INSTITUTE OF CATALYSIS
AND SURFACE CHEMISTRY
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DETAILED RESEARCH REPORT

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Statutory research

Nanotechnology as the Basis of New Catalytic Materials

Monodispersed, Colloidal Suspensions of the Zeolite Nanocrystals and their Use for the Preparation of New Porous Systems for Catalytic and Sorption Processes

(Assoc. Professor Mirosław Derewiński DScEng, Jerzy Podobiński MSc)

The aim of the work was to prepare a highly porous system by assembling protozeolitic nanoclusters into a mesostructured material of wormhole-layered arrangement. The applied approach was reported to be effective in generation of acidic active sites in the mesoporous materials, leading to a highly active and thermally stable catalytic system. The protozeolitic clusters of the MFI molecular sieve (containing Al or Fe atoms) were chosen as building units for the preparation of new mesoporous catalytic systems.

The synthesis of MFI type protozeolitic nanoclusters was performed under conditions ensuring formation of very small particles. Size of the Al containing nanoclusters synthesized at 50^{o}C was in the range 4-6 nm, whereas of these prepared at 100^{o}C and containing Fe was in the range 13-18 nm. Band at ~550 cm^{-1} in the FTIR spectra of the protozeolitic particles indicated presence of five member rings, i.e. secondary building units (SBU), in the structure.

Mesoporous, hierachical materials (PMM) were prepared by mixing suspension of the protozeolitic cluster containing Al and Fe with solution of surfactant. The layered-wormhole mesoporous character of the obtained materials was confirmed by SEM (Fig 1) and TEM analysis. The obtained preparations were characterized by XRD, SEM, DRSUV/VIS, TEM ^{27}Al MAS NMR, FTIR spectroscopy (acidity determination) and N_2 sorption.

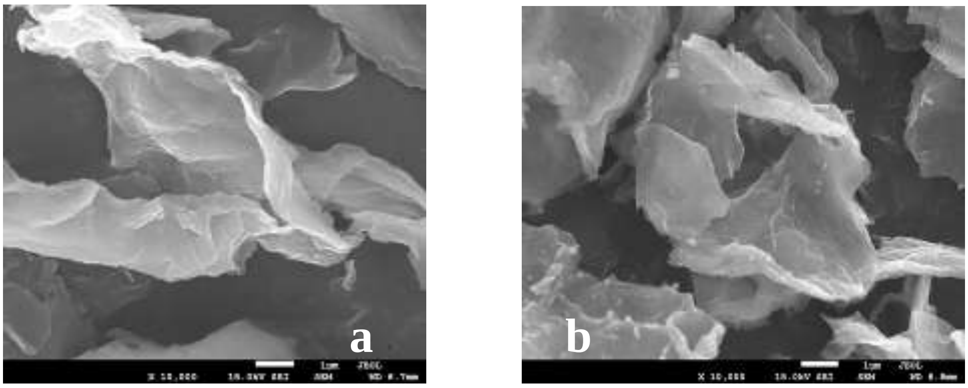


Figure 1. SEM micrograph of mesostructured materials containing Al (a) and Fe (b)

A very high BET specific surface area (909-1167 cm^{-1}) and adsorption/desorption isotherms of N_2 proved the presence of mesopores (2.5-3 nm in diameter).

^{27}AlMAS NMR data of the calcined Al-PMM materials showed that most of Al was tetrahedrally coordinated. It was supported by the results the study of the acidity of the obtained porous solids with pyridine sorption monitored with FTIR spectroscopy. Bands attributed to the vibration of pyridine molecules bonded to the active centers were found in the IR spectra recorded after desorption of pyridine at 350^{o}C. On the other hand analysis of the Fe-PMM materials with DRSUV/VIS technique has showed, that most of the iron present in the hierarchical material remained octahedrally coordinated and did not generate protonic acidity.

Conclusion on the different coordination and structural environment of Al and Fe atoms in mesoporous materials were confirmed by the catalytic tests, i.e. liquid phase isomerisation of α-pinene. Whereas Al-PMM material was highly active (~85% α-pinene conversion in 1 h), the hierarchical material prepared with the protozeolitic species containing Fe was no active (about 5% conversion of α-pinene).

Structural Properties and Dynamics in Epitaxial Oxide and Metal Nanostructures Studied with Microscopic and Spectroscopic Techniques Radiation

(Professor Józef Korecki DSc, Nika Spiridis PhD, Jacek Gurgul PhD, Robert Socha PhD, Dorota Wilgocka-Ślęzak PhDEng, Barbara Figarska MSc, Kinga Freindl MSc, Tomasz Giela, MSc, Ewa Madej (Zackiewicz) MSc, Ewa Młyńczak MSc [in cooperation with AGH University of Science and Technology])

A number of thin-film systems, such as MgO, CoO, FeO, Fe_3O_4, which are ideal substrates supports for metallic nanostructures were obtained by three different methods: oxidation of a native metal, reactive deposition of a metal in oxygen atmosphere using molecular beam epitaxy and by evaporation of a bulk oxide using electron-beam bombardment. Especially, the growth of FeO(111) films, as thick as several nanometers was documented. Stabilization of such thick films exposing the polar surface was not reported before, whereas it can be an important step in investigations of model metal catalysts on oxide supports.

Tri-layers Fe/MgO/Fe (a typical tunnel junction system) was studied in view of correlation between their structural (morphology of interfaces) and magnetic properties, such as perpendicular anisotropy and interlayer exchanger coupling and their properties on the thickness of the MgO spacer. The STM data indicated that MgO as thin as one monolayer, deposited on Fe, is continuous. This is connected with the formation of a FeO layer during deposition of MgO, as shown by conversion electron Mössbauer spectroscopy. On the contrary, when a top Fe layer is deposited on MgO/Fe, completing a magnetic tunnel junction (MTJ) structure, the Fe/MgO interface is chemically sharp. An antiferromagnetic coupling between the Fe films was evidenced by magnetooptic Kerr effect microscopy for an ultimately thin (~2 Å) MgO spacer.

Preparation of self-organized magnetic nanostructure requires well defined substrates with a unique surface pattern, which can be used as a template. Single-crystalline substrate usually involve a laborious process of surface cleaning such as ion bombardment, gas treatment and annealing. Alternatively, in nanostructure studies one can use a refractory metal surface to grow on it a film exposing the surface of interest. In such an approach, by using molecular beam epitaxy and LEED and STM characterization techniques, we optimized the growth of gold films on the tungsten W(110) surface for stabilization of a characteristic "herring bone" reconstruction, which was then used as a template for growing nanostructures of cobalt and silver. The growth parameters were deposition and post-deposition annealing temperature, as well as the film thickness. We analyzed the long-range ordering of the unidirectional reconstruction domains and the influence of surface defects. An important finding was the observation and explanation screw dislocation pairs and their grouping. Using the Au(111) surface with anisotropic reconstruction we analyzed the nucleation and growth of cobalt and silver. The results were gathered in the master thesis "Metal nanostructures (Au, Ag, Co) on the W(110) surface for engineering of magnetic anisotropy" by Tomasz Giela.

Nanomaterials Based on Layered Minerals

(Professor Ewa Serwicka-Bahranowska, DSc, Małgorzata Zimowska PhD, Alicja Michalik-Zym PhDEng, Roman Dula PhD, Elżbieta Bielańska PhD, Daria Napruszewska MScEng

Mixed oxides derived from hydrotalcite-like precursors are characterized by nanocrystalline structure and high dispersion of constituting elements, which makes them attractive materials from the point of view of catalytic applications. Properties of a hydrotalcite precursor depend critically on the preparative conditions. The aim of the present work was to determine the influence of reagents concentration on the properties of CuMnAl (1:2:1) hydrotalcite, frequently used as a catalyst precursor. Carbonate forms of hydrotalcite were prepared by co-precipitation at constant pH=9, at temperature 55°C. In all experiments a mixture of nitrates containing respective cations in quantities: Cu^{2+}-0,01 M, Mn^{2+}-0,02 M, Al^{3+}-0,01 M was used. Two series of hydrotalcites were prepared a) using constant quantity of sodium carbonate (0,018 M) and changing the volume of water used for dissolution of reagents, b) using the same amount of water for dissolution and changing the amount of Na_2CO_3. XRD analysis showed the presence of well crystalline CuMnAl hydrotalcite in all studied samples, accompanied by various amounts of $MnCO_3$ (rhodochrosite) admixture. SEM image in Fig. 1 shows well developed hydrotalcite plates co-existing with fine grains of rhodochrosite. Analysis of results indicates that increase of the water volume used for synthesis leads to better crystallinity of the hydrotalcite phase and results in better structural order within the layer. It enhances also the amount and crystallinity of rhodochrosite admixture. Growing amount of carbonate used during synthesis results in worsening of hydrotalcite crystallinity and increase of the amount of poorly crystalline rhodochrosite. The findings are of significant importance for the synthesis of catalytic materials, because the presence of rhodochrosite means that the mixed oxides obtained during thermal decomposition contain, next to CuO and spinel phases, also strongly dispersed Mn oxides, which, depending on the catalytic reaction, may or may not be advantageous.

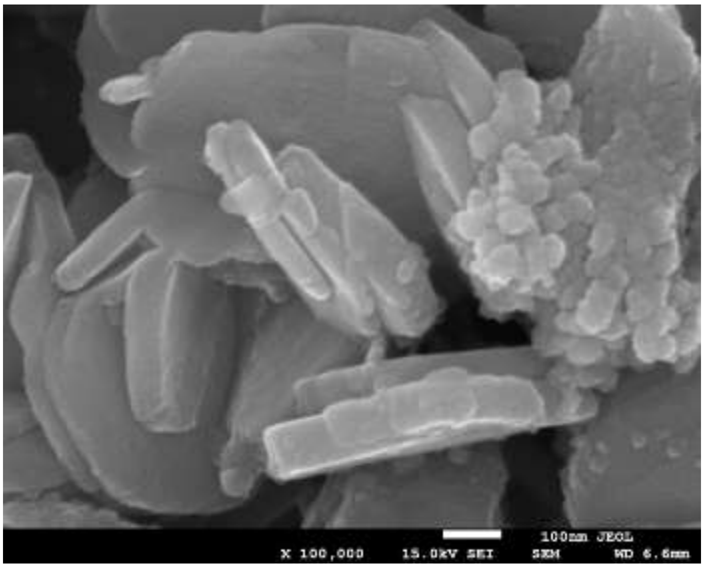


Figure 1. SE image of surface morphology of CuMnAl (1:2:1) sample with well developed hydrotalcite plates and fine grains of rhodochrosite

New Peroxo-compounds of Mo(VI), W(VI) i V(V) – Synthesis, Crystal Structure, and Physico-chemical Investigations.

(Professor Wiesław Łasocha DSc, Dariusz Mucha, PhD, Anna Dobija MSc, Marta Grzesiak MSc)

As a result of research we have carried out recently, we obtained several new peroxy-compounds of molybdenum and tungsten. Very promising (for reasons of efficiency, speed and ease of synthesis) is yellow, tetragonal, peroxomolybdate of nicotinic acid. This compound is obtained by dissolving of $Na_2MoO_4.H_2O$ in hydrogen peroxide, then to the acidified solution nicotinic acid is added.

An additional, important achievement was the refinement, in terms of yield and purity of the compound, of synthesis conditions of diperoxo-molybdates of nicotinic acid N-oxide. This result will allow in the future, conducting a series of studies of physical properties of this compound (XRD vs. temp, catalytic studies, etc.)

In addition to investigations of perokso compounds, we obtained a few new polymolybdates, including γ-octamolybdate of 3.4-dimethylpyridine, and we examined the thermal degradation of selected γ-octamolybdates. We have also obtained a new complex of molybdenum oxide with 1,2-phenylenediamine. A characteristic feature of this compound, is its chain structure, and the connection of each molecule of diamine with the molybdenum atoms by two nitrogen atoms (Fig. 1). This compound is formed as a result of prolonged heating of solutions of molybdic acid with an excess of 1,2-phenylenediamine. This result suggests that in order to obtain the cationic salts, the synthesis should be carried out at low pH. To obtain a gamma octamolybdates (with only two N atom connected with 2 Mo atoms in Mo_8O_{26} moiety), one should avoid excessive use of amine and apply short time of reaction.

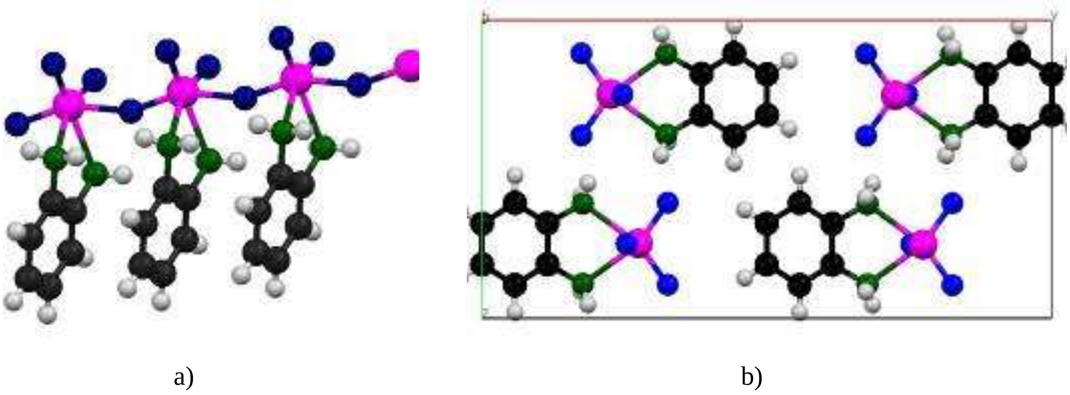

a) b)

Figure 1. Infinite chain of MoO_3 substituted by 1,2-phenylenediamine (**a**), and the projection of the structure along [010] (**b**).

Formula – $C_6H_8MoN_2O_3$**,** FW - 252.0811 g/mol, T - 293(2) K
SG - Pnma, a,b,c [Å] 19.429, 10.109, 3.833, 90.0, 90.0, 90.0, V [$Å^3$] 752.831, Z=4.

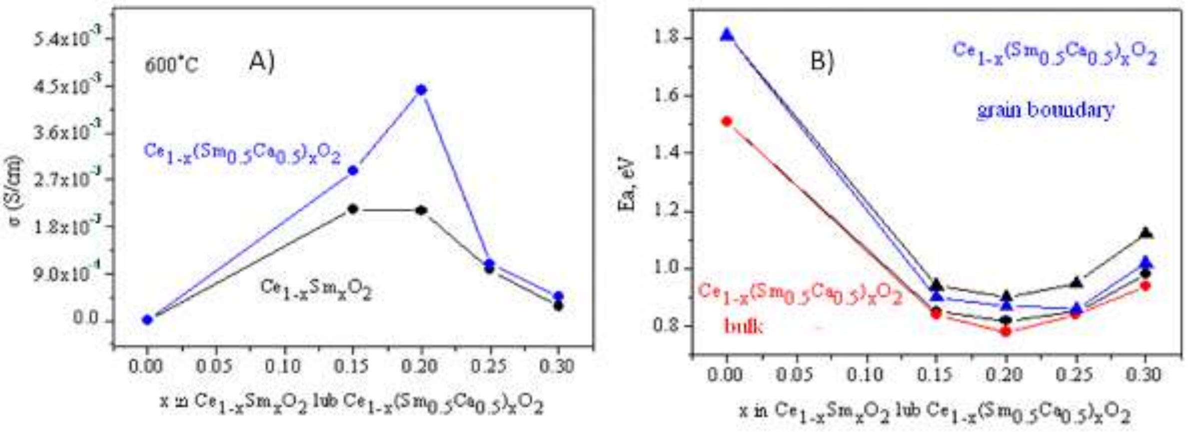
In addition, we conducted researches in the field of crystal engineering, including the synthesis and crystal structure studies, of new coordination polymers and complexes of cadmium halides and aromatic amines.

Determination of Electrical and Electrochemical Characteristics of Solid Solutions in Systems M_2O_3-CaO, and CeO_2-M_2O_3-Nd_2O_3, where M = Sm, Gd, in Terms of their Possible Application in Fuel Cells

(Professor Paweł Nowak DSc, Michał Mosiałek PhD, Grzegorz Mordarski PhDEng, Magdalena Dudek PhD
[AGH University of Science and Technology]

The possibility of improving the ionic conductivity of solid solutions $Ce_{0.8}M_{0.2}O_2$, M = Sm, Gd, through the gradual replacement of Sm^{+3} cation or Gd^{+3} cation by the cation with bigger ionic radius - Nd^{+3}, leading to $Ce_{0.8}M_{0.2-x}Nd_xO_2$ M = Sm, Gd was investigated. Single-phase solid solutions in the form of powders and compsition $Ce_{0.8}M_{0.2-x}Nd_xO_2$, M = Sm, Gd, were obtained by Pechini method. A series of samples was prepared from those powders by firing in the furnace at 1500°C for 2 hours. The ionic conductivities of prepared mixed oxides were measured by the method of electrochemical impedance spectroscopy at temperatures from 200 to 800°C. The results showed that the partial substitution of Sm^{+3} cations by Nd^{+3} cations in solid solution $Ce_{0.8}Sm_{0.2-x}Nd_xO_2$ leads to the increase in ionic conductivity compared to electrolytes $Ce_{0.8}M_{0.2}O_2$, M =Sm or Gd. Thus, $Ce_{0.8}Sm_{0.2-x}Nd_xO_2$ solid solutions could be better electrolytes for intermediate temperature solid oxide fuel cells (IT-SOFC) applications in comparison to $Ce_{0.8}Sm_{0.2}O_2$.

The effect of the introduction of divalent cations Ca^{+2} to the structure of the solid solution $Ce_{1-x}Sm_xO_2$ was also investigated. The single-phase powders $Ce_{1-x}(Sm_{0,5}Ca_{0,5})_xO_2$, x = 0.0, 0.15, 0.20, 0.25, 0.30 were prepared by Pechini method. A series of samples was prepared from those powders by firing in the furnace at 1500°C for 2 hours. The ionic conductivities of the obtained electrolytes were measured by the method of electrochemical impedance spectroscopy at temperatures from 300 to 800°C. Introduction of equal amounts of calcium and samarium cations to the obtained solid solutions leads to a compound of higher ionic conductivity than in the case of the corresponding compound doped with samarium ions only. In figure 1 a-b, the conductivity (calculated as the sum of the conductivity of the bulk and the conductivity of grain boundaries) and the activation energy of ionic conductivity of investigated solid solutions is presented.



Electrocatalytic Properties of Nanostructured Metal Oxides and Metal Oxide/Carbon Composites Prepared with the Use of Hydrotalcite-like Material as a Metal oxide Precursor

(Assoc. Professor Paweł Nowak DSc, Aleksandra Pacuła PhDEng)

The object of the work was the preparation of hybrid materials involving metal oxide/carbon composites and metal oxide composites and characterization of their physicochemical and electrocatalytic properties. At first metal oxide/carbon composites were synthesized by heating hydrotalcite-like material containing Ni, Co and Al (Ni:Co:Al = 1:1:1) at temperatures of 800^oC and 900^oC under the flow of argon saturated with CH_3CN. During synthesis both substrates decomposed leading to metal oxides formation and carbon deposition. Moreover, transition metal oxides (containing Ni and Co) were reduced to metallic species, which acted as catalysts for growing carbon nanostructures. Metal oxide composites were obtained by heating metal oxide/carbon composites at high temperature (800^oC or 900^oC) in air, which resulted in the combustion of carbon component and the conversion of metals (Ni, Co) to oxides. Newly prepared composite materials were characterized by means of X-ray diffraction, thermal analysis, nitrogen sorption, X-ray photoelectron spectroscopy and scanning and transmission electron microscopy. Electrocatalytic properties of the composites in the oxygen reduction reaction were examined by cyclic voltammetry in alkaline medium (0.1 M NaOH). In the electrochemical measurements, a glassy carbon electrode coated with tested composites acted as a working electrode, whereas saturated calomel electrode was used as a reference electrode.

Metal oxide/carbon composites were composed mainly of carbon constituent (70%) including multiwall carbon nanotubes with the average diameter in the range of 20-150 nm. The remaining part of the composites (30%) contained crystalline metal particles (Ni, Co) and amorphous Al_2O_3. Metal oxide/carbon composites were macroporous. Specific surface area of the composites synthesized at temperatures of 800^oC and 900^oC was 90 m^2/g and 44 m^2/g, respectively. Both metal oxide/carbon composites showed similar electrocatalytic performance in the reduction of oxygen to water molecule via transfer of 4 electrons. The oxygen reduction peak in the CV curve recorded for metal oxide/carbon composites prepared at 800^oC and 900^oC was observed at -0.28 V and -0.30 V, respectively. Metal oxide composites were a mixture of crystalline oxide phases such as NiO, Co_3O_4, $NiAl2O_4$, $CoAl_2O_4$ and amorphous Al_2O_3. Metal oxide composites showed lower electrocatalytic activity towards the oxygen reduction reaction than metal oxide/carbon composites. The oxygen reduction peak in the CV curve recorded for metal oxide composites prepared at 800^oC and 900^oC was observed at -0.43 V and -0.46 V, respectively. It seems that lower electrocatalytic activity of metal oxide composites is at least partly connected to its lower conductivity.

Statutory research

Catalytic Processes for Sustainable Development

Reduced Copper and Palladium Salts of Heteropolyacids as Bifunctional Catalysts

(Professor Adam Bielański, Urszula Filek MScEng)

The aim of our investigation in 2010 was to synthesize the copper and palladium salts of Wells-Dawson heteropolyacid $H_6P_2W_{18}O_{62}$ and the measurement of their catalytic properties as bifunctional (acid-base and redox) catalysts.

Copper (II) salt, $Cu_3P_2W_{18}O_{62}$ (CuD), was obtained by the addition of stoichiometric amount of copper (II) acetate to the aqueous solution of heteropolyacid. The pale blue solution was evaporated on water bath and dried at 50 ^oC and subsequently kept over saturated solution of $Mg(NO_3)_2$. Thermal analysis of such sample exhibited 26 mol H_2O per one mole of salt. Palladium salt $Pd_3P_2W_{18}O_{62}$ (PdD) was obtained in a similar way using palladium chloride $PdCl_2$.

The catalytic properties of both heteropolyacid salts were tested using ethanol conversion in gas phase. The reduced catalysts exhibited both acid-base function due to their Brønsted acidy and production of ethylene (C2) as well as diethyl ether (DEE). Redox activity was signalled by the formation of acetaldehyde (AcAl).Each catalytic test comprised two stages:

- stage I - reduction of the catalyst with ethanol at 210-290^{o}C – 150 min.

$$(\text{e.g. } Cu_3P_2W_{18}O_{62} \xrightarrow{\text{reduction}} 3Cu + H_6P_2W_{18}O_{62})$$

- stage II - catalytic reaction in an oxygen free atmosphere (helium gas as the carrier gas) or at the presence of oxygen (air as the carrier gas)

Sample	Reduction temp. [^{o}C]	Conversion of ethanol [%]	Selectivity [%]		
			DEE	C2	AcAl
CuD	210	13,0	48,7	51,3	0
	230	15,9	36,1	62,4	1,5
	250	16,0	20,7	79,3	0
	270	18,3	14,1	85,1	0,8
	290	14,8	9,2	89,6	1,2
PdD	210	42,4	32	67,4	0,6
	230	26,4	28,6	70,7	0,7
	250	49,7	15,9	83,2	0,9
	270	45,5	13,1	85,7	1,1
	290	53,8	6,5	92,4	1,1

Both salts exhibited the highest activity after several minutes of the reducing treatment. In stage I activity gradually decreased and then became constant. The Table shows typical results of reduction for both CuD and PdD. Conversion of ethanol on the palladium salt was 3-4 times larger than that of copper salt tested at the same conditions. The increase of temperature resulted in the increased selectivity to C2 but the decreased one to DEE. At the absence of oxygen selectivity to AcAl never exceeded 1.5%

When air was introduced into the catalytic system in the stage II selectivity to AcAl increased to 76% at 250^{o}C. However, selectivity to C2 decreased. Simultaneously ethanol conversion is increased. In the case of PdD the formation of ethyl acetate both on acidic and redox centres was registered.

Transesterification of Triglycerides with Methanol in the Presence of Zinc-derived Catalysts

(Assoc. Professor Alicja Drelinkiewicz DSc, Adam Zięba MSc PhD student)

Transesterification of triglycerides with methanol to give methyl esters (Bio-esters) was studied in the presence of solid alkaline catalysts, the $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$-based catalysts. The Zn-derived catalysts were selected for the studies taking into account high activity of various Zn-derived catalysts for transesterification of triglycerides. Moreover, a mixed oxide ZnO-Al_2O_3 catalyst is applied in industrial synthesis of bio-esters. The latter catalyst, however, gradually deactivates during the transesterification reaction due to slow dissolution in methanol. Moreover Mg-Al hydrotalcite catalysts exhibit high activity in the transesterification reaction. The structure of $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ salt and that of Mg-Al hydrotalcite both are of similar double layered anionic structures. In the present work physicochemical properties of catalysts were characterized using number of techniques, BET, SEM, FT-IR, XRD. The studies were performed for fresh catalysts and the samples after catalytic test. Transesterification with methanol was studied for two triglycerides, triacetin (short triglyceride molecule) and for vegetable oil, castor oil composed of triglycerides of ricinoleic acid. In the first part of studies, the role of calcination temperature (60-300^{o}C) in activity of Zn-catalysts was evaluated. It was observed that calcination resulted in gradual decomposition of salt accompanied by the formation of various intermediate products (the salts of various contents of NO_3^-, OH^- and H_2O) and ZnO was the final product of decomposition. These structural changes resulted in the decrease of specific surface area, porosity and alkalinity of catalysts with consequent decrease of catalytic activity in the transesterification of both triglycerides triacetin and castor oil. Therefore in systematic studies, the catalysts dried at temperature of 60^{o}C were used. The $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ salt slowly deactivated during methanolysis reaction due to relatively strong adsorption of partial glycerides, di- and mono-acetin. This deactivation was fully reversible. The regeneration of catalyst by washing with THF resulted in complete restoration of catalyst activity and this activity was stable during several catalyst recycling experiments. Methanolysis experiments showed that activity of $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ salt was determined by the methanol/ /triglyceride molar ratio. The procedure of catalyst pretreatment prior to catalytic experiment (contacting with methanol or triglyceride) was found to be crucial for catalyst activity. Moreover, the presence of co-solvents in the reaction mixture exhibited a strong effect on the rate of methanolysis because it affected the course of triactin transformation via consecutive reactions, i.e. the formation of di- and mono-glycerides. Therefore, the role of co-solvent was ascribed to the modification of catalyst adsorption ability towards the individual reagents.

Oxide-Silver Catalyst for Total Oxidation of Organic Compounds

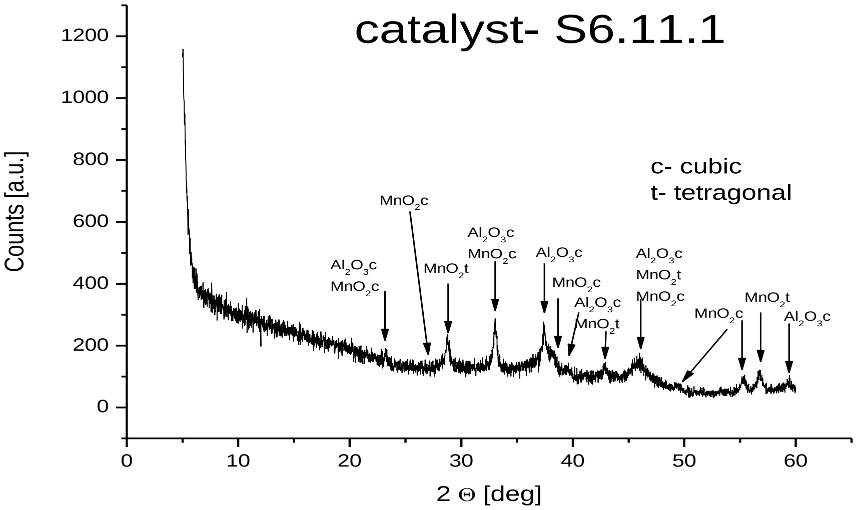
(*Tadeusz Machej PhD, Wojciech Rojek MSc)*

Volatile organic compounds (VOC) can be destroyed by means of thermal or catalytic combustion. These compounds are combusted in air to CO_2 and water when VOCs contain carbon, hydrogen and oxygen. In the best case the heat of reaction sustains the combustion process.

Catalytic combustion takes place at much lower temperatures (200-500°C) than the thermal combustion (750-900°C). So, the catalytic combustion is a self-sustaining process taking place at much lower concentration of VOCs than in the case of thermal combustion. The catalytic combustion is a better economic solution because of low operation costs. The operation costs can be further decreased by using catalysts operating at the temperature range 100-200°C. Standard catalysts can not be used below 200°C because of the adsorption of VOCs and the reaction products.

Aim of the research was a development of the catalyst which would be effective in the VOCs combustion below 200°C, i.e. exhibiting high VOC conversion without adsorption of substrates and products.

The catalyst is composed of Mn_2O_3, MnO_2 and silver ions dispersed on γ-Al_2O_3 (see figure below).



The catalytic activity of the catalyst was checked in the total oxidation of methanol and ethanol.

Total oxidation of methanol and ethanol was carried out in a flow reactor at GHSV=10,000 h^{-1}.The concentration of reagents were 0.2 g/m^3. The conversion of alcohols was monitored by measuring the concentration of CO_2 in outlet of the reactor. It was found that the oxidation of methanol is effective below 200°C. The methanol conversion and selectivity to CO_2 attain 100% at 175°C whereas in the case of ethanol the temperature 200°C is necessary.

The stability of the catalyst activity was checked in long-term experiment. The catalyst was kept at 400°C for 500 hours in air containing the reagents. Then, the catalyst was cooled down to the temperature below 200°C and its activity in oxidation of methanol and ethanol was measured. The conversion of alcohols and selectivity to CO_2 did not change after the long-term experiment.

Transformations of the Monoterpene Hydrocarbons over Micro- and Mesoporous Molecular Sieves

(Professor Bogdan Sulikowski DScEng, Ewa Włoch PhD, Urszula Filek MScEng, Łukasz Mokrzycki PhD)

Terpenes encompass a number of hydrocarbons with various structures. α-Pinene is one of the important monoterpene hydrocarbons used for the synthesis of raw materials as: camphene, limonene and *p*-cymene. Catalytic transformation of α-pinene by, e.g., isomerization route, is nowadays carried out industrially using acidic TiO_2 contacts. The process has, however, some disadvantages, such as the low reaction rate coupled with corrosion of the equipment. We have therefore decided to develop other viable catalysts, exhibiting micro- and mesoporous regular architecture and containing acid centres. Our earlier studies led to the selection of a few zeolites for this purpose. Development of a highly active and selective catalyst is however retarded and requires further rationalization, by understanding on a molecular level the processes taking places whilst a zeolite under question is being modified. In the period reported, our work was concerned with, first of all, on catalytic studies concerning the isomerization and oxidation processes proceeding in the liquid-phase.

Zeolite Y (FAU) is a molecular sieve manufactured on a large industrial scale. It is characterised by the presence of smaller cages and larger supercages. In the supercages of zeolite Y many catalytic processes can proceed readily. First, the parent zeolite should be modified purposedly, by e.g. changing the amount of the cations neutralising the negative charge of an aluminosilicate framework, varying the SiO_2:Al_2O_3 ratio, or forming a secondary mesopores system in the crystals. The last feature leads to better transportation properties of the solid, thus enabling higher diffusion rate of substrates and products within zeolitic crystals.

Commercially available zeolite Y was used as a pristine material. The zeolite was modified using two routes. The first one removes partly silicon atoms in the presence of sodium hydroxide solution of optimized concentration. The samples obtained were characterised by XRD, SEM, and adsorption of nitrogen. Finally, the samples were tested in liquid-phase isomerization of α-pinene.

The second method of modification was carried out by dealumination, a method which removes in part aluminium from the zeolite framework. Dealumination is usually performed by applying the combination of ion exchange, calcination at proper temperature and treating a sample with solutions of mineral or organic acids. We have studied treatment with ethylenediaminetetraacetic acid. Physicochemical properties of the dealuminated samples were carried out, as well as catalytic screening in the isomerization of α-pinene.

Within the frame of co-operation with a Cambridge group (Prof. J. Klinowski) studies of properties of the partly and fully deuterated ammonium perchlorate samples were continued.

Finally, within the frame of co-operation with a Stuttgart group (Prof. M. Hunger) studies of heteropolyacids and their salts were studied using the solid-state NMR. The changes occurring upon heating of the samples were documented. For some chosen samples studies on oxidation of norbornene towards epoxynorbornane were carried out.

Ag-ZnO-(ZrO_2) Systems as the Catalysts for Hydrogenation of CO_2

(Assoc. Professor Ryszard Grabowski DSc, Michał Śliwa MSc, Dariusz Mucha PhD, Robert Socha PhD, Małgorzata Ruggiero-Mikołajczyk PhD, an. Mizera MSc)

Synthesis of methanol from CO_2 has been widely studied during the last years. Processing cheap raw materials such as CO_2 and the need to mitigate the greenhouse effect have been among reasons behind this research. Systems containing copper and ZrO_2, also in combination with other oxides (ZnO, Al_2O_3, Ga_2O_3), are active in the reaction of hydrogenation of CO_2 to methanol. Alternative catalysts, containing silver in the place of copper, are less active in the methanol synthesis and for that reason they have been less investigated. Structure and operational mechanism of the copper catalysts have been extensively studied. A synergy between active metal and ZrO_2 or ZnO was found in these systems and it is believed that the stabilization of Cu^{+1} ions on the surface of the catalyst plays an important role in this phenomenon. The aim of this work was to find out if the synergy effect, analogical to that postulated for the copper catalysts, exists in the Ag/ZrO_2 and Ag/ZrO_2/ZnO systems and to elucidate the mechanism of such synergy. Structural modifications in the Ag/ZrO_2 and Ag/ZrO_2/ZnO systems were introduced by changing the composition and preparation methods and these modifications were correlated with the activity and selectivity of the catalysts in the hydrogenation of CO_2 to methanol.

Ag/ZrO_2 and Ag/ZrO_2/ZnO catalysts obtained by the co-precipitation method were studied in the CO_2 hydrogenation to methanol. The catalyst structure was determined using XRD and TPR. The XPS and Auger spectroscopies were used to determine the silver electronic state. It was found that selection of the appropriate conditions of the catalyst preparation influences silver dispersion degree, its electronic state and contents of the zirconia polymorphic phases (tetragonal and monoclinic). The presence of oxygen vacancies stabilizes both the thermodynamically unstable t-ZrO_2 phase and the Ag^{+1} cations, which are present in the vicinity of oxygen vacancies. The catalytic activity to methanol increases with increasing t-ZrO_2 content but RWGS reaction is accelerated by dispersed metallic silver. The implications of the obtained results for the mechanism of the catalytic hydrogenation of CO_2 are discussed.

Comparison of Catalytic Activity of Salen and Porphyrin Cationic Metallocomplexes in Oxidation of Phenol

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

Chemical, petrochemical and pharmaceutical industry produce large amounts of pollutants and among them phenol and its derivatives are extremely dangerous. They are highly toxic already at relatively low concentrations. Biomimetic oxidation of environmental pollutants using ecological oxidant like H_2O_2 is a useful degradation method for phenol and its derivatives.

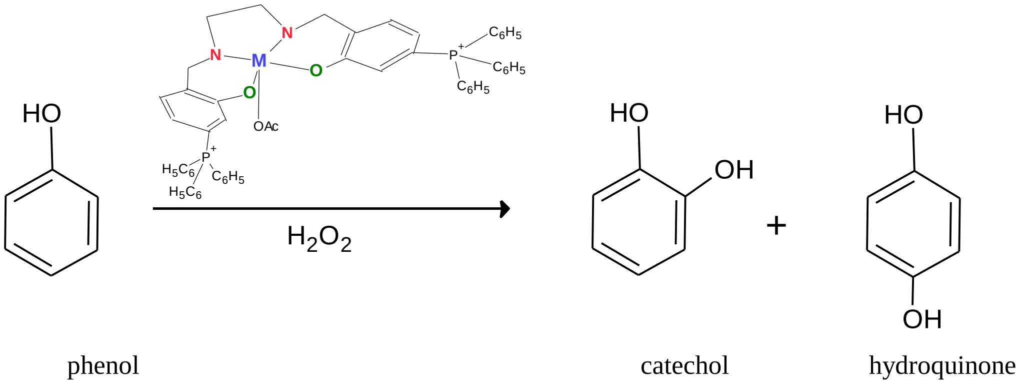


Figure1. Investigated reaction scheme

The main goal of the work was the synthesis of water soluble cationic macrocyclic metallocomplexes and their use as catalysts in oxidation of phenol by hydrogen peroxide. Porphyrin metallocomplexes MnTMPy, FeTMPy, CoTMPy, MnTAP and salen metallocomplexes Mnsalen-$[CH_2\text{-}P\text{-}(C_6H_5)]_2$, Fesalen-$[CH_2\text{-}P\text{-}(C_6H_5)]_2$, Cosalen-$[CH_2\text{-}P\text{-}(C_6H_5)]_2$ were applied as catalysts. The main reaction products are catechol and hydroquinone. All the synthesized metallocomplexes were active in the investigated reaction. The type of metal centre and properties of substituents influence the conversion of substrate and the yield of reaction products. Among metalloporphyrins FeTMPy is the most active and it shows the highest activity among all the tested metallocomplexes. The following order of activity of metalloporphyrins was established:

FeTMPy > MnTAP > MnTMPy > CoTMPy

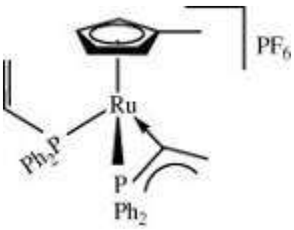
Among salen complexes Fesalen-$[CH_2\text{-}P\text{-}(C_6H_5)]_2$ turned out to be the most active catalyst. For metallosalen complexes the order of activity, quite similar to metalloporphyrins, was observed:

Fesalen-$[CH_2\text{-}P\text{-}(C_6H_5)]_2$ > Mnsalen-$[CH_2\text{-}P\text{-}(C_6H_5)]_2$ > Cosalen-$[CH_2\text{-}P\text{-}(C_6H_5)]_2$

Summarizing, one may state that the structure of ligand influences the catalytic properties of the studied catalysts. Cationic metalloporphyrin complexes with a positive charge on nitrogen atoms are more active than cationic metallosalen complexes with a positive charge on phosphorus atom. All water soluble cationic metalloporphyrin catalysts were more active than metallosalen complexes. The highest selectivity to catechol was observed for MnTMPyP while to hydroquinone CoTMPyp catalyst was the most selective. On the basis of our results and literature reports a mechanism for the oxidation of phenol has been proposed.

Ruthenium Catalysts for Selective Hydrogenation Processes

(Professor Ewa Serwicka-Bahranowska DSc, Dorota Duraczyńska PhD, Assoc. Professor Alicja Drelinkiewicz DSc, Małgorzata Zimowska PhD, Robert Socha PhD)



Cationic ruthenium complex Ru(II) $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\eta^3\text{-PPh}_2\text{CHCH}_2)(\eta^1\text{-PPh}_2\text{CHCH}_2)]^+$, showing catalytic activity in hydrogenation reactions due to the presence of hemilabile phosphine ligand, was deposited on alumianted mesoporous molecular sieves of FSM-16 and SBA-15 types. The characteristic feature of the selected supports is the presence of uniform pores with diameters in the range 2-10 nm. Cation exchange was used as a method of complex anchoring. This method does not require any additional surface and/or ligand modification and allows for immobilization to be carried out at low temperature and neutral pH, which is of importance for the stability of metallorganic species. Synthesized heterogeneous catalysts were characterized with XRD, XPS, UV-Vis, NMR (^{27}Al, ^{29}Si, ^{31}P), FTIR, TG/DTG/DSC and analysis of nitrogen sorption isotherms. On the bases of physico-chemical characterization it has been concluded that in the case of supports prepared by direct alumination, i.e. by addition of Al source to the synthesis gel, the metallorganic cations occupy preferentially the inner space of the channel system, while in the case of post-synthesis aluminated carriers, prepared by impregnation of purely siliceous mesoporous materials with Al compound, a substantial part of Ru complex is localized at the external, morphological surface of the catalyst. This is evidenced, among others, by the results of nitrogen sorption experiments, which show a much larger reduction of pore size and pore volume upon Ru complex deposition on directly aluminated supports. The effect is a consequence of the fact that, as demonstrated by our previous research, distribution of Al sites, whose charge is compensated by the cationiuc Ru complexes, depends on the employed method of alumination.

In the test reaction of phenylacetylene to styrene and ethylbenzene the catalysts prepared with directly aluminated supports show activity distinctly higher than that of catalysts containing similar Ru complex loading on post synthesis aluminated supports (Table). In the latter case, even the use of SBA-15 molecular sieve with large pores facilitating diffusion, does not result in higher catalytic activity. ^{31}P MAS NMR spectra show that in catalysts with low activity, the peak assocaited with hemilabile phospine ligand becomes suppressed, which suggests its involvement in the binding of the complex to the support surface with formation of an adsorbed form incapable of interaction with the reagents. It is argued that the advantageous influence of the complex location within the channel system is due to steric hindrances, which prevent the formation of the inactive structure and impose an alternative mode of complex binding with the pore wall.

Catalyst	Rate of phenylacetylene hydrogenation $[\text{mol}_{\text{Phac}}\times\text{min}^{-1}\times\text{g}_{\text{com}}^{-1}\times10^{-5}]$
5.2 wt%Ru(II)/FSM-16(Si/Al=40)(d)*	15.9
4.6 wt%Ru(II)/FSM-16(Si/Al=40)(p)	4.1
4.6 wt%Ru(II)/FSM-16(Si/Al=20)(d)	20.3
5.6 wt%Ru(II)/FSM-16(Si/Al=20)(p)	7.1
4.1 wt%Ru(II)/SBA-15(Si/Al=10)(d)	4.8

*(d) – direct alumiantion, (p) – post-synthesis alumiantion

Statutory research

Adsorption and Catalytic Processes Modeling

Structural and Electronic Factors in Catalytic Activi
Enzymes and Nanoporous Materials: Quantum Chen

(Professor Ewa Brocławik DSc, Paweł Rejmak PhD)

Molecular modeling for ethane and ethyne interacting with Cu(I) or Ag(I) sites in MFI zeolite was performed by means of combined QMPot method. Electronic structure was calculated by DFT with B3LYP and PBE exchange-correlation potential and TZVP basis set. ETS-NOCV analysis, providing the direction and symmetry of independent electron flow channels, was done by using recent implementation in ADF software. QM models were based on the cluster cut-off the wall on main channel in ZSM-5.

ETS-NOCV analysis allowed unequivocal separation of charge redistribution accompanying molecule adsorption into donation and backdonation processes. The example of two important electron density flow channels for ethene interacting with Cu(I)-ZSM-5 are shown in Fig. 1.

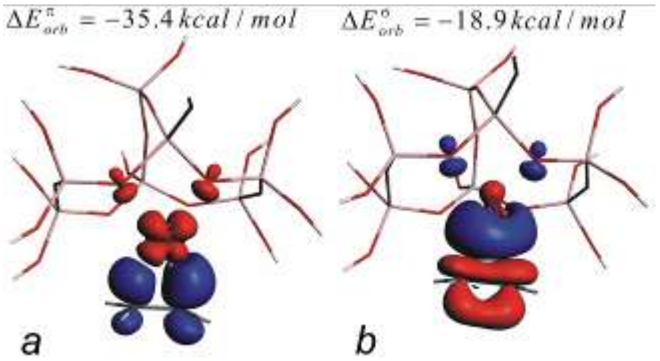


Figure 1. Contours for most important electron flows for ethene on Cu(I)ZSM-5: backdonation (a) and donation (b). Blue - gain of electron density, red - loss of electron density.

Energetic measures for electron flow channels (ΔE^{i}_{orb}) give quantitative estimate of the efficiency of the cation-to-molecule π^*-backdonation and σ donation in the activation of the molecule on cationic site. Measured IR C=C frequency shifts after adsorption of ethene on Cu(I) and Ag(I) with the calculated elongation of C=C bond, increase of bond orders and contributions to electronic orbital interaction energy for the channel corresponding to π^*-backdonation are given in Table 1. The analysis of these data together with the results obtained for ethyne shows that it is the π^*-backdonation process that discriminates the two cationic sites.

Table 1. IR frequency shifts for ethene adsorbed on Cu(I) and Ag(I) sites, change in C=C bond lengths and bond orders, orbital energy interaction component for π^*-backdonation .

	$\Delta\nu_{exp}{}^{*}$ [cm^{-1}]	ΔR_{CC} [Å]	Δb.o.	ΔE_{orb} [kcal·mol^{-1}] for σ donation	ΔE_{orb} [kcal·mol^{-1}] for π^* backdonation
Cu	-85	0.048	–0.43	-18.9	-35.4
Ag	-41	0.037	–0.30	-15.5	-18.7

[*] *frequency shifts are related to absolute value in gas phase - 1623 (exp)*

Additional analysis of electron density flow channels between the framework and the cation shows that the framework more efficiently supports the backdonation process in the case of copper than silver site. This clearly indicates that the activation ability of the catalytic site is determined not only by intrinsic donor properties of transition metal cation but also depends to large extent on its electronic interaction with framework oxygens.

Molecular modeling of enzymatic reaction mechanisms

(Assoc. Professor Tomasz Borowski DSc)

One of the research problems concerned the chemical identity of a catalytic cycle intermediate observed by Lipscomb and co-workers for a representative extradiol dioxygenase. Using less reactive substrates and X-ray crystallography these authors were able to trap a gem-diol intermediate, which according to our prior works, is a metastable O-O cleavage product. From the fact that it could be trapped, it follows that the observed species is considerably stable, which is at odds with the computational results obtained for the radical gem-diol suggesting that it is very reactive. This apparent discrepancy was the motivation for additional computational study. Several redox forms of the gem-diol species were considered, and it was found that the reduced species (obtained by $H^{\bullet}$ uptake) is the best candidate for the observed intermediate, as it is a stable form with substantial barrier for transformation into an epoxide. Thus, the discrepancy between experimental and computational studies has been resolved.

Another research project concerned the mechanism of a catalytic reaction between dioxygen and a biomimetic complex for intradiol dioxygenases. Results of quantum-chemical calculations suggest that the reaction takes place on sextet and quartet potential energy surfaces, yet, the critical steps, involving O-O bond cleavage and insertion of an oxygen atom into the ring, occur in the quartet spin state. In addition, the computations reproduced the observed product specificity (intradiol cleavage) and revealed the factors controlling it.

The final research problem tackled in 2010 in our group concerned the mechanism of selective chlorination of threonine side chain, which is a reaction catalyzed by SyrB2 – an Fe(II) and 2-oxoglutarate dependent halogenase. The conducted theoretical studies, involving molecular docking of the organic substrate, DFT and CASPT2 calculations on the electronic structure of the reactive oxoferryl species, and DFT computations of Mossbauer spectra parameters and reaction mechanism allowed us to propose the structure for two experimentally observed forms of the key oxoferryl intermediate and put forth a coherent mechanistic hypothesis explaining selective chlorination of threonine.

Properties of Active Centres in Model Heteropolyacids - Cluster and Periodic DFT Investigations

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

Investigations of the properties of active centres in heteropolyacids were carried out within the DFT approach with cluster (Turbomole code) and periodic (VASP code) models. Calculations were performed for two groups of compounds: (i) modified anions of molybdenum and tungsten heteropolyacids (HPMo and HPW) and (ii) hydrated salts of HPW.

Simulations of modified anions of HPMo and HPW focused on the influence of the central cation on the properties of active centres. The compounds investigated were $XMo_{12}O_{40}^{3-}$ and $XW_{12}O_{40}^{3-}$, where X = P, Si, Fe. Calculated density of states spectra show that in all cases the valence band close to the Fermi level is dominated by orbitals of the oxygen centres (Ob, Oc) which are bridging the addenda atoms. Middle part of the valence band originates from the singly coordinated oxygen centres (Od) while the conduction band comes mainly from the addenda metal cations. Central cation influences the positions of frontier orbitals and the size of the band gap (ca. 2 eV for P and Si; ca. 0.5 eV for Fe). Table 1 shows changes in the atomic charges for different molybdenum heteropolyacids. Change of the central cation does not influence significantly the properties of bridging (Ob, Oc) and the terminal oxygen centres (Od). Largest charge changes are observed for oxygen centres that are directly connected to the central cation. In IR spectra of different systems shifts of main peaks are observed.

Table 1. Atomic charges of the active centres in $XMo_{12}O_{40}^{3-}$

	$PMo_{12}O_{40}^{3-}$	**$SiMo_{12}O_{40}^{3-}$**	**$FeMo_{12}O_{40}^{3-}$**
Mo	1,06	1,05	0,97
P/Si/Fe	0,88	1,18	1,37
Oa	-0,59	-0,72	-0,75
Ob	-0,44	-0,43	-0,44
Oc	-0,37	-0,38	-0,41
Od	-0,37	-0,40	-0,49

Periodic calculations for HPW salts were performed for a series of compounds in which the structural water molecules were gradually exchanged with caesium atoms: $(H_5O_3)_3PW_{12}O_{40}$, $Cs(H_5O_3)_2PW_{12}O_{40}$, $Cs_2(H_5O_3)PW_{12}O_{40}$, $Cs_{2.5}(H_5O_3)_{0.5}PW_{12}O_{40}$, $Cs_3PW_{12}O_{40}$. Obtained optimal geometries are rather similar, while the size of the band gap shows a moderate dependence on the amount of caesium introduced (Fig. 1). Results for the $Cs_{2.5}(H_5O_3)_{0.5}PW_{12}O_{40}$ salt do not offer a satisfactory explanation of unique catalytic properties of this compound observed experimentally (they most probably stem from the macroscopic structure of the salt crystallites covered with a layer of pure heteropolyacid). Comparison of salts of different alkali metals $X_3PW_{12}O_{40}$, where X = Na, Rb, Cs, show that with decreasing atomic radius of the alkali cation the size of the band gap increases (Fig. 1).

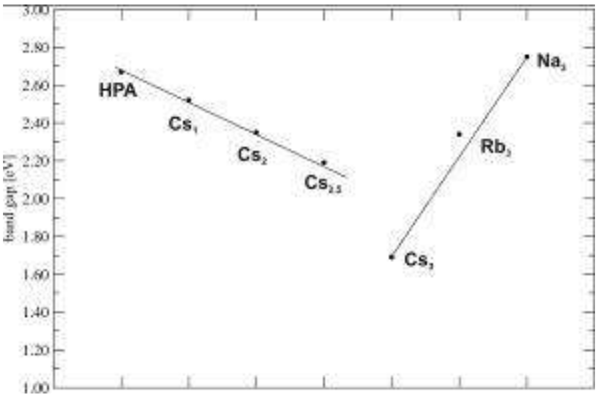


Figure.1 Band gaps of selected HPW salts

Modeling the Influence of Surface Heterogeneity and Electrostatic Interactions on the Adsorption Kinetics and Equilibrium of Metal Ions and Protons

(Professor Władysław Rudziński DSc, Wojciech Płaziński PhD)

Adsorption of ions at a solid/solution interface is one of the most common physical process occurring in nature and (in the case of heavy metal ions) applied in the purification of waste waters. Understanding mechanisms of both kinetics and equilibria of this process is crucial for designing adsorption processes effectively.

The influence of non-controlled pH conditions on the kinetics of metal ions adsorption at solid/solution interfaces was studied by applying the SRT (statistical rate theory) approach. The quasi-equilibrium assumption inherent in SRT imposes the identical mathematical form of expressions for both the competitive adsorption and ion exchange models. These two mechanisms can be differentiated on the basis of the time-dependent profile of pH in the bulk solution. The developed model accounts for both multidentate binding mode and different proton/metal exchange ratios. The results provide a relatively simple way to simultaneous description of the kinetics of metal ion adsorption and time-dependent pH changes and explains the impossibility of finding the constant (time-independent) ratio of metal-proton exchange observed in experimental systems. The proposed model can be treated as a starting point for building more complex descriptions of the phenomenon including e.g. ionic strength effects or surface heterogeneity.

The applicability of certain family of the models (corresponding to the Langmuir model in which the maximum uptake value is pH-dependent) was studied; these models are used for description of the pH-dependent equilibria of metal ion adsorption. It was shown that these models are approximations for more general approach in which both the metal ion speciation in the bulk solution and the formation of multidentate surface complexes are important.

Furthermore, the preliminary study focused on the interactions of glucuronate chains and the calcium ions was performed. This included the parameterization of the GROMOS96 force field with respect to interactions between negatively charged uronate residues and calcium ions.

Studies of the Influence of the Translational and Rotational Energies and the Energy Dissipation Mechanism on the Initial Sticking Probability of Water on Platinum Surface Using Molecular Dynamics Simulations

(Assoc. Professor Tomasz Pańczyk DSc)

Water adsorption on metal surfaces can be regarded as a prototype of a system where the hydrogen bonds play dominant role. Supersonic molecular beam measurements of the initial sticking probability of water on Pt{110}-(1x2) led to the results which need closer theoretical analysis. The striking observation is a strong increase of the initial sticking probability with the increasing translational energy of water molecules though there are no premises concerning the existence of the activation barriers for adsorption. Another interesting feature is very complex influence of the rotational energy of water molecules on the shape of the initial sticking probability profile.

Studies, carried out using molecular dynamics simulations, revealed the dominating role of the energy dissipation mechanism during collision with the surface. We found that this mechanism is mainly controlled by the electron-hole pair creation and, when accounted for in the model, the results of simulations compare well to the experimental data of the initial sticking probability as the function of the water molecule translational energy.

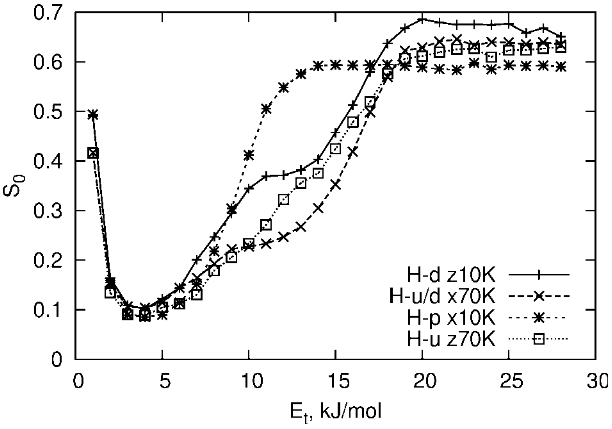


Figure 1. Initial sticking probability calculated for various orientations of the water molecule and various rotational energies.

Extension of the studies aimed at understanding the effects related to the rotational excitation of the water molecule, led to the conclusion that the simulation model is too simplified and cannot give satisfactory description of the influence of the rotation energy on the initial sticking probability. Therefore, in the next step the simulation model has been subjected to numerous modifications in order to properly account for the effects of the incidence angle of the water molecule in the probability of the kinetic energy dissipation. Finally we got a good correlation between theoretical and experimental results in the range of kinetic energies greater than 10 kJ/mol. (Fig. 1) Therefore, we concluded that the probability of the kinetic energy dissipation depend also on the angular coordinates of the water molecule. In the range of kinetic energies less than 10 kJ/mol we had to assume that another factor comes to play a significant role. It is the dispersion of the kinetic energy in the molecular beam – a common experimental factor - which had not been accounted for so far. Final results involving also that dispersion effects allowed us to explain some discrepancy between the theoretical and experimental results also in the range of that low incident energies.

Studies on the Relationship Between Molecular Structure and Chemical Activity of Reagents

(Professor Małgorzata Witko DSc, Maciej Szaleniec PhD, Dorota Rutkowska-Żbik PhD)

The aim of the research was the elucidation of relationship between molecular structure of reagents and their chemical reactivity. The research programme covered the influence of structural modifications in aromatic systems and their alkyl substituents on selected reaction rates in two groups of compounds: alkyl aromatic and alkyl heterocyclic hydrocarbons in bio-catalytic oxidation of alkyl substituents by ethyl benzene dehydrogenase (EBDH) and chlorophyll derivatives in metalation reactions.

The studies were performed by experimental (kinetic measurements, spectroscopy, chiral chromatography LC-MS) and theoretical techniques (quantum-chemical calculations within density functional theory (DFT) – B3LYP, BP).

In order to obtain the relationship between molecular structure of alkyl aromatic and alkyl heterocyclic hydrocarbons and reaction rates a set of activity data in reaction with EBDH for 46 compounds was prepared. Their structures were additionally investigated by DFT method. Various types of descriptors were calculated such as the typical quantum chemical (such as partial charges, orbital energies, dipole moments, H and C NMR shifts etc.), the thermodynamic parameters (ΔG of C-H bond activation reaction to radical and carbocation) and electrostatic potential in nuclei (as an alternative for experimental Hammet constant). These parameters were then selected by an algorithm of automatic net architecture algorithm implemented in Statistica code (IPS), and the neural model was constructed which defined the relationship between experimental activity and theoretical descriptors of the selected molecules. The best performance in prediction was observed for MLP 12-7-1 model ($R^2 = 0.929$).

The influence of molecular modifications on stereoselectivity was studied for a series of chromatography analyses of EBDH reaction mixtures with a set of compounds with varying para substituents with respect to ethyl group. 100% S-selectivity was observed for p-H, p-CH_3, p-C_2H_5, p-F, p-OCH_3, substituents, 80% and 55% S-selectivity for p-OH, p-NH_2, respectively, and only ca. 5% for p-Ph. The performed analysis showed high correlation ($R^2=0.87$) between stabilization of radical intermediate state ($\Delta\Delta G^{radical}$) by a given substituent and the amount of R-isomer formed. Similarly, the relationship between HOMO-LUMO gap and the stereoselectivity exhibited linear character for 4-Ph, 4-NH_2, 4-OH, 4-OCH_3 ($R^2=0.98$),

The second focus was the metalation of eight chlorophyll derivatives, in which both macrocycle and substituents were varied, by Zn and Pt. It is concluded that the reaction rate depended on the size of π–electron system, ring rigidity and the presence of macrocycle substituents. It seems that the latter drastically reduced macrocycle affinity towards metal ions, what may be explained by lowering of electron density on pyrrolenine nitrogen atoms and by imposing greater ring rigidity through steric interactions. Kinetic data suggest also that the solvent had an important role by complexating incoming ions and facilitating their insertion into the macrocycle.

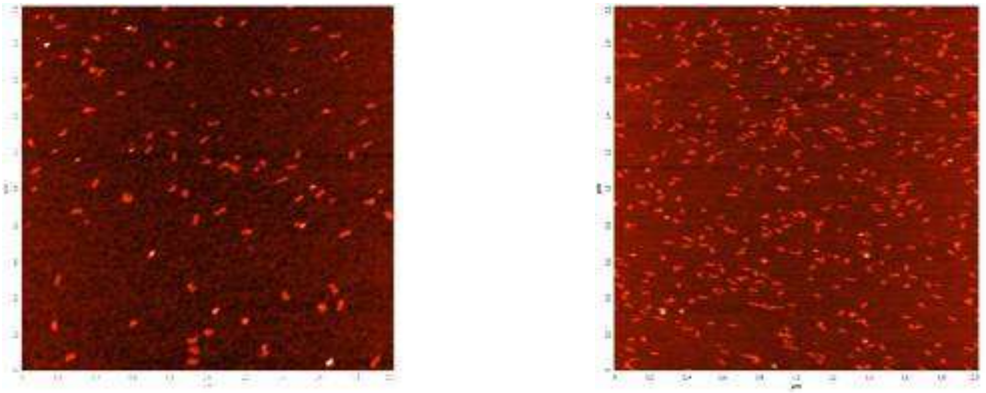
Statutory research

Dynamics of Nanoparticle and Colloid Systems

Determination of the Topology of Globular Proteins on Heterogeneous Interfaces Using the Streaming Potential, Colloid Deposition and AFM Methods

(Profesor Zbigniew Adamczyk DScEng, Monika Wasilewska MSc, Małgorzata Nattich PhD, Barbara Jachimska PhD, Jakub Babrasz PhD)

Extensive measurements of the kinetic of adsorption and conformations of fibrinogen (Fb) on mica surface have been performed. This protein, one of the most important in serum, plays an essential role in blood clotting. In order to select the optimum parameters for adsorption kinetic measurements, bulk characteristics of Fb suspensions were carried out including the diffusion coefficient and the electrophoretic mobility for various ionic strength and pH. In this way the number of uncompensated (electrokinetic) charges on protein surfaces was determined. The electrophoretic mobility data were also converted to the zeta potential values, which allowed one to determine the isoelectric point (i.e.p.) of Fb , which was found to be at $pH = 5.8$. Hence, for $pH < 5.8$ the Fb acquired a positive charge reaching the maximum value of 34 elementary charges for $pH = 3.5$. This important finding suggested that a significant adsorption in the side-on orientation of the molecule can take place on negatively charged substrate surfaces, e.g., mica, whose electrokinetic properties also were determined using the streaming potential method. Afterwards, extensive kinetic measurements of Fb on mica were performed for $pH = 3.5$ under diffusion-controlled transport using the direct AFM method working in the semi-contact mode. Typical fibrinogen monolayers on mica acquired by AFM for different surface concentration of $N = 20$ and 125 [μm^{-2}], are shown in Fig. 1. By determining the dependence of the surface concentration of Fb on the adsorption time, one can evaluate in a quantitative and direct way the kinetics of adsorption of this protein. This enables one in turn to determine, using the square root of time formula pertinent to the diffusion transport, the bulk concentration of the protein below 1 ppm, which is not possible by commonly used chemical methods.



$N = 20\ \mu m^{-2}$ $N = 125\ \mu m^{-2}$

Figure 1. Monolayers of fibrinogen on mica surface for differnet surface concentration N formed under diffusion-controlled transport ($pH = 3.5$ and $I = 10^{-2}$ NaCl). The mocrographs were taken using AFM (semi-contact mode).

It should be also mentioned that the AFM measurements enabled one to determine not only the surface concentration of adsorbed molecules but also their conformations and dimensions of molecules (length and diameter). It was found in this way that fibrinogen molecules retain a strongly anisotropic shape upon adsorption on mica surface, characterized by the dimensions of 47 x 6 x 6 nm.

Influence of pH and Ionic Strength on Profiles of the Bubble Local Velocity in Solutions of Anionic Surfactants

(Professor Kazimierz Małysa DSc, Marcel Krzan PhD, Jan Zawała PhD,
Anna Niecikowska MScEng, Agnieszka Olszewska MSc, Dominik Kosior MScEng)

The studies aimed at determination of influence of anionic surfactants concentration and variations of the solution pH and ionic strength on motion parameters of the rising bubbles. As a result of viscous drag exerted by fluid on interface of the rising bubble an uneven distribution of surfactant molecules over the bubble surface is induced. This Dynamic Adsorption Layer (DAL) is established over the bubble interface under steady-state conditions, that is, when the bubble starts to rise with a constant velocity (terminal velocity of the bubble). Establishment of the DAL architecture means that the adsorption coverage is at minimum on the bubble top pole, while on the bottom the coverage is higher than the equilibrium one. These differences in adsorption coverage mean that the surface tension gradient is induced over interface of the rising bubble, which retards mobility of the bubble interface. As a result of the bubble interface immobilization the hydrodynamic drag for the bubble motion is increased and the bubble rising velocity is significantly reduced.

Influence of the dynamic adsorption layer (DAL) formation on local velocities and shape deformations of the rising bubbles was studied. Profiles of the bubble local velocity, that is, variations of the bubble local velocity with the distance from the point of the bubble formation (capillary), were determined in solutions of sodium n-alkilsulfates and sodium n-alkanoates (C8,C10,C12). It was found that the bubble velocity profiles are strongly dependent on concentration of anionic surfactants studied, especially within their lowest concentration range. In clean water and at high concentrations of anionic surfactant solutions the local velocities were increasing steadily till reaching a value of their terminal velocity. The bubbles terminal velocity was 34.8±0.3 cm/s in distilled water and decreased to a value ca. 15 cm/s in concentrated solutions of the surfactants studied. In the case of low solution concentrations the detached bubbles attained, after initial acceleration period, a maximum velocity value and then the bubble decelerated prior a plateau value of the terminal velocity was attained. Height, width and position of the maximum were diminishing with increasing solution concentration. Presence of the electrolyte and/or the pH variation affected significantly the bubble velocity profiles in solutions of the anionic surfactants studied. Addition of 0.05M of the electrolyte (NaCl/KCl/NaOH/KOH/HCl) and/or the pH variation (pH 2-11) caused drastic changes in the bubble velocity profiles in solutions of sodium n-alkilosulfates: maxima on the velocity profiles were disappearing and the terminal velocity stage was achieved immediately after the acceleration period. The effect of the electrolyte presence and/or pH changes on the velocity profiles is related to variations in degree of adsorption coverage at the bubble surface. Numerical calculations of degrees of the adsorption coverage showed that for example in the case of non-ionic form of the n-octanoic acid the initial adsorption coverage of ca. 2% was sufficient for full immobilization of the bubble interface. The dissociation of the surfactants shifted the value of the minimum adsorption coverage needed for the bubble interface immobilization up to ca. 10% in the case of full dissociation (pH 10). It shows that the effect observed is related to variations of the degree of adsorption coverage and surfactant adsorption kinetics.

Statutory research

Self-Organized Structures and Nanoparticles Monolayers

Thin Polymeric Films Containing Nanoparticles and Proteins

(Professor Piotr Warszyński DScEng, Marta Kolasińska-Sojka PhD,
Magdalena Elżbieciak-Wodka MSc)

The objective of our research activities in 2010 was the determination of optimal conditions for formation of polyelectrolyte films considering the effect various types of polyanion/polycation pairs, ionic strength and pH of their solution on films' thickness and internal structure for their application for embedding ionoselective fluorescent markers, quantum dots, electroactive nanoparticles or proteins.

For the multilayer films formation either synthetic, biocompatible polyelectrolytes like poly-L-lysine (PLL), polyglutamic acid (PGA) or natural polyelectrolytes–polyanions: alginate, carageenean and polycations: chitosan or poly-L-arginate. Combinations of natural polyelectrolytes with synthetic ones were also considered. Multilayer films were formed by the sequential adsorption from polyelectrolyte films with concentration 100 ppm in various ionic strength and pH conditions. Effect of branched polycation (PEI-polyethylenoimine) on thickness and permeability of films was also investigated.

Similarly as in the case of model, synthetic polyelectrolytes, thickness of the multilayer films formed with natural polyelectrolytes increases with the ionic strength of the solutions the films are formed from. Since majority of natural polyelectrolytes are the weak ones, pH of their solutions determines the thickness of the multilayer films formed. As the example, shown in Fig 1, in the case of PLL/PGA pair the largest film thickness is observed at pH 4, when the degree of ionization of PGA is low and the lowest for pH 7.4 when both polyelectrolytes are strongly charged. For the chitosan/alginate pair the optimal conditions for films formation are in the pH range 4-7 and at the ionic strength 0.15 M NaCl.

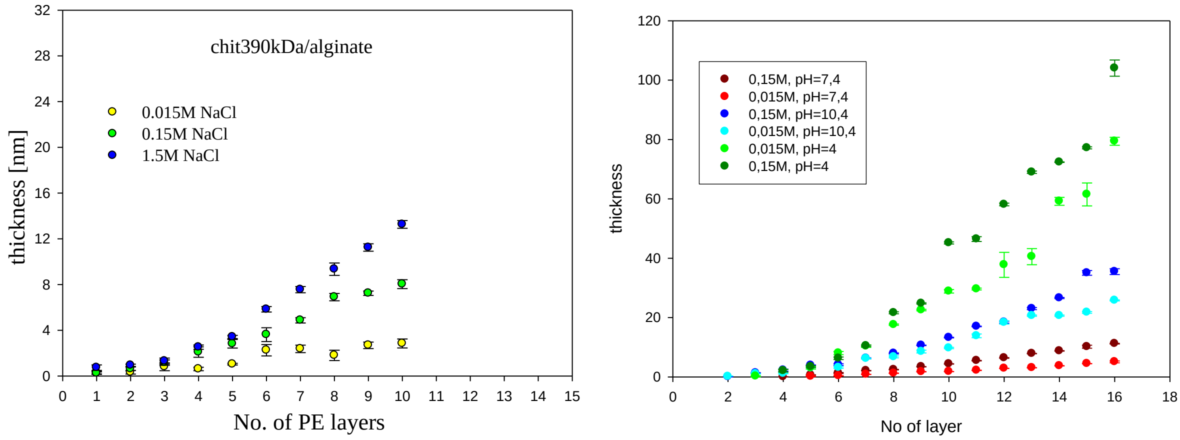


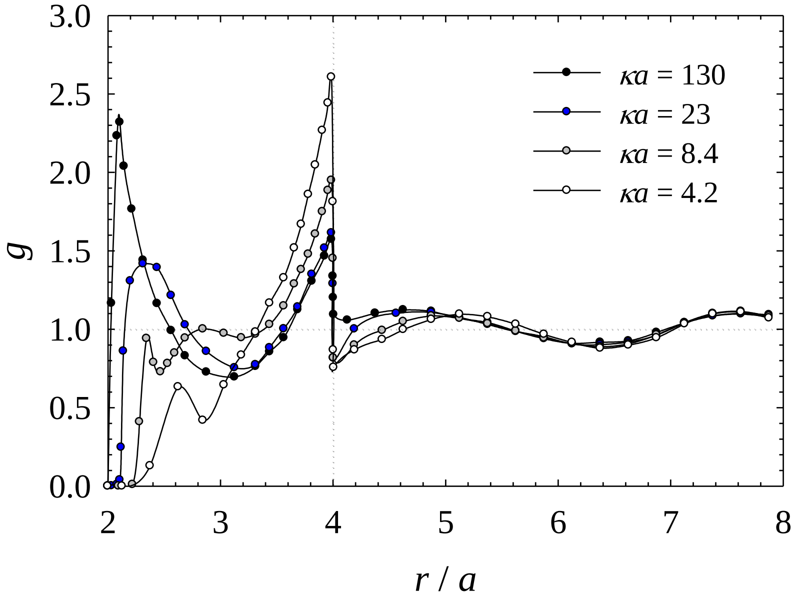
Figure 1. The dependence of ellipsometric thickness of multilayer films chitosan/alginate (left) and PLL/PGA (right) on the number of deposited layers in various ionic strength and pH conditions.

Permeability of polyelectrolyte films were determined by cyclic voltamperometry using electroactive particles with various sizes. We also determined properties of films containing Prussian blue nanoparticles with chitosan.

Modeling of Nanoparticle Adsorption – Theoretical Description of Curvilinear Trajectory Random Sequential Adsorption of Spherical Brownian Particle

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

The earlier developed theoretical model of multilayer adsorption of soft (electrostatically interacting) colloidal particles CT-RSA were used for simulation of layer by layer adsorption of colloidal particles. As a result of simulations we obtained multilayer structures of spherical colloidal particles of the size of the order of micron. We conducted the simulations for several surface concentrations of first layer particle and for several values of the solution ionic strength. We described quantitatively the structures using the two- and three-dimensional correlation functions, as well as the function of multilayer density distribution. The obtained results suggest that the porosity of multilayer formed in a lower ionic strength solution is higher. Multilayer structure analysis also suggests that with the increase of surface concentration of first layer particle the semi-spherical clusters of particles decline and the multilayer structure geometry becomes planar. We conducted a detailed analysis of calculated correlation functions and we identified the characteristic distances between adsorbed particles, corresponding to minima and maxima of density of particle adsorption probability. We also identified the most and the least probable particle configurations corresponding to extrema of correlation functions. In the Figure below we present a comparison of three-dimensional correlation functions obtained for multilayers formed in solutions with various ionic strength, represented by the parameter κa.



Statutory research

Physical Chemistry in the Protection of Cultural Heritage

Monitoring of Preservation State of Surfaces of Historic Objects Using Optical Methods

*(Professor Roman Kozłowski DSc, Łukasz Bratasz PhD, Leszek Krzemień PhD,
Michał Łukomski PhD, Łukasz Lasyk MSc)*

The statutory task of 2009 was continued in 2010. It consisted in the development of optical methods for monitoring and tracing damage development on decorated surfaces of historic objects. The development of non-invasive, non-contact techniques is a very important task for conservation science, as works of art are usually both fragile and extremely valuable.

Further works on the development of interferometric methods for analysis of the surface preservation state were carried out in the reporting period. The results of the local strain field measurements for the wooden supports subjected to an external load or relative humidity changes were particularly important in the context of a further development of the optical methods. The measurements performed using the Digital Image Correlation method showed that the micro-cracks pattern of the design layer is strongly correlated with the distribution of the annual growth rings in wood, which is a substrate of a panel painting. To trace precisely this correlation, it was decided to expand the interferometer (and the software analysing the interferometric images) so that it became possible to perform measurements of surface deformations in the direction perpendicular to the axis of the optical system. Preliminary results of the measurements obtained using the in-plane interferometer showed that the minimum and maximum local deformations of lime wood are the same irrespectively if they are caused by an external load or a relative humidity change. The result demonstrates that the mechanical simulation of the fatigue processes resulting from recurrent changes of relative humidity in the vicinity of the object is a correct procedure reflecting a real behaviour of the panel paintings.

Further calibration and measurements on specimens of different wood species are necessary to obtain a more detailed specification of the critical climatic fluctuations leading to damage of polychrome wood.

Research projects
of the Ministry of Science and Higher Education

Mechanism of Catalytic Activity of "Nano-Au/Oxide" in Oxidation of CO

Research Project N204 089 32/2633 [2007-2010]
(project leader: Professor Józef Korecki DSc)

Nano-Au/oxide support catalysts have been widely studied in the last decade, following the discovery of Haruta of high activity of such systems in CO oxidation at low temperatures, even below room temperature. Iron oxides were frequently used as the support, however there is a strong indication that the surface stoichiometry of the support is Fe_3O_4. This motivated us to study nano-Au/ Fe_3O_4 systems, both as model and real catalysts.

Cluster - support interaction in a model Au-Fe_3O_4(001) system was studied using scanning tunneling microscopy, X-ray photoemission spectroscopy and Mössbauer spectroscopy, in situ, under ultra high vacuum conditions. Gold deposition on epitaxially grown octahedral Fe_3O_4(001)/MgO(001) surface resulted in formation of two- and three-dimensional Au clusters. A positive shift of the electron binding energy was observed in the Au 4f core excitations for the smallest clusters. The source of this relatively low (0.4 eV) BE shift can be assigned to three overlapping effects: the positive cluster charging due to both (1) the photo-ionization process (final state effect) and (2) the particle-support interaction, and (3) the surface effect resulting in a negative shift. This implies modification of the electronic structure, which is crucial for the catalytic properties. Based on the analysis of the Mössbauer spectra we showed that for the Au-Fe_3O_4(001) system this modification lies in the charge transfer between the cluster and the support resulting in the valence shift of surface Fe atoms toward a lower oxidation state. It is remarkable that for the conducting Fe_3O_4(001) surface the charge flow spreads over a surface area considerably exceeding the area occupied by the gold clusters. On the other hand, locally, at the cluster-support interface, the iron ions gain a metallic character by proximity of gold atoms. By simple arguments, such effects make the gold clusters positively charged, because electrons must be transferred from the clusters to the support. The electron transfer from Au to the support is limited by the ability of an iron ion to accept electrons and by the number of iron ions involved in this process, which must be neighbors to a gold cluster. With increasing cluster size, this number certainly grows more slowly than the number of the gold atoms per cluster. Hence, while the total positive charge of the clusters increases with increasing size, the charge per single gold atom decreases. This explains why only the smallest clusters become catalytically active.

Real catalysts were obtained by deposition-precipitation of gold at room temperature and pH = 9.5-10, with the aqueous solution of $AuCl_3$ (5.0 wt % Au), and ammonia as a precipitating agent. To obtain different state of reduction of the support the precursors were calcined in the air atmosphere (oxidizing) and in Ar at 350^oC and 400^oC. The catalysts were tested in CO oxidation and characterized by XRD, Mössbauer and XPS spectroscopies and electron microscopy (TEM). To follow the changes of the catalysts in the reaction medium, the reaction of the catalysts was examined in a reactor equipped with mass spectrometric analysis, attached to an XPS spectrometer. The samples after the treatment in different atmospheres and temperatures in the reactor were transferred directly to a XPS UHV set-up without contacting air atmosphere. The properties of Au/FeO_x catalysts prepared at different calcination temperatures (350 and 400^oC) and in different calcination atmosphere (Ar, or air) were different in respect to the support properties (phase composition) but not with respect to the gold particle size. Catalytic activity of Au/FeO_x catalysts in CO oxidation was higher for catalysts prepared in air and it was higher for all the catalysts after treatment in hydrogen. Moreover, the reaction mixture ($CO+O_2$) induces considerable changes in the Au/FeO_x catalyst structure and properties.

Employment of Macrocyclic Metallocomplexes of Transition Metal Ions in Self-Assembling Systems for Catalytic Oxidation of Hydrocarbons

Research project N204 122 32/3142 [2007-2010]
(project leader: Assoc. Professor Ryszard Grabowski DSc)

The studies carried out within the framework of the accomplished research project consisted of two stages. In the first stage, 30 macrocyclic complexes i.e. porphyrins, phthalocyanines, salenes and their metallocomplexes as well as inorganic metallocomplexes, heteropoly compounds were synthesized. Metallocomplexes were heterogenized using chitosan, alginine and liposome as polyelectrolyte carriers. The catalysts were characterized by different techniques such as UV-Vis, FT-IR spectroscopy, DSC calorimetry, measurements of the hydrodynamic radius of the vesicles by DLS method and zeta potential measurements. These studies confirm the correctness of the synthesis methods of ligands and metallocomplexes.

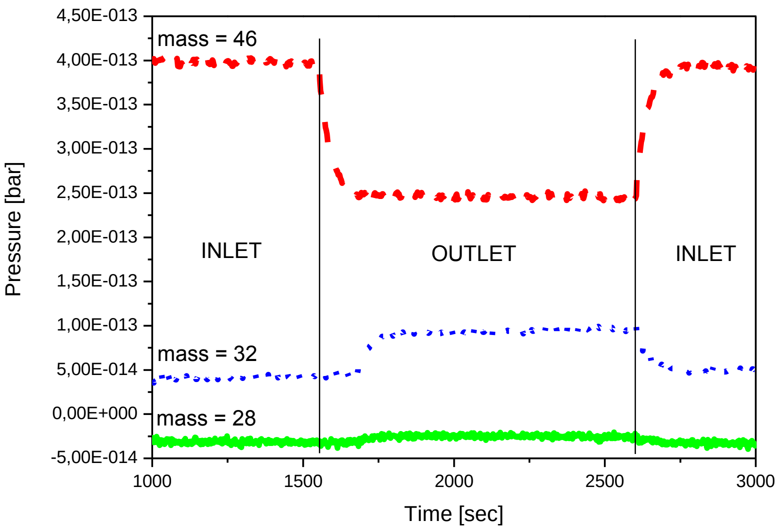
In the second stage the catalytic properties of metallocomplexes and their heterogenized counterparts in epoxidation of cyclohexene and oxidation of cyclooctane were studied. The epoxidation of cyclohexene was carried out in homogenous system and in the presence of sodium hypochlorite as an oxygen donor. The anionic complexes of phthalocyanine (FePcS, MnPcS, CoPcS, CuPcS, NiPcS) and anionic porphyrin complexes (FeTPPS, MnTPPS, CoTPPS) as well these complexes introduced on/in liposome were applied as the catalysts. Propene oxide, 2-cykloheksen-1-ol and 2-cykloheksen-1-on are the products of cyclohexene epoxidation. All synthesized catalysts were active in this reaction. The yield and selectivity of the examined reaction depend on the structure of macrocyclic complex and on the character of the metallic center. In the case of metalloporphyrins, manganese porphyrin MnTPPS was the most active. Its activity was also the highest among metallocomplexes immobilized on/in liposome. Immobilization of macrocyclic complexes on/in liposome results in significant increase of the catalytic activity and prevents their dimerization. Among phthalocyanine metallocomplexes, both before and after immobilization, on/in liposome manganese complexe MnPcS and MnPcS/liposomes were the most active.Molecular oxygen was an oxidizing agent in the case of cyclooctane oxidation. Anionic metalloporphyrins FeTPPS, MnTPPS, CoTPPS and anionic metallophthalocyanines FePcS, MnPcS, CoPcS supported on chitosan, cationic metalloporphyrins MnTMPyP, FeTMPyP, CoTMPyP supported on alginate and cobalt salts of tungstophosphoric and molybdophosphoric acids $H_{3-2x}Co_xPX_{12}O_{40}$, where X= W or Mo, x = ½, 1, 1 ½ supported on chitosan were used as the catalysts. For comparison, the unsupported complexes were also studied. Cyclooctanon and cyclooctanol were the main products of the reaction. All the studied catalysts were active in catalytic oxidation of cyclooctane. Cobalt complexes were the most active for both anionic metalloporphyrins and anionic metallophthalocyanines. The catalytic activity of anionic metalloporphyrins increased with the zeta potential decrease in accordance with the row: CoTPPS > MnTPPS > FeTPPS. Similar order of activity was obtained for metallophthalocyanine catalysts: CoPcS > MnPcS > FePcS. In the case of cationic metalloporphyrins the highest activity is observed for manganese complex MnTMPyP. For supported cationic metalloporphyrins catalytic activity increased with the increase of the positive zeta potential charge: MnTMPyP > CoTMPyP > FeTMPyP. It was also shown that structure and the type of metallic center influenced the reaction selectivity. Cobalt salts of tungstophosphoric acid were more active than phosphomolybdic cobalt salts and their activity only slightly decreased after deposition on chitosan.

The Influence of Kind of Central (P, Si) and Addenda Atoms (W, Mo) in the Silver Salts of Heteropolyacid with Keggin Structure on Direct Decomposition of Nitrogen Oxide NO_x

Research project N204 149433 [2007-2010]
(projects leader: Tadeusz Machej PhD)

The investigations including catalytic oxidation of NO to NO_2 and direct decomposition of NOx on $Ag_3PW_{12}O_{40}$, $Ag_3PMo_{12}O_{40}$, $Ag_4SiW_{12}O_{40}$, $Ag_4SiMo_{12}O_{40}$ salts were finished in 2010 year. The results showed that all silver salts of different heteroplyacids are active in oxidation of nitrogen monooxide to nitrogen dioxide in ambient temperature, especially, in the presence of water vapour. The highest conversions were obtained with $Ag_3PMo_{12}O_{40}$, $Ag_4SiW_{12}O_{40}$ and $Ag_4SiMo_{12}O_{40}$ salts what can be correlated with the high NO_2 sorption on these salts. It can be supposed that NO_2, appearing as a result of NO oxidation, is sorbed by silver salt. Since, it can be suggested that diffusion of NO_2 to active centres existing in silver salts plays an important role influencing reaction rate. Further investigations confirmed that the diffusion of reagent to active centres existing in the bulk of silver salts is the limiting step of NO to NO_2 oxidation reaction. It is presumably because silver salts were characterized by very small surface area.

The investigations concerning direct decomposition of NOx were performed in anaerobic atmosphere, with the presence of oxygen and with water vapour. The obtained results shown that silver salts of heteropolyacids are active in decomposition of nitrogen dioxide what is presented in the Figure. However, the decompostion of nitrogen monooxide proceeds in the presence of oxygen, only. It can be assumed that oxygen allows for oxidation of NO to NO_2, which is sorbed and decomposed in the next step. The experiments performed with nitrogen dioxide confirmed proposed mechanism of decomposition. The positive influence of addition of water vapour on the reaction was also observed. Unfortunatally, the decomposition of NO_x on silver salts of different heteropolyacids is also limited by diffusion process in the wide range of GHSV 600-6000h^{-1}. It makes that these compounds can not be applied in practice.



Presented above results clearly show that the described problem can be solved by the preparation of silver salts with developed surface area or by supporting these salts on different carriers.

Multiple Cationic Surfactant Complexes with Polyelectrolytes as Elements of Nanostructures

Research project N N204 248634 [2008-2011]
(project leader: Grażyna Para PhD)

Influence of molecular structure on the adsorption of double chain, cationic surfactants: *N,N*-(didodecyl)-*N,N*-dimethyl ammonium bromide as well as gemini type *N,N,N',N'*-tetramethyl-*N,N'*-di(dodecyl)-alkylenediammonium bromides and their interactions with polyanions: sodium poly(styrene sulfonate) (PSS) at free solution surface was examined. The molecular structure of investigated surfactants was elucidated by molecular mechanics simulations using AMBER99 force field and Hyperchem 8.0 chemical computation software. The surface tension was measured by a pendant drop shape analysis method and the equilibrium surface tension isotherms of investigated ammonium salts solutions were determined. The extended "surface quasi two-dimensional electrolyte" (STDE) model was applied for the description of experimental data of surfactants adsorption.

Surface activity of investigated gemini-type cationic surfactants, due to their multiple charge, was in concentration range between that of dialkyl and single chain ammonium surfactants. It was observed that cmc of dimeric gemini surfactants first increased (up to $(CH_2)_6$ spacer chain) and then decreased with the length of the spacer and this dependence can be explained as result of flexibility of long spacer chain.

Fig. 1 presents the dependence of the N-N distance on the number of -(CH_2)- groups in the spacer for its fully extended (circles) and maximally folded (squares) conformations. One can conclude that minimal distance between amine groups grows for the spacer length from 2 to 6, then, for longer spacer, it remains the same, which means that degree of folding of the spacer increases. The molecular dynamic simulations confirmed that this effect is caused by increased flexibility of long spacer, which can bend out of the aqueous phase.

Using various types of investigated cationic surfactants and of polyanion PSS, surfactant-polyelectrolyte bulk complexes were formed for further encapsulation by layer-by-layer adsorption of polyelectrolytes (polycation PDADMAC (polydiallyl dimethyl ammonium chloride) and polyanion PSS).

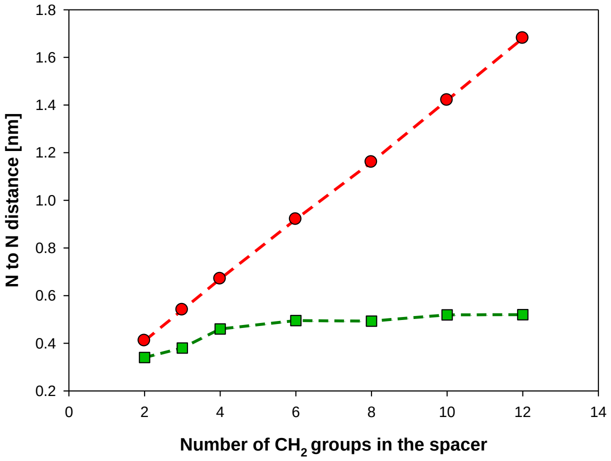


Figure 1. The dependence of the N to N distance on the number of CH_2 groups in the spacer of N,N,N',N'-tetramethyl - N,N'-di(ndodecyl)-alkylenediammonium bromides calculated using molecular dynamics simulation; circles – fully extended spacer, squares – maximally folded spacer

The Study on the Application of Heterogenized Chiral Ruthenium Complexes in Enantioselective Hydrogenation of Ketones

Research project N N204 249034 [2008-2011]
(project leader: Dorota Duraczyńska PhD)

Ruthenium catalysts supported on amine functionalized methacrylate-styrene FCN resin (Fig. 1) prove very active and highly selective in the hydrogenation of carbonyl group in acetophenone (Fig. 2). In the presence of 4%Ru/FCN catalyst 1-phenylethanol is formed with ca. 80% selectivity. The essential feature of the catalytic set-up is the use of a biphasic isooctane/water solvent system. An important aspect of reaction carried out in the biphasic isooctane/water solvent is that acetophenone becomes transformed preferentially via hydrogenation of C=O group rather than hydrogenation of aromatic ring. The role of biphasic isooctane/water solvent system has been attributed to the solvation of acetophenone phenyl ring by non-polar isooctane, which enhances appropriate orientation of the reactant and facilitates adsorption and catalytic transformation of polar carbonyl group at the surface of the catalyst. Superior selectivity to 1-phenylethanol over polymer supported ruthenium catalyst with respect to the reference Ru/Al_2O_3 catalyst is tentatively assigned to steric effects induced by the polymer chains which enhance favorable orientation of acetophenone molecule towards Ru active sites.

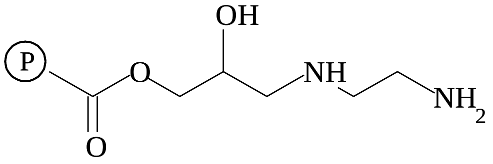


Figure 1. The structure of FCN resin

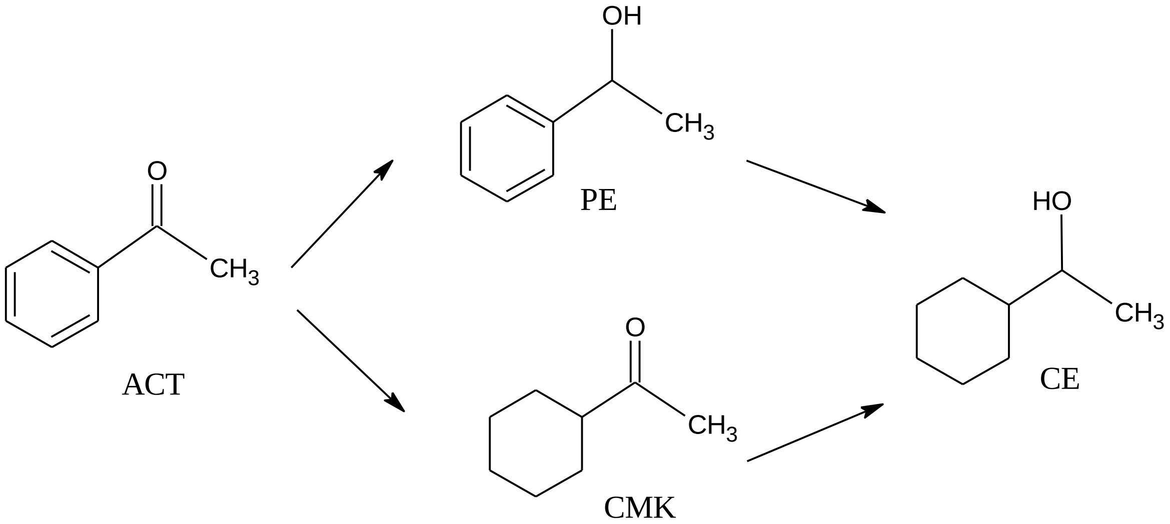


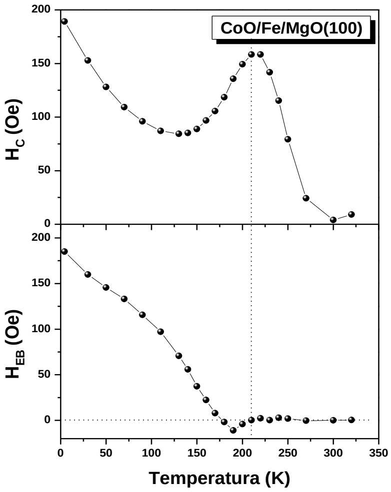
Figure 2. Hydrogenation of acetophenone

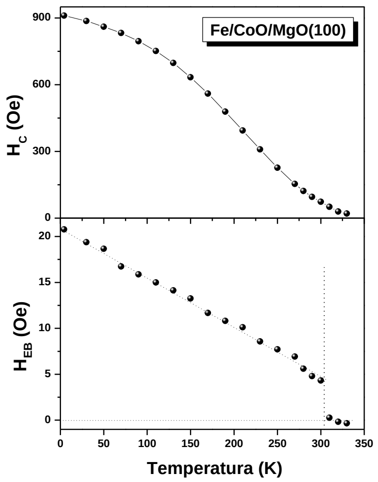
Exchange-bias Effect in the Epitaxial Systems Obtained by Deposition of the 3d and 4f Metals on Polar and Non-polar Transition Metal oxide Substrates

Research project N N202 248535 [2008-2011]
(project leader: Jacek Gurgul PhD)

In year 2010, studies of CoO/Fe/MgO(100) and Fe/CoO/MgO(100) systems prepared by molecular beam epitaxy (MBE) were continuing. Special attention was focused on the modification of Fe/CoO and CoO/Fe interfaces. For this purpose several samples were prepared,

e.g. Fe/CoO/MgO(100) system with 50 Å thick homoepitaxial layer of MgO, CoO/Fe-O(1x1)/MgO(100) with oxidized Fe layer and CoO/Co/Fe/MgO(100) sample with 2 Å cobalt layer deposited to prevent oxidizing of Fe surface. The quality of layers was verified by low energy electron diffraction (LEED) at every stage of preparation process. Then, 50 Å thick layer of MgO was deposited on every sample to prevent surface modification during the *ex situ* VSM magnetic measurements, magnetooptical Kerr effect (MOKE) studies and ^{57}Fe conversion electron Mössbauer spectroscopy (CEMS).





The detailed magnetic measurements allowed to determine coercive field H_C and exchange-bias field H_{EB} as a function of temperature, what is shown above for two typical systems with different interfaces. The analysis of results shows that magnetic properties of multilayer systems are closely connected to the interface chemical structure and to the morfological layer structure. Due to the more precise analysis of structural factors influence on magnetic properties of Fe-CoO systems, CEMS measurements were performed on the samples with additional layer containing pure ^{57}Fe Mössbauer nuclei, where appropriated procedure of samples preparation let us know some information concerning hyperfine interactions in the interface. The forthcoming results show that Fe/CoO bilayers are characterized by large coercive fields, small H_{EB} fields and relatively high blocking temperature $T_B \sim 290$ K, from time to time even exceeded Néel temperature of CoO. On the other hand in CoO/Fe interfaces one can observed small coercive fields, large H_{EB} fields and much lower blocking temperature $T_B < 260$ K. It is worth mentioning that temperature characterisitics of H_C and H_{EB} are significantly different (see Figure) what is caused by Fe layer oxidation in the Fe-CoO interface.

Molecular Mechanisms Determining Product Specificity of 2-Oxoglutarate Dependent Oxygenases

Research project N N301 093036 [2009-2011]
(project leader: Professor Ewa Brocławik DSc)

Within this project an α-ketoglutarate dependent halogenase, abbreviated in the literature to SyrB2, has been studied with theoretical methods. This nonheme iron enzyme catalyzes chlorination of threonine (L-Thr) side chain, which is one of the biosynthesis steps leading to an antibiotic – syringomycin.

Since the structure of a Michaelis complex for SyrB2 is not yet known, the first step of our studies was simulations of molecular docking of the organic substrate into the enzyme active site, which was accomplished with the use of AutoDock program. The resulting structure of a macromolecular complex was a starting point for construction of an active site model used in quantum-chemical investigations into the electronic structure of the reactive oxoferryl species and the catalytic reaction mechanism.

The electronic structure of the oxoferryl species was investigated with DFT and CASPT2 methods, and in addition, Mossbauer spectra parameters were calculated for two proposed forms of the reactive intermediate (a and a’, see Figure) in three plausible spin states. The results allowed us to interpret the experimentally derived spectra.

Based on the fact that the oxoferryl species exists in two inter-converting forms, corresponding to a and a’, a mechanistic hypothesis has been formulated which explains selective chlorination of L-Thr, and preferential hydroxylation of non-physiological substrates (see Fig. 1). Here, it is assumed that both forms (a and a’) can activate the C-H bond, yet with slightly different rate, and subsequently transfer to the aliphatic radical either Cl or OH. The results have been published in JACS.

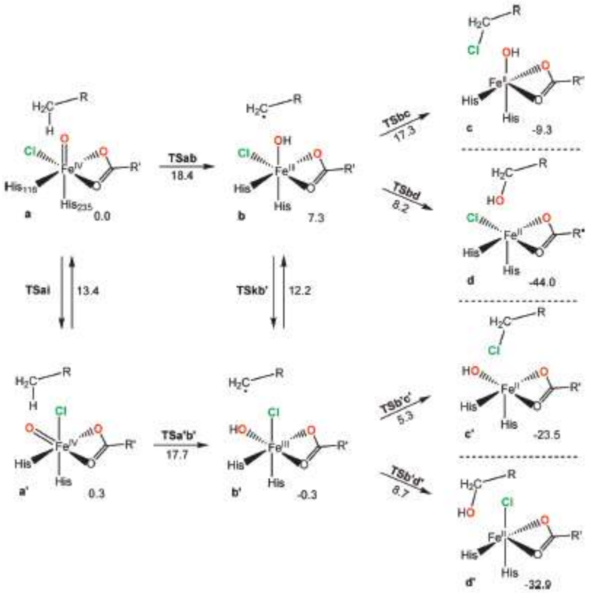


Figure 1. Suggested reaction mechanism for chlorination and hydroxylation of L-Thr by SyrB2

Developing of the Methods of Formation Biologically Active Multilayers Contained Polyelectrolytes - Proteins - Dendrimers

Research Project N N204 028536 [2009-20012]
(project leader: Barbara Jachimska PhD)

The controlled assembly of colloidal particles has potential application in the production of nano and microstructured materials of desired functionality. Understanding and control of these phenomena can be achieved only by acquiring information on specific interactions between the particles under dynamic conditions. The dynamic interactions can be effectively studied through the model particle deposition on substrate of homogenous and controlled surface properties. By adsorbing particles under well defined condition it becomes possible to control the degree of surface heterogeneity.

Dendrimers can be used for elucidation an adsorption mechanism of globular protein and to calibrate the indirect methods of measuring protein surface coverage like: ellipsometry, reflectometry or streaming potential.

Characterization of poly (amido amine) PAMAM dendrimers in an aqueous solution was carried out by measuring their electrophoretic mobility and diffusion coefficients using the dynamic light scattering (DLS) method. This allowed one to determine the effective charge and the hydrodynamic radius of PAMAM molecules. These physicochemical characteristics were supplemented by dynamic viscosity measurements. From these data, the intrinsic viscosity of PAMAM solutions was derived. The viscosity behavior was successfully interpreted in terms of dense-core/dense-shell structure of dendrimers as postulated in literature.

A detailed study of the adsorption of PAMAM dendrimers to the mica surface was performed using atomic force microscope (AFM). By determining the maximum coverage and the topology of the adsorption layers we could extract information about the dendrimer adsorption dynamics and interactions between the surfaces and dendrimers molecules. These experimental results obtained for the model dendrimer system can be used as useful reference states for analyzing protein adsorption.

New Nanostructured Carbon Materials, Oxide Materials and their Composites as Components of Capacitors

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

1. A series of layered double hydroxides (LDHs) were synthesized. According to a plan, obtained materials have different elemental composition, e.g. cobalt-aluminium, nickel-aluminium, cobalt-nickel-aluminium and various M^{2+}/M^{3+} atomic ratio equals 2 or 3. Additionally, in the case of cobalt-nickel-aluminium systems, cobalt to nickel atomic ratio also varies, e.g. Co:Ni = 3:7, 5:5, 7:3. Elemental composition of LDHs was confirmed by chemical analysis using ICP OES. LDHs were prepared by co-precipitation method by addition of aqueous solution of sodium hydroxide to aqueous solution of cobalt and/or nickel and aluminum nitrates at constant pH=10. Hydrothermal synthesis was carried out at room temperature applying 30-minute precipitate ageing. XRD analysis confirmed that obtained materials possess a hydrotalcite-like layered structure; moreover they indicate a different degree of crystallinity. In general, samples with a lower M^{2+}/M^{3+} atomic ratio equals 2 are less crystalline than samples with a higher M^{2+}/M^{3+} atomic ratio equals 3. Nickel-aluminium LDHs have a higher degree of crystallinity in comparison to analogue samples containing cobalt instead of nickel. Among all the LDHs, cobalt-nickel-aluminium LDHs are the least crystalline. Thermal analysis carried out in the air up to 1000^oC revealed that LDHs have different thermal stability.
2. A series of composites were synthesized via chemical vapour deposition (CVD) method. CVD experiments were carried out in a horizontal tube furnace under a flow of inert gas. LDHs (Co/Al=2, Ni/Al=2) were heated for 30 minutes at various temperatures of 600, 700, 800^oC, under a flow of argon saturated with acetonitrile (CH_3CN) vapour.
3. A series of carbon materials were obtained from the composites via treatment with acid. The carbon materials were extracted from the composites with the use of dilute hydrochloric acid during 24-hour process enhanced by 1-hour sonication.
4. Several techniques including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and volumetric nitrogen sorption were employed to characterize physicochemical properties of newly prepared materials.
5. Electrode properties of the composites and the carbon materials were examined by cyclic voltammetry in alkaline media (0.1 M KOH). The electrical double layer capacity was measured and the electrocatalytic performance was tested in the oxygen reduction reaction.
6. The poster entitled „Electrode materials containing cobalt species and nitrogen-doped carbon nanotubes" was presented during the 61st Annual Meeting of the International Society of Electrochemistry in Nice (France) 26th September – 1st October 2010.

Acoustic Emission for Monitoring Museum Objects as a Universal Method of the Preventive Conservation

Research project N N105 278536 [2009-2012]
(project leader: Łukasz Bratasz PhD)

During the second year of the project, which started on May 5, 2009, scientific equipment for the measurement of acoustic emission generated during crack propagation in cultural heritage objects was developed. It was achieved by an acquisition of a high quality system for acoustic emission recording, a low-noise amplifier and a set of sensors sensitive to a frequency range from 10 to 1000 kHz. These pieces of equipment were integrated into one set up and programmed to effectively analyse the recorded signals. Development of an automatic module for the analysis, classification and recording of the acoustic events on site i.e. in museum display conditions, has been also finished. The entire system was tested in the laboratory by using wooden specimens and by the standard Nielson test. The developed equipment was optimised to achieve a proper amplification of the signals and to filter out undesired frequencies.

Several model material samples imitating historic objects were prepared according to historic recipes such as gypsum, stucco marble and various wood species as lime, spruce, walnut, oak and poplar.

Developed equipment was used for characterization of relations between acoustic emission and type of wood, anatomic direction and water content in investigated woods under externally induced loading in universal testing machine.

Obtained results indicated strong dependence of mechanical parameters of investigated materials on the rate of load application. This relationship was caused by material relaxation processes. For materials tested characteristic times of relaxation were obtained, which allowed to carried out consistent experiment and then compare results of acoustic emission activity induced by ‘fast’ and ‘slow’ application of load. Analysis of acoustic emission indicated lack of significant difference in characteristic frequency between two tests, which allowed to set one universal testing procedure for all materials under investigation.

Similarly to woods, characteristic frequency and envelope of acoustic signals were determined for gypsum and stucco-marble.

For all investigated materials key mechanical parameters such as: Young modulus, strength, yield point as well as sorption properties were found.

At present, experiments aiming at determination of impact of real environmental variations, in particular relative humidity changes, on damage development, are continued. To achieve this, new experimental set up was prepared. It combines programmable climatic chamber coupled with laser system of dimensional changes monitoring with the acoustic emission system.

Work aiming at selection of adequate reference objects for acoustic emission monitoring in the collection of the National Museum in Krakow, has been started.

Controlled Adsorption as a Method of Protection against the Environment Contamination Caused by the Oxidation of Metal Sulfides

Research project N N523 451336 [2009-2011]
(Assoc. Professor Paweł Nowak DSc)

Wastes from the mineral and non-ferrous metal industries contain frequently metals in the form of metal sulfides. The solubility of metal sulfides is very low, however when left on the depository places they undergo the influence of atmospheric oxygen and other oxidizing species and oxidize to better soluble compounds (carbonates, sulfates, hydroxides), liberating metal ions to the environment during the contact with natural waters. Weathering of metal sulfides may be considered as a corrosion process and, like in the case of metals it may be prevented by the application of inhibitors. The object of the present work was the selection of the compounds that adsorb strongly on the surface of metal sulfides forming a protective layer preventing the oxidation of the surface, which might be used as inhibitors of the reaction of metal sulfide oxidation.

Copper sulfide of the composition $Cu_{1.87}S$, synthesized from high purity copper and sulfur, similar in the composition to many non-stoichiometric copper (I) sulfides occurring in Polish copper ores as well as several pieces of natural copper sulfides, natural pyrite and galena isolated from the ores were used in the experiments. Metal sulfides are good electrical conductors, so electrochemical methods (mainly electrochemical impedance spectroscopy) were used in the investigations. Adsorption of the chemical compounds that might be used as the inhibitors of the reaction of metal sulfide oxidation was investigated by measuring the capacitance of the electrical double layer at the interface: metal sulfide / aqueous solution. Adsorption of following chemical compounds was investigated: sodium oleate, sodium phosphate, sodium stearate, sodium hexadecylsulfate, sodium dodecylsulfate, polyvinyl alcohol, sodium silicate, dodecyltrimethylammonium chloride, n-octanol, N-dodecylpyridinium chloride, 2-mercaptobenzthiazole, dodecylpyridinium chloride, sodium bis(2-ethylhexyl)phosphate, potassium ethylxanthate and humic acid sodium salt. It was established that in the range of potentials establishing on copper sulfide electrode in oxygenated solutions the surface of the electrode bears negative charge, so only cationic surfactants can adsorb, but the physical adsorption is too weak to prevent the oxidation of the surface. Only those compounds that adsorb at the surface by strong chemisorptive bond or react with the surface giving the overlayer of precipitated reaction product may become the effective inhibitors.

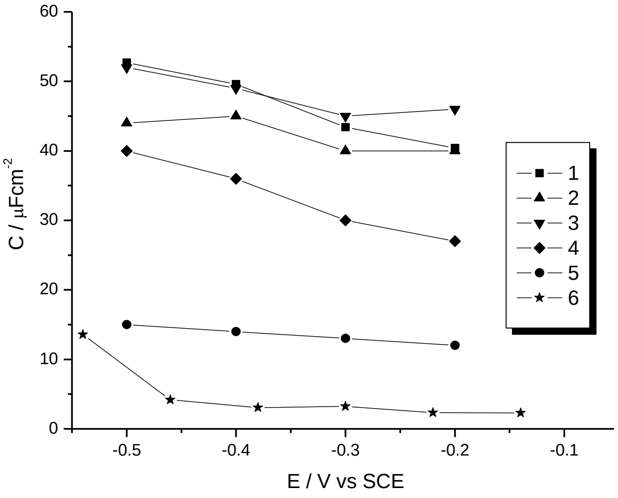


Figure 1. The dependence of the electrical double layer capacitance at the surface of non-stoichiometric copper sulfide electrode in: 1 - the solution of pure base electrolyte (0.5 mol dm^{-3} Na_2SO_4) and in the solutions containing surface active substances at the concentration of 1 mmol dm^{-3}: 2 - sodium dodecylsulfate, 3 - sodium oleate, 4 - n-octanol, 5 -dodecyltrimethylammonium chloride, 6 -N-dodecylpyridinium chloride

Theoretical and Experimental Analysis of Multilayered Spherical Colloidal Particles Porosity

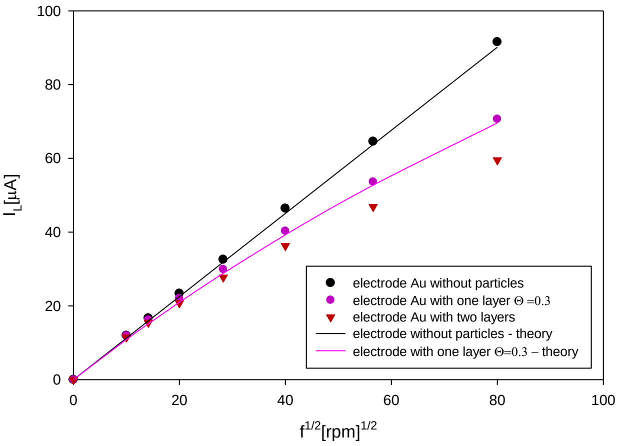
Research project N N204 347737 [2009-2012]
(project leader: Assoc. Professor Paweł Weroński DSc)

We used the dynamic light scattering method to measure the size and surface potential of several kinds of colloid latex particles as a function of pH and electrolyte concentration. We developed a method of mechanical polishing and cleaning of gold rotating disk electrode, allowing preparation of smooth and clear surface with reproducible parameters. We quantitatively characterized the physicochemical properties of electrode surface using optical microscopy, atomic force microscopy, electrochemical methods, as well as by investigation of adsorption kinetics of charged latex particles. We conducted measurements of limiting diffusion current at a gold rotating disk electrode in 1 mM solution of potassium ferricyanide at various rotation speeds. We also conducted measurements of limiting diffusion current at a rotating disk electrode covered with a monolayer or bilayer of colloidal particles of the size of 1 μm. We demonstrated that in the range of medium and high surface coverage the measured limiting currents agree well with the Levich theory and can be calculated with the equation:

$$I = \frac{I_L}{1 + 2a[1 + (\pi/8 - 1/3)\theta]/(\delta_d \varepsilon^2)}$$

Here $I_L = 0.62\ D^{2/3}\ \omega^{1/2}\ \nu^{-1/6}\ c\ S\ e$ is Levich current at a bare electrode surface, D and c are the diffusion coefficient and concentration of ferricyanide ions, respectively, ω and S are the electrode rotation speed and surface area, respectively, ν is the kinetic viscosity of solution, e is the proton charge, a is the colloidal particie radius, $\theta = n\ \pi\ a^2\ /\ S$ is the coverage of electrode surface, n is the number of adsorbed particles, $\delta_d = 1.61\ D^{1/3}\ \omega^{-1/2}\ \nu^{1/6}$ is the thickness of the diffusion boundary layer, and $\varepsilon = 1 - 2\ \theta / 3$ is the porosity of adsorbed layer.

In the figure below we present a comparison of experimental and theoretical results for the limiting diffusion current at a gold disk electrode without colloidal particles, as well as with mono- and bilayer of latex particles.



New Method of Evaluating Colloid Particle and Protein Interactions with Interfaces based on Streaming Potential Measurements

Research project N N204 026438 [2010-2013]
(project leader: Professor Zbigniew Adamczyk DScEng)

The knowledge of hydrodynamic mobility tensors and intrinsic viscosity has an essential significance for predicting conformations of proteins in electrolyte solutions for determining kinetics of aggregation processes, and mechanisms of their interactions with interfaces leading to mono- and multilayer adsorption. Because of complicated shapes of proteins, deviating significantly from the spherical shape, theoretical calculations are very tedious. Thus, the aim of this work was elaborating a new, efficient hydrodynamic model of proteins, based on the bead concept. According to this model, the real shape of the molecule is replaced by a constellation of beads of various sizes, having the same volume as the molecule. Using this model, extensive calculations were carried out, aimed at determining the hydrodynamic resistance matrix, the diffusion tensor and the intrinsic viscosity of proteins. Our calculations were based on the linear Stokes equations describing fluid velocity fields. The no-slip boundary conditions were applied on solid surfaces, the ambient flow was assumed to be zero and the fluid was assumed unbounded. Using the formalism of induced forces, and the Oseen tensor as the Green's function for the infinite system geometry, the Stokes equations are transformed into a set of boundary integral equations at the surfaces of all spheres. These equations are next projected onto a complete set of spherical multipole functions. Contrary to previous approaches, the hydrodynamic resistance and the diffusion tensors were evaluated by taking into account the coupling between translation and rotation of protein molecules. Results of calculations performed for fibrinogen are shown in Fig. 1 as the dependence of the hydrodynamic radius R_H on the length of the side arms of the molecule, modeled as the number of beads N_R.

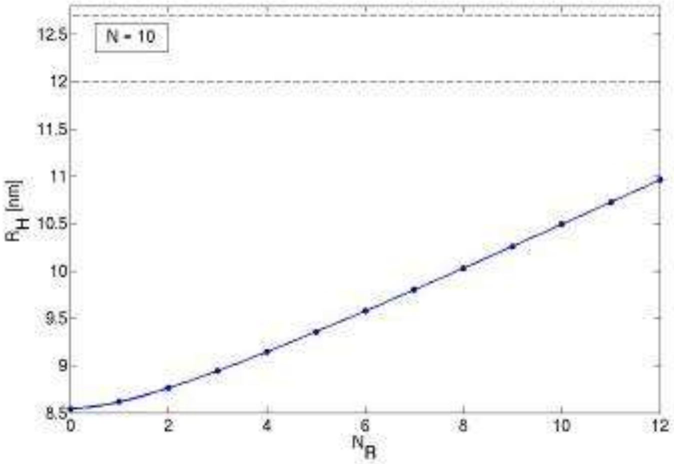


Figure 1. The dependence of the hydrodynamic radius of fibrinogen R_H on the length of the side arms modeled by the number of beads N_R.

A comparison of these theoretical calculations with experimental data acquired by DLS indicated that there is a significant hydration of the molecule, reaching 30%.

Modeling of Kinetics and Equilibrium of Heavy Metal Ion Sorption by Materials of Biological Origin

Research project N N204 271238 [2010-2012]
(Professor Władysław Rudziński DSc)

Binding of heavy metal ions by calcium alginate has been described by applying many different models. We used two most basic approaches to systematically compare their simultaneous description of metal uptake dependence on pH and metal ion concentration in the bulk solution. Eleven experimental data sets corresponding to the binary sorption systems containing protons and heavy metal ion (cadmium, lead or copper) were taken from the literature. The applicability and limitations of both models are discussed. Neither of the models gave a completely satisfactory description of all data but the two-site occupancy model yielded better results compared to the one-site-occupancy model when considering the coherence of the parameters (e.g. affinity constants and Donnan factors). However, the quality of the obtained fits is similar in both cases.

The analysis of various models assumed to represent the influence of pH on heavy metals biosorption equilibrium was studied. It appeared that all of them lead to the same mathematical expressions (e.g. the Langmuir or the Flory adsorption isotherm equations) when the pH effects are neglected. Even if considering the pH effects, some of them (competitive adsorption and ion-exchange models, for instance) still lead to analogical expressions for sorption isotherm equations. The accepted mechanism of biosorption may, however, influence strongly the differences between the initial and equilibrium states of biosorption system. This effect was qualitatively and quantitatively described.

Finally, complementary studies were performed aiming at molecular modeling of interactions of alginates and alginic acid with phenol and two phenol derivatives (*o*-chlorophenol and *p*-chlorophenol).

Biocatalytic Synthesis of Chiral Alykaromatic and Alkylheterocyclic Alcohols with Ethylbenzenee Dehydrogenase- Theory and Experiment

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

Within task 1 the activity of 10 new substrates was investigated: 4-ethylresorcinol, 4-ethylcatechol, 2-, 3-, 4-propylphenol, 4-ethylbenzoic acid, 3-ethylaniline, 3-ethylpyridine, indane and cumarane. Moreover, a full kinetic characterization has been conducted for 3-ethylaniline, 3-ethylpyridine, 4-ethylresorcinol, indane, cumarane, 2-, 3-, 4-propylphenol fitting Michaelis-Menten model to experimental results. Among studied compounds there high activity was observed in case of 4-ethlrezorcine (360% activity in respect to ethylbenzene), cumarane (80% activity), indane (80% activity), 4-propylphenol (40 % activity). The rest of compounds exhibited low activity (3-ethylaniline 25%, 3-ethylpyridine 3.7%, 3-propylphenol 3.14%, 2-propylphenol 6.3%), was an inhibitor (4-ethylbenzoic acid) or due to non-enzymatic background reaction with ferrocenium tetrafluoroborate (enzyme re-oxidation agent) prevented kinetic characterization (4-ethylcatechol). The obtained kinetic parameters will be used in construction of the reactivity model within task 3.

The stereospecifity of EBDH reactions was investigates with chiral liquid chromatography with DAD and MS (APCI) detection. The chiral analyses were performed for 3-ethylpyridine, indane and cumarane reaction mixtures proving 100%, 100% and 95% stereoselectivity, respectively.

The studies conducted within Task 3 comprised of construction the EBDH substrates and inhibitors collection that contained 46 compounds. As a next step following quantum chemical theoretical descriptors (DFT level of theory, B3LYP, double-zeta basis set) for the studied compounds were calculated: the partial alpha-carbon charge, the highest and the lowest atomic charges, the difference between the highest (positive) and the lowest (negative) charge in both Mulliken and NBO analyses, the ν_sC-H symmetrical stretching frequency, the H-NMR shift of substituted hydrogen, the C-NMR shift of alpha-carbon, the dipole moment μ, frontier orbital energies i.e. E_{LUMO} (as an approximation of electron affinity) and E_{HOMO} (as an approximate measure of ionization potential) and GAP - the energy difference between E_{LUMO} and E_{HOMO} (as a measure of absolute hardness). Substituents influence on the relative changes in Gibbs Free Enthalpy of radical and carbocation formation ($\Delta\Delta G^{radical}$ and $\Delta\Delta G^{carbocation}$) was calculated according to previously described methods. Moreover, a computational alternative to Hammet σ, an electrostatic potential at the nuclei was calculated according to the procedure described by Galabov *et al*. Compound's bulkiness was described by the molecular weight (MW), total energy of the molecule (SCF) and zero point energy (ZPE) (derived from DFT calculations) as well aw molecular surface area (Mol_Surf), molecular fractional polar surface area (Pol_Mol_Surf) and molecular refractivity (MR) (calculated in the Accerlys Discovery Studio 2.5). Moreover, the logP and logP_MR (hydrophobicity), Kier and Hall molecular connectivity indices χ^0, χ^1, χ^2 as well as Balban and Zagreb indexes (topology) were also calculated in Accerlys Discovery Studio 2.5. The topology descriptors were supplemented with the mutual location of the substituents (ortho, metha, para) taking ethylbenzene structure as a reference core. Such description of EBDH substrates and inhibitors will be used in further modelling studies of the enzyme reactivity.

The studies conducted within task 2 focused on QM;MM modeling of ethylbenzene activation mechanism in the full EBDH alpha subunit. The model utilized mechanical embedding of the active site that was treated with full quantum chemical level of theory. The obtained reaction energy profile showed chemical analogy to results obtained before with cluster *in vacuo* approach (i.e. radical C-H activation and transfer of second electron during OH rebound). Preliminary calculation with electrostatic influence of the protein (electronic embedding) showed its profound influence on the stabilization of transition states and electron transfer.

Functional Nanostructures of Manganese Oxides Doped with Other Metals

Research project N N204 269238 [2010-2013]
(project leader: Robert Socha PhD)

Knowledge about manipulation of atomic size structures allow obtaining new systems of specific and dedicated properties. Low dimensional structures of manganese oxides (II-VII) have found growing interest due to their morphologic, electronic and magnetic properties. Only few approaches to synthesis epitaxial structures of manganese oxides (mainly MnO and Mn_3O_4) have been undertaken recently. This gives an opportunity for synthesis new systems of interesting properties, different that the ones existing in nature and leading to dispersed forms of higher catalytic selectivity.

There have been two tasks of the project performed partly in 2010 i.e. preparation of the epitaxial nanostructures of manganese oxide (II,III) Mn_3O_4 (spinel) and the spinel substituted by other metal on single crystal oxide support. Polished and cleaved MgO(001) single crystals were chosen as the support. As the test method of oxide synthesis, the oxidation of metal layer was applied. Low energy electron diffraction (LEED) was used for analysis of obtained structure and X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES and XAES) for composition and electronic states analysis of the elements on the studied surfaces.

Applied procedure allowed obtaining of (001) oriented epitaxial layer of metallic manganese on polished and cleaved MgO(001) substrate. Oxidation of manganese layer in the temperature range of 150-250^{o}C led to manganese oxide (III) Mn_2O_3 of weakly formed structure. Annealing of such a layer at 400^{o}C led to good (001) epitaxy.

A sample test of synthesis of mixed oxide was performed with iron as a dopant metal. In this synthesis, the iron layer (0.2 nm) was deposited on manganese layer epitaxially grown on polished MgO(001). The bi-metallic system was annealed at 400^{o}C that led to partial dissolution of iron in manganese but the structure remained unchanged. Mixed oxide was obtained by oxidation of bimetallic layer. XPS analysis showed presence of oxidized iron forms Fe^{2+} and Fe^{3+} at the structure of resulting oxide layer. Annealing of mixed oxide at 400^{o}C led to the (001) substrate surface structure.

Composite Cathodes for Solid Oxide Fuel Cells (SOFC) Working at Temperature 600^{o}C and Lower Containing Silver

Research project N N507 616638 [2010-2013]
(project leader: Michał Mosiałek PhD)

Solid oxide fuel cells are promising electric energy generators. The most important difference between the fuel cell and the internal combustion engine is that the efficiency of the later is limited by the condition imposed by the Carnot cycle whereas the former not. Nowadays the technology is at the beginning of the end user testing step. Many word-wide known enterprises like Google and Microsoft are using fuel cell power supply systems. The main problem in construction of SOFC is the low rate constant of the oxygen reduction reaction and low mobility of oxygen at low temperature. The goal the project is to develop a new type of cathode showing better catalytic properties than traditional materials, that would be able to work at lower temperatures. The promising material, that could improve the performance of the SOFC cathode is silver. The project started in 2010 year with the task entitled "Synthesis and characterization of the composite electrode materials containing silver". $La_{0.8}Sr_{0.2}MnO_3$ LSM, $Sm_{0.5}Sr_{0.5}CoO_3$-SSC, $Gd_{0.5}Sr_{0.5}CoO_3$-GSC cathode materials and $Ce_{0.8}Sm_{0.2}O_{1.9}$-20SDC, $Gd_{0.8}Sm_{0.2}O_{1.9}$-20GDC, 8-YSZ electrolyte materials were synthesized and characterized by XRD, SEM, EDS and XPS methods. Dense and non-porous disc shaped electrolytes were produced. An attempt to introduce particles of silver to the cathode material $Gd_{0.5}Sr0_{.5}CoO_3$ at the initial stage of synthesis of mixed oxide was made.

Electromigration of silver in the prepared materials was investigated at negative bias potential by chronoamperometric method. The growth of the area of the contact between silver electrode and YSZ electrolyte was observed. No such growth was observed in the case of the Ag/LSM contact. It was noticed, that 1 mμ thick dendrites grew around the contact area during electrolysis. Kinetics of that process was investigated with the use of electrochemical methods. The decrease in the manganese content in LSM below the contact with silver was observed.

A LSM|YSZ half cell was constructed. Preliminary measurements in the system LSM/YSZ with the use of the point electrode measuring configuration were performed. The EIS spectra were recorded at various temperatures and potentials. It was proved that in this case no permanent changes in the electrode system characteristics under the influence of prolonged polarization were observed.

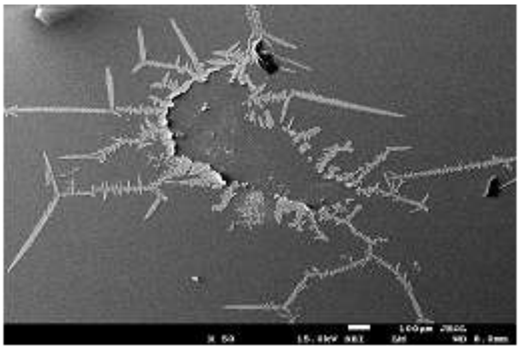


Figure 1. SEM image of 8-YSZ electrolyte after 24 hours at -0.5 V in air at 600°C

New Methods for Powder Diffraction Studies of Structural Materials, Partially Amorphous, Disordered and of Reduced Dimensionality

Research project N N204 546439 [2010-2012]
(project leader: Professor Wiesław Łasocha DSc)

Structural studies, using modern methods of powder diffraction for moderately complex preparations, with no texture or other disturbing factors, are generally fast and reliable.

However, for many important materials, we amorphous or largely amorphous materials, with 1- or 2-dimensional ordering. These materials can be valuable catalysts and composites with interesting physical properties. Their diffraction studies are very difficult, due to very poor quality (in the classic sense of the structural studies) diffraction patterns.

Within the project we plan the following:

- The application of Patterson and the 'charge flipping' methods to test 'nonstandard' specimens with reduced dimensionality, including hybrid inorganic - organic layered materials.
- In later stages, we plan structural studies conducted on the basis of formalism PDF (pair distribution function). Their goal is not only putting the hypotheses regarding the construction of structural elements, but also the quantitative verification of the created models by their refinement in a manner similar to the Rietveld method.
- The independent verification of models of structures by non-diffraction methods is expected. Support of computational methods, such as DFT methods (Density Functional Theory) may be crucial for a correct selection and refinement of the structure model.

A test of the phenomenon of different X-ray absorption in the detection and description of the texture, will be performed. Such studies will be conducted in terms of intensity distribution of overlapping lines, and further structural studies.

The aim of this project is therefore - to adopt and supplement existing procedures (for measurements and computation) by the essential elements (X-ray Ag tube, CHARGE FLIPPING, PDF or DFT methods), allowing wider use of powder diffraction methods to the structural characteristics of new materials exhibiting a high degree of disorder, the presence of nano-phase or partially amorphous phases, based on a laboratory X-ray sources.

Stability, Functionality and Mechanism of Creating Polymer-Casein Multilayer Structures

Research project N N204 546639 [2010-2013]
(project leader: Lilianna Szyk-Warszyńska PhD)

Casein is one of the intrinsically unstructured proteins (IUP), which in their natural state do not adopt stable folded structure. These proteins play an important role in living organisms, therefore many researches are focused on their biological activity. However, even though their function is well understood, our knowledge about self-organization and adsorption of these proteins is limited. Casein is surface active in aqueous solution and forms micellar aggregates. On the other hand single protein molecules behaves like polyelectrolyte-like molecule so it can be easily integrated into polyelectrolyte films. A major biological function of casein is its ability to bind calcium ions. Therefore, materials covered with casein containing films can be potentially used in medicine or diary industry. Sorption of heavy metal toxic ions by micellar solution of casein was also recognized.

In this work we investigated formation of polyelectrolyte multilayer films containing α- and α-casein. Since in neutral pH casein is negatively charged it was used as a polyanionic layer for the film build-up with polylysine (PLL) as polycation. We used sequential adsorption of polyelectrolytes (layer-by-layer technique) to form films at surface of silicon wafers and quartz crystals. Thickness of the films was determined by ellipsometry and QCM. We investigated dependence of the thickness of deposited layer on the ionic strength of the polyelectrolyte solution and exposure to solutions of various composition and pH. We found the optimal conditions for film formation at I = 0.15 M NaCl (films had maximum thickness). Films were not resistant to solutions of pH 2 due to charge reversal of casein and pH 11 due to neutralization of PLL. At the isoelectric point of casein pH 4.5, only films containing α-casein were stable. In neutral conditions, as well, these films were more stable than ones with β-casein, when contacted with the solutions with various composition.

Ph.D. research projects
of the Ministry of Science and Higher Education

Deposition of Model Microcapsules on Metallic Surfaces Modified by Adsorption of Polyelectrolyte Mulitayers

PhD research project N N204 214533 [2007-2010]
(Professor Piotr Warszyński DScEng, Anna Trybała MSc)

According to the project work plan in year 2010 the following tasks were realized:

- Preparation of microcapsules containing fluoresceine core (size 4-9 μm) and shell consisting of model polyelectrolytes: polycations - PAH poly(allylamine hydrochloride), PEI poly-(ethyleneimine), polyanion PSS poly(sodium 4-styrenesulfonate or natural polyelectrolytes CHIT – chitosan and ALG - alginate prepared by 'layer by layer' (LbL) method. Shell consisted number of layers ranging from 1 to 50.
- Study of the permeability of microcapsules shell.

The microcapsules were prepared in a solution of pH=4, in which the fluorescein core remains insoluble, the measurement of fluorescence intensity followed when changing the pH to 8 (by addition of phosphate buffer) caused the dissolution of the core. During the core dissolution, changes in the intensity of dye fluorescence were monitored using the spectrofluorymetry. During the core release from the capsule fluorescence intensity increased until the entire core was dissolved. The release rate of the dye from the capsule was compared with the dissolution rate of fluorescein crystals without polyelectrolyte shell. The results of the permeability of capsule shells were normalized to the capsule concentration.

We found that for the capsules with (PAH/PSS)n shells the release of dye from the capsule coated with film consisting of 50 layers is about 30 times slower compared to the dissolution of the uncoated fluorescein core.

We found the large influence of first layer of PEI on the permeability of the shell. The time required for the release of fluorescein from the capsule coated with $(PAH/PSS)_{25}$ film was about 360s, while from the capsule coated with PEI $(PSS/PSH)_{24}$PSS film was about 3300s. That means that the capsules, with the same number of layers containing the first PEI layer retard the release of the dye about 9 times more than the capsules without PEI.

For capsules with shells consisting of natural polyelectrolytes, it was found that the release of fluorescein from capsules coated with film (CHIT/ALG) was very fast. Fluorescein enclosed by $(CHIT/ALG)_{25}$ film was released from the capsules in about 40s, that means $(CHIT/ALG)_{25}$ film slows down the release of fluorescein from the capsule only 4 times more than from pure fluorescein core. On the other hand the effect of the first PEI layer on the release rate of encapsulated fluorescein was much stronger than for model polyelectrolytes PAH/PSS. The dye was released from the capsule PEI$(ALG /Chit)_{24}$ALG about 40 times slower than from the capsule with $(CHIT\ ALG)_{25}$ film.

In conclusion use of PEI as a first layer makes the polyelectrolyte layer more dense and thus, the capsule shell much less permeable.

Influence of Modification of Electron Density of Catalysts Active Centre on its Activity in Hydrocarbons Oxidation

PhD research project N N205 018934 [2008-2010]
(Professor Ewa Serwicka-Bahranowska DSc, Robert Karcz MScEng)

Heteropolyacids are wide group of chemical compounds. The most important for catalysis are these of Keggin structure. Keggin anion consist of central tetrahedron containing heteroatom (Al, Si, P) surrounded by 12 oxygen-addenda metal (W or Mo) octahedra. Heteropolyacids possess some useful properties like high acidity and ability to catalyze redox reactions. These properties could be tuned by modification of composition of Keggin anion. Such modification allows preparation of selective catalyst, active at low temperatures.

In our research tungstophosphoric and molybdophosphoric acids were modified by the exchange of counter cations and by the formation of lacunary anions followed by introduction of the transition metal cations into the lacunary position. Lacunary anions are formed by removal of one metal-oxygen species from Keggin anion and formation of empty coordination site. Such site can incorporate transition metal cation and form transition metal substituted polyoxometalate (TMSP). Hill and co-workers in their paper compared lacunary Keggin anion containing transition metal cations with metalloporphyrins due to the similarity in coordination of transition metals and possibility of the removal one by one of two electrons, controlled modification of the redox potential by using different atoms of the addenda and well defined active sites. To improve solubility in organic media phase transfer agent was used to prepare tetrabutylammonium salts. Organic salts of lacunary anions containing iron, manganese, cobalt or copper were prepared.

The synthesized lacunary catalysts were characterized by XRD, DSC-TG, FT-IR and UV-Vis spectroscopy. Physicochemical methods confirmed the introduction of transition metal atom into the addenda position of the Keggin structure. Prepared salts were applied as catalyst for oxidation of cyclooctane with air.

Table 1. Product yields for cyclooctane oxidation in presence
of tetrabutylammonium salts of transition metal substituted heteropolyacids.

Catalyst	Cyclooctanol	Cyclooctanone	C-ol + C-on
TBAPMoCo	7,0	1,7	8,7
TBAPWCo	6,8	0,7	7,5
TBAPWMn	5,5	1,1	6,6
TBAPWFe	4,0	1,2	5,2
TBAPWCu	3,6	0,8	4,4

The best activity is obtained with catalyst containing molybdenum and cobalt in addenda and lacunary positions respectively. The Co containing salts prepared from tungstophosphoric acid known to be strong acid yield more cyclooctanone than Co salts of molybdophosphoric acid, which is known to possess redox properties. The catalytic activity of prepared salts strongly depends on the type of transition metal.

Encapsulation of active compounds in emulsions cores.

PhD research project N204 255934 [2008-2010]
(Professor Piotr Warszyński DScEng, Krzysztof Szczepanowicz MSc)

The sequential adsorption of polyelectrolytes (PE) is considered as a convenient method to obtain microcapsules' shells on colloidal cores. Solid particles (polystyrene latex, porous silica, $CaCO_3$) are most often used as cores for formation of capsules, which may contain some active ingredient. Alternatively the solid core can be dissolved to leave the hollow shell, which can be then refilled with the desired composition. The disadvantage of that method can be traces of the destructed core trapped in the capsule and, what is even more important, low efficiency of the loading of the active substance into the hollow shells. Use of emulsions droplets as liquid cores give us the possibility to encapsulate oil soluble active components with control of size and shell properties of obtained capsules.

In 2010 we were concentrated on preparation of polyelectrolyte capsules containing model drugs (Vitamin A or beta-carotene) based on emulsion droplets. The multilayer shells on emulsion droplets were constructed by subsequent adsorption of polyelectrolytes from their solutions without the intermediate rinsing step (using saturation method). Capsules were obtained with average droplets size 60-100nm (Fig. 1). Figure 2 illustrates typical zig-zag dependence of zeta potential of capsules on the adsorption of subsequent PLL and PGA layers.

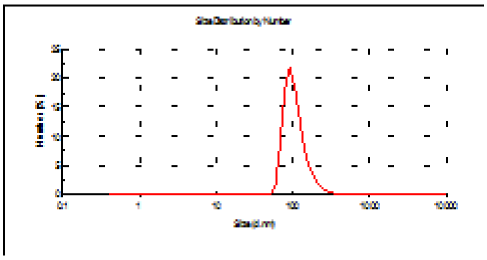


Figure 1. Size distribution of nanocapsules AOT(PLL/PGA)$_n$

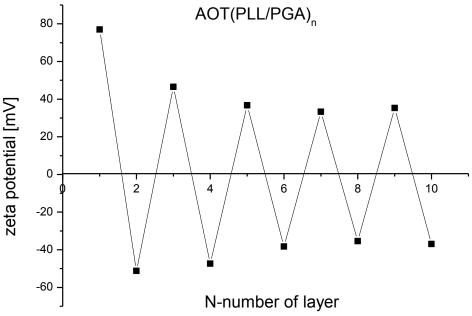


Figure 2. Zeta potential of capsules on formation of the consecutive layers of polyelectrolyte shell.

Bio-medical applications of nanocapsules require the selection of biocompatible polyelectrolytes and the specific shell modification. In particular formation of PEG corona at the capsules surface is a one of the available methods to prevent serum protein adsorption and non-specific binding of capsules to cells. We synthesized the PGA-g-PEG copolymer, which was then used to create pegylated outermost layer of the AOT(PLL/PGA)$_n$ capsules.

Conformations of Selected Globular Proteins in Aqueous Solutions and on Interfaces of Controlled Heterogeneity

PhD research project N N204 166336 [2009-2011]
(Professor Zbigniew Adamczyk DScEng, Monika Wasilewska MSc)

Mechanisms of fibrinogen adsorption on the mica/electrolyte interface were investigated using the streaming potential method. From these measurements, the apparent zeta potential of fibrinogen monolayers was calculated, which exhibits the unique relationships with the coverage of the protein. In Fig. 1 results of these measurements are show, carried out for pH=3.5 and the ionic strength of 10^{-2} M, NaCl. These experimental data were interpreted in terms of known theoretical approaches, especially the Gouy-Chapman model neglecting the heterogeneity of charge distribution due to adsorbed protein molecules. As can be seen (dashed line in Fig. 1) this model proved inadequate. Similarly, the theoretical model postulating an unoriented adsorption of fibrinogen was also improper (dashed-dotted line in Fig. 1). On the contrary, the experimental data were properly reflected by our model postulating a side-on adsorption of fibrinogen (solid line in Fig. 1). It is also interesting to mention that the experimental results for fibrinogen are very similar to experimental data obtained for the A500 latex monolayer (depicted by hallow circles in Fig. 1). Therfore, these measurements enabled one to conclude that fibrinogen adsorption on mica proceeded according to the side-on, irreversible mechanism.

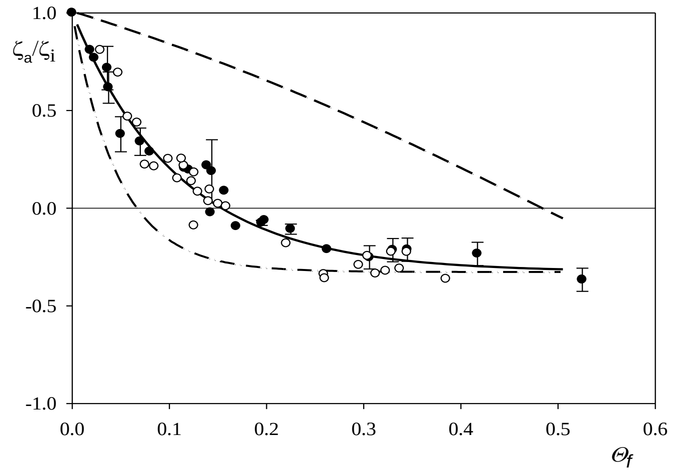


Figure 1. The dependence of the normalized zeta potential of mica ζ_a/ζ_i on the coverage of fibrinogen, Θ_f. The full points (●) denote experimental results obtained for pH=3.5, T=293 K, I=10^{-2} M, ζ_p/ζ_i=-0.46. The empty points
(○) denote results obtained for the A500 latex particles on mica. The dashed lines show the results calculated from the Gouy-Chapman model (GC). The solid lines represent exact theoretical results derived from our model, postulating
a side-on adsorption mechanism of fibrinogen and the dashed- dotted lines show theoretical results predicted for the end-on adsorption model.

The Physico-chemical Properties of Bifunctional Catalysts and their Catalytic Activity in Direct Syngas-to-Dimethyleter Process

PhD research project N N204 279937 [2009-2011]
(Assoc. Professor Ryszard Grabowski DSc, Michał Śliwa MSc)

The synthesized mixed oxide catalysts consisting of Cu, Al, Zr, Zn, Ga, Mn were obtained by co-precipitation and citric method. Next, these catalysts were characterized by the following techniques: TPR, SEM/EDS, ICP-OES and used as a metallic component of bifunctional catalyst for the direct synthesis of dimethyl ether from syngas (STD process). The commercially available montmorillonite K10 was applied as an acidic function of bifunctional catalyst. These two components were combined by mechanical mixing in the volume ratio of metallic to acidic function equal 2:1.

The ICP-OES analysis showed that experimental composition of the metallic components is in good agreement with the theoretical composition.

The TPR measurements revealed that catalysts from both metallic series are described by one sharp TPR peak, related to CuO reduction. The metallic catalysts obtained by co-precipitation method are easier reduced then their equivalent catalysts, which were synthesized by citric method. The lower reduction temperatures, in case of catalysts from co-precipitation series result from the smaller CuO crystallites present in these samples and higher Cu dispersion in comparison with catalysts from citric series. The substitution of Al with Zr leads to the catalysts of better reducibility.

The results obtained form XRD, TPR and N_2O decomposition clearly show the existence of proportionality between crystallites seizes of CuO in fresh catalyst and the Cu present on the surface of the reduced catalyst (Fig. 1).

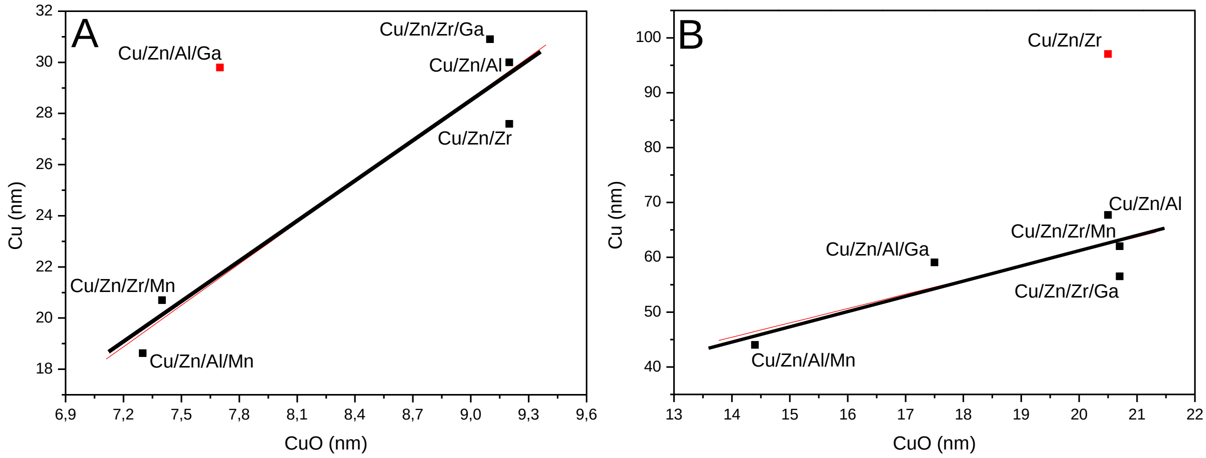


Figure 1. Correlation between crystallites sizes of CuO and Cu: A – co-precipitation method, B – citric method

The SEM/EDS analysis confirmed the higher concentration of Cu on the surface of the samples with higher Cu dispersion.

All bifunctional catalysts are active in the STD process and show maximum activity in the temperature range between 290-300^{o}C. The bifunctional catalysts, which contain Zr instead of Al exhibit higher yields to dimethyl ether. The observed improvement in the activity is connected with facilitated reduction of CuO in these samples. The highest yield to dimethyl ether was obtained for the bifunctional catalyst composed of Cu, Zn, Zr, Mn, (Y_{dme}=45%) and Cu, Zn, Zr, (Y_{dme}=35%) which were synthesized by co-precipitation and citric method respectively.

Mechanisms of Irreversible Adsorption of Nanoparticles and Selected Proteins on Interfaces Determined by Electrokientic Methods and the AFM

PhD research project N 204 137537 [2009-2011]
(Professor Zbigniew Adamczyk DScEng, Maria Zaucha MSc)

model, enabling calculations of the streaming potential for surfaces covered by nanoparticles, polymers and proteins. This has an essential significance for elaborating of a sensitive method for detection of trace amounts of proteins in solutions, working for the range below 1 ppm. In the first stage of our work, experimental measurements were performed for model colloid suspension of positively charge polystyrene latex particles (the A500 sample) having a well-defined surface charge and a high monodispersity degree. Results of these experiments can be used as convenient reference systems for interpreting adsorption kinetics of globular proteins, in particular the mechanism of the antigen/antibody interactions. In Fig. 1 results of these measurements performer by the streaming potential method are presented for the A500 latex, having the average diameter of 520 nm. As can be seen, the normalized zeta potential of mica surface determined in these measurements increased abruptly with the coverage of latex coverage. Then, it attains the limiting value equal to 0.71 of the bulk zeta potential of the latex. Thus, as can be noticed, contrary to intuition, this limiting value is much smaller than the zeta potential value of the latex determined in the bulk using the microelectrophoretic method. It is also worthwhile to mention that the experimental data are well reflected by the theoretical predictions derived by assuming the irreversible, 3D adsorption mechanism of latex (solid line in Fig. 1). An important conclusion, chich can be derived from the results shown in Fig. 1 is that the streaming potential method can be used as an effective tool for a precise determination of the kinetic of adsorption of colloid particles on solid substrates.

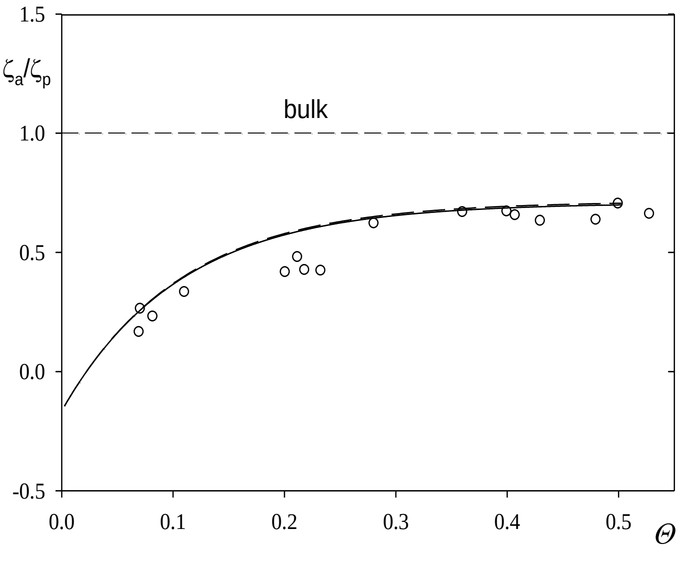


Figure 1. The dependence of the normalized zeta potential of mica ζ_a / ζ_p on the coverage of particles, Θ. The points denote experimental results obtained for the A500 latex, (pH = 5.5, T = 293 K and $I = 9\text{x}10^{-3}$ M, $MgCl_2$). The solid line represent exact theoretical results derived from our theoretical approach. The dashed line denotes the limiting results of zeta potential for the latex particles in the bulk determined by microelectrophoresis.

Influence of Cationic Surfactants and pH on Kinetics of the Three Phase Contact Formation at Solid Surfaces of Low Hydrophobicity

PhD research projekt No: N N204 179439 [2010-2012]
(Professor Kazimierz Małysa DSc, Anna Niecikowska MScEng)

The project aims at determination of influence of cationic surfactants and the solution pH on kinetic of the three-phase contact (gas/liquid/solid) formation at solid surfaces of low hydrophobicity, under dynamic conditions. Three-phase contact is formed when a liquid (wetting) film is ruptured during the bubble collisions with the solid surface. Stability of the wetting films is affected by many factors amongst which the most important are hydrophilic/hydrophobic properties of solid surface, surface roughness, presence of surface active substances at film interfaces (type and concentration), state of the adsorption layers. Electrostatic interaction between liquid/gas and liquid/solid interfaces can stabilize or destabilize the wetting films formed at solid surfaces of low hydrophobicity. The electrical properties of liquid/gas and liquid/solid interfaces can be modified by adsorption of surface active substances and variations of the solution pH.

The experiments performed aimed at evaluation of the influence of cationic surfactants on course of the bubble collisions with solid surface and kinetic of the three-phase contact formation. Mica, which is the solid having well defined and characterized the electrical surface properties was used in the experiments. Mica surface is completely wetted by water and is negatively charged practically within entire range of pH. Properties of the liquid/gas interface (bubble surface) were modified by adsorption of cationic surfactants; dodecyltrimathylammonium bromide (DDTABr) and cethymtrimethylammonium bromide (CTABr). Measurements were carried out for two locations of the solid/liquid interface, 10mm and 100mm, from the point (capillary orifice) of the bubble formation. When the bubble rises in surfactant solution then the dynamic architecture of the adsorption layer, i.e. non-equilibrium distribution of surfactant particles over the bubble surface, can be established. Formation of the dynamic adsorption layer (DAL) means that the adsorption coverage is at minimum at the upstream pole of the moving bubble (practically devoid of any surfactant), while at the rear pole is higher than the equilibrium coverage. Processes of adsorption and de-sorption of surfactant molecules at the bubble surface occur simultaneously and continuously during the bubble motion and collisions. State of the adsorption layer and its dynamic architecture influence the bubble velocity and it important factor affecting the kinetic and time of the three-phase contact formation, because top pole of the rising bubble forms bottom interface of the liquid film formed during the bubble collision with solid surface. It was found that the time of the three-phase formation at mica surface located at longer distance from the capillary orifice (100mm) was significantly prolonged. The results so far obtained show that the dynamic adsorption layer formation, over the bubble surface, affects kinetics of the three phase contact formation at mica surface in solutions of the cationic surfactants studied (DDTABr and CTABr).

Scientific networks
of the Ministry of Science and Higher Education

SURUZ Surfactants and Dispersed Systems in Theory and Practice

(project coordinators: Professor Piotr Warszyński DScEng,
Professor Kazimierz Małysa DSc)

The main aim of the Scientific Network SURUZ is the development of scientific cooperation and taking advantage of apparatus backup present in different research centres in Poland, which carry on studies on the surface active agents (surfactants) and colloidal systems. The teams of Scientific Network work on both basic and applicable researches on the new surfactants and technologies employing dispersed systems, thin films, adsorptive layers and so forth. The SURUZ project is accomplished by the teams from 11 research centres in Poland and the coordinator of the Network is Professor Piotr Warszyński (IKiFP PAN).

The tasks planned to carry on within the activity of the Network can be divided as following:

- The implementation of mutual research topics, supplemental or complementary to the tasks pursued within the basic, statutory activity of the units creating Scientific Network. The aim of these research is presented below.
- The exchange of scientific personnel as well as PhD students for optimalization of using the research infrastructure accesible for several participants of the Network. Theextend of the possibility of using complementary research methods aiming at the solution of scientific problems.
- The organization of workshops intended mainly for young scientists, which will give them an opportunity to discuss about their research results and to solve emerging problems with more experienced scientists.
- The organization of meetings of the teams participating in the project for the presentation of main achievements, as well as for the discussions.
- The extend of the research area which aims at the preparation of mutual scientific projects, both national and international, especially within the 7th Framework Programme of the European Union.
- The establishing, controlling and coordinating of the researches performed within the Network; planning expenses for several tasks and controlling if the granted funds are utilized in a correct way.

The research proposed within the Scientific Network SURUZ include three priority scientific topics:

I. Surfactants and dispersed systems – synthesis and physicochemical characteristic.
II. Dispersed systems of importance for biomedicine.
III. Dispersed systems of importance for technology.

PV-TECH Development of New Technologies and Research Techniques in Area of Photovoltaic Cells

(subject leader: Robert Socha PhD)

The increase of industrial and household demand on electricity and the necessity to fulfill the CO_2 regulations result with growing importance of the ‘pure’ energy obtained from photovoltaic cell. Additionally, the silicon shortage in the global market, followed by increasing silicon price, results in the need to utilize silicon waste from the electronic industry that leads to ‘multicrystalline silicon ribbon’ production, which can be applied in photovoltaic. PV-Tech network should help solution of above mentioned problems. Therefore, the project has following tasks:

a) development of new technologies in photovoltaic cell production i.e. dedicated mainly to multicrystalline silicon ribbon cells,
b) development of the research techniques dedicated to production and to analysis of the final product.

In the frame of the project, ICSC PAS performs analytical survey of intermediate and final stages of the silicon wafer/ribbon preparation. The stages consist: catalysts deposition for silicon etching, silicon surface etching and electric contacts formation. In these studies, the surface characterization of the delivered samples is performed by the means of microscopy (SEM) and spectroscopy (XPS, AES, EDX). Moreover, ICSC PAS delivers the test samples of the chemicals that can be applied as catalysts for silicon etching process or as materials that increase the internal reflection of light in the photovoltaic cell body.

BIONAN Molecular Mechanisms of Interactions in Biological Nanosystems and in Biologically Active Systems modified with Nanoparticles

(subjects leaders: Professor Piotr Warszyński DScEng, Professor Józef Korecki DSc)

Understanding of molecular mechanisms responsible for alterations in the liquidity of biological membranes is of primary importance for both biologists and physicians, pharmacists as well as for physicists and chemists working on catalytic processes. It is known that destructive processes due to oxidative stress take place in living organisms. As a result singlet oxygen or free oxygen radicals are produced, causing the destruction of lipid and protein structures. Thus, the recognition of molecular mechanism which enables controlling these processes is crucial for designing of new generation drugs. These medicines exploit the encapsulation of pharmaceutically active substances. Such created capsules should be specifically delivered to the target in the organism. Moreover, the dosage of drug released should also be controlled. Therefore, a non-invasive method of controlling the transport and the permeability of the capsules is required. The implementation of nanosensors/nanomarkers based on modified carbon nanofibers, whose minor toxicity for living organisms has been proved, might significantly improve the selectivity and effectiveness of encapsuled drugs.

The researches proposed within BIONAN project are meant for studying of the activity of biologically active systems depending on their interaction with the surfaces with well defined physicochemical properties or with the nanoparticles in solution. Understanding of adhesive mechanisms at molecular level (interactions at membrane - nanolayer interface) will contribute to the conscious modelling of systems of required molecular dynamic and its affinity to specified structures.

The aim of research carried on within BIONAN project is:

I. A built-in actions of physicians, chemists and biologists in the study of natural photosyntetic membranes and their artificial model equivalents suspended in solutions or moved onto defined solid surfaces.
II. The study of physicochemical properties of natural and artificial systems under the influence of controlled, variable exterior factors.
III. The establishment of optimal environment conditions and properties of the surfaces for obtaining the highest possible activity of examined, biologically active systems, or for obtaining the biochemical activity in model systems.
IV. The development of manufacturing methods of biologically active systems with specific surface properties.
V. The evaluation of biological nanosystems (components of photosyntetic membranes) as a platform for the construction of nanosystems that converts light energy into chemical energy.

The BIONAN network is coordinated by the Institute of Physics and Applied Informatics of AGH University of Technology.

Commissioned research projects of the Ministry of Science and Higher Education

Chemistry of Perspective Carbon Transformation

Multifunctional Catalysts Derived from Layered Minerals for Single Stage Process Syngas→Methanol→Dimethyether

Commissioned research project PBZ-MEiN-2/2/2006 [2006-2010]
(project leader: Professor Ewa Serwicka-Bahranowska DSc)

In 2010 realization of the project devoted to development of novel bifunctional catalyst for direct transformation of syngas to dimethylether (STD), via methanol as an intermediate, has been completed. Catalysts for the stage of methanol synthesis were derived from hydrotalcite-like precursors, those for methanol dehydration to DME were prepared by modification of montmorillonite. The hybrid catalyst was prepared by mechanical mixing of redox and acid components. Reaction was carried out at in a fixed bed flow reactor at 40 bar pressure, using syngas of composition H_2:CO:CO_2=65:30:5, in the temperature range 250-290^{o}C and GHSV=3600 h^{-1}.

Investigations carried out within the project resulted in:

a) identification of main factors controlling the catalytic activity in methanol synthesis from syngas of hydrotalcite-derived systems containing Cu, Zn and Al as chief structure-forming elements. In particular, it has been found that the key prerequisite for achieving high dispersion of metallic copper is preparation of a hydrotalcite precursor with possibly high crystallinity.

b) synthesis of acid catalysts efficient in methanol dehydration to DME basing on natural silicate - montmorillonite,

c) selection of hydrotalcite-derived catalysts most active and selective in methanol synthesis, and catalysts based on silicate-based catalysts most active and selective in methanol dehydration as potential components of hybrid catalyst for STD process and optimization of its composition. It has been found that best performance in STD process is ensured by hybrid systems built of CuZnAl redox component derived from non-aged hydrotalcite co-precipitated at pH=7, and acid component constituting either untreated montmorillonite K10 or montmorillonite K10 covered with monolayer of $H_3PW_{12}O_{40}$ heteropolyacid.

Hybrid catalysts prepared in the course of this project belong to the most active reported in the literature.

Investigations of the Physicochemical Properties of the Passive Layers on Aluminum, Magnesium and Titanium Alloys and Zn-Ni, Zn-Co, Sn-Zn, Co-P and Ni-P Alloy Coatings on Steel

Commissioned research project PBZ-MNiSW-01/I/2007 [2008-2010]
(project leader: Assoc. Professor Paweł Nowak DScEng)

Titanium and its alloys show very high corrosion resistance and excellent mechanical properties. So, they found wide application both in the aerospace industry, as a construction material, as well as in medicine, as a material for implants (due to their biocompatibility). Corrosion of titanium and its alloys at the temperature of 37^{o}C degree and in the solutions similar to physiological solutions is widely described in the literature. However from the point of view of the aerospace industry much more important would be the corrosion resistance in more aggressive media, that the parts of the machines are subjected to during their exploitation (salt brines present in airports during the winter). 5% NaCl solution may be used as a medium simulating such aggressive environment. The second metal which alloys are widely used in aviation is aluminum. Aluminum alloys has very high hardness and low specific gravity. The goal of the works, conducted jointly with the team from Silesian Technical University in 2010 year was the development of new procedures enabling the preparation of the protective layers on the surface of aluminum and titanium alloys, which would increase the corrosion resistance of these materials in aggressive environments occurring during the exploitation of airplanes.

The measurements were carried out on samples prepared at the Technical University of Silesia. Three series of samples were investigated - two series of alloys of titanium and a series of aluminum alloy. On the surfaces of investigated samples the conversion coating layers were produced, representing the first protection against corrosion. Different passivation baths (fluorosilicate, silicate, phosphate and oxalic acid for aluminum alloy) and passivation conditions (time, temperature and voltage of passivation) were applied in sample preparations. The measurements of corrosion resistance were performed in 5% NaCl solution at the temperature of 25 or 30^{o}C. For each sample a series of impedance spectra at the predetermined time intervals was registered to follow changes in the corrosion resistance. The equation describing the impedance of a selected electrical equivalent circuit was least-squares fitted to measured impedance data which enabled the calculation of the corrosion resistance.

The corrosion resistance of the samples differed strongly, depending on the procedure of preparation. The best corrosion resistance showed samples prepared in the silicate bath. Corrosion resistance of some samples from that series practically did not change for three months. Protective layers obtained using phosphate bath showed lower resistance, the samples obtained at highest voltage were more stable. Finally, the samples prepared using fluorosilicate bath showed the lowest corrosion resistance, practically similar to uncoated titanium alloy. The best coatings having highest corrosion resistance obtained on aluminum alloy surfaces were those that were anodised for 60 minutes at 40V. The most corrosion resistant coatings were obtained when concentration of oxalic acid in the solution equaled 80 g dcm^{-3}.

"Technological Initiative I" programme projects of the National Centre of Research & Deverlopment

Development of a New, Wasteless Technology of Cyclohexanol/Cyclohexanone Synthesis (Intermediates in Nylon 6 and Nylon 66 Synthesis) from Benzene *via* Cyclohexene

Research Project Technological Initiative 1 KB/69/13848/IT1-B/U/08 [2008-2010]
(project leader: Professor Ewa Serwicka-Bahranowska DSc)

Year 2010 was devoted to realization of stage B of the project, which aimed at paving way for implementation of the newly developed technology. The project was realized in collaboration with the Institute of Industrial Chemistry (IIC) in Warsaw. The basis for stage B were the results of research performed in stage A, presented in the final report in December 2009, in particular those obtained in the experiments carried out at large laboratory scale. The outcome of stage A allowed for optimization of pressure and temperature conditions for hydrogenation of benzene and hydration of cyclohexene, and selection of most promising catalysts for both processes. In the case of hydrogenation metallic ruthenium was the catalyst of choice, in the case of hydration a zeolite catalyst was selected. ICSC PAS carried out complementary studies aimed at further improvement of the hydrogenation catalyst, concentrating at modification of the preparation procedure and the manner of reagent addition. It has been demonstrated that in some cases it is advantageous to use powdered materials instead of solutions. It was concluded that among factors vital for the engineering analysis are the physicochemical properties of the materials (reagents and catalysts) and quantitative assessment of their consumption. Detailed process design of pilot installation for the synthesis of cyclohexanol from benzene via cyclohexene as an intermediate, with output capacity of 1000 ton of cyclohexanol per year was prepared by specialist engineering department Biuro Projektów Zakładów Azotowych "***Biprozat***", under author's supervision by ICSC PAS and IIC. Conceptual design assumed continuous work of all key production centers, with the exception of the catalyst manufacturing centre, working periodically. Engineering design of the pilot installation considers the following aspects:

1. 8000 hour work per year
2. 15 years exploitation time,
3. 20 % design reserve of the installation,
4. possibility of the total emptying of hydrogenation reactors,
5. minimum quality requirements for reagents,
6. transportation of raw materials, products and catalysts,
7. volume of the reactors,
8. type of the construction materials,
9. process steering,
10. catalyst regeneration.

Designed installation manufacturing cyclohexanol from benzene via cyclohexene does not produce wastes. Cyclohexane appearing as a byproduct in hydrogenation centre is an important substrate for manufacturing of cyclohexanol/cyclohexanone mixture.

"Homing Plus" programme projects of the Polish Foundation for Science

Structure and Electric Properties of the Composite Films Containing Conductive Nanoparticles

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

As the goal of the project is to obtain chemical sensors, nanoparticles chosen have to follow some specific criteria. They have to be sensitive to the presence of some particular compounds in the environment, i.e. hydrogen peroxide, to be able to detect them. According to the scientific literature Prussian blue nanoparticles seem to fulfill those conditions. Thus, they were chosen as model electroactive nanoparticles. Some different methods of synthesis of the Prussian blue nanoparticles were tested. For all obtained nanoparticles their size, zeta potential and the stability in time was determined using Zetasizer Nano from Malvern Instruments Ltd. Basing on the results of conducted experiments, the nanoparticles obtained with the most optimal method had the size c.a. 10nm in diameter and they met all the criteria to be used in further studies.

Nanocomposites: polyelectrolyte/Prussian blue nanoparticles were obtained using alternative adsorption from the solutions of oppositely charged polyions/nanoparticles. Deposition of Prussian blue nanoparticles on polyelectrolyte monolayer/multilayer was proved by *in situ* experiments using Quartz Crystal Microbalance. It was found that the amount of Prussian blue deposited depended on the polyelectrolyte film used to modify quartz crystal. Some of the results of the kinetics of Prussian blue deposition on the layer of polyethylenimine (PEI) are depicted in Fig.1. Black curve refers to nanoparticles' deposition on PEI layer adsorbed from the solution of pH=10.3 (natural for PEI). Red curve refers to nanoparticles' deposition on PEI layer adsorbed from the solution of pH=7.

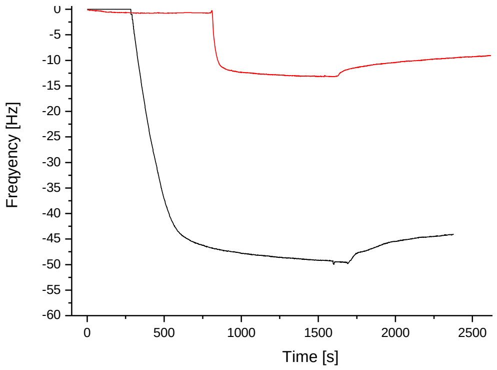


Figure 1. Decrease of the vibration frequency of the QCM crystal referring to the increase of the mass due to the adsorption of Prussian blue on polyethylenimine layer deposited from the solution of pH=10.3 (black curve) and from the solution of pH=7 (red curve).

As the next step electroactive properties of polyelectrolyte multilayers with embedded nanoparticles were studied with cyclic voltammetry. It was done using rotating disc electrode from Metrohm Autolab B.V. We found that the current increased with number of deposited Prussian blue layers.

EU 6th Framework Programme projects

IDECAT Integrated Design of Catalytic Materials for a Sustainable Production

UE NoE Project IDECAT NMP2-011730-2 [2005-2010]
(project leader: Professor Małgorzata Witko DSc)

IDECAT (Integrated Design of Catalytic Naomaterials for a Sustainable Production) is a Network of Excellence (NoE) launched in 2005 within 6th EU Framework Programme for Research and Technical Development. The Network is coordinated by the Consorzio Interuniversitario per la Scienza e Tecnologia dei Materiali, Italy and integrates 37 laboratories from 17 institutions: Consorzio Interuniversitario per la Scienza e Tecnologia dei Materiali, Italy; Ghent University, Belgium; Katholieke University Leuven, Belgium; J. Heyrovsky Institute of Physical Chemistry, Czech Republic; Helsinki University of Technology, Finland; Centre Nationale de la Recherche Scientifique, France; Max-Planck-Gesellschaft, Germany; Leibnitz Institute of Organic Catalysis, Germany; Technische University Munchen, Germany; Consiglio Nazionale delle Ricerche, Italy; NRSC-Catalysis, Tha Netherlands; Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Poland; Consejo Superior de Investigaciones Cientificas, Spain; Stockholm University, Sweden; University St. Andrews, United Kingdom; University of Southampton, United Kingdom; Ecole Polytechnique Federale de Lausanne, Switzerland.

The aim of the IDECAT NoE is to achieve a lasting integration between the main European Institutions in the area of heterogeneous, homogeneous and bio-catalysis via creating a coherent framework of research, know-how, training, promotion of science, spreading of excellence and technology transfer between those various catalysis communities. The Network is divided into 5 programmes (Joint Programme of Integration, Joint Programme of Research, Joint Programme of Spreading Excellence, Joint Programme of Science and Technology Transfer and Management) and 13 Workpackages.

Joint Programme of Integration has been aimed to achieve long-term integration within European Research Institute of Catalysis (ERIC) which has been established as a legal entity under the Law of Belgium in the form of a non profit association - A.I.S.B.L (Association International Sans Bout Lucratif). ERIC is basically composed of the vast majority of IDECAT partners, integrating the remaining institutions with the Framework Agreement. According to the Mission, ERIC aims to gather highly specialised expertise and know-how at the excellence level and serve as interface and platform to communicate industrial and societal needs in the field. Moreover, within the JPI, electronic tools to facilitate the gathering of information and allow better communication between the integrated groups have been further improved. Director of the ICSC as appointed as a member of the Council of Directors of ERIC.

On February 16th, 2010 in Firenze the meeting of the Council of Directors of ERIC was held on which the www page of ERIC was presented and some aspects of acceptation new non-IDECAT academic and industrial members were discussed.

ISCS together with Ghent University coordinates the preparation of internet tools for effective communication and information exchange between network members.

In frames of package "Creating and mastering nano-objects and nano-organisation" ICSC participated in bi- and multilateral research projects "Nanostructured multimodal porous materials with grafted organometallic single-sites – new catalysis for alkane metathesis ans C-H bond activation", "Design of new catalysts based on nanostructured micr-mesoporous solid acids for environmentally clean diesel fuels", "Nanostructured carbon composites for bio-sensing applications" and "Novel catalysts based on organometallic macrocycles supported on porous structures derived from layered minerals".

ICSC was actively participating in the vast majority of the Network activities and tasks.

NANOMEDPART Multifunctional Particulate System for Nanomedicine

NANOMEDPART [2007-2010] in frameworks of ERA-NET MATERA project
(project coordinator: Professor Piotr Warszyński DScEng)

Due to their great application potential, the development of nanocontainers is currently one of the main topics in scientific research and in the last few years the major progress in the synthesis and applications of various types of micro and nanocontainers has been achieved. Nanoencapsulation has the high application potential in medicine since it can be used to improve the compatibility of lyophilic, poorly water-soluble or even water-insoluble active compounds with physiological fluids and can protect therapeutic molecules from the destructive influence of external environment. Nanocapsules can be also used in the specific drug delivery system, as they can penetrate the cell membrane. Moreover they can be functionalized for the delivery to the specific cells or organs.

The objective of the project was to develop effective methods for preparation of nanoparticles/nanocapsules and modification of their surfaces for targeted drug delivery (anticancereous, antimicrobial). The main scientific and technical challenges of the project were the formation of stable particles and capsules in the nanosized range containing active compounds with shells tailored for cancer therapy and antimicrobial applications. The project was realized by the consortium consisting of: Institute of Catalysis and Surface Chemistry PAS, SINTEF Materials and Chemistry Oslo, Hebrew University Jerusalem, Institute for Cancer Research at the Norwegian Radium Hospital Oslo and Chemistry Dept. of Wrocław University of Technology.

In 2010 we concentrated on the specific shell modification/functionalization for bio-medical application of nanocapsules (Fig.1). Formation of PEG corona at the capsules surface is one of the available methods to prevent serum protein adsorption and non-specific binding to cells (stealth effect). In addition, the PEG side chains can be functionalized with bio-ligands (antibodies), while retaining resistance to unspecific protein adsorption. The immobilization of antibodies on capsules' surface allows intelligent drug targeting. Biotinylated nanocapsules were prepared using synthesized PGA-g-PEG-Biotin copolymer. Streptavidin was used as a bridge between capsules and antibody. Binding of streptavidin was achieved by specific interaction with biotin groups (biotinylated capsules and biotinylated antibody).

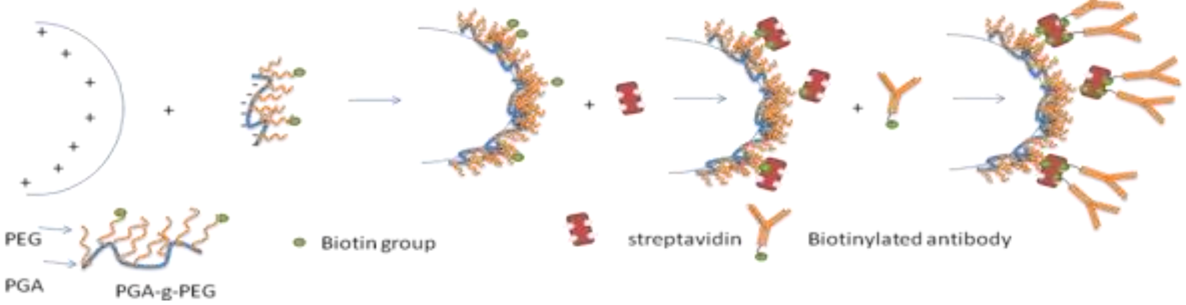


Figure 1. The schematic representation of modification and fictionalization of nanocapsules

We tested biocompatibility of the nanocapsules AOT(PLL/PGA)$_{3,5}$PGA-g-PEG in co-culture with a human cell line, which is very sensitive to toxic components such as surfactants and other chemicals. The cytotoxicity of the samples of nanocapsules was tested in a proliferation assay. Results indicated that the capsules can be used in high concentrations without harming the cells. Additionally they exhibited minimal non-specific binding to the white blood cells.

PARFUN Nanoscale Surface Treatments to Functionalise Polymer Particles for Electronic Applications

Controlled attachment of polystyrene particles at PEI modified surfaces

PARFUN [2007-2010] in frameworks of ERA-NET MNT project
(project leader: Professor Piotr Warszyński DScEng)

The main objective of the project is to develop a new generation of spacer particles for LCD based on new concepts for surface treatment of polymer particles, and thereby also greatly improve the manufacturing process of LCD screens. There is a strong need for spacers with a careful control of the particle size and size distribution together with suitable surface properties. The introduction of flexible displays that can be bend and twisted during their use will need better adhesion between the spacers and the inner surface of the display. Also new and improved techniques for distribution of the spacers in the display is needed.

The aim of our activities in the project was to develop methods for surface modification of glass and/or plastic plates (polyimid - PI) in order to obtain better adhesion of micron size polystyrene particles in well controlled patterns. For surface modification cationic polyelectrolyte polyethyleneimine (PEI) was used. PEI of molecular weight 700 kD was adsorbed from 500 ppm aqueous, ethanol, and isopropanol solutions by microcontact printing. The adhesion of latex particles, provided by project partners was examined from water, ethanol and isopropanol suspension. Figure 1 illustrates pattern on the surface of silicon wafer obtained by the microcontact printing of PEI and successive adsorption of CONPART latex particles provided by project partners.

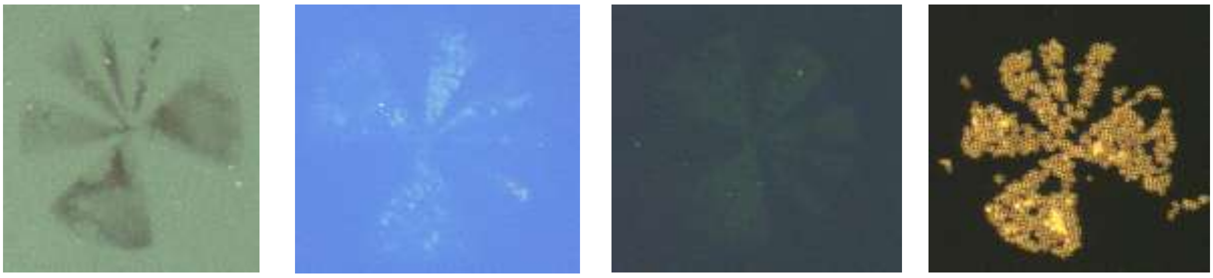


Figure 1. Patterns received by the microcontact painting technique followed by adsorption of latex particles. From left: PEI pattern with the average thickness 10 nm (polarization microscope), the same pattern observed with SARFUS technique, PEI pattern with adsorbe fluorescent latex particles (diameter 100 nm), PEI pattern with deposited latex particles with diameter3.8 μm.

We found high selectivity of particle adhesion at the surfaces covered with PEI film. The ratios of CONPART particles deposited from isopropanol suspension at covered surface to the uncovered one were: 10:1 for polyimide plates and 300:1 for glass plates.

In order to obtain conductive spacer particles they were coated with silver nanoparticles in combination with conductive polyelectrolytes (PDOT-PSS, polypyrrol). The mechanical properties of coated particles were examined.

NANOREP II Multifunctional Surface Coatings and Highly Scratch Resistant Plastic Parts

Surface Modification of Nano- and Micron Size Plastic Modifiers

NANOREP II [2007-2010] in frameworks of ERA-NET MNT project
(project leader: Professor Piotr Warszyński DScEng)

The main objective of the NANOREP II project is the development of technology that will allow application of nanosized particles and nanostructured coating materials with multifunctional properties for (near)future high quality polymer products. The project is aiming to create a strong transnational network of research activities in the field of nanoparticle materials and bring the partners a step forward into implementation of nanotechnology in their products and applications.

The aim of our investigation was to determine the optimal conditions to obtain the surface treated glass beads with good adhesion and compatibility with termo- and fluoroplastics. Adhesion of microspheres was examined by colloidal probe AFM, based on the force measurement between glass beads with various surface modification attached to the cantilever of AFM probe and different surfaces (glass, silicon, bare and modified with surfaktants and polyelectrolytes). Fig. 1. illustrates summary of the results of measurements of adhesion forces between surface modified glass microspheres (diameter 20-50 μm) and glass, silicon and polyimide surfaces. We found that measured adhesion forces were in the range from $8.2\cdot10^{-7}$ N to $1.6\cdot10^{-4}$ N. The largest forces were observed between surfaces with the same type of modification.

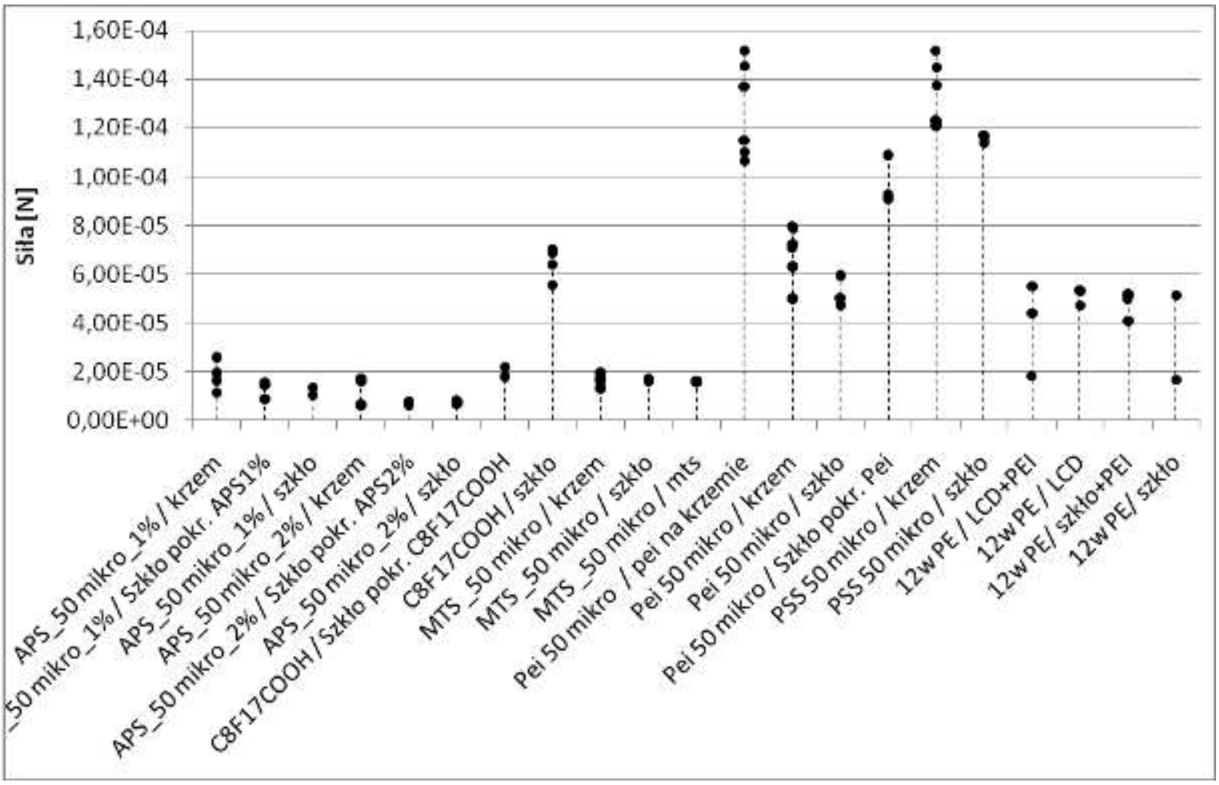


Figure 1. Summary of the adhesion forces between surface modified glass microspheres and glass, silicon and polyimide surfaces

EU 7th Framework Pprogramme projects

InGAS Integrated Gas Powertrain – Low Emission, CO_2 Optimised and Efficient CNG Engines for Passenger Cars and Light Duty Vehicles

EU 7th FP InGAS Collaborative Project [2008-2011]
(project leader: Professor Ewa Serwicka-Bahranowska DSc,
principal investigator: Tadeusz Mache, PhD)

InGAS is a large-scale international collaborative research project launched within 7th EU Framework Programme for Research and Technical Development. The project integrates 28 partners from 11 European Countries: Austria, Czech Republic, Denmark, Finland, France, Luxemburg, Germany, Poland, Sweden, Switzerland and Italy. The Consortium is coordinated by Centro Ricerche Fiat SCpA. Starting date of the project is 1st October 2008.

Main objective of the InGAS project is to deploy custom designed CNG engine integrated with specific aftertreatment systems applied to passenger cars and light duty vehicles able to achieve 10% higher fuel conversion efficiency than that of a corresponding 2006 Diesel vehicle and complying with an emission level lower that Euro 6.

Institute of Catalysis and Surface Chemistry is involved in Sub-project B2 "Aftertreatment for passengers cars CNG engines", Workpackage B2.2 "Advanced Catalysts Development". Research aims at design, synthesis, characterization and catalytic testing of new catalyst formulations for methane oxidation in CNG fueled engine exhausts, based on mixed transition metal oxides.

In 2010 most effort was directed at optimization of synthesis of catalysts based on mixed oxides derived from hydrotalcite-like precursors or prepared by sol-gel procedure from citrates. The synthesized solids were characterized with XRD, SEM, XPS, FT-IR, thermal analysis, chemical analysis (ICP-OES), nitrogen adsorption at 77 K, and TPR in the hydrogen flow. It has been demonstrated that addition of certain promoters at the stage of precursor synthesis resulted in a synergetic effect and was beneficial for the catalyst activity. Also, the use of appropriate support offers means for catalyst improvement, as it stabilizes dispersion of spinel phases, prevents rapid thermal degradation of mixed transition metal oxide active component, and renders the material ready for washcoating. Selected mixed oxide catalysts survive the 600^{o}C ageing conditions without loss in activity.

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

EU 7th FP NEXT-GTL Large-scale Integrating Project [2008-2011]
(project leader: Professor Małgorzata Witko DSc)

Electronic structure of heteropolyacids

DFT calculations were performed on the electronic structure of molybdenum and tungsten heteropolyanions ($PMo_{12}O_{40}^{3-}$ and $PW_{12}O_{40}^{3-}$), also with one addenda atom substituted by another transition metal (Co, Fe, Cu, V, Mo, Mn). The calculations were carried out using both cluster (Turbomole code) and periodic (VASP code) models. Results allowed for a detailed comparison of the Mo- and W-containing heteropolyacids. Main differences are in: distribution of the atomic charges; position of frontier orbitals; size of the band gap; bond lengths; positions of main peaks in IR spectra. Ion exchange in addenda position has a profound effect on the energy of oxygen vacancy formation in the Keggin structure, what directly influences activity in oxidation processes.

Theoretical modeling of interaction between $Pt/Pd(NHC)Cl_2$ complexes and methane

Calculations of the electronic structure of $Pt/Pd(NHC)Cl_2$ complexes and selected steps of methane (as CH_3^+ cation) adsorption were performed. Both metals form slightly distorted square structures in which HOMO and LUMO orbitals are mostly localized on metal centers. Two scenarios for methane activation are investigated. According to the first one, it is postulated that the Cl^- ligand is dissociated and methane is bound to the three-coordinate complex. The Cl^- dissociation is thermodynamically favourable. The geometry and electronic structures of the resulting $Pt/Pd(NHC)ClCH_3$ and $Pt/Pd(NHC)ClHCH_3$ complexes are described. The second possibility is the direct involvement of the chlorine ligand in C-H bond activation. The calculations preformed thus far indicate that the excitation from the singlet ground state to the triplet state of the catalyst is required. In that case, the interaction between methane and active center results in a considerable elongation (by 0.83 A) of one of the metal – ligand bonds.

Electronic structure of MoOxCy system

Calculations were performed for small Mo-O clusters (using Turbomole code) in order to establish a reference basis for simulations of oxycarbides, which are successfully used in conjunction with zeolites to activate the C-H bond in methane. Initial research consisted of calculating the electronic properties of active centres in small Mo-O clusters possessing geometries of the MoO_3 and MoO_2 oxides. Results showed: strong dependence of the atomic charges on metallic and bridging oxygen centres on the cluster size; weak dependence of the atomic charges on singly coordinated (molybdenyl) oxygen centres on the cluster size; strong dependence of the bond orders on the cluster size. Periodic simulations (using the VASP code) were also performed on the MoO_3 structure in which two oxygen atoms in every unit cell were exchanged with carbon. Considerable geometry changes were observed. In several cases CO groups were formed, bridging two neighbouring Mo centres. Also creation of C-C bonds was observed. Geometry changes were accompanied by a strong stabilization effect (ca. 4 eV).

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

EU 7th FP MUST Collaborative Project [2008-2011]
(project leader: Professor Piotr Warszyński DScEng)

The object of the MUST project is the development of new active ("self-healing") multi-level protective systems for future vehicle materials based on "smart" release nanocontainers incorporated in the polymer matrix, containing anticorrosive agents. Main objects of the investigations at the Institute of Catalysis and Surface Chemistry in 2010 year was the compatibility of nanocontainers and water traps with the polymer matrix as well as diffusion of water in the polymer matrix.

Two model coatings were chosen for the investigations: one organic solvent based epoxy resin and one water based epoxy resin, both supplied by other partners of the project. Synthetic layered silicate mineral (Laponite) and synthetic hydrogel (both as water-traps) as well as selected nanocontainers containing anticorrosive agents (mercaptobenzothiazole and cerium ions) were dispersed in the polymer matrix. The main investigation methods used were Infrared Attenuate Total Reflection Spectroscopy (IR ATR), Scanning Electron Microscopy (SEM), Fluorescence Microscopy (FM), Electrochemical Impedance Spectroscopy (EIS) and X-ray Photoelectron Spectroscopy (XPS).

The package of programs for the digital simulation of the water diffusion in the polymer matrix was developed. Results of the measurements of diffusion performed by IR ATR were compared with the results of digital simulation. Good agreement between the predictions of the digital simulation and the experimental results was obtained. Diffusion coefficients for water diffusion in the polymer matrixes used in the investigations were calculated. Those coefficients were used later on in the simulation of the behavior of protective coatings during the contact with corrosive environment.

One of the nanocontainer materials used were the multiwall carbon nanotubes (CNs). The crucial step in the preparation of the coatings was filling the CNs with the cerium nitrate (see fig. 1). The anticorrosive coatings on the surface of zinc galvanized steel and aluminum were prepared using cerium nitrate filled CNs. Preliminary results of the measurements of corrosion resistance by EIS showed the beneficial influence of cerium nitrate on the corrosion resistance of prepared coatings.

Figure 1. SEM picture of the carbon nanotube filled with $Ce(NO_3)_3$. Picture was made in the "compo" mode (reflected electrons). In that mode of acquisition the brightness of the pattern is proportional to z^2, where z is the atomic number of the atoms constituting the sample surface. Because cerium has much higher atomic number than carbon, regions rich in cerium look bright. Presented pictures strongly suggest that cerium was located inside the carbon nanotubes

Smart Monitoring of Historic Structures

EU 7th FP SMOOHS Collaborative Project [2008-2011]
(project leader: Michał Łukomski PhD)

The main aim of the project is to develop a wireless monitoring system of historic structures which could be used by conservation practitioners in the field. It will have a modular structure so that one can select monitoring modules and combinations of sensors to answer specific questions arising at an object.

An acoustic emission (AE) sensor will be utilized for monitoring the progress of damage for historic objects. It is necessary to elaborate a measuring methodology which will allow a continuous monitoring of materials for a long period of time (up to two years) especially that the system will be power supplied by a battery. The most important task is defining characteristics of the acoustic emission signals related to the damaging processes for different historic materials, as well as the elaboration of a method capable of separating the relevant signal from the environmental noise.

During the second year of the project the emphasis was placed on developing the best possible AE detection system capable of long-term monitoring in noisy environments (building facades or objects displayed in museums). In such a case, a very low level of signal in comparison to the environmental noise is expected. This situation requires especially effective filtering of any possible noise resulting from processes different than fracturing of object structure. Laboratory tests showed that it is not possible to find a single, characteristic frequency of acoustic emission signals correlated with the micro-damage. Signals are attenuated when passing through the material; their frequency is also disturbed by characteristics of the utilized detectors and amplifying electronics. As a result, it was decided to use a high-pass filtering just to cut off the low-frequency background noise rather than measure signals in a narrow, well-defined frequency window. The developed system was tested on a historic material – almost 100 year old wooden beams, taken from the roof construction of Palace Malvezzi (1560) in Bologna, Italy. The measuring schemes based on various AE detectors (wide-band: flat and multi-resonant and also narrow-band) as well as different frequency thresholds were tested during the mechanical loading of the wood. The results showed that the frequency filtering significantly improves the signal-to-noise ratio and allows discarding most of the unwanted signals obscuring the monitoring results.

The developed system was used also to monitor damaging processes induced by salt phase transitions and crystallisations. The measurements were performed in the Rathgen Research Laboratory (Berlin, Germany) on samples originating from the Ishtar Gate (575 BC, collection of the Pergamon Museum in Berlin) contaminated by NaCl and Na_2S04. The results will be processed at the beginning of the next year.

ROCARE ROman Cements for Architectural REstoration to New High Standards

EU 7th FP 226898 ROCARE Collaborative Project [2008-2011]
(project leader: Professor Roman Kozłowski DSc)

Highly hydraulic binders, known as natural or Roman cements, were key materials to decorate façades of buildings during the nineteenth and early twentieth centuries, a period of rapid urban growth in Europe. The former EU project ROCEM (2003-2006, coordinated by the institute) has re-established manufacturing of Roman cements at a pilot scale and initiated their use in conservation practice. The main steps of the new ROCARE project implemented in 2009-2012 are: scaling up of the production, laboratory studies to fully understand optimum conditions of mortar processing and handling in the conservation practice, and broad dissemination measures.

A number of elements of the mechanism of shrinkage cracking of Roman cement pastes and mortars, which is the key research task of the institute, were elucidated in the reporting period:

- the desiccation shrinkage of the materials diminishes strongly with the increasing aggregate content
- the desiccation shrinkage of the materials increases considerably with hydration time and change in the pore structure, related to the progressing hydration
- the critical strain at which the materials fail at tension, increases with the hydration time
- surface cracking of the pastes proceeds during fast drying and considerably weakens the structure of the specimens
- the total shrinkage of the paste and the mortar with the aggregate-to-cement ratio of 0.5 is greater than the critical strain at failure for all hydration times
- the total shrinkage of the mortar with the aggregate-to-cement ratio of 3.0 is greater than the critical strain at failure only for long hydration times, exceeding 28 days
- surface cracking caused by fast drying of the pastes considerably weakens structure of the specimens
- fast drying of mortars rich in aggregate and low shrinkage does not lead to the surface cracking, in contrast a slow relaxation of stresses due to creep is observed, which increases the critical strain.

The institute leads Workpackage 3 “Dissemination and marketing”. During the reporting period all meetings and reports required in the project schedule were prepared, as well as activities within this Workpackage in the subsequent phase of the project, in particular model conservation treatments of facades in various countries.

F3 Factory Flexible, Fast and Future Factory – European Chemistry Consortium Begins the Journey into the Future of Production

EC 7th FP CP-IP 228867-2 F3 Large-scale Integrating Project [2009-2013]
(project leader: Professor Piotr Warszyński DSc)

The F3 consortium's vision is that the EU's chemical industry's competitive position would be strongly enhanced if it could operate modular continuous plant (F3 plant), which combines world scale continuous plant efficiency, consistency and scalability with the versatility of batch operation. Our project will deliver such a radically new production mode based on:

- Plug–and–play modular chemical production technology, capable of widespread implementation throughout the chemical industry. This technology uses generic backbone facilities designed for rapid interfacing with standardized process equipment containers (PEC). The PEC house process equipment assemblies (PEA) composed of intensified process equipment for fast, flexible future chemical production
- Holistic process design methodology applying process intensification concepts and innovative decision tools. This will accelerate process development and provides a substantial reduction in energy consumption, raw material usage and plant volumes.

The F3 consortium of leading academic & research institutions and 7 major synthetic chemical producing industrial companies has 3 main goals:

1. To prove the technical feasibility of the F3 mode of manufacturing by building and operating a 0.1 to 30 kg/hr demonstration facility,
2. To demonstrate that operation of F3 plant will be more economical, eco-efficient and more sustainable than conventional production modes like large scale continuous or small to medium scale batch processing.
3. To drive a step change in the technology available to EU chemical production and engineering companies by designing intensified equipment for reaction and down stream processing, dissemination of standards for plug and play modular plant and providing open access to the backbone facility.

The main task of ICSC in the F3 project is to model properties of polyelectrolytes and copolymers based on the polyacrylic acids and to evaluate their adsorption properties, formation of thin polymer films and validation of performance of copolymers produced by project partners for the encapsulation of active compounds. This activity started in late 2010. Initial simulations of the polyelectrolyte adsorption at the charged, homogeneous surface were performed. The example of the snapshot of such simulations is illustrated in the figure.

EU COST Actions projects

Molecular Structure-Performance Relationships at the Surface of Functional Materials

Interfacial functionalization of (bi)-metallic nanoparticles to prepare highly active and selective catalysts: understanding synergy and/or promotion effect

EC COST Action D36 research project [2006-2011]
(Polish representative: Professor Józef Korecki DSc)

In catalytic processes, sintering of the active clusters can lead to the lost of activity. The Au clusters size and their electronic properties can be changed by adding a second metal, e.g. iron. Bi-metallic Au-Fe nanoclusters were deposited under UHV on a rutile-$TiO_2(110)$ substrate. The influence of the deposition sequence (Au, Fe or Fe, Au) on cluster morphology and electronic properties was studied *in situ* by STM and XPS as a function of annealing between 25°C and 700°C.

Analysis of the STM images collected at RT showed that in the $AuFe/TiO_2$ system (Fe as precursor), the cluster density is approximately three times larger than for $FeAu/TiO_2$. Annealing of $AuFe/TiO_2$ resulted in cluster ripening and a decrease of their density, accompanied by dissolution of iron in the TiO_2 lattice. For the $FeAu/TiO_2$, only limited influence of the annealing temperature on the cluster number was observed suggesting stabilization of the Au clusters by iron.

The analysis of Fe 2p XP spectra obtained for different annealing temperatures showed presence of three iron species: metallic Fe, Fe^{2+} and Fe^{3+}. After 400°C annealing, metallic Fe had a maximum, whereas Fe^{2+} approaches minimum. Fe^{3+} concentration remained stable in whole annealing range. Deposition of Au on Fe/TiO_2 resulted in a decrease of metallic Fe intensity, which suggests nucleation of Au on metallic Fe species. At the temperatures below 300°C, the BE value of Au $4f_{7/2}$ suggests an interaction of the TiO_2 substrate with the Au deposit. Above 300°C, Au showed a similar electronic state in both systems. Our studies results indicated that the size bimetallic clusters can be tuned by annealing temperature and preparation recipe, which can be used for modeling real catalysts.

Colloid and Interface Chemistry for Nanotechnology

EU COST Action D43 research project [2006-2011]
(Polish representative: Professor Zbigniew Adamczyk DScEng)

By exploiting physicochemical measurements performed in this work two complementary methods of determining trace amounts of proteins were developed, characterized by a precision superior to commonly used, chemical methods. The first method consists in measurements of the streaming potential of surfaces covered by protein mono- or multilayers. The second method is based on non-specific (driven by electrostatic interactions) or specific (driven by chemical covalent bound formation) interaction of colloid microparticles with protein layer. The presence of colloid particles on surfaces can be determined in a convenient way by optical or fluorescent microscopy. The precision of the colloid deposition method is exceptionally high, enabling one to determine bulk protein concentration for the range of 0.01 ppm (10 ppb). Moreover, using this method, one can determine the electric charge of proteins on various solid substrates and their isoelectric points that is rather difficult using conventional bulk methods. The applicability of the method in the case of fibrinogen is demonstrated in Fig. 1, where the dependence of the normalized coverage of latex particles Θ_L / Θ_{max} on the fibrinogen coverage Θ_f is shown. As can be seen, the latex coverage increased abruptly with fibrinogen coverage attaining the value of 0,8 for Θ_f=0.05 (5%). It is interesting to mention that the experimental data are well reflected by the theoretical results derived from our fluctuation theory (solid line number 2 in Fig. 1) whereas the often applied, classical DLVO theory (dashed line in Fig. 1) is not applicable in this case.

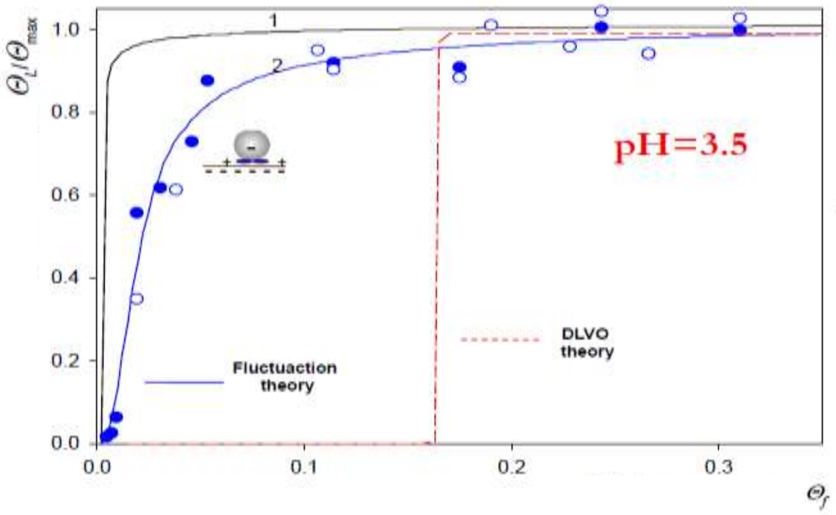


Figure 1. The dependence of the normalized coverage of the negative latex particles L800, Θ_L / Θ_{max} on the fibrinogen coverage Θ_f. The points denote experimental results obtained by optical microscopy (•) and AFM (○), for $I=10^{-3}$ M, pH=3.5, $n_b=1.77\text{x}10^{10}$ cm^{-3}, latex deposition time 20 hours. The solid lines 1-2 represent theoretical results calculated from the fluctuation theory, developed in this assuming that adsorption sites consist of one or two fibrinogen molecules. The dashed line shows theoretical results predicted by the DLVO theory, assuming a continuous distribution of electric surface charge.

Wood Science for Conservation of Cultural Heritage

EU COST Action IE0601 research project [2006-2011]
(Polish representative: Professor Roman Kozłowski DSc)

Professor Roman Kozlowski of the Institute, representing Poland in the Action's Management Committee, is member of the eight-person Steering Committee as leader of Working Group 2 "Assessment and diagnosis". He participated in a Steering Committee meeting organized in 2010 and worked as a member of the Scientific Committee of the Action's 4th International Conference organized in Izmir, Turkey in October 2010. During the conference, members of staff of the institute presented 1 oral presentation. Professor Kozlowski co-organized in Oslo in February 2010 Action's International Workshop "Allowable microclimatic variations for polychrome wood". During the workshop, members of staff of the institute presented 3 oral presentations and 2 posters. Dr Michał Łukomski organized a focused meeting in Krakow in April 2010 "Modelling mechanical behaviour of wooden cultural objects", a joint event of two COST Actions IE0601 "Wood Science for Cultural Heritage" and FP0802 "Experimental and Computational Micro-Characterisation Techniques in Wood Mechanics". During the focused meeting, members of staff of the institute presented 1 oral presentation.

Management of the Museum Collection Based on Computer Modeling of the Impact of the Microclimatic Fluctuations on Historic Objects

(Professor Roman Kozłowski DSc, Marcin Strojecki PhD, Bartosz Rachwał MSc)

The project concerns development of management strategies for the microclimatic control for museum collections consisting of wooden objects. Partners of the project – the National Museums in Krakow and Warsaw are particularly interested in the optimum microclimatic control in their galleries and storage rooms as they own the most important collections of medieval and modern art consisting of wooden objects in Poland. The main aim of the project is to develop management strategies for the microclimate control, which will on the one hand reduce the costs and on the other ensure the effective protection of art objects.

Fulfilment of this objective requires a scientific assessment of the impact of microclimatic parameter fluctuations on the process of destruction of historic objects. The tools for achieving this objective will be computer simulations, supported by measurements of the physical properties of materials and monitoring of the micro damage of objects caused by fluctuations of the air temperature and humidity.

The principal research tool was developed in the reporting period - the use of finite element analysis (FEA) to model the moisture movement, strains, and stresses, in panel paintings and polychrome wooden sculpture, in response to changing climate condition. A key feature of the selected approach was the coupling of moisture diffusion with FEA that allows for accurate "real time" analysis of cultural artefacts. In addition to developing the rigorous mathematics for the model, the properties of the materials constituting the polychrome wood such as sorption of water vapour, moisture related swelling and shrinkage, water vapour diffusion and surface emission coefficients, and tensile properties were determined experimentally The accuracy of the model has been verified by comparing the model's dimensional response to those of objects displayed in real-world museum conditions.

The method developed was used to establish important parameters of the response of panel painting supports, to changing climate conditions. Critical amplitudes of cyclic sinusoidal RH fluctuations generating strain of 0.002 in the most responsive tangential direction of the wood support, which the design layer can endure without damage, were derived for the mid-RH region as a function of cycle duration, panel thickness and diffusion configuration. It was established that panel paintings do not respond significantly to diurnal fluctuations or shorter. The panels respond more and more significantly when the duration of the fluctuations increases until the panel fully responds to each cycle. These duration periods are 14 and 90 days at 20^{o}C for a panel thickness of 10 and 40 mm, respectively, with two faces of a panel diffusively opened. The critical amplitude corresponding to the wood's full response is ± 6% RH.

Numerical modelling of the moisture movement and strain in a composite system – a wood panel coated with a layer of gesso - was advanced.

Physics of Droplets

UE COST Action P21 research project [2006-2010]
(Polish representative: Professor Kazimierz Małysa DSc)

The COST Action P21 “Physics of droplets” was completed on October 3, 2010 (the project started on October 4. 2006). 27 research teams from various scientific institutions of 17 European countries, and the Ian Wark Research Institute of University of South Australia, Australia participated in the project. From Poland the research teams from the Institute of Catalysis and Surface Chemistry Polish Academy of Sciences (ICSC PAS, Institute of Fundamental Technological Research Polish Academy of Sciences (IFTR PAS) and the Warsaw University of Technology, Department of Chemical and Process Engineering (WUT-CPE) participated in the project, and Professor Kazimierz Malysa from ICSC PAS was the Polish representative in the Management Committee. Professor N.Vandewalle, GRASP, Institut de Physique B5a Sart Tilman, Université de Liège, B-4000 Liège, Belgium was the project coordinator.

In 2010 the official meetings of the Management Committee (MC) was held in Borovets, Bulgaria. The MC meeting was coupled with the Joint Meeting of the Working Groups WG1, WG2 and WG3 organized in Borovets on July 14-16, 2010. During this Meeting the following contributions were presented by K. Małysa and J. Zawala: i) J. Zawala, D. Terwagne, S. Dorbolo, N. Vandewalle, K. Malysa "On Mechanism of the Bubble and Droplet Bouncing from the Liquid/gas Interface" (result of scientific collaboration developed between ICSC PAS and Université de Liège, Institut de Physique, GRASP, Belgium within the frame of the COST P21 Action), and ii) D. Kosior, J. Zawala, M. Krasowska, K. Malysa "Air at Hydrophobic Surfaces and the Three-Phase Contact Formation". The Table below presents data on the organized meetings of the working groups (WG), training schools (TS), short technical scientific mission (STSM) and management committee meetings (MC).

Year	WG1	WG2	WG3	MC	TS	STSM
2006	1	1	1	2	0	5
2007	2	2	1	2	0	7
2008	1	1	2	2	1	5
2009	2	2	2	2	0	24
2010	1	1	1	1	1	3
TOTAL	7	7	7	9	2	44

Anna Niecikowska MScEng from ICSC PAS applied and obtained financing from the COST P21 Action for the scientific visit to Ian Wark Research Institute of University of South Australia in Australia, within the frame of the Short Term Scientific Mission (STSM), for the period January 29-February 16, 2010. During her visit A. Niecikowska attended the 27th Australian Colloid & Surface Science Student Conference (ACSSSC) and had oral presentation: A. Niecikowska, M. Krasowska, J. Ralston, K. Malysa "Mutual Interdependences of Electrostatic Interactions and Hydrophobicity for Three Phase Contact Formation at Titania Surface". After the Conference she stayed in Ian Wark Research Institute of University of South Australia in Adelaide where she carried out studies related to the common work on formation of TiO_2 solid films and influence of the film modification on stability of wetting films formed during the bubble collisions with TiO_2 surface.

Dynamics of Interactions of the Moving Micro-objects (Particles, Droplets, Bubbles) with Interfaces

The project was completed on October 29, 2010. The final report describing results obtained during 36 months of the project realization was sent to Ministry of Science and Higher Education on December 21, 2010. The project was aimed at deepening the knowledge about phenomena related to motion and mutual interactions between micro-objects (droplets, particles, bubbles) as well as between these objects and various interfaces having modified, in a controlled manner, their surface properties (electrical charge, hydrophobicity, heterogeneity, roughness) in respect to their importance for coalescence and deposition processes, the three phase contact formation, etc. The project was realized by research teams from three different Polish scientific institutions, namely: i) Institute of Catalysis and Surface Chemistry Polish Academy of Sciences (ICSC PAS), ii) Institute of Fundamental Technological Research Polish Academy of Sciences (IFTR PAS) and iii) Warsaw University of Technology, Department of Chemical and Process Engineering (WUT-CPE). The project was carried out also in cooperation with research teams from various countries of European Union and from Australia participating in activities of COST P21 "Physics of Droplets" Action. Institute of Catalysis and Surface Chemistry Polish Academy of Sciences was the institution coordinating the project (coordinator - Professor Kazimierz Małysa).

Results of the research carried out during the project realization have been presented in 32 papers, 45 oral and poster presentation at international conferences and meetings of the working groups (WG) of the COST P21 "Physics of droplets" Action. As a result of the project realization the existing international collaboration was strengthened and new international contacts were formed, which resulted in: i) common papers, ii) common oral and/or poster presentation at international conferences, iii) exchange of scientists and research carried out in collaborating institutions, iv) formulation of projects of common studies (for example ICSC PAS and GRASP University of Liege in Belgium, ICSC PAS and IWRI University of Adelaide in Australia, IFTR PAS and Institute of Fluid Mechanics and Heat Transfer, Graz University in Austra, IFTR PAS and Physics of Complex Fluids, University of Twente in The Netherlands).

Theoretical and experimental studies carried out using complementary possibilities of the teams, which realized the project, enabled obtaining a lot of new results on mechanisms of interactions of various micro-objects with different interfaces. Results obtained from theoretical and experimental studies are important for deepening and widening the knowledge on fundamentals of flows of particles, droplets and bubbles, as well as in application aspects by supplying data necessary for elaboration more effective separation processes in multiphase systems and for optimization methods of drugs supply through inhalation. All tasks planned ware fulfilled.

EEA Financial Mechanism projects

NOMRemove Effective Photocatalytic-Membrane Methods of Removal of Organic Contaminants for Water Treatment

EEA PL0084 NOMRemove [2007-2010]
(project leader: Professor Piotr Warszyński DScEng)

The project was realized from July 1st 2007 to June 30th 2010 by scientific consortium consisted of two partners: Institute of Catalysis and Surface Chemistry Polish Academy of Science in Krakow and The Foundation for Scientific and Industrial Research at the Norwegian Institute of Technology, SINTEF - Material Science and Chemistry, Oslo, Norway.

The main objective of the project was to develop a sustainable and environmentally friendly methods for treatment of water, which otherwise may not be applicable for drinking water supply, due to contamination by Natural Organic Matter (NOM), by failing to fulfill all standards of directive 98/83/EC on the quality of water intended for human consumption. That overall objective was achieved on model water solutions of NOM. We concentrated our investigations on the heterogeneous photocatalysis - the advanced oxidation process to remove organic contaminants from water, which is economical and safe for the environment. We synthesized and used several types of modified TiO_2 photocatalysts with different activity in the decomposition of dissolved model organic substances. These photocatalysts were tested as fluidized bed mainly. Several oxidants were checked for the synergistic activity with photocatalyst for humic acid decomposition. Sodium persulphate appeared to be the most effective. It was then encapsulated in the porous silica capsules modified with polyelectrolyte layers to obtain slow release capsules. Photocatalytic membranes of various geometries (water flow through the membrane pore (Ft), or over the membrane (Fo) in the contactor system) were developed. The laboratory scale water treatment equipment was assembled at ICSC (Fig. 1a). It can utilize either membrane or fluidized bed reactor. Testing unit for membranes of various geometries was developed at SINTEF (Fig. 1b and 1c). The two methods for removal of organic contaminants by photocatalityic membrane and fluidized bed treatment processes, which allow removing 98% of model organic substance - humic acid sodium salt from water solutions was developed. For natural waters we did not obtain full mineralization as demanded. That requires further studies.

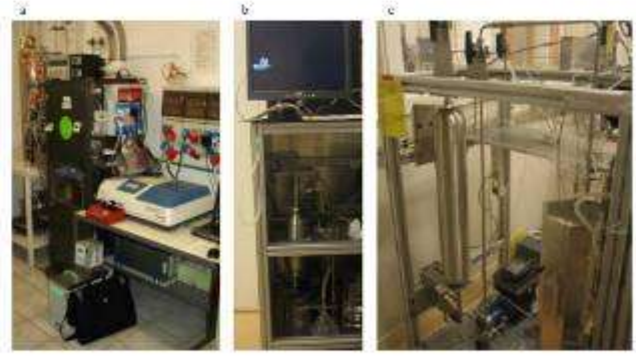


Figure 1. The laboratory scale equipments developed and constructed in the frame of the project PL0084. a) the water treatment equipment, which can utilize either photocatalytic membrane or fluidized bed reactor, b) testing unit for flat membrane c) testing unit for tubular membranes.

Establishing Standards for Allowable Microclimatic Variations for Polychrome Wood

EEA PL0086 WOOD [2007-2010]
(project leader: Professor Roman Kozłowski DSc)

Panel paintings, polychrome wooden sculpture and paintings decorating wooden architectural surfaces are an important part of the artistic heritage. The protection of this heritage is particularly important for Poland and Norway in which a group of polychrome wooden churches, unique on a world scale, has been preserved. The most valuable of them are inscribed on the UNESCO World Heritage List.

Uncontrolled variations of the air parameters in the environment of polychrome surfaces, leading to the deformation and mechanical damage of wood, gesso and paint layers, are principal hazards to their preservation. The main aim of the project was establishing precisely and quantitatively the variations of air parameters that are safe for the painted wooden surfaces. The implementation of the project ended in April 2009.

During the last months of project's implementation, the last research task concerning measurements of the local strain field in wood in response to applied force and adsorption of water vapour from the environment, were performed. The measurements were carried out at the Technical University of Eindhoven, the Netherlands using an in-plane speckle pattern interferometer. The measurements revealed that minimum and maximum magnitudes of the local strain in the wood are identical in the mechanical and humidity tests, which demonstrated that mechanical simulation of the fatigue processes is a correct procedure as far as the damage mechanism of the design layer induced by climate impacts is concerned.

An international workshop in Oslo and a national workshop in Warsaw were organised to disseminate project's results. The international workshop was co-organised by the Norwegian partner to the project, the Institute for Cultural Heritage Research NIKU in Oslo, and COST Action IE0601 "Wood Science for Conservation of Cultural Heritage". 70 participants from Europe and USA took part in the workshop. The national workshop was organised in the collaboration with the Mazowsze Regional Conservator of Monuments. Approximately 100 participants took part in the workshop.

A brochure prepared by the project team and printed in 1500 copies has been an important platform for the dissemination of knowledge on the protection of polychrome wood. The brochure contains information on microclimate in historic buildings, threats to the polychrome wood, preservation strategies, international recommendations and standards. The brochure was distributed to the participants of the national workshop in Warsaw. It was also sent to the offices of regional conservators of monuments Poland-wide.

All publications which has been an outcome of project's implementation, oral presentations and posters from the both workshops, and the brochure have been made available in the electronic from at the project website. They have met with a considerable interest of Polish and international conservation community.

Projects OF EU structural funds programmes

MPD Krakow Interdisciplinary PhD Projects in Nanoscience and Advanced Nanostructures

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

Project MPD "Krakow Interdisciplinary PhD-Projects in Nanoscience and Advanced Nanostructures" is implemented within the Innovative Economy Operational Programme, Priority 1. Research and development of new technologies, Measure 1.2 - Strengthening the human potential of scienceThe Project Coordinator is Professor Bartłomiej Szafran affiliated at Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, who is the partner in the Project. The project is also carried out in cooperation with the following foreign partners: Universiteit Antwerpen (Belgium), University of Leeds (United Kingdom), National Research Centre INFM-CNR (Italy), University of Stockholm (Sweden), Max Planck Institut für Molekulare Pflanzenphysiologie (Germany), Max Planck Institut für Kolloid und Grenzflächenforschung (Germany), Basque Country University (Spain), SINTEF Material and Chemistry (Norway), VŠB-Technical University of Ostrawa, (Czech Republic), Institute of Physical Chemistry Bulgarian Academy of Sciences (Bulgaria).

The five-year Project started on 1st November 2008 aims to accomplish twelve PhD thesis within twelve individually defined PhD projects. Recruitment procedure of the PhD students was in the form of the open calls. In 2009 the recruitment procedure was completed and since that time in the ICSC the following five individual PhD project are being implemented:

1. Anna Wójcik MSc (supervisor: Professor Ewa Brocławik DSc)"Computer Modeling of Biological Nanostructures"
2. Małgorzata Adamczak MScEng (supervisor: Profesor Piotr Warszyński DSCEng) "Surfactants, Polyelectrolytes and Nanoparticles as Building Blocks for Surface Nanostructures"
3. Dominik Kosior MScEng (supervisor: Professor Kazimierz Małysa DSc) "Nanostructures and Stability of Thin Liquid Layers"
4. Katarzyna Luberda-Durnaś MScEng (supervisor: Professor Wiesław Łasocha DSc) "Hybrid Organic-Inorganic Layered Materials - Precursors of Semiconducting Nanostructures"
5. Ewa Młyńczak MScEng (supervisor: Professor Józef Korecki DSc) "Surface and Interface Properties of Metal-Oxide Magnetic Nanostructures"

ISD Advanced Materials for the New Technologies and Energy of the Future

PO KL 4.1.1 ISD [2008-2012]
(project leader: Assoc. Professor Renata Tokarz-Sobieraj DSc)

The Interdisciplinary PhD Project entitled "Advanced Materials for the New Technologies and Energy of the Future" is implemented within the Human Capital Operative Programme funded form the European Union Structural Funds and the national budget sources. The project is coordinated by the Faculty of Physics & Applied Computer Science AGH University of Science and Technology and carried out in the partnership with the Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences and the Institute of the Nuclear Physics of the Polish Academy of Sciences.

The aim of the Project is to educate high level specialist with the PhD diploma in the disciplines considered as strategic in the European and national research policy, i.e. Info, Bio, Nano, Techno. Research and education within the project involve physical, chemical and technological aspects of material science and modern energy science.

Implementation of the Project will be based on the 3 recruitment editions, starting form 2009. In each recruitment edition about 20 students will be recruited for the 4 years PhD studies.

The first recruitment was launched in 2009 and as a result the following individual PhD projects are being implemented in the ICSC PAS:

1. Magdalena Nosek MSc (supervisor: Assoc. Professor Paweł Weroński DSc) "Analysis of the Porosity of the Multilayered Colloidal Materials of the Controlled Architecture"
2. Anna Pajor MSc (supervisor: Professor Piotr Warszyński DSCEng) "Electroactive multilayers polyelectrolytes films with embedded nanoporticles'
3. Małgorzata Krzak MSc (supervisor: Assoc. Professor Paweł Nowak DScEng) "High-performance anticorosive coatings prepared from composite meterial based on organic polymers"
4. Magdalena Oćwieja MSc (supervisor: Professor Zbigniew Adamczyk DScEng) "New Layered Materials of Controlled Architecture and Functionality Containing Silver Nanoparticles – Biomedical Applications"
5. Justyna Dziedzic MSc (supervisor: Professor Piotr Warszyński DScEng) "Photocatalytic decomposition of organic compounds in water enhanced by encapsulated oxidants"
6. Katarzyna Onik MSc (supervisor: Assoc. Profesor Mirosław Derewiński DScEng) "The new catalytic systems based on hierarchic porous materials"

The second recruitment was launched in 2010 and as a result the following individual PhD projects are being implemented in the ICSC PAS:

7. Piotr Batys MSc (supervisor: Assoc. Professor Paweł Nowak DScEng) "Multiscale modeling of irreversible adsorption of nanoparticle at the solid - liquid interface"
8. Anna Dobija MSc (supervisor: Professor Wiesław Łasucha DSc) "New peroxo- and polymetalate materials for catalysis, medicine and new technology"
9. Anna Dziedzicka MSc (supervisor: Professor Bogdan Sulikowski DScEng) "Physicochemical properties of hierarchic molecular sieves"
10. Marta Grzesiak MSc (supervisor: Professor Wiesław Łasucha DSc) "Metalorganic structures of MOF-type materials for catalysis, crystal engineering and gas containers"
11. Żaneta Kalemba MSc (supervisor: Assoc. Professor Alicja Drelinkiewicz DSc) "Research for the selection of catalysts for the reaction of glycerol etherification"
12. Anna Miłaczewska MSc (supervisor: Assoc. Professor Tomasz Borowski DSc) "Molecular modelling of structure and catalytic activity of biological materials"
13. Dorota Szepietowska MSc (supervisor: Profesor Bogdan Sulikowski DScEng) "Physicochemical properties of zeolites/heteropolyacids hybrid types catalysts"
14. Maciej Tatko MSc (supervisor: Assoc. Professor Paweł Nowak DScEng) "Highly conductive ionic conductors based on lantanide metal oxides for high-temperature solid oxide fuel cell"

SPINLAB National Centre of Nanostructures for Spintronic Applications

PO IG 2.2. SPINLAB [2009-2011]
(project leader: Professor Józef Korecki))

Adaptation of laboratory space (38m^2 area) for PEEM-LEEM microscope purposes has been executed in the frame of the task no 12: "Adaptation of laboratory space of Surface and Nanostructure Laboratory for purposes of PEEM-LEEM microscope". The room has been equipped with following installations:

- Wiring, network, telephone, and fire protection systems
- Ventilation and air conditioning systems
- Airlines

The laboratory has been equipped with computer infrastructure and set of furniture.
The task is accomplished.

In 2010 in the frame of the task no 13: "Purchase of PEEM-LEEM microscope" following actions were taken up towards purchasing PEEM-LEEM microscope:

- Preparation to call for tender:
    - appointments at companies supplying LEEM-PEEM microscopes: ELMITEC in Clausthal-Zellerfeld and SPECS in Berlin;
    - preparation of specification for systems in demand;
- Opening of call for tender for PEEM-LEEM microscope and preparation chamber.
- Selection of the winner tender – signing the contract with ELMITEC company for purchasing the systems.

Preparatory actions have been taken up for realization of next steps of the project:

- Staff training in the use of the microscope operating at synchrotron
- Microscope installation and testing at synchrotron

The actions are directed to find the optimal place at one of the European synchrotrons. The cooperation project has been presented to:

- MAX-lab, Lund
- ESRF, Grenoble
- Elettra, Trieste

Promotional activities:

- Installation of the outdoor information board promoting SPINLAB project
- Inclusion of the SPINLAB informative site into the website of ICSC
- Poster contribution promoting SPINLAB project to "10 International School and Symposium on Synchrotron Radiation in Natural Science- ISSRNS'10" in Szklarska Poręba, Poland
- Poster contribution promoting SPINLAB project to "Joint European Magnetic Symposia - JEMS 2010" in Krakow, Poland.

BIOTRANSFORMACJE Biotransformations Useful in Pharmaceutical and Cosmetics Industry

Task 6. Biocatalytic Methods for Synthesis of Chiral Alcohols

POIG 1.3.1 BIOTRASFORMACJE [2009-2014]
(project leader: Maciej Szaleniec PhD)

Researches in task 6 were conducted according to the quarterly schedule and concerned two enzymatic systems catalyzing synthesis of chiral alcohols: i) ethylbenzene dehydrogenase (EBDH) and ii) phenylethanol dehydrogenase (PEDH). The research conducted in the quarter of 2010 concentrated on the transfer of PEDH research topic to Poland. To attain this Agnieszka Dudzik MSc undertook 2.5 months research visit in Johann Heider's team in Marburg. The research and training conducted in laboratory of our German co-operator covered PEDH overexpression in E.coli mutant strain, enzyme purification and activity assay protocols. The biological material brought to Poland from Marburg allowed independent research on the further stages of the project.

Tasks performed in the second quarter of 2010 comprised of the optimization of cultivation of E.coli as well as purification protocols of PEDH and EBDH (due to new purification equipment and new stationary phases). Moreover, multiple preparative purifications of both enzymes were conducted in order to provide sufficient material for further analyses. During that stage the characterization of PEDH substrate spectrum was initiated and expansion of EBDH substrate characterization was expanded. These studies were continued during following months of the project. As a result 25 ketones and 17 alkilaromatic and alkylheterocyclic compounds were tested as PEDH and EBDH substrates in the reactions of steroselective reduction and oxidation, respectively. Due to complicated cooperative kinetics of PEDH only approximate relative values were obtained while in case of EBDH full kinetic characterization was conducted based on Michaelis-Menten model with or without substrate inhibition.

The next step of research conducted in third and fourth quarter of 2010 aimed at development of methods of chiral analysis of studied reaction mixtures. This required also custom synthesis of non-commercially available chiral standards (required for product identification and LC-MS optimization of ionization). Additionally, based on literature references the post-column sol vent addition method was developed which allows APCI ionization in a normal phase solvent system (with high content of n-hexane). In determination of reaction enantioselectivity two methods were used: chiral (Chiracel OB) LC-MS in NP system and GC-MS with cyclodextran chiral column. These analyses allowed characterization of PEDH reaction stereoselectivity for 14 compounds and for EBDH in case of 7 compounds. As a next step the quantitative calibration s were prepared for 14 substrate-product pairs. Based on such tools it was possible to start determination of reaction conversion rates (12 reaction for PEDH and 3 for EBDH). This allowed optimization of reaction environment of biosynthesis for PEDH in the cofactor regeneration system with co-substrate (isopropanol). The optimization showed high PEDH resistance to organic solvents.

FUNANO Functional Nano- and Microparticles, Synthesis and Applications in Innovative Materials and Technologies

POIG 2.1.1 FUNANO [2009-2014]

(project leader: Professor Zbigniew Adamczyk DScEng)

A complex characteristics of polymeric and ionic stabilizers used in the synthesis of noble metal nanoparticles was performed. Then, syntheses of silver nanoparticles were performed under various conditions according to the method of Creighton et al. by reduction of $AgNO_3$ solutions with $NaBH_4$ in the presence of these stabilizing agents. Bulk characteristics of silver sols obtained in this way involved plasmon absorption spectrum, fluorescence, diffusion coefficients using the PCS method and the electrophoretic mobility. In this way, a reproducible method of silver suspensions of controlled particle size within the range 12 to 70 nm was elaborated. It was shown that these suspensions were stable within a prolonged storage time reaching one year. These silver suspensions were used in subsequent measurements of the kinetics of nanoparticle deposition on mica modified by adsorption of various cationic polyelectrolytes. The surface coverage of particles was determined directly by counting the number of particles over various surface areas using the atomic force microscopy and the scanning microscopy. In Fig. 1, the silver particle monolayer (average particle size 16 nm) on mica modified by PAH is shown. The monolayer was obtained under diffusion-controlled transport conditions. The maximum surface coverage obtained in these kinetic measurements exceeded 30%, which is the highest value reported in the literature. It is also interesting to mention that both the kinetic runs and the maximum coverage determined in experiments were in a good agreement with theoretical predictions derived from the random sequential adsorption (RSA) model.

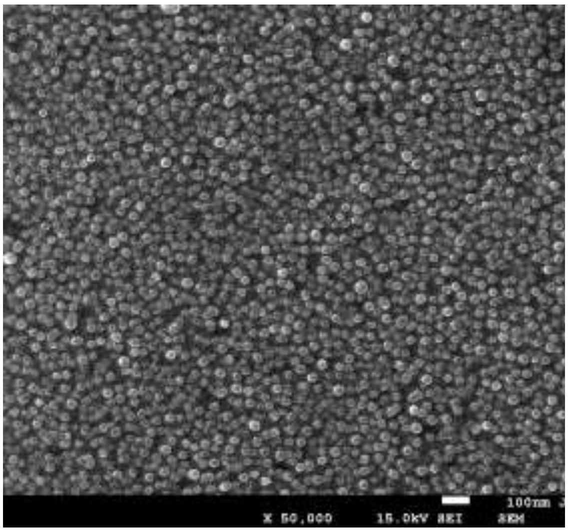


Figure 1. Monolayer of silver particles (average diameter 16 nm) on mica modified by the cationic polyelectrolyte (PAH) pre-adsorption. Particle deposition was carried out under diffusion-controlled transport for the bulk concentration c_b=35 ppm, t=11 h, pH=5,5, I=10^{-4} M NaCl. The surface concentration of particles was 615 μm^{-2}.

Our investigations confirmed that it is feasible to produce uniform silver nanoparticle monolayers on solid substrates, characterized by controlled density and structure using the colloid self-assembly from aqueous sols.

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

PO IG 2.1.1. VOX [2009-2013]
(project leader: Professor Ewa Serwicka-Bahranowska DSc,
principal investigator: Tadeusz Machej PhD)

Project aims at development of efficient and cheap oxide catalysts for purification of industrial flue gases from toxic volatile organic compounds. The basis for catalytic design are synthetic layered minerals isomorphous with hydrotalcite, of general formula $[(M^{2+})_{1-x}(M^{3+})_x(OH)_2](A^{n-})_{x/n}\cdot mH2O$, whose specific structure allows for uniform mixing of catalytically active elements at atomic level. Mixed oxides resulting from thermal decomposition of hydrotalcites are characterized by topotactic relations between oxidic nanstructured components, which generates unique properties, unattainable by other synthetic methods. In particular, our study of catalytic systems based on copper-chromium hydrotalcites demonstrated that the materials surpass Cu-Cr commercial catalyst, and their properties can be easily tuned to the requirements of a particular catalytic reaction by introduction of appropriate elements into the precursor structure. On the basis of to date results it is expected that the performance of hydrotalcite derived catalysts will be comparable or better than that of costly precious metal based catalysts. In 2010 a series of hydrotalcite precursors has been prepared, based on the synthetic procedure constituting know-how of the project authors. Synthesis encompassed, among others, preparation of transition metal containing hydrotalcite precursors from aqueous or aqueous-organic solutions, in the conditions of constant or variable pH, in the temperature range 0-90°C, employing hydrothermal conditions and controlled oversaturation of the reaction mixture. Prepared hydrotalcites and mixed oxides obtained by their thermal decomposition, were characterized by means of ICP OES, XRD, XPS, TPR, TG/DTG/DTA, BET, SEM, TEM methods. The materials were tested for their activity in the reaction o total oxidation of toluene.

ISD MOLMED Molecular Sciences for Medicine

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

The Interdisciplinary PhD project entitled "Molecular Sciences for Medicine" is implemented within the Operational Programme Human Capital, Priority IV Higher Education and Science, sub-measure 4.1.1 Strengthening and development of didactic potential of universities. This project is co-financed by the European Social Fund (ESF).

ISD MOLMED is coordinated by Professor Małgorzata Witko DSc from Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences (the project leader), and involves the following participants: Jagiellonian University Faculty of Chemistry, Jagiellonian University Medical College, and Institute of Pharmacology Polish Academy of Sciences.

The five-year project has been running since October 1, 2010. Its goal is to improve the quality of interdisciplinary education at doctoral level in the fields of: chemistry, advanced materials, nanotechnology, (bio)catalysis, medicinal chemistry, pharmacology and medicine by opening and implementation of PhD studies. Simultaneously, a parallel goal of the project is to increase the didactic potential of university by broadening and enriching the training at tertiary education level and to improve teaching competence of academic staff.

In the first quarter (October-December 2010) of the project a contest on the topics of doctoral dissertations was conducted, and as a result 17 topics were selected. Ultimately, the project will provides 40 topics, under which 40 doctoral dissertations will be completed.

Other international projects

Enzymes as Nanotools - Development of a New, Enzyme-Based Technology for Engineering Selectivity Permeable, Nano-Structured Membranes

GRDE France [2007-2010]
(project leader: Professor Piotr Warszyński DScEng)

The objective of the project, which was concluded in the present year, was to acquire necessary knowledge allowing to use the enzymes as nanotools for obtaining new biomedical material with surface nanostructure or biomedical sensors. Our investigations concentrated on the determination of influence of enzymatic reaction on structure and physicochemical properties of phospholipids layers at free interface and deposited on solid supports.

For the investigations the enzyme - phospholipase A2 (PLA2), which in the presence of calcium ions is able to selectively cut fatty acids off the sn-2 position of phospholipids, was selected. The product of this reaction is either soluble or insoluble in water depending on the hydrocarbon chain length. Wide range of experimental methods was applied to determine the progress of the enzymatic reaction. For example, the plates with phospholipid layer (containing 1% of phospholipids with fluorescent labeled head group) were investigated before and after the enzymatic reaction by using spectrofluorimetry and results were correlated with contact angle measurements (Fig. 1). Wetting measurements revealed that increase of hydrophilicity were connected with cut-off the parts of hydrophobic chain, which was evidenced by increase of fluorescence intensity.

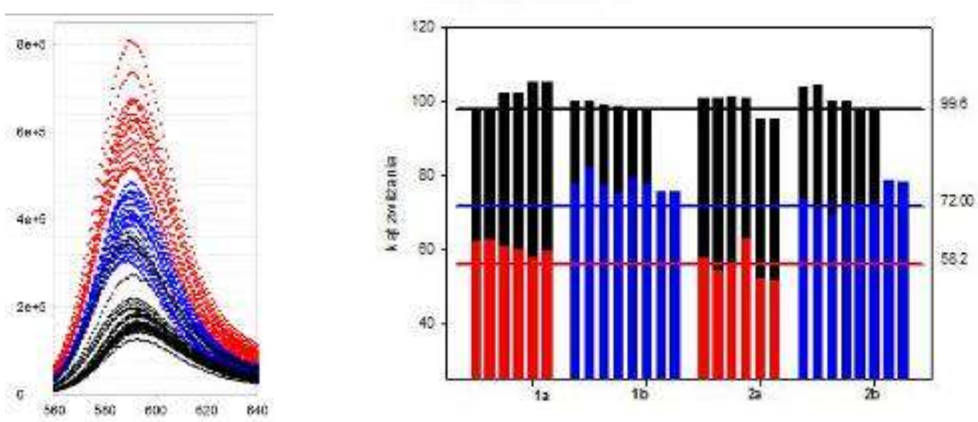


Figure 1. Dependence of fluorescence intensity and contact angle on the way of treatment of mica plates with deposited phospholipids. Black color – dry plate with deposited phospholipids 1% DPPE –Rod 99% DLPE, red color – the same plates after enzymatic reaction, blue color – plates treated only by calcium chloride solution.

The adsorption of phospholipids and loss of mass after enzymatic reaction were measured by using Quartz Crystal Microbalance (QCM). In that case the phospholipids layers were deposited on the quartz crystal with gold sputtered layer either from the chloroform solution or by using L-B technique. The analysis of the results showed that, first that enzyme had been adsorbed on the phospholipids layer surface (mass increase) and then, after a short steady state, the mass loss was observed, especially in the rinsing phase. The course of enzymatic reaction was also investigated by measurements of local and terminal velocities of rising bubbles. The measured velocities were decreased when the water soluble product of enzymatic reaction – dodecanoic acid had appeared in solution. Moreover, the kinetics of enzymatic reaction for phospholipids at free interface was determined by measuring changes of surface potential using vibrating plate method.

Adsorbates on Fe Monolayer on W (110)

Intergovernmental Polish-Austrian project [2009-2010]
(project leader: Professor Józef Korecki DSc)

Oxygen adsorption on iron surface (110)

Oxygen adsorption on iron surfaces attracted a lot of interest because of its importance in such processes as oxidation, passivation, corrosion and catalysis. In literature it is well established that on Fe(110) molecular oxygen is adsorbed dissociatively from a precursor diffusing on the iron substrate. However, despite quite a number of papers, the data are fragmentary and often contradictory. Here, we report on concern room temperature adsorption of oxygen on the Fe(110) surface of epitaxial Fe films grown on W(110). The low energy electron diffraction (LEED) was used to identify the symmetry of the adsorbate structure. We found three well defined structures of oxygen adsorbate: the well known (2x2) (at oxygen exposure 3 L), the so called split 3x1 (at oxygen exposure 17 L) and a new one (3x2), to our knowledge not reported before. We studied also modification the Fe electronic structure induced by oxygen the nuclear resonance scattering (NRS) of synchrotron radiation at the beamline ID 18, ESRF Grenoble.

Oxygen adsorption on the bulk Fe(110) surface was compared with that on a pseudomorphic Fe monolayer on W(110). In complementary LEED, AES and STM experiments different surface structures could be identified, covering the whole range of oxygen coverages, Additionally, NRS and conversion electron Mössbauer spectroscopy results revealed a distinct transition in electronic structure interpreted as the onset of oxide formation at oxygen doses of about 100 L.

Differences in the oxygen adsorption on Fe(110) surface and Fe/W(110) monolayer were interpreted in terms of Fe lattice expansion and influence of the tungsten substrate.

Spin reorientation transition in Fe/W(110) monolayers

Using nuclear resonant scattering (NRS) of synchrotron radiation we investigated the details of thickness induced spin reorientation transition (SRT) in ultrathin Fe/W(110) films. During SRT the easy direction of magnetization changes from the [110] out-of-plane to the [1-10] in-plane crystallographic direction. Our results reveal the complex character of this intensively studied in the past transition. Extremely fast acquisition of the experimental NRS spectra, in connection with the high NRS sensitivity to the orientation of the magnetic hyperfine fields, allowed us to get insight into pristine (free from adsorption effects) magnetic configuration during SRT. The non-collinear magnetic structure appears due to the exchange and possibly dipolar interactions between the mono-, double-, and tri-layer areas coexisting due to the deviation from the layer-by-layer growth mode of Fe/W(110). We also report the striking observation of perpendicular magnetization in double layer areas at temperature as high as 300K. The obtained profiles of the local magnetization across the film are unique and were up to now not accessible with any other method.

Metal and Oxide Epitaxial Nanostructures as Seen by Nuclear Resonance Scattering of Synchrotron Radiation

Intergovernmental Polish-French POLONIUM Project [2010-2011]
(project leader: Professor Józef Korecki DSc)

Ultrathin FeO(111) oxide was grown on a Pt(111) single crystal. The best FeO structures were obtained by oxidizing of single Fe monolayers at 2 L oxygen exposition at $5x10^{-8}$mbar O_2 and 280°C substrate temperature, followed by UHV annealing at 600°C. FeO could be stabilized for many monolayer cycles, contrary to previous papers reporting that FeO on Pt(111) is stable only up to 2.5ML.

LEED and STM investigations of the oxides surfaces indicated a high degree of the structural order. For FeO a layer-by-layer growth was observed. A characteristic feature of the FeO surface was a Moire superstructure being a consequence of a large lattice misfit (11%) between FeO(111) and Pt(111). CEMS studies performed in a wide range of thickness and temperature exhibited a long range magnetic order in FeO films of several angstrom thickness.

Using nuclear resonant scattering (NRS) of synchrotron radiation at the ESRF Grenoble we performed in December 2010 time spectra and inelastic measurements for the FeO oxide films on Pt(111). The results indicate a strong correlation between magnetic properties of the two dimensional oxide and its crystal structure but more detailed analysis of these measurements is planned for the next project phase.

The cooperation with the ESRF Grenoble has been continuing already for many years and the Polonium project was started much before the funding by the Polish Ministry of Science and Education was granted. As the result in 2010 the paper "Non-collinear Magnetization Structure at the Thickness Driven Spin Reorientation Transition in Epitaxial Fe Films on W(110)" was published in the Phys. Rev. Let. 105 (2010) 027206.

Other activities

Sixth Edition of a University Textbook: "An Introduction to Inorganic Chemistry"

(Professor Adam Bielański, PhD, DHC)

The sixth edition of the textbook "Podstawy Chemii Nieorganicznej - An Introduction to Inoganic Chemistry"(1045 pages, ed. PWN, Warszawa, in Polish) has been revised from the point of view of actuality of the information and also several new chapters (elements in the earth's core, elements in the cosmic space) were added and some others enlarged (water and hydrogen bond in the inorganic chemistry, IR spectrometry in the inorganic chemistry, condensation of cations in aqueous solutions etc.).

Centre for Environmental Pollution Analyses "CezaŚ"

(Janusz Janas MSc, Joanna Kryściak-Czerwenka PhD,
Joanna Opalińska-Piskorz MSc)

In the beginning of 2010 the final works in the course of preparing the CezaŚ Laboratory for the accreditation of declared research methods were completed.

In March 2010, the CezaŚ Laboratory was subjected to the "initial assessment visit" (accreditation audit), e.g. special evaluation *in-situ* carried on by the Polish Centre for Accreditation (PCA) assessors.

In the course of evaluation 6 minor nonconformities with the demands in technical area was found. The sources of these nonconformities were then identified and the proper correction procedures have been initiated and finally completed. These attempts were positively appreciated by the PCA what finally resulted in obtaining the Accreditation Certificate of Testing Laboratory No. AB 1221.

In the said reporting period the activity of the CezaŚ Laboratory comprised the following works:

1. Realization of 5 external orders amounted on 5,490 zloty (gross).
   The scope of all orders comprised the measurements of:
   - VOC conversion in various industrial plants,
   - exhaust gases purification efficiency,
   - chemical composition and concentration of organic and inorganic atmospheric contaminants,
   - adsorption-desorption process characteristics,
   - emission of gaseous organic contaminants and efficiency of RCO (regenerative catalytic oxidizer) units.
2. Realization of 13 internal orders in the Institute of Catalysis comprising 14 different measuring series using the following experimental techniques:
   - GCMS (gas chromatography with mass detection)
   - FT-IR based on DRIFT, transmission and ATR equipment,
   - EDXRF (energy dispersion X- fluorescence spectroscopy).
3. Participation in the two interlaboratory comparisons:
   - "Silesialab-2010, Interlaboratory Comparison BT0110"
   - "Measurements of benzene vapours in waste gases" in cooperation with LabAnalityka Ltd in Brzeg Dolny.

   Both comparisons were completed with satisfactory results.
4. Two internal proficiency testing comprising the following Standard Operating Procedures:
   - PB-04 „Determination of epichlorhydrin by means of Gasmet DX-4000 analyzer”, 2nd ed., 6th Aug 2010
   - PB-06 "In-situ determination of organic substances concentration in vapour mixture by means of Gasmet DX-4000 analyzer according to FT-IR method", 2nd ed., 6th Aug 2010.

The obtained results confirmed the proficiency of CezaŚ Laboratory in employment of said methods.