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Fields of research

- Advanced catalytic oxidation processes
- Catalytic combustion of volatile organic compounds in waste gases
- Catalytic decomposition of N₂O
- Design of new theoretical models for structure-activity relationships
- Morphology and application properties of catalysts based on functional polymers
- Preparation of hierarchic nanomaterials
- Temperature programmed techniques in characterization of catalysts
- Texture and transport processes in porous solids
- Theoretical analysis of the structure of molecules with complicated bonding pattern
- Preparation and characterization of the electrospun nanofibrous membranes and catalytic supports
- Unconventional preparation of metal oxide nanostructures by pressurized fluid extraction and supercritical drying

Applied research

- Catalytic combustion of volatile organic compounds
- Oxidation processes for environment
- Textural characteristics of structural materials
- Green chemistry for biomass utilization to the high added-value products

Research projects

Hydrogen oriented underground coal gasification (UCG) for Europe - environmental and safety aspects (HUGE2)

(O. Šolcová, solcova@icpf.cas.cz; joint project with GIG, Politechnika Slaska, Kompania Węglowa S.A. and Lubelski Węgiel Bogdanka S.A., Poland, Institut National de l'environnement industriel et de risques, France and UCG Engineering Ltd, UK; supported by Research Fund for Coal and Steel (RFCS), project No. RFCR-CT-2011-00002)

This project is focused on safety and environmental aspects of underground coal gasification. Underground trial has been performed in mine testing two borehole system and reactive barriers usage. The most serious environmental concerns related to UCG have been investigated that is contamination of underground aquifers and potential leakage of poisonous and explosive gases into the surrounding strata. The work is focused on finding practical solutions of possible leakages prevention by use of reactive barriers. Complex system of environmental telemetric monitoring was built and tested. Also technical and ecological risk assessment was performed.

During the UCG process as well as a long time after the process termination a great number of hazardous environmental contaminants (both inorganic and organic species) can be released into the groundwater environment. Within this project, the solute transport processes in groundwater were modeled using the saturated zone model of groundwater flow including phenomena that incorporates advection, both mechanical and hydrodynamic dispersion, solute diffusion as well as adsorption of solutes on the rock inner surfaces. Used model was formulated under consideration of the rock saturation with water. Water fills completely all volume of voids in porous rocks and creates a saturation zone. From a mathematical point of view, the model description takes into consideration Darcy's law, Fick's law of diffusion and equation of adsorption isotherms.

Fly ash from coal combustion have been chosen as potentially best fill material for filling of UCG voids and control of release and migration of contaminants due their widely known ability to isolate contaminants, between other in landfilling, beneficial physical properties and availability. From the point of the view of isolation of contaminants a very important factor is the filtration coefficient of solidified (stabilized) fly ash – water mixtures, what become subject of laboratory measurements. [Ref. 26]



Pilot reactor with reactive barrier made by active carbon after 5 days processing

Removal of heavy metals and radionuclides from water using ceramic membranes

(O. Šolcová, solcova@icpf.cas.cz; joint project with Institute for Single Crystals of NAS of Ukraine and University of Maribor, Slovenia; supported by NATO, project No. SFP 984398)

The problem of environmental pollution with radionuclides is especially acute in Ukraine after the Chernobyl catastrophe in 1986 which caused serious radioactive contamination of the surface aquatic environment. Even currently uranium concentration in liquid low-level radioactive wastes from the object "Shelter" in Chernobyl Exclusion Zone exceeds 30-40 mg/l. These wastes require treatment to meet discharge regulations to the inland waterways and to minimize the volume of radioactive material to be stored. Additionally, Ukraine ranks sixth place in the world and first in Europe regarding the reserves of uranium ores. Large volumes of drainage and process water contaminated with uranium and other radionuclides are formed during mining and enriching of uranium ores. Unfortunately, this polluted water as a rule enters the environment without adequate treatment.

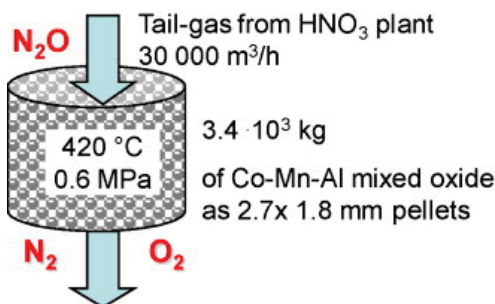
Therefore, the main objective of the project is to develop a family of advanced nano- and ultrafiltration ceramic composite membranes containing functionalized mesoporous silica layers which will be capable of selective binding of heavy metals (Hg, Cd, Cr) and uranium from surface and waste waters and thus preventing or minimizing the environmental exposure to hazardous substances. [Ref. 24]

Abatement of N₂O emissions in off-gas from nitric acid technology

(K. Jirátová, jiratova@icpf.cas.cz; joint project with TU of Ostrava, and ICT; supported by TACR, project No. TA01020336)

Alkali promoted Co₄MnAlO_x mixed oxide (molar ratio of alkali metal/Co = 0.037) were prepared by impregnation of calcined Co-Mn-Al hydrotalcite (molar ratio Co : Mn : Al = 4:1:1) with an aqueous solution of Li, Na, K, Rb or Cs nitrate. N₂O conversion over alkali promoted Co₄MnAlO_x mixed oxide decreased in order Cs > Rb > K > Na = Co₄MnAlO_x > Li in inert gas and was shifted to the lower values in the presence of typical components (NO_x, O₂ and H₂O) of flue gas. The addition of alkali promoters to the Co₄MnAlO_x mixed oxide resulted in a modification of both electronic properties of active metals and acid-base function of the catalyst surface. The promotional effect of alkali metals is connected with their ionization potential, the charge transfer to the catalyst and a decrease in binding energies of all catalyst components (Co, Mn, Al and O). Pilot plant verification of N₂O decomposition over K-promoted Co₄MnAlO_x is shown.

A catalyst for N₂O removal from effluents of nitric acid plants was patented. The catalyst consists of calcined beta-cobalt hydroxide and Cs. The catalyst is prepared by action of NaOH on cobalt nitrates solution in molar NaOH / Co(NO₃)₂ = 0.5 to 2.0 at 20 to 25 °C under mixing for 5-10 min, then is dried, formed into pellets, calcined and impregnated with water solution of Cs compounds to meet molar ratio Cs to Co₃O₄ in the range from 0.003 to 0.060 and again is calcined. Concentration of N₂O in the treated gas is lower than 150 ppm, when initial concentration of N₂O is 1000 ppm and GHSV 0.001 g min ml⁻¹. [Refs.19, 31]

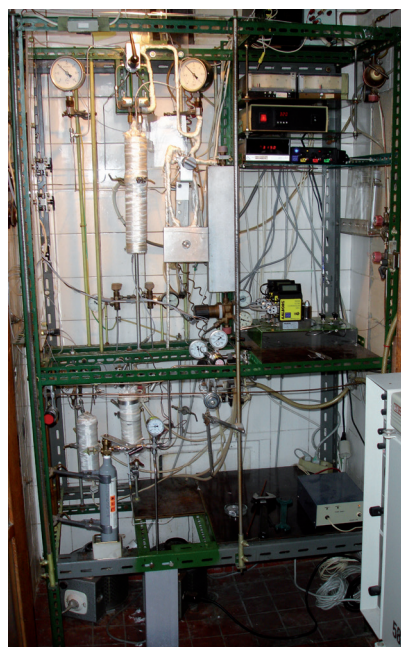


Scheme of the reactor arrangement for N₂O decomposition

Study of hydrodesulfurization and its inhibition by hydrogenation (denitrogenation) over catalysts containing small amounts of noble metals

(Z. Vít, vít@icpf.cas.cz; joint project with Department of Chemistry, Physics and Environment, University of Udine, Italy; supported by GACR, project No. 104/09/0751)

Acidic supports and active phases containing noble metals were studied for hydrodesulfurization (HDS) of model compounds such as thiophene and benzothiophene. Silica-alumina's modified by post-synthesis acid extraction were studied as possible supports of bimetallic Pd-Pt catalysts. The extraction of support increased the surface areas and exposed more Brønsted acidic sites which improved the HDS activity of catalysts. HDS activity was greatly affected by metal precursor and the way of catalyst pretreatment. It was shown that a fraction of active phase, enriched by Pd, accumulated hydrogen in the form of β -Pd hydride phase. Amounts of hydrogen held by hydride phase correlated with thiophene HDS activities showing that activated hydrogen participated in HDS. The inhibition effects of pyridine and quinoline on HDS of thiophene and benzothiophene were studied on Mo and Pd-Mo/alumina catalysts. Noble metal containing catalysts were generally less sensitive to nitrogen bases than conventional CoMo catalysts. Activities and nitrogen tolerance were in relation to C-N bond breaking activity of nitrogen inhibitor.



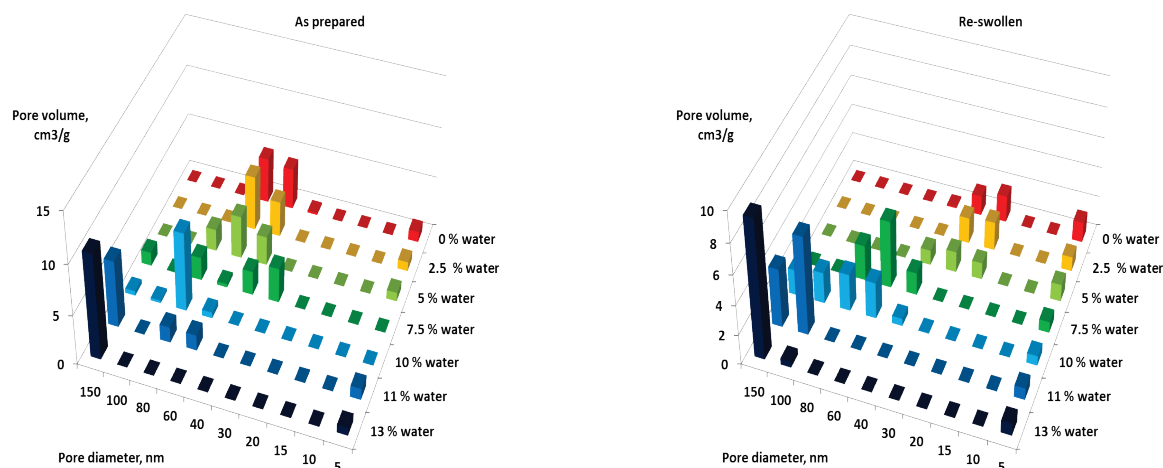
Pressure flow microreactor with fixed bed of catalyst for hydrodesulfurization

Morphology and application properties of mesoporous poly(divinylbenzenes)

(K. Jeřábek, kjer@icpf.cas.cz; joint project with Zhejiang University, Hangzhou, China; supported by MEYS, project No. LH12194)

Chinese colleagues discovered a novel polymerization method producing porous polymers with very high surface area and unique mesoporous morphology, completely different from conventionally prepared materials of similar chemical nature. In their preparation is used exceptionally high dilution of monomers with porogenic solvents. With help of inverse steric exclusion chromatography method developed in Prague providing information on the polymer morphology in its native, swollen state undeformed are investigated relations between preparation conditions of mesoporous functional polymers and their morphology and applications for which the exceptional properties of the mesoporous functional polymers could be advantageous. It was found that the pore volume in the polymer examined just after preparation corresponded to the volume of the porogen used. Resulting high porosity exceeding 90 % can be explained only on the basis of pore formation through

microsyneresis rather than the macrosyneresis mechanism that is common in the synthesis of conventional porous polymer materials. Drying of the polymers of course induces extensive collapse of the porous structure. Water, as additive to the porogenic solvent, influences ability of the polymer morphology to re-swell to its original state.

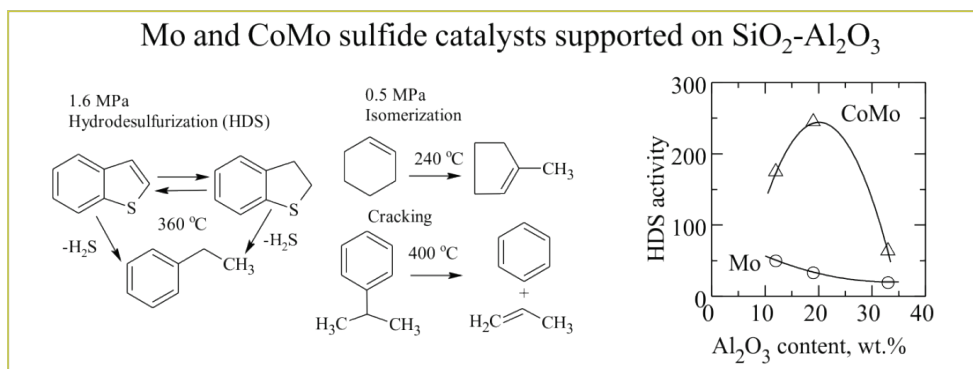


Influence of addition of water to porogenic solvent on the swollen-state morphology of mesoporous poly(divinylbenzenes)

Unconventional composition and preparation of sulfide hydrotreating catalysts

(L. Kaluža, kaluza@icpf.cas.cz; supported by GACR, project No. 106/11/0902)

Catalysts with various MoO₃ and Al₂O₃ contents were prepared by a reaction of acidic SiO₂-Al₂O₃ supports with aqueous slurry of MoO₃. The saturated adsorption amount of MoO₃ corresponded with the amount of Al₂O₃ in the supports. The deposited and sulfided Mo species were accessible for promotion of the activity and selectivity in benzothiophene hydrodesulfurization reaction by Co. The acidity of the SiO₂-Al₂O₃ supports modified by dealumination by leaching with nitric acid in terms of cyclohexene isomerization and cumene cracking were preserved after deposition of the CoMo sulfide phase. Furthermore, a new method based on impregnation of unconventional supports (i.e. activated carbon and ZrO₂) by the nitrilotriacetic acid (NTA) assisted spreading of molybdenum trioxide with cobalt carbonate, or ammonium heptamolybdate with cobalt carbonate was investigated. The NTA systematically increased the promotion effect of Co in the sulfided catalysts in comparison to samples prepared without NTA from ammonium heptamolybdate and cobalt nitrate. The promotion effect of Co was expressed as ratio of activity of CoMo catalyst and its Mo counterpart and NTA increased it by the factor 1.13-1.58 for the studied supports. [Refs. 8, 9]



Model hydrotreating reactions for unconventional catalysts

Microalgae as a promising sources of omega-3 unsaturated fatty acids and their incorporation into the human food chain

(F. Kaštánek, kastanek@icpf.cas.cz; joint project with Rabbit Trhový Štěpánov a.s., IBOT, EcoFuel Laboratories, Institute of Microbiology ASCR, Mydlářka a.s., Rabbit CZ a.s., Rabbit Chotýšany a.s., CU, ICPF, ICT Prague; supported by TACR, project No. TA03011027)

The project is focused on utilization of the lipid new sources with the high content of the healthy polyunsaturated fatty acids (PUFAs), omega-3 types. Microorganisms, mainly biotechnologically produced eustigmatofit microalgae with the high content of PUFA, have been applied. New types of mixotrophic bioreactors were designed to obtain the optimal content PUFA in biomass. Products will be used as the feeding additives for poultry.



The newly designed biophotoreactor

Innovative autoMotive MEA Development - implementation of Iphe-genie Achievements Targeted at Excellence (IMMEDIATE)

(L. Kaluža, kaluza@icpf.cas.cz; supported by European Union's 7th Framework Programme FP7/2007-2013 for the Fuel Cells and Hydrogen Joint Undertaking Technology Initiative, project No. 303466 and co-supported by MEYS, project No. 7HX13003)

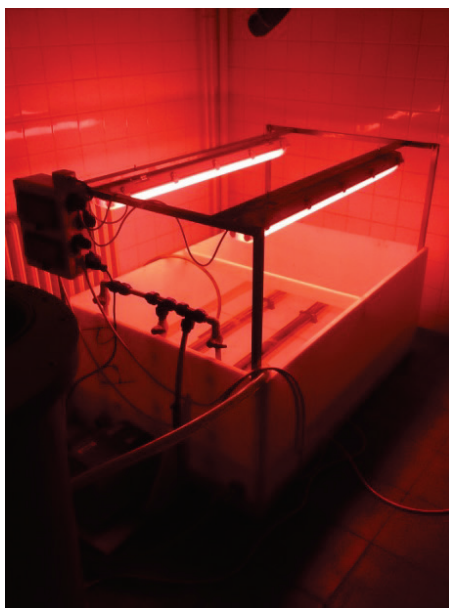
Fulfilling of increasingly stringent environmental restrictions imposed on transportation drives the research on alternative energy resources such as hydrogen and fuel cells. Preparation of carbon black supported 60 wt. % Pt was studied as a conventional catalyst for membrane electrode assembly. Platinum was deposited on the supports XC72R, XC72 (Vulcan, Cabot Corp.), and ENSACO 290G, 350G (Timcal Graphite & Carbon Ltd.) and a research grade PT-P (Timcal Graphite & Carbon Ltd.): (i) from true solutions of H_2PtCl_6 , $Pt(C_5H_7O_2)_2$, $Pt(NH_3)_4(NO_3)_2$, or $Pt(NH_3)_2(NO_2)_2$, and (ii) from fine dispersions of $Pt(C_5H_7O_2)_2$, PtO_2 , $Pt(NH_3)_4(OH)_2$. Atomic adsorption spectroscopy and scanning electron microscopy were used for elemental analysis and determination of Pt content. N_2 adsorption-desorption measurements revealed highly developed mesoporous system with maximum on the pore-size distribution curve at pore-size radius 7 nm for Pt-P, which was quite unique among the studied supports. Deposited Pt species were dried, calcined or reduced and were subjected to temperature programmed reduction (TPR). After degassing at increased tempera-

ture, the Pt dispersion was determined by hydrogen chemisorption at - 60 °C. TPR revealed that PtO_2 , H_2PtCl_6 , $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$, and $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ deposited on carbon blacks and dried in rotary vacuum evaporator at 95 °C were reduced to metallic Pt at 0, 70, 120, 140, 150 °C, respectively. Specific interaction of the Pt precursor with support surface was considered necessary for formation of the desired 4-6 nm Pt particles from H_2PtCl_6 or $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$. The deposition of colloidal form of PtO_2 or $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ seemed to be particularly promising because it represented relatively clean and gentle method of Pt deposition. This was manifested by the sharp reduction peaks but the tailored high Pt dispersion was not reached.

Reactive chemical barriers for decontamination of heavily polluted waters

(P. Klusoň, kluson@icpf.cas.cz; joint project with Dekonta a.s.; supported by MIT, project No. FR-TI1/065)

The project was focusing on the final studies of the special oxidations of contaminants in industrially polluted waters. Special attention was paid to aniline and nitrobenzene waters, to waters with dissolved chlorinated compounds and to inorganic contamination with certain specific ions. The used methods were the photocatalytic oxidations with phthalocyanines, name with Zn phthalocyanine, and with UVC and hydrogen peroxide. Among other techniques electrocoagulation was also tested to reduce both the organic as well as the inorganic pollutants. The project thus deals in a complex manner with the problem of industrial pollution of various types and origins. The Recheba concept represents a kind of passive approach, however, assisted with highly advanced processes for effective water decontamination. The systems had been still tested on a laboratory scale, however, much more attention was now paid to the large scale operations. [Ref. 30]



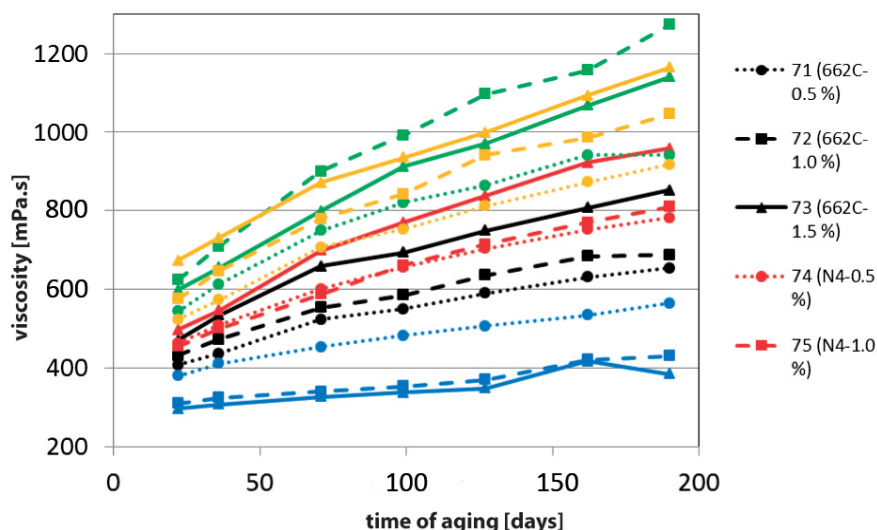
Detail of the phthalocyanine decontamination unit

Research and development of special dyes using ionic liquids as efficient functional additives

(P. Klusoň, kluson@icpf.cas.cz; joint project with Teluria, Techem; supported by MIT, project No. FR-TI3/057)

This project deals with utilization of special types of ionic liquids based on tetra-alkylammonium bistriflateamides as additives for new types of dyes. These additives may

bring special properties to the final product, such as higher mechanical stability, higher effect of the pigment addition and lower amounts of various pigments, more complex compositional solutions, etc. The project comprises preparation of the selected ionic liquids, their characterization by many types of physical methods (viscosity, contact angle, density, etc.), and then their direct application together with other characteristic components. The project addresses completely new way to obtain modern dyes useful both in industry as well as for standard and common customers.



Viscosity change (at $T = 23^{\circ}\text{C}$) in time of alkyde resin with various ionic liquids at three concentrations (additives do not change the Newtonian character of resin)

Research and development of advanced thin film elements for direct evaluation of the time variable with by means of the precisely calibrated color change

(P. Kluson, kluson@icpf.cas.cz; joint project with INVOS Ltd., COC Ltd., CU, ICPF, TU Brno; supported by TACR, project No. TA03010548)

Aim of the project, shortly named *Color Clocks*, focuses on the applied research & development and testing of the advanced thin film elements for direct evaluation of the time variable by means of precisely calibrated color change. These elements represent a highly specific form for time measurement under highly specific conditions and for very specific practical purposes. These structures are supposed to be used as tools for simple visual and intuitive evaluation of the time variable under very different circumstances. It is a kind of standard memory element collecting a certain type of data, which are then assessed in the cumulative form as the absorbed light dose of characteristic energy, or characteristic energetic region. The light sensitive films are based on uniformly organized nanoparticles that exhibit an adjustable photocatalytic activity toward the decomposition of selected organic structures deposited onto their surfaces. The decolorization process is then carefully calibrated for many different types of probe organic molecules. There are many possible practical applications of these materials, among others dermatology, conservation and storage of historical monuments and artefacts, should be mentioned.

Use of PFG NMR, stochastic reconstruction and molecular simulation to estimate transport-related texture characteristics of advanced porous materials

(O. Šolcová, solcova@icpf.cas.cz; joint project with CU and JH IPC; supported by GACR, project No. P204/11/1206)

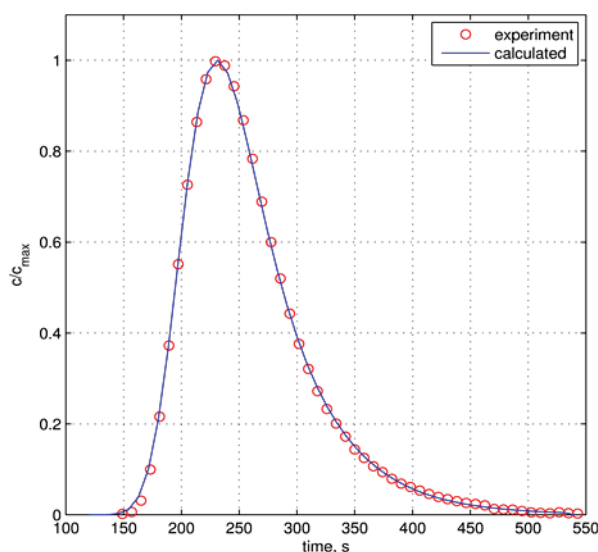
Searching after the functional relationship between diffusion of fluid in disordered solids (e.g. porous solids) and their microstructure is an active field of research in membrane sci-

ce, catalysis, biophysics, civil engineering and other branches of research and development. During several past decades the pulsed field gradient (PFG) NMR technique has proved to be a powerful tool for measuring of self-diffusion in such systems. The focus of the project is on transport investigation of liquid species contained in porous materials (non-consolidated and consolidated) with monodisperse and bidisperse porous structure with excursions to adjacent supercritical regions. A rational system of transport-related structure characteristics to predict transport behavior of liquids and supercritical fluids will be searched by combined application of PFG NMR, image analysis of porous materials and molecular simulation of self-diffusion in selected two-phase systems.

The effective transport properties of advanced porous materials based on hydroxyapatite nanopowders were characterized by means of the effective diffusion coefficients. Polystyrene molecules substituted a role of biofluids transported in human body (especially in bones) were used as appropriate model compounds.

The effective diffusion coefficients for two polystyrene samples with different relative molecular weights (1000 and 100,000) in cyclohexane on hydroxyapatite were evaluated. Comparison of the chromatographic response signals for polystyrene tracers with different molecular weights is depicted in Fig. Furthermore, Fig. illustrates a very good fit between experimental data (circle marks) and the calculated chromatographic response signals (solid lines) based on the optimized model parameters.

It was found that the binary effective diffusion coefficients revealed much lower values in comparison with the binary bulk ones due to the strong influence of hindered diffusion in hydroxyapatite pore network. [Refs. 25, 29].



Response curve for polystyrene ($M_w = 100,000$) in cyclohexane on hydroxyapatite. Experimental (°), calculated (—)

Removal of endocrine disruptors from waste and drinking water by photocatalytic and biological processes

(O. Šolcová, solcova@icpf.cas.cz; joint project with Dekonta, a.s. and Institute of Microbiology ASCR; supported by TACR, project No. TA01020804)

Endocrine disruptors represent the group of chemical substances disrupting the hormonal indication of vertebrates and thereby they could encroach on the organism function. To the group of endocrine disruptors belong surfactants, softeners, fungicides, insecticides and some kinds of medications and hormonal contraception. They are commonly presented not only in

the waste water but also in the natural water. Endocrine disruptors are persistent to degradation by common chemicals as well as biological and photolytic processes. The necessity of finding the alternative solutions leads to development and use of the new technologies. Photo-catalysis using semiconductor particles have found increasing interest to solve the endocrine disruptors remove problems.

This study is focused on verification of the specially designed photoactive materials and their modified versions suitable for photo-processes carried out upon illumination in the UV-light. Ethynylestradiol, nonylphenol and bisphenol A were chosen as typical compounds belong to the endocrine disruptor group. In this work the water decontamination with various concentrations of endocrine disruptors in the two types of reactors; batch and plug flow arrangement on the titania thin layers were studied. Moreover, the application of the specially designed pilot plan photoreactor has been studied. [Ref. 16]



Pilot plant photo-reactor

Ionic liquids as additives for special pigments

(O. Šolcová, solcova@icpf.cas.cz; joint project with Synthesia, Techem; supported by MIT, project No. FR-TI4/189)

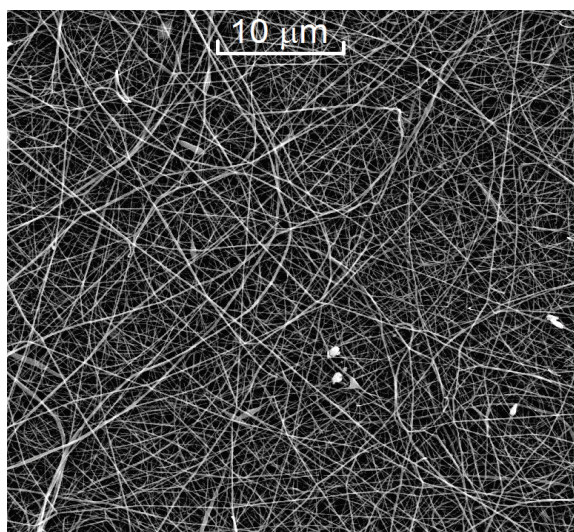
Ionic liquids are composed of large ions with a low degree of the overall molecular symmetry. Very high coulombic interactions are behind their impressive electrical and mechanical stabilities, thermal and pressure resistivity, and extremely low tension of vapors. Low flammability, very good electrical conductivity, high thermal capacity and unusual phase behavior might be added to the previous list of exceptional properties. No doubts these features qualify them for a broad band applications ranging from “green solvents” due to their negligible volatility, over templates for synthesis of nanoparticles (some of them tend to form organized ionic clusters), liquid electrolytes in solar cells and fuel cells, to liquid adhesives, special lubricants, chromatography mobile phases, incombustion additives, etc.

One of the most prominent applications is their use as special additives for pigments and dye compositions. If the side-chains are too short, they do not disturb the ionic network significantly and, also, they do not possess enough conformational freedom to adopt a low energy configuration. However, increasing the chain-length the role of its spatial arrangement becomes much more important. In this respect this project pays special attention to the utilization of quaternary ammonium ionic liquids, namely n-alkyl-triethylammonium bis(trifluoromethane sulfonyl) imides ($N_{R222}Tf_2N$, $R = 6, 7, 8, 10, 12, 14$) with a variable length of an alkyl chain are specially promising.

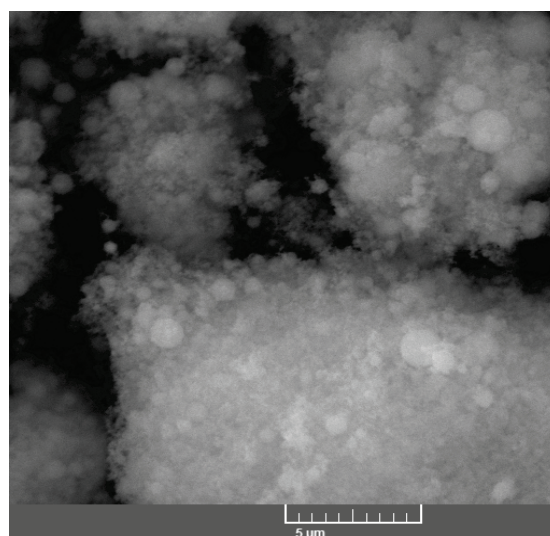
Transport characteristics of novel biocompatible materials

(K. Soukup, soukup@icpf.cas.cz; supported by GACR, project No. P106/11/P459)

The aim of the project was focused on comprehensive characterization of the microstructure properties of the novel biocompatible porous solids included both electrospun polymeric membranes and bone-like hydroxyapatites. In order to prepare materials having the targeted effects for the required applications (both in medical and chemical), the knowledge of the transport characteristics typical of its pore network is of the prime importance. Four experimental setups were utilized for the transport characteristics determination: Graham's diffusion cell, Wicke-Kallenbach cell, and permeation cell were used for the gas transport measurements and inverse liquid chromatography technique for diffusion measurements in liquids. Special attention was paid to the detailed statistical analysis of the optimized transport parameters and effective binary diffusion coefficients. The statistical reliability of the calculated transport parameters was assessed by means of their confidence regions (from diffusion measurements) and confidence intervals (from permeation measurements) computed at a significance level of 5%. It was found that the confidence of the optimized transport parameter ψ (from diffusion) and $\langle r \rangle \psi$ (from permeation) reflecting the influence of the molecular and Knudsen mass transport mechanism, respectively, was much higher than transport parameters $\langle r \rangle \psi$ (from diffusion) and $\langle r^2 \rangle \psi$ (from permeation). It was additionally found that tracer solute with the larger molecular weight shows shorter retention time compared to tracer solute with the lower molecular weight. The observed difference in retention times corresponds to expectation that the short-chain solute will penetrate deeper to the pore system of biocompatible nanopowders and will be more retained in comparison with the long-chain solute. [Refs. 25, 26, 29]



Micrograph of nanofibrous chitosan



Micrograph of bone-like hydroxyapatite

New heterogeneous catalysts for environmental protection

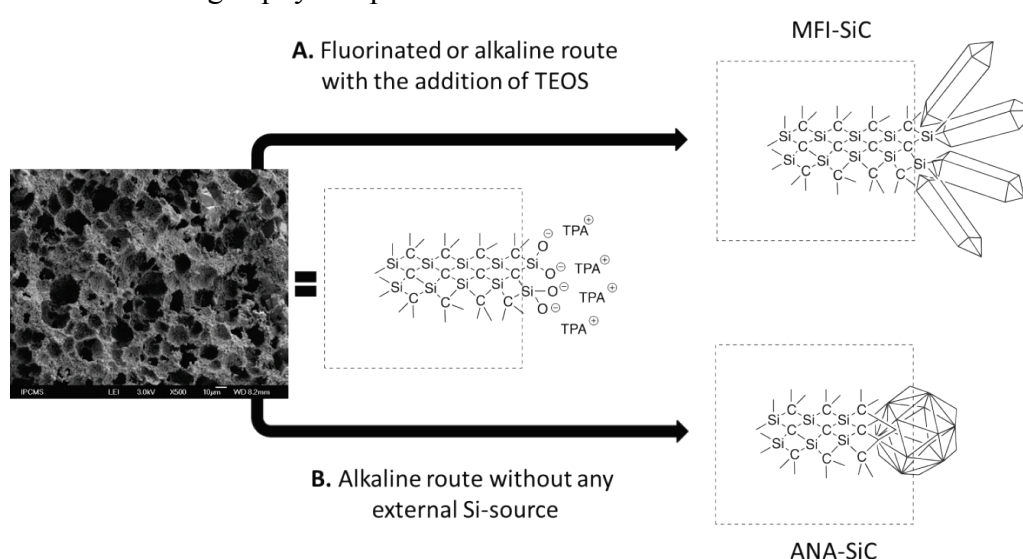
(L. Kaluža, kaluza@icpf.cas.cz; joint bilateral co-operation with Institute of Catalysis, BAS, Sofia, Bulgaria; supported by ASCR)

High surface area TiO₂ nanotubes (Ti-NT) synthesized by alkali hydrothermal method were used as a support for NiW hydrodesulphurization catalyst. Nickel salt of 12-tungstophosphoric acid (Ni_{3/2}PW₁₂O₄₀) was applied as oxide precursor of the active components. A polytungstate phase evidenced by Raman spectroscopy was observed indicating the destruction of the initial heteropolyanion. The catalytic experiments revealed two times higher thiophene conversion on NiW catalyst supported on Ti-NT than those of catalysts supported on alumina and titania. Increased HDS activity of the NiW catalyst supported on Ti-NT could be related to a higher amount of W oxysulfide entities interacting with Ni sulfide particles as consequence of the electronic effects of the Ti-NT observed with XPS analysis. [Ref. 20]

Novel materials with hierarchical pore structure: preparation and evaluation of the transport characteristics

(K. Soukup, soukup@icpf.cas.cz; joint bilateral project with University of Strasbourg; supported by MEYS, project No. 7AMB12FR029)

In the present bilateral project, we would like to propose strategies towards the design of structured catalytic beds made of hierarchical zeolites with improved hydrodynamics (compared to extrudates or conventional pellets), combining both the advantages of zeolitic catalysts and of a tailored porosity (triple level of porosity: micro-, meso- together with an appropriate macroporosity). Several syntheses have been performed to allow the growth of zeolite crystals on α -silicon carbide supports (α -SiC). Silicon-carbide foams exhibit a duplex macroporous structure. Framework type MFI and ANA of zeolites have been successfully coated to this relatively inert supporting material. While the synthesis of MFI/SiC required the presence of an additional Si-containing source, in contrast, ANA/SiC composites have been unexpectedly obtained through the self-recrystallization of the silicon contained in the α -SiC substrate. The different composite materials were thoroughly characterized by SEM, comprehensive textural and gas transport measurements and XRD. The coating rates as well as the coverage by ANA zeolite crystals on SiC surface were determined by both SEM observations and nitrogen physisorption measurements.

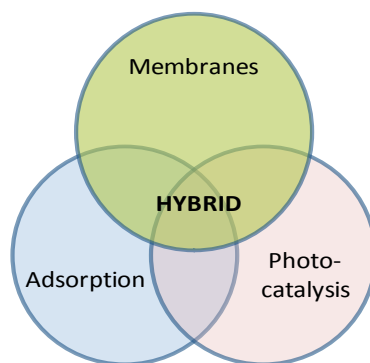


Two different approaches followed to grow zeolites on α -SiC, resulting in; (A) MFI-crystals and (B) ANA-crystals. Schematic representation of the crystal morphology at the SiC interface.

Hybride membrane process for water treatment (HYMEPRO)

(O. Šolcová, L. Matějová (member of the steering group), solcova@icpf.cas.cz, matejova@icpf.cas.cz; joint project with University of Oulu, Lappeenranta University of Technology, Corvinus University of Budapest, National University of Engineering in Lima and 12 industrial partners; supported by Finish funding agency TEKES)

Project deals with the development of a novel, active and sustainable hybrid wastewater treatment process that removes simultaneously heavy metals, arsenic and nutrients from waters. The developed technology is designed based on the green chemistry and engineering principles. [Ref. 13]



Production of 3rd generation biofuels by enzymatic catalyzed transesterification of microalgal oil

(O. Šolcová, solcova@icpf.cas.cz; joint project with EcoFuel Laboratories, TransBiodiesel, Ltd. Israel; supported by MEYS, GESHER/MOST, project No. LJ12002)

The objective of the project is to develop a closed process for autotrophic cultivation of microalgae and biorefinery approach using novel extraction techniques for production of algal oils and high-value feed additives from wet algal biomass. The oil will be further converted to biodiesel utilizing a novel immobilized enzymatic technology.

Project makes huge benefit from connecting algae cultivation and photo-bioreactor design experience together with the down-stream chemical engineering experience of Czech partners with the complementary experience of Israel partner in the area of biodiesel production. Important benefit lies in the transfer of developed algal biotechnologies to Israel where conditions of warm Mediterranean climate with high level of photosynthetic solar radiation will allow efficient year-round large-scale cultivation of algae mainly using deserted non-arable land for photobioreactors installation. In comparison, climatic conditions in Czech Republic allows for only approx. 150 days cultivation period.

The process consists of cultivation of microalgae in the novel high-rate photobioreactors using waste streams as nutrients, the novel low-energy cell harvesting techniques and lipids extraction directly from wet biomass coupled with advanced high-yield enzymatic transesterification of algal oil into biodiesel. The extraction of oil from algal biomass will be environmentally friendly, leaving residual algal biomass with high content of proteins and carotenoids, suitable for use as animal feed supplement. This biorefinery approach influences positively the feasibility of production of algal biodiesel.

Utilization of vast knowledge of microalgae cultivation techniques and photo-bioreactor existing by partners in Czech Republic will facilitate development of techniques for production of biodiesel feedstock from algal oil. In Israel - TransBiodiesel will contribute to development of non-lipid high tolerance enzymes. Such technologically advanced enzymes will be used in a "pilot unit" for transesterification algal oil using environmentally friendly and energy saving advanced enzymatic process for 3rd generation of biodiesel production.



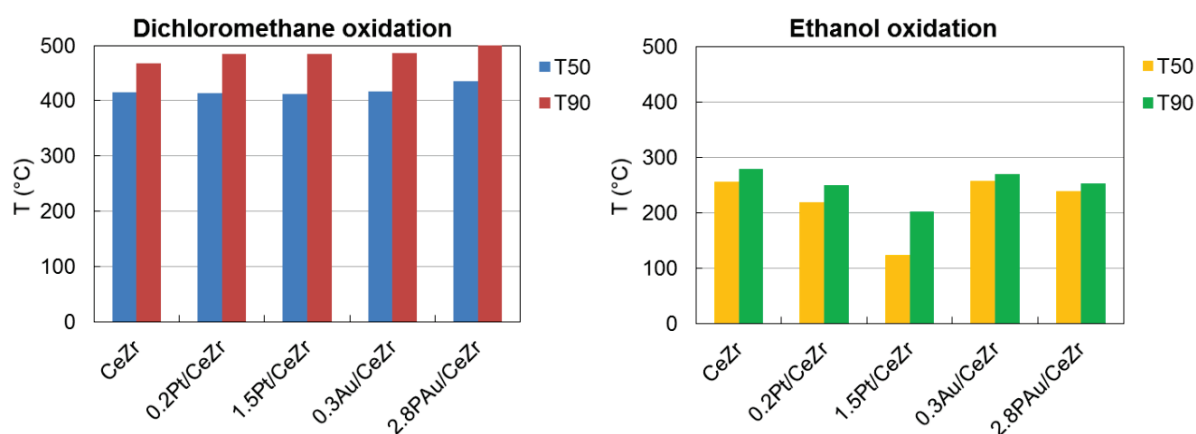
Pilot plant bioreactor

Washcoated ceramic monoliths for total oxidation of volatile organic compounds

(P. Topka, topka@icpf.cas.cz; supported by GACR, project No. 13-24186P)

This project is focused on the development of monolithic catalysts for total oxidation of volatile organic compounds based on ceria-zirconia mixed oxide doped by noble metals. Volatile organic compounds are one of the major contributors to air pollution and their emissions are strictly regulated by the directives of European Union. Catalytic oxidation is efficient, cost-effective and environmentally friendly way to treat VOC emissions. In industrial applications, large volumes of gases have to be treated and therefore monolithic catalysts have to be used. Ceramic monoliths are chosen due to their successful application in automotive catalysts and in the industry. The aim of the project is to propose methods for the preparation of highly active and selective monolithic catalysts and to develop the strategy for their tailored synthesis. [Ref. 15]

Activity of CeO₂-ZrO₂ supported Pt and Au catalysts



Activity of ceria-zirconia supported platinum and gold catalysts in the oxidation of dichloromethane and ethanol

International co-operations

Institute of Catalysis, BAS, Sofia, Bulgaria: New heterogeneous catalysts for environmental protection

University of Oulu, Oulu, Finland: New catalysts for VOC oxidation

University of Oulu, Oulu, Finland: Hybrid membrane process for water treatment

University of Paris VI, Paris, France: Theory of chemical bond

University of Poitiers, Poitiers, France: New catalysts for VOC elimination

University of Strasbourg, Strasbourg, France: Determination of transport characteristics of novel materials with hierarchical pore structure

University of Stuttgart, Stuttgart, Germany: Transport characteristics for coal gasification

Department of Chemical Sciences, University of Padua, Padua, Italy: Polymer-based catalysts

University of Maribor, Maribor, Slovenia: PolyHYPE polymers

University of Graz, Graz, Austria: Porous polymers

Silesian University of Technology, Gliwice, Poland: Transport characteristics for coal gasification

Central Mining Institute, Katowice, Poland: Transport characteristics for coal gasification

University of Barcelona, Barcelona, Spain: Ion exchanger catalysts

Zhejiang University, Hangzhou, China: Mesoporous poly(divinylbenzenes)

Institute of Surface Chemistry NAS, Kiev, Ukraine: Preparation of nanoporous materials

University of Bangor, Bangor, Wales, United Kingdom: New sensors based on optically active nanomaterials

UCG Partnership Ltd, Woking, United Kingdom: Transport characteristics for coal gasification

University of Udine, Udine, Italy: Characterization of noble metal catalysts and desulfurization on unconventional catalysts

Istanbul Technical University, Istanbul, Turkey: Synthesis and Thorough Characterization of Composite Functionalized Polymeric Nano-Structure

Institute of Computational Chemistry, University of Girona, Spain

IRD Fuel Cells A/S, Svendborg, Denmark: fuel cells electroactivity

Centre National de la Recherche Scientifique, Montpellier, France: non-carbonaceous supports, catalysts

FUMA-TECH Gesellschaft für Funktionelle Membranen und Anlagentechnologie MBH, St Ingbert, Germany: ionomers

Shanghai Jiao Tong University, Shanghai, China: ionomers and polymers

Volvo Technology AB, Göteborg, Sweden: MAE test protocols

SGL Carbon GmbH, Meitingen, Germany: electroconductive gas diffusive layers

JRC Joint Research Centre-European Commission, Brussels, Belgium: FCH tests

TimCal SA, Bodio, Switzerland: carbon black supports

Visitors

L. Benoit, University of Strasbourg, France

M. Boltz, University of Strasbourg, France

P. Losch, University of Strasbourg, France

P. Krajnc, University of Maribor, Slovenia

J. Grabowski, Central Mining Institute, Katowice, Poland

M. Green, UCG Engineering Ltd, United Kingdom

A. Lobnik, University of Maribor, Maribor, Slovenia

A. Sezai Sarac, Istanbul Technical University Faculty of Sciences

R. Palcheva, Institute of Catalysis, BAS, Sofia, Bulgaria
K. Stanczyk, Central Mining Institute, Katowice, Poland
Y. Zub, Institute of Surface Chemistry NAS, Ukraine
M. Rodlert, TimCal SA, Bodio, Switzerland
F. Mornaghini, TimCal SA, Bodio, Switzerland
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I. Galbiati, SGL Carbon GmbH, Meitingen, Germany
H. Gao, Shanghai Jiao Tong University, Shanghai, China
B. Bauer, FUMA-TECH, St Ingbert, Germany
W. Zhang, FUMA-TECH, St Ingbert, Germany
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J. Roziere, Centre National de la Recherche Scientifique, Montpellier, France
J.L. Bonde, IRD Fuel Cells A/S, Svendborg, Denmark
M. Odgaard, IRD Fuel Cells A/S, Svendborg, Denmark
M.J. Larsen, IRD Fuel Cells A/S, Svendborg, Denmark
D.N. Tito, Elysium Projects Ltd., Bangor, United Kingdom

Teaching

P. Klusoň: UJEP, Faculty of the Environment, course "Toxicology"
R. Ponec: CU, Faculty of Science, course "Structure and Reactivity"
O. Šolcová: ICT, Faculty of Chemical Technology, postgraduate course "Texture of Porous Solids"

Publications

Original Papers

- [1] Bučinský L., Büchel G.E., Ponec R., Rapta P., Breza M., Kožíšek J., Gall M., Biskupič S., Fronc M., Schiessl K., Cuzan O., Prodius D.: On the Electronic Structure of the mer, trans-[RuCl₃(1H-indazole)₂(NO)], a Hypothetical Metabolite of the Antitumor Drug Candidate KP1019: Experimental and DFT Study. *Eur. J. Inorg. Chem.* 14, 2505-2519 (2013).
- [2] Centomo P., Bonato I., Hanková L., Holub L., Jeřábek K., Zecca M.: Novel Ion-Exchange Catalysts for Reactions Involving Lipophilic Reagents: Perspectives in the Reaction of Esterifications of Fatty Acids with Methanol. *Top. Catal.* 56(9-10), 611-617 (2013).
- [3] Cooper D.L., Ponec R.: Bond Formation in Diatomic Transition Metal Hydrides: Insights from the Analysis of Domain-Averaged Fermi holes. *Int. J. Quant. Chem.* 113(2), 102-111 (2013).
- [4] Hejtmánek V., Veselý M., Čapek P.: Pore Structure and Effective Permeability of Metallic Filters. *J. Phys. Conf. Ser.* 410, 012110 (2013).
- [5] Hrabánek P., Zikánová A., Drahošoupil J., Prokopová O., Brabec L., Jirka I., Matějková M., Fíla V., de la Iglesia O., Kočířik M.: Combined Silica Sources to Prepare Preferentially Oriented Silicalite-1 Layers on Various Supports. *Micropor. Mesopor. Mat.* 174(JUL 1), 154-162 (2013).
- [6] Jeřábek K., Hanková L., Holub L., Slavík H.: Changes in Ion Exchanger Catalysts after Extremely Long Exposition to the Reactor Environment. *Ind. Eng. Chem. Res.* 52(2), 985-989 (2013).
- [7] Jeřábek K., Zecca M., Centomo P., Marchionda F., Peruzzo L., Canton P., Negro E., Di Noto V., Corain B.: Synthesis of Nanocomposites from Pd0 and a Hyper-Cross-Linked Functional Resin Obtained from a Conventional Gel-Type Precursor. *Chem. Eur. J.*, 19(28), 9381-9387 (2013).
- [8] Kaluža L., Gulková D., Vít Z., Zdražil M.: Water-Assisted Spreading of MoO₃ onto SiO₂-Al₂O₃ Supports for Preparation of Sulfide CoMo Hydrodesulfurization Catalysts. *Fuel* 112, 272-276 (2013).

- [9] Kaluža L., Zdražil M., Gulková D., Vít Z.: The Influence of the Chelating Agent Nitrilotriacetic Acid on Promotion of Hydrodesulfurization Activity by Co in CoMo Catalysts Prepared on Al₂O₃, C, and ZrO₂ Supports. *Chem. Eng. Trans.* 32(2), 841-846 (2013).
- [10] Kovačič S., Matsko N.B., Jeřábek K., Krajnc P., Slugovc Ch.: On the Mechanical Properties of HIPE Templated Macroporous Poly(dicyclopentadiene) Prepared with Low Surfactant Amounts. *J. Mater. Chem. A* 1(3), 487-490 (2013).
- [11] Kovanda F., Jirátová K., Ludvíková J., Raabová H.: Co-Mn-Al Mixed Oxides on Anodized Aluminum Supports and Their Use as Catalysts in the Total Oxidation of Ethanol. *Appl. Catal., A* 464, 181-190 (2013).
- [12] Ludvíková J., Jirátová K., Klempa J., Raabová H., Zapivovarski Votipka Z., Kovanda F.: Ethanol Total Oxidation Over Calcined Layered Double Hydroxides Modified with Organic Components. *Kemija u industriji* 62(5-6), 137-146 (2013).
- [13] Matěj Z., Matějová L., Kužel R.: XRD Analysis of Nanocrystalline Anatase Powders Prepared by Various Chemical Routes: Correlations between Micro-structure and Crystal Structure Parameters. *Powder Diffr.* 28(Suppl. 2), 161-183 (2013).
- [14] Matějová L., Kočí K., Reli M., Čapek L., Matějka V., Šolcová O., Obalová L.: On Sol-Gel Derived Au-Enriched TiO₂ and TiO₂-ZrO₂ Photocatalysts and Their Investigation in Photocatalytic Reduction of Carbon Dioxide. *Appl. Surf. Sci.* 285(Part B), 688-696 (2013).
- [15] Matějová L., Topka P., Kaluža L., Pitkääho S., Ojala S., Gaálová J., Keiski R.L.: Total Oxidation of Dichloromethane and Ethanol over Ceria-Zirconia Mixed Oxide Supported Platinum and Gold Catalysts. *Appl. Catal. B-Environ.* 142-143, 54-64 (2013).
- [16] Matějová L., Valeš V., Fajgar R., Matěj Z., Holý V., Šolcová O.: Reverse Micelles Directed Synthesis of TiO₂-CeO₂ Mixed Oxides and Investigation of Their Crystal Structure and Morphology. *J. Solid State Chem.* 198, 485-495 (2013).
- [17] Mikulová Z., Šeděnková I., Matějová L., Večeř M., Domek V.: Study of Carbon Black Obtained by Pyrolysis of Waste Scrap Tyres. *J. Therm. Anal. Calorim.* 111, 1475-1481 (2013).
- [18] Morozová M., Klusoň P., Dzik P., Veselý M., Baudys M., Krýsa J., Šolcová O.: The Influence of Various Deposition Techniques on the Photoelectrochemical Properties of the Titanium Dioxide Thin Film. *J. Sol-Gel Sci. Technol.* 65(3), 452-458 (2013).
- [19] Obalová L., Karásková K., Wach A., Kustrowski P., Mamulová-Kutláková K., Michalík S., Jirátová K.: Alkali Metals as Promoters in Co-Mn-Al Mixed Oxide for N₂O Decomposition. *Appl. Catal., A* 462-463, 227-235 (2013).
- [20] Palcheva R., Dimitrov L., Tyuliev G., Spojakina A., Jirátová K.: TiO₂ Nanotubes Supported NiW Hydrodesulphurization Catalysts: Characterization and Activity. *Appl. Surf. Sci.* 265, 309-316 (2013).
- [21] Pitkääho S., Nevanperä T., Matějová L., Ojala S., Keiski R.L.: Oxidation of Dichloromethane over Pt, Pd, Rh, and V₂O₅ Catalysts Supported on Al₂O₃, Al₂O₃-TiO₂ and Al₂O₃-CeO₂. *Appl. Catal., B* 138, 33-42 (2013).
- [22] Ponec R., Beran P.: On the Mechanism of Dihydrogen Activation by Frustrated Lewis Pairs. Insights from the Analysis of Domain Averaged Fermi Holes and Generalized Population Analysis. *J. Phys. Chem. A* 117(12), 2656-2663 (2013).
- [23] Ponec R., Ramos-Cordóba E., Salvador P.: Bonding Guandary in the [Cu₃S₂]⁽³⁺⁾ Core. Insights from the Analysis of Domain Averaged Fermi holes and the Local Spin. *J. Phys. Chem. A* 117(9), 1975-1982 (2013).
- [24] Sliesarenko V.V., Dudarko O.A., Zub Y.L., Seisenbaeva G.A., Kessler V.G., Topka P., Šolcová O.: One-Pot Synthesis of Mesoporous SBA-15 Containing Protonated 3- Aminopropyl Groups. *J. Porous Mater.* 20(5), 1315-1321 (2013).
- [25] Soukup K., Hejtmánek V., Petráš D., Šolcová O.: Determination of Texture and Transport Characteristics of Electrospun Nanofibrous Mats. *Colloids Surf., A* 437(SI), 133-140 (2013).
- [26] Šolcová O., Rogut J., Soukup K.: Chemical Engineering Application of Transport Characteristics. *Kemija u industry* 62(5-6), 215-218 (2013).

Review papers

- [27] Jeřábek K.: Ion Exchanger Catalysts. *Kemija u industriji* 62(5-6), 171-176 (2013).

Books and monographs

- [28] Topka P.: *Molybdenum Oxide & Mesoporous Silica Metathesis Catalysts. New Catalysts for Alkene Metathesis and Alkyne Polymerization*. 152pp., LAP LAMBERT Academic Publishing, Saarbrücken 2013.

Chapters in books

- [29] Soukup K., Hejtmánek V., Šolcová O.: Determination of Transport Characteristics of Porous Bio-compatible Materials. In: *Recent Advances in Chemical Engineering, Biochemistry and Computational Chemistry*. (Moller J.A.D., Kibler M.R., Hefferlin R., Ed.), pp. 66-71, WSEAS Press, Athens 2013.

Patents

- [30] Žebrák R., Wimmerová L., Mašín P., Klusoň P., Krystyník P., Domín T., Hejda S.: Způsob dekontaminace odpadní vody s obsahem rozpuštěných organických látek a zařízení k provádění tohoto způsobu. (Czech) The Method of Decontamination of Wastewaters Containing Dissolved Organic Substances and the Apparatus for Performing this Method. *Pat. No. 304222/PV 2012-830*. Applied: 12.11.23, Patented: 13.11.27.
- [31] Kovanda F., Obalová L., Jiráková K., Šrámek J.: Katalyzátor pro odstranění N₂O z odpadních plynů a způsob jeho výroby. (Czech) Catalyst for N₂O Removal from Effluents and Way of Its Manufacture. *Pat. No. PV 2013-1070*. Applied: 13.12.27.
- [32] Warshavsky A., Strikovskiy A., Jeřábek K.: Selective sorbent for separation of heavy metal ions and method for its preparation. *Israel Pat. Appl. 121369*.
- [33] Kaštánek F., Šolcová O., Maléterová Y., Spáčilová L., Maternová H., Mašín P., Žebrák R.: Zařízení pro fotokatalytickou dekontaminaci vod s obsahem organických látek, zejména endokrinních disruptorů. (Czech) Device for Photo-Catalytic Decontamination of Water Containing Organic Compounds, Especially Endocrine Disruptors. *Pat. No. PV 2013-522*. Applied: 13.07.03.