics is an opportunity to get acquainted with different views on the same research problems. The implementation of such a program creates the possibility of an innovative and modern way of educating a doctoral student, prepared for independent interdisciplinary and multi-domain scientific research, aware of his own values, prepared to continue scientific work and ready to take up tasks in the industrial and biomedical sciences.

Doctoral students carry out their scientific research on an ongoing basis, under the care of two supervisors from two different partner units, representing different scientific disciplines. They present the results of the research at doctoral seminars. They broaden their knowledge by participating in scientific conferences, both domestic and foreign and carrying out scientific internships. In 2018 PhD students took 4 internships abroad, 36 doctoral students participated in domestic and foreign conferences.

Interdisciplinary Environmental Doctoral Studies "Physical, Chemical and Biophysical Foundations of Modern Technologies and Materials Engineering" (FCB)

Project of Operational Program Knowledge Education Development (POWER) for interdisciplinary doctoral study programs POWR.03.02.00-00-I004 / 16 [2017-2022]
(deputy project manager: DSc Eng. A. Micek-Ilnicka)

The project is financed by the Foundation for the Development of the Education System and is a result of a competition announced by The National Centre for Research and Development (NCBiR) in 2017 for interdisciplinary doctoral studies programs. This project is coordinated by the Faculty of Physics and Applied Computer Science (WFiIS) at the AGH University of Science and Technology (AGH) with the participation of the Faculty of Materials Science and Ceramics (WIMiC) at the AGH, the Faculty of Chemistry at Jagiellonian University (WCh UJ), The Henryk Niewodniczański Institute of Nuclear Physics (IFJ) of the Polish Academy of Sciences and Jerzy Haber Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences (IKiFP).

FCB doctoral studies are interdisciplinary. The interdisciplinary nature of FCB doctoral studies results from the participation of doctoral students in lectures and seminars in natural sciences in the discipline of chemical sciences and physical sciences.

The project has been implemented since October 1, 2017. The recruitment of doctoral students to the project was carried out in three stages, in the winter semester (September 2017) and in the summer semester (February 2018, September 2018). Currently, according to the project assumptions, FCB is studying 75 doctoral students, including 5 persons at IKiFP, 34 persons at WFiIS, 15 persons at WIMiC, 9 persons at IFJ, 12 persons at JHC.

FCB doctoral studies gives opportunity to:

- conducting independent scientific research, including outside the unit providing education;
- scientific cooperation in research teams, including international ones;
- preparation by a doctoral student of a scientific publication in the form of a book or at least one scientific publication accepted for publication in a peer-reviewed scientific journal of at least national coverage or in a peer-reviewed report from an international scientific conference;
- implementation of the study program, including compulsory, optional and apprenticeships;
- preparation for doctoral examinations and preparation of a doctoral dissertation under the supervision of a promoter or an assistant supervisor;
- participation in the life of the scientific community in the country and abroad.
- participating in interdisciplinary activities - within the disciplines represented by the units conducting the studies (physics / chemistry / biophysics / materials engineering / chemical technology).
- implementation of interdisciplinary scientific research and preparation of the doctoral dissertation
- as part of interdisciplinary doctoral dissertations.

As part of developing soft skills, doctoral students participated in training workshops in Poronin on 15-17 June 2018.

Other International Research Projects

Immobilization of Metal Nanoparticles on Organo-Modified Layered Silicates

Joint research project of the Polish Academy of Sciences and Slovak Academy of Sciences cooperation [2016-2018]
(project leaders: Małgorzata Zimowska PhD, Helena Pálková PhD)

Hybrid inorganic–organic nanomaterials based on layered silicates, serve as a solid supports, creating suitable templates for guest species like metal nanoparticles. Selection of both, layered silicates and polymeric substance has significant effect on immobilization process and on final distribution of metal nanoparticles within matrix of composite.

The aim of this project was to determine the effect of synthesis parameters on the physicochemical properties of composites obtained as a result of clay minerals modification by poly(diallyldimethyl ammonium) cationic polymer (PDDA) and immobilization and stabilization of ruthenium metal nanoparticles. The catalytic properties of the obtained composites were tested in the hydrogenation reaction of 2-butanone under mild conditions that were determined by the room temperature, atmospheric pressure and the solvent (aqueous solution) which were used to conduct the reaction.

Three synthetic procedures were applied, differing in the order of components addition and the step of metallic Ru particles generation. The obtained materials were characterized with the use of various techniques: XRD, XRF, EDS, AFM, TEM/HRTEM and TG/DSC. Thorough analysis indicated that via tuning the preparation method the structural and thermal properties of the composites can be controlled. The applied approach controlled the distribution and size of Ru particles and affected the activity of the obtained catalysts in the hydrogenation reaction of 2-butanone to butanol. The test reaction, carried out for 30 minutes in the aqueous solution, showed complete inactivity of the polymer-unmodified sample. All polymer-modified catalysts were active in the hydrogenation of 2-butanone. Optimization of the catalytic efficiency was associated with the optimization of the size of the Ru particles by appropriate loading of polymer and selection of Ru / PDDA ratio. The best catalytic properties and the highest conversion values (over 90%) were obtained for Ru/polymer/clay composite with the intermediate size of Ru particles (5 nm) obtained by generation of metallic Ru species in the polymer solution before intercalation into the clay mineral structure.

Studies on the stability of catalysts as a function of time showed that the size of Ru crystallites affected the susceptibility of the catalysts to reoxidation, and the state of reduction of the metallic phase is essential for the course of hydrogenation reactions of 2-butanone.

Biocompatible Particle-Stabilized Foams and Emulsions as Carriers for Healing Agents

Joint research project of the Polish Academy of Sciences and CNR National Resreach Council[2017-2019]
(project leaders: Marcel Krzan PhD, Francesca Ravera PhD)

During the project, we want to develop technology for generation and application of stable foam and emulsions formulated from mixtures of hypoallergenic, non-toxic biological polymers, mainly “green surfactants”. Such surface thin film could in the close future become the basis of the cosmetic and dermatological composition for the multiple use products. The application of other biologically active particles, like i.e. chitosan, silk fibroin or liposomes will also be carefully studied. Similar multicomponent film layer (created after foam or emulsion injection on the human body) would be the first line of the skin body defence against various pathogens. Thanks for them the skin will be simultaneously protected, lubricated and regenerated. Similar thin surface film (created from our foams or emulsions) could also be used as a pathogen barrier in the food industry as natural preservatives. The same technology may be utilized in the agricultural production in natural green pesticides. The similar application of the technology let us in close future reduce the number of synthetic surfactants incorporated into the natural environment.

During the second year of the project, the foaming properties were studied in saponin solutions (saponin reagent grade, VWR, catalogue no. 0163-100g) and its mixtures with chitosan (HD chitosan, low molecular weight, cosmetic ingredient) using a modified apparatus for measuring the stability of foams based on eight foaming columns. The complementary foam was done using the double-syringe method. The research was carried out simultaneously using the facilities of both institutes in Poland and Italy.

The bilateral project funds allowed us to perform two two-week research internships in Genoa - for dr. Marcel Krzan and dr. Ewelina Jarek. We also had two independent one-week project visits to our Cracow institute - dr. Frances Ravera (Italian PI of the project) and dr. Eva Santini.

The obtained results were presented during national and international scientific conferences 61st Polish Chemical Society conference, Krakow, Poland, International Conference on Catalysis and Surface Chemistry, Krakow, Poland, Eufoam 2018, Liege, Belgium, and 17th Food Colloids Conference, 2018, Univ. Of Leeds, UK. They were also used to prepare publications, including one chapter in the book (published in 2018) and two publications in ISI / JCR journals (to be reported at the turn of 2018/2019).

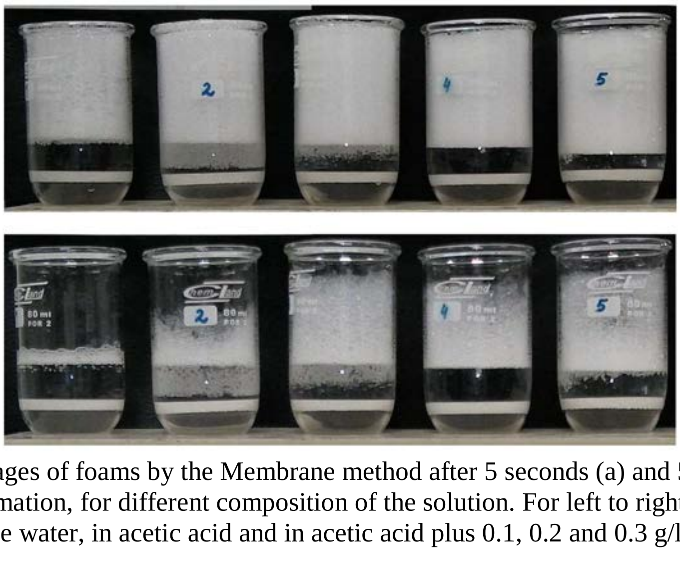


Figure 1 Images of foams by the Membrane method after 5 seconds (a) and 5 hours (b) from the formation, for different composition of the solution. For left to right: 0.1 g/l of saponin in pure water, in acetic acid and in acetic acid plus 0.1, 0.2 and 0.3 g/l of chitosan.

Biocompatible Particle-Stabilized Foams and Emulsions for Biomedical Applications

Joint research project of the Polish Academy of Sciences and the Bulgarian Academy of Sciences cooperation [2018-2020]
(project leader: Marcel Krzan PhD)

During the project, we want to develop technology for generation and application of stable foam and emulsions formulated from mixtures of hypoallergenic, non-toxic biological polymers, mainly biosurfactants. The medical impact of the biological foams and emulsions, which could be used as the thin cover film, will be further strengthened by the addition of silver nanoparticles. The application of other biologically active particles, like i.e. chitosan, silk fibroin, liposomes or dendrimers will also be carefully studied. Similar multicomponent film layer (created after foam or emulsion injection on the human body) would be the first line of the skin body defence against various pathogens.

During the first year of the project, measurements of dynamic and equilibrium surface activity and surface elasticity were made in solutions of one of the so-called "green surfactant": n-dodecyl-ethyl-arginate, which was enriched with the presence of colloidal silica nanoparticles (with different particle sizes - 6, 9 and 30nm). From the obtained results, the concentration ranges of the tested substances and mixtures necessary for the development of a stable foam film were determined. Our assumptions were verified in the experiment in the foam stability tester.

The research was carried out simultaneously using the facilities of both institutes in Poland and Bulgaria. The bilateral project funds allowed us to perform two one-week research internships in Sofia - for dr. Marcel Krzan and dr. Ewelina Jarek. We also had one one-week project visits in our Cracow institute - dr. Hristina Petkova.

The obtained results were presented during national and international scientific conferences 61st Polish Chemical Society conference, Krakow, Poland, International Conference on Catalysis and Surface Chemistry, Krakow. They were also used to prepare publications, including one chapter in the book (published in 2018) and two publications in ISI / JCR journals (to be reported at the turn of 2018/2019).

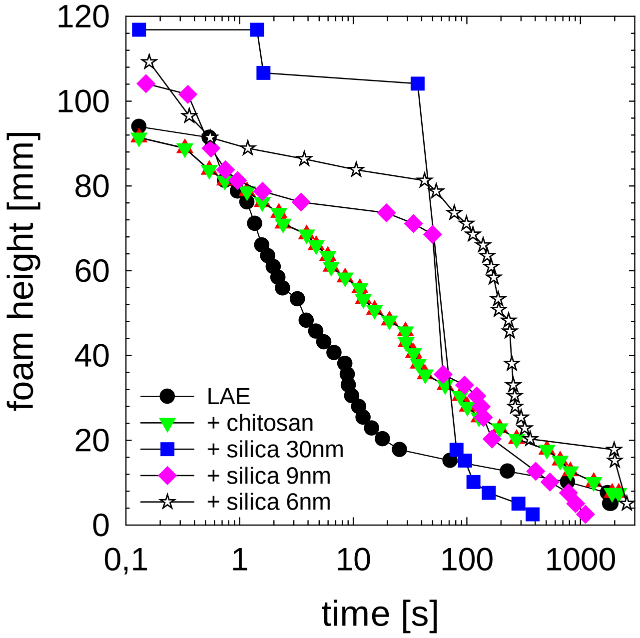


Figure 1. Foam height evolution in lauroyl ethyl arginate foams (all experiments performed in presence of 1%wt. acetic acid). Foams generated from 100ppm solution of lauryoly ethyl arginate (LAE) alone and from mixtures of 100ppm LAE with: i) 100ppm chitosan; ii) silica particles Levasil 100/45% (30nm diameter); iii) silica particles Levasil 300/30% (9nm diameter); iv) silica particles Levasil 500/15% (6nm diameter).

Synthesis of Novel Organic-Inorganic Hybrid Materials to Use as Catalysts for Fine Organic Synthesis

Projekt badawczy Polskiej Akademii Nauk i National Academy of Sciences of Ukraine
[2018-2019]
(project leader: Professor Ewa Serwicka-Bahranowska)

The project is focused on the optimization of the catalytic properties of nanoporous silica materials by introducing additional functionality (e.g., phosphonic, ammonium, ethylammonium groups) on sulfur-functionalized surfaces. Such modifications may lead to the higher catalytic activity of bifunctional compounds as compared to monofunctional materials. Thorough physicochemical investigations involving numerous techniques (IR, Raman, and XPS spectroscopies, SEM, TEM, XRD, and BET analysis as well as water contact angle and zeta potential measurements) will be conducted. The physiochemical characterization will employ quantum chemical calculations as well. The impact of such changes will be explored in test reactions e.g. alcohol dehydration and the Baeyer-Villiger transformation of cyclohexanone to ε-caprolactone.

In the reported period Dr Oksana Dudarko visited the Institute of Catalysis and Surface Chemistry PAS. During this stay a series of catalysts based on mono- and bifunctionalized SBA-15 mesoporous silicas, prepared by the Ukrainian partner, have been subjected to physico-chemical characterization by means of thermal analysis and nitrogen adsorption/desorption at 77 K. In addition, a draft of a book chapter co-authored by the project team, has been prepared.

Other Scientific Activity

Acoustic emission monitoring of historical furniture in Knole, UK

Research contract from the National Trust, UK (2016-2018)
(*project leader: Marcin Strojecki PhD*)

Acoustic emission (AE) monitoring of historical furniture has been continued at Knole House in Kent, UK in the framework of a research and conservation project being implemented in 2016-2018. The analysis of the results collected during almost 1.5-year monitoring as well as the condition survey performed by visual inspection strongly suggested possible infestation by wood boring insect. Therefore, it has been decided to apply the thermolignum heat treatment process for all Gole suite objects. The treatment started at 15:00 on Friday 16/02/2018 and lasted approximately 3 days. The kill-temperature of insects was targeted at 52 °C in the objects' core, consequently to reach this value an ambient temperature around 55 °C was required. Relative humidity was set to a target value of 57% and was maintained at around 65% RH during the treatment. The AE monitoring conducted during the thermal treatment of the Gole suite objects was intended to double-check objects' safety during the thermolignum process. The Gole suite objects as well as the AE equipment in the course of the treatment are shown in Figure 1.

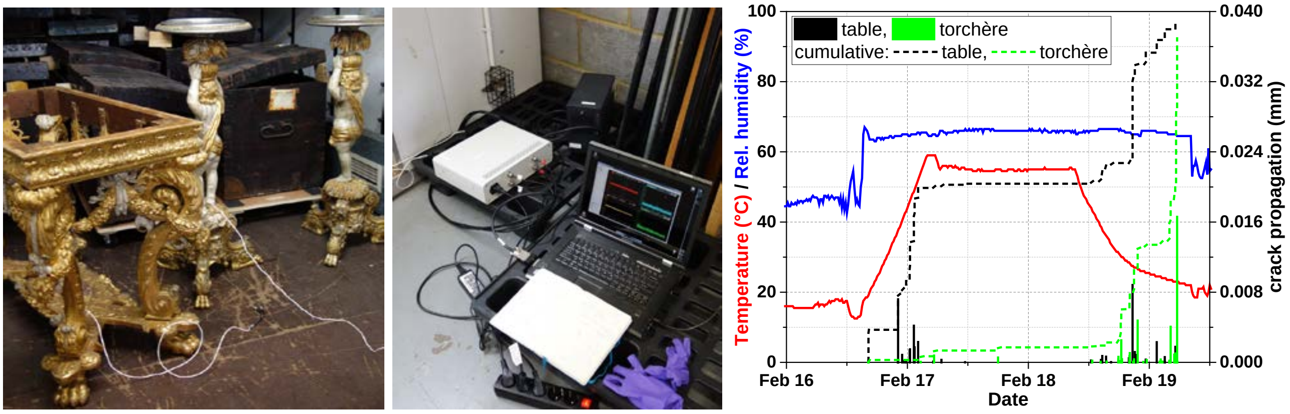


Figure 1. Gole suite table and torchères in the thermolignum chamber - left. The acoustic emission system installed outside the chamber - middle photo. AE activity recorded from the Gole table (black) and torchère (green) during thermolignum treatment correlated with temperature (red) and relative humidity (blue) inside the chamber - right.

The results of the AE monitoring recorded from the Gole suite table and torchère during the thermolignum process correlated with temperature and relative humidity in the vicinity of the objects inside the treatment chamber are shown in Fig. 1. The data analysis showed that the most of AE activity was recorded during elevating the temperature up to 53 °C as well as during the cooling phase. For both objects similar AE energy was recorded, however the proportions of energy corresponding to the heating and the cooling phase for both objects are different. For the table during the heating and the cooling phase almost the same AE energy was recorded, whereas for the torchère almost all AE energy was recorded during the cooling phase. This may be due to different stresses induced in objects resulting from their different geometry – construction with the joints in case of the table and bulky for the massive torchère. During the whole thermolignum treatment 40 and 36 AE events were recorded for the table and torchère, respectively. It corresponds to 22535 and 21432 of AE energy in arb. units, which in turn correspond to 0.039 and 0.038 mm of the cumulative crack propagation for the table and torchère, respectively.

After the thermolignum treatment all Gole suite objects returned to their original place of exposition *i.e*. the Cartoon Gallery, where the AE monitoring was continued till July 2018. The results obtained confirmed the effectiveness of the thermolignum treatment after which the AE energy decreased more or less about one order of magnitude and the correlation of the AE with temperature reversed.