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Instytut Katalizy i Fizykochemii Powierzchni im. Jerzego Habera PAN

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Komitet Chemii PAN

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PL-1

Methanol partial oxidation to formaldehyde (MTF) over silver – new kinetic and structural insights

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About half of the world's production of formaldehyde (>25 Mt/year) proceeds via methanol oxidation over silver in the form of a shallow bed of Ag particles. Short residence time and product temperature quench facilitate yields up to 90%, but 8-10% of the feedstock is non-selectively oxidized to CO_2. The catalysis is difficult to study at industrially relevant conditions, especially those involving steam co-feed (water ballast). This is due to the high temperature (600-700°C), very fast reactions, homogeneous contributions, challenging product stability and quantification, and interplay with a - dynamic – Ag catalyst surface and bulk morphology. We have therefore proceeded along several directions, i.e., investigation of sub-reaction systems (e.g., CO/H_2 oxidation), detailed characterization (e.g., FIB/TEM), and development of an annular reactor configuration that enables reaction data at high temperature and low conversion without impact of mass transfer limitations or reactions in the gas phase [1,2].

Dissolution of oxygen atoms into the bulk Ag lattice has been reported as important to the Ag surface activity as well as the refacetting and pinhole formation commonly observed post-reaction. Through different high temperature treatments, we established that exposure to oxygen alone or in ($CO/H_2/CH_3OH$) oxidation mixtures was sufficient to induce significant morphology changes of this type, i.e. hydrogen-oxygen interaction seems not prerequisite although hydroxyls may still have specific effects. Additional characterization revealed that while the electrolytically produced, high-purity Ag particles applied in industry initially are large/single crystals in the µm range with a high density of dislocations and inclusions, the catalyst post MTF is recrystallized into small (<100 nm) and randomly oriented grains.

In the annular reactor, exceptionally high formaldehyde selectivity (93-97%) could be obtained under practically isothermal reaction conditions, at low methanol and oxygen conversion, and without contributions from gas phase reactions. CH_2O and CO_2 turned out to be the only carbon containing products, showing that CO is formed by homogenous decomposition of CH_2O and should not be considered a main precursor to CO_2 as assumed in prevailing reaction mechanisms. Complementary investigations of CO and H_2 oxidation support this notion and provide additional insight. Extracting kinetic parameters was challenging due to a correlation between activity, oxygen dissolution, and the temperature-dependent silver restructuring. Nevertheless, the data indicate 1st order with respect to oxygen and an apparent activation energy of ~41 kJ/mol for the 525-560°C temperature range. The lecture will discuss these and further results and implications.

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PL-2

Operando surface spectroscopy and microscopy during catalytic reactions

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Operando characterization of working catalysts, requiring the simultaneous measurement of catalytic performance, is crucial to identify the relevant catalyst structure/composition and how molecules interact with interfaces [1]. Three examples, covering supported nanoparticles, meso-scale aggregates and single particle catalysis, bridge the "materials and pressure gaps".

i) *Area-averaging operando spectroscopy*: CO oxidation on Pt/ZrO_2 prepared by atomic layer deposition (ALD) was examined by sum frequency generation (SFG) spectroscopy and near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), combined with mass spectrometry (MS) [2]. Complemented by Density Functional Theory (DFT), we show that the reaction onset is determined by a delicate balance between CO disproportionation (Boudouard reaction) and oxidation (Fig. 1i).

ii) *Spatially-resolved operando microscopy*: A combined photoemission electron microscopy (PEEM) and DFT study of supported meso-scale Pd particles demonstrates how a minute fraction of sites at the perimeter of the metal-oxide interface affects the CO oxidation performance of an entire Pd aggregate [3]. The initiation of CO-poisoning fronts is visualized at the perimeter (Fig. 1ii), at a CO pressure two times higher for oxide-supported Pd aggregates than for unsupported ones. DFT calculations reveal stronger oxygen binding at the perimeter sites, explaining the higher CO-tolerance. As long as catalyst deactivation is not initiated, metal sites on oxide-supported Pd particles that are as far as several tens of μm away from the metal-oxide boundary maintain high catalytic activity even at increased CO pressure.

iii) *Single particle catalysis*: Using the apex of a Rh-nanotip as model of a single catalytic particle and field emission microscopy (FEM) as imaging tool (Fig. 1iii), ongoing catalytic reactions can be visualized on the nm-scale [4]. Novel effects were revealed for H_2 oxidation, such as multifrequential oscillations on the nanoscale and limited interfacet coupling. Using ionized water as imaging species, the active sites were directly imaged by field ion microscopy (FIM). Local nano-pacemakers [5] were identified as being surface atomic configurations at the border between strongly corrugated Rh{973} regions and adjacent atomically flat terraces.

The insights by monitoring *ongoing* reactions may stimulate new ways of catalyst design.

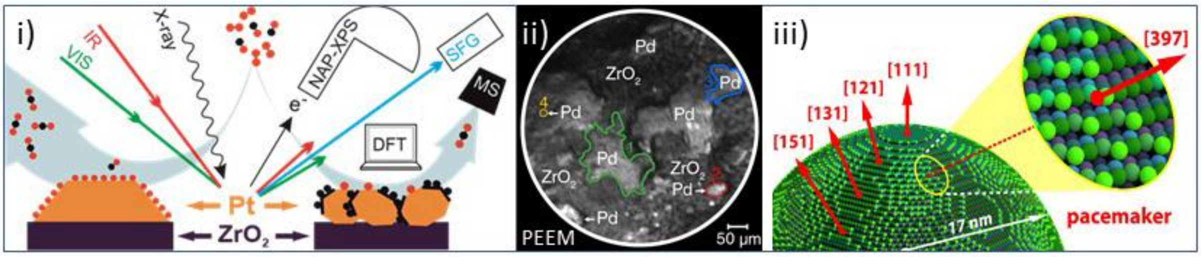

Fig. 1. Operando surface spectroscopy (i) and microscopy (ii, iii). From refs. [2-5].

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Design of a photocatalyst as a coating for removal of organic pollutants from air and water

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The aim of the field of catalyst/photocatalyst design for heterogeneous catalysis is to establish the desired composition and structure of these materials in the form of non-supported or supported systems which form powders, shaped powders (e.g. granules) or coatings. The lecture is based on the case study of supported titanium dioxide as a coating for photocatalytic removal of organic pollutants from air and water. Titanium dioxide (TiO_2) is the most used material for mentioned application due to its interesting characteristics: low cost, high stability, shows high photocatalytic activity, it can promote ambient temperature oxidation of the major class of organic pollutants. However, due to the hindered applications of TiO_2 as non-supported systems for photocatalytic air and water cleaning, design and development of TiO_2 supported systems are very important. Common support materials are SiO_2, Al_2O_3, zeolites (aluminosilicates), carbon etc. These materials exhibit high specific surface areas, high porosities in a variety of pore sizes, and high thermal and mechanical stability, while they are mostly chemically inert. Here, an overview on the design and development of coatings [1] from a) SiO_2 supported TiO_2 for removal of volatile organic pollutants from indoor-air under UV light [2] and b) SiO_2 supported TiO_2 functionalized with transition metals for removal of organic pollutants from wastewater under visible light [3] will be given.

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PL-4

Integrating sonochemistry, flow chemistry, and heterogeneous photocatalysis towards environmental and energy applications

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This lecture is a report of selected recent research experiences on mechanochemical approaches, and especially sonication, to expand the design and synthesis fields in materials chemistry, leading to new surface features arisen as a result of recombination of traditional inorganic and organic materials into unique multifunctional entities, and on photocatalysis intensification using flow microphotoreactors (fabricated by an ultrasound-based technique) for photocatalytic selective oxidation of benzyl alcohol to benzaldehyde (in the frame of the concept of lignin valorization). More specifically the lecture will be on:

a. **Ultrasound-driven synthesis of a multiphase heterogeneous nano- designed photocatalyst:** The herein presented low-power high-frequency (500 kHz) sonication-assisted precipitation synthesis (LPHF-US) leads to a unique multiphase nano-structured titanium dioxide, grafted with oxygen-containing organic functionalities [1]. The main goal of our catalyst design was to avoid the energy demanding step of calcination, and to exploit the potential of an organic residue in order to increase the chemical heterogeneity and enhance light absorption and thus, photoreactivity. The material exhibits high porosity (surface area 326 m^2g^{-1} and total pores volume 0.484 cm^3g^{-1}) and heterogeneous surface chemistry. In the used LPHF-US synthetic protocol, the energy-demanding calcination step leading to crystallization is eliminated and an organic residue is simultaneously grafted to the surface. That organic residue affects the anatase nanocrystals, size (4–7 nm), which are embedded in an amorphous titanium hydroxide network. This nanomaterial shows superior performance as heterogeneous photocatalyst either in a gaseous phase by decomposing toxic vapors of chemical warfare agents (a mustard-gas surrogate), or in a liquid phase by selectively oxidizing benzyl alcohol, a model lignin-biomass-derived compound.

b. **TiO_2 coated microflow reactor for selective oxidation:** The current work introduces an efficient ultrasound-based TiO_2 deposition on the inner walls of a perfluoroalkoxy alkanes (PFA) microtube under mild conditions [2]. The experiments were carried out using commercial TiO_2 and sol-gel synthesized TiO_2. The rough surface formed during sonication is the site for the deposition of these nanoparticles in the inner walls of the microtube. The photocatalytic activities of these semiconductor coated fluoropolymer based microreactors were evaluated for the selective oxidation of benzyl alcohol to benzaldehyde in liquid flow phase. The analysis of the results showed that various features/parameters are crucial and by tuning them, it is feasible to improve the conversion of benzyl alcohol and benzaldehyde selectivity. For instance, prepared TiO_2 showed better benzaldehyde selectivity, which is much higher compared to TiO_2-P25. Because of the high surface area of synthesized TiO_2, there is a higher availability of the active sites upon the deposition in the microtube.

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PL-5

How to design an efficient photocatalyst? On intrinsic and extrinsic factors influencing activity of photocatalysts

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We reveal the role of the TiO_2 phase composition in various types of photocatalytic reactions, controlled either by reduction or oxidation counterparts. We hypothesize that the choice of the optimal phase composition of TiO_2 should take into account both the nature of photocatalytic reaction and intrinsic physicochemical properties of the composite photocatalyst. To verify this hypothesis, we report the phase-tuneable syntheses of TiO_2 nanoparticles under mild temperatures (up to 200°C), which resulted in two series (A and B) of materials characterized by different anatase-to-rutile ratios, but otherwise similar morphologies. The synthesized materials were examined in water oxidation, hydrogen peroxide reduction, photocurrent generation and methanol-assisted water reduction [1]. The optimal phase composition depends on the reaction type – high contents of rutile or anatase should be considered for H_2O_2 reduction and water oxidation, respectively, while water reduction requires moderate contents of both polymorphs. The A series appeared more active in oxidation-controlled reactions, while the B series facilitated reduction-controlled processes. The DOS analysis confirmed, that rutile is a significantly better reducer, whereas anatase is a better oxidant [2-4]. Presented data show that a synergistic effect observed usually for anatase/rutile composites can result from both, intrinsic and extrinsic factors. The intrinsic factors are responsible for the improved photocatalytic activity of the material related to its physicochemical properties, *e.g.*, efficiency of charge separation, lifetime of photogenerated charges, absorption properties, redox characteristics, porosity, specific surface area, *etc*. The extrinsic factors are strongly related to the redox reactions to be performed at the photocatalyst surface, both oxidation and reduction. Therefore, the design of the optimal photocatalyst must take into account both, intrinsic and extrinsic factors.

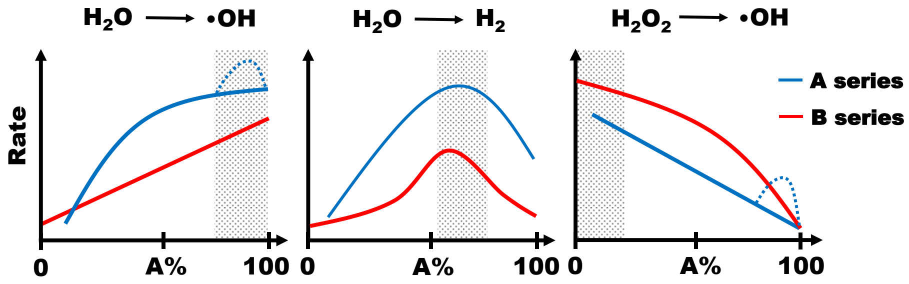

Figure. Reactivity of various anatase/rutile TiO_2 composites in different photocatalytic reactions as the function of the phase composition.

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Komunikaty ustne
Oral communications

O-1

Application of active carbon supported copper catalysts for the synthesis of 2-methyl-3-buten-2-ol in continuous-flow hydrogenation

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Selective hydrogenation of alkynes to alkenes is one of the essential reactions. It is widely used for the fine synthesis of alkene building blocks allows obtaining vitamins, fragrances, drugs, and many other critical products for which the demand increases in recent years [1,2]. Traditional hydrogenation catalysts, including supported nanoparticles of Pd and Pt, usually lead to low catalyst selectivity [1]. Moreover, the high cost of such catalysts drew the industry's attention to develop new cost-effective, well-defined, efficient, and environmentally friendly catalytic systems for the hydrogenation reaction [3].

Herein, our studies present the selective continuous catalytic semi-hydrogenation of the alkyne 2-methyl-3-butyn-2-ol (abbr. MBY) to 2-methyl-3-buten-2-ol (abbr. MBE) over a catalytic flow system to manage greater control over process parameters than classical, other technologies [1,2]. In particular, the implementation of continuous-flow systems seems to be particularly important in the pharmaceutical industry, where one of the most strategic fields is innovation toward greener manufacturing methods [3]. Therefore, it is worth mentioning that not a lot of attention was paid to using flow conditions for this reaction until now [3–5].

Very interesting results obtained for the palladium-loaded catalyst used in continuous-flow hydrogenation of MBY [6,7] motivated us to investigate other materials' catalytic potential like catalysts consisting of easily accessible support as active carbon and a non-noble metal of the transition group like copper as an active phase in the same reaction. Our work investigates the effect of copper loading and the determination of optimal pressure and temperature conditions to obtain high selectivity to MBE by semi-hydrogenation. Among the analyzed materials, 6 wt.% Cu/CNR115 showed ~100% selectivity to MBE in mild conditions 3 bars and 25°C.

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O-2

Węgle aktywne otrzymane z biomasy - porównanie właściwości teksturalnych oraz aktywności katalitycznej w reakcji izomeryzacji α-pinenu

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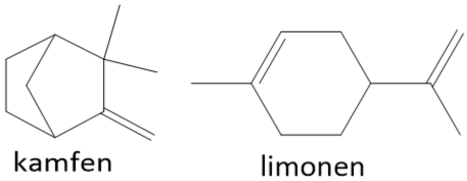
Wykorzystanie materiałów odpadowych z przemysłu i rolnictwa do produkcji węgli aktywnych stało się głównym kierunkiem ówczesnych badań materiałowych [1]. Biorąc pod uwagę ilość wytwarzanych bioodpadów w postaci skórek pomarańczy, łupin słonecznika i fusów kawowych, a także mając na uwadze problem z ich składowaniem i bezpieczną dla środowiska utylizacją, należy dążyć do rozwoju technologii zagospodarowania tych bioodpadów. α-pinen pozyskiwany jest z płynnej żywicy (terpentyny), głównie drzew iglastych. Związek ten jest tanim surowcem do syntezy wielu cennych substancji stosowanych jako zapachy, dodatki do żywności [2], farmaceutyki [3] i rozpuszczalniki [4].

Celem pracy było otrzymanie węgli aktywnych z biomasy, a następnie sprawdzenie ich aktywności katalitycznej w reakcji izomeryzacji alfa-pinenu. Biomasą do pozyskiwania węgli aktywnych były skórki pomarańczy, fusy z kawy i łuski słonecznika. Jako aktywator chemiczny wykorzystano KOH. Próbki aktywowano w piecu (800˚C) w obecności N_2. Na podstawie izoterm sorpcji N_2 (-196˚C) wyznaczono następujące parametry charakteryzujące strukturę porowatą: pole powierzchni właściwej (SBET), całkowitą objętość porów (Vtot) oraz objętość mikroporów (Vmic). Reakcję izomeryzacji α -pinenu prowadzono w szklanym reaktorze umieszczonym w łaźni olejowej z chłodnicą zwrotną. Do badań nad izomeryzacją zastosowano α-pinen oraz odpowiednią ilość węgla aktywnego. Aktywność otrzymanych materiałów węglowych badano w najkorzystniejszych warunkach ustalonych podczas badań wstępnych: temperatura reakcji - 160°C, ilość węgla aktywnego w mieszaninie reakcyjnej - 5% wag., czas reakcji - 3h, szybkość mieszania - 400 obr/min. Głównymi produktami otrzymywanymi w procesie izomeryzacji α-pinenu były kamfen oraz limonen. Oba te związku znajdują szerokie zastosowanie w wielu gałęziach przemysłu.



Rysunek 1 Główne produkty izomeryzacji α-pinenu

Najwyższą konwersję α-pinenu (58% mol) osiągnięto przy zastosowaniu materiału węglowego na bazie skórek pomarańczy. Najwyższą selektywność dla wszystkich badanych materiałów odnotowano dla kamfenu.

Na podstawie powyższych wyników badań założono, że materiały węglowe otrzymane z biomasy wykazują aktywność katalityczną w reakcji izomeryzacji α -pinenu.

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O-3

Fine crystalline Mg-Al hydrotalcite-like compounds as catalysts for Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone

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Baeyer-Villiger (BV) oxidation of cyclohexanone yields ε-caprolactone – an important monomer for production of biocompatible and biodegradable polymers. Recently we have demonstrated that diminishing the crystal size of Mg-Al hydrotalcite-like (Htlc) materials improves their catalytic activity in BV reaction [1]. The present work reports preparation, characterization and catalytic testing of a number of fine crystalline HTlc prepared by two novel synthetic procedures: 1) using inverse microemulsion method (described as Htlc/mic) and 2) using starch as a structure controlling biotemplate (described as Htlc/s). In the first case, the particle size was limited by the dimension of formed micelles, in the second, the spatial constraint for the particle growth was provided by the gelatinous medium used for synthesis.

Htlc with the intended Mg/Al ratio equal 3 and different interlayer anions (Cl^-, Br^-, CO_3^{2-}) were investigated. The materials were synthesized by double microemulsion method described by Bellezza et al. [2] and by co-precipitation in starch solution, as described by Michalik et al. [3]. Reference materials (Htlc/ref) were prepared using co-precipitation at a constant pH=10, followed by anionic exchange to produce materials with the desired interlayer anions.

The catalysts were characterized by means of PXRD, SEM, FTIR spectroscopy and chemical analysis. The crystallite size was calculated using Scherrer equation. Catalytic reaction was performed in a thermostated glass reactor at 70 °C, using 30% hydrogen peroxide as an oxidant and acetonitrile as a solvent.

Physico-chemical characterization confirmed formation of Htlc materials with the intended anions in the interlayer. Htlc prepared via procedures 1) and 2) possessed much smaller crystallites in comparison with the reference samples. In the case of Cl^- as interlayer anions, the average D_{003} crystal size was equal 5.9 Å for Htlc/mic, 8.5 Å for Htlc/s and 18.7 Å for Htlc/ref.

The synthesized Htlc samples proved catalytically active in BV oxidation of cyclohexanone using hydrogen peroxide/nitrile system, but their performance was strongly affected by the nature of interlayer anions, with chloride yielding the best catalysts. Double microemulsion method using chloride surfactant produced the most active and selective catalyst. The performance of starch bio-templated Htlc catalysts also surpassed that of the reference samples, showing that bio-templating may be considered as an efficient and cheap alternative to double microemulsion method for preparation of fine crystalline Htlc catalysts.

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O-4

Physicochemical properties of the structurally modified TiO$_2$ system decisive for its high-performance in photocatalytic oxidation of terephthalic acid

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It is well known, that conventional TiO$_2$-based photocatalysts cannot respond to visible light. Here, we describe TiO$_2$ samples active in terephthalic acid (TA) oxidation under visible light. It is demonstrated in the present work, that □-TiO$_2$ nanocrystals can be successfully synthesized by one-step hydrothermal process. The crystal structure of the obtained samples was confirmed by XRD. The most promising photocatalysts exhibit a remarkable enhancement of oxidation of terephthalic acid (TA) to hydroxyterephthalic acid (TAOH).

The role of such preparative variables as the parameters of hydrothermal synthesis, nature of a chosen precursor, its concentration and calcination temperatures has been investigated in detail. Interestingly, it was observed, that in some favorable cases the uncalcined TiO$_2$ samples exhibited a higher conversion rate of TA than those calcined at 450°C. Simultaneously, the TiO$_2$ samples synthesized at low precursor concentrations showed the highest photocatalytic activity towards TAOH equal to 0.00136 M during 30 min of irradiation. It was confirmed that the phase composition of the photocatalysts controlled by synthetic conditions belongs to the most decisive parameters determining photocatalytic activity of the investigated TiO$_2$ samples. This work may provide practical guidelines for designing efficient □-TiO$_2$-containing photocatalysts suitable for oxidation of organic compounds under visible light.

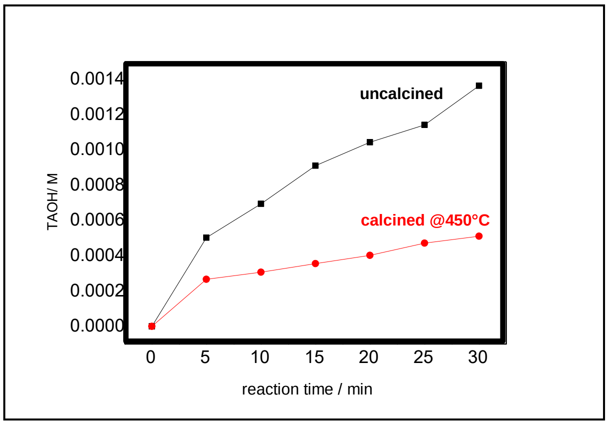

Fig. Example of the photogeneration of TAOH during the photocatalytic oxidation of TA in the presence β-TiO$_2$-containing sample under Xenon lamp irradiation.

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O-5

Influence of catalyst's Co-loading on a sedative drug precursor synthesis by continuous-flow 2-methyl-2-pentenal selective hydrogenation

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Although readily available 3d transition metals require higher H_2 pressure and higher temperature to attain comparable performance like noble metals, they are intensively being explored in selective hydrogenation processes, especially in the flow conditions [1]. Because, in contrast to batch systems, continuous-flow hydrogenation allows superior contact between the reactants and the catalytic phase, improving catalytic performance, eventually requiring softer reaction conditions [2].

In this context, the present work analyses the chemoselectivity toward 2-methylpentanal (MPAA) from catalytic hydrogenation of 2-methyl-2-pentenal (MPEA) as a function of the catalyst's Co-loading. 2-methylpentanal is used as a flavouring agent and an intermediate for dyes, resins, and especially for the sedative drug - meprobamate [3].

Four different Co/CNR115 carbon catalysts ranging from 2 to 14 wt.% of metal have been characterized and compared. We studied the effects of process parameters like pressure and temperature on the activity and the selectivity to the desired product (MPAA). As a result of our research, we have found values over 95% of selectivity toward the desired product for the 2% and 6% Co-loading catalysts, corresponding to the latest one, the best activity towards MPAA (Fig. 1).

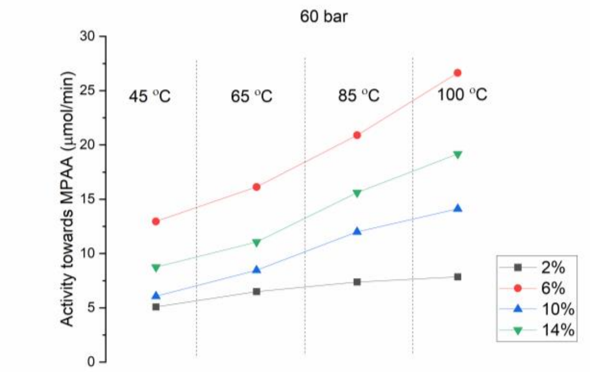

Fig. 1. Activity towards MPAA obtained for the four catalysts (2, 6, 10 and 14 wt.% Co) at 60 bar and four different temperatures (45 °C, 65 °C, 85 °C and 100 °C).

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O-6

Hydrodechlorination of $CHClF_2$ (freon R-22) on carbon-supported Pd-Pt catalysts. Search for synergistic effect

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Commercial activated carbon, pretreated in helium at 1600 °C and largely free of micropores, was used as a support for two series of 2 wt% Pd-Pt catalysts, prepared by impregnating the support with metal acetylacetonates or metal chlorides. The catalysts were characterized by temperature-programmed methods, H_2 chemisorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning transmission electron microscopy (STEM) with energy dispersive spectroscopy (EDS). The results confirmed the existence of well-dispersed and homogenized Pd–Pt nanoparticles in the bimetallic catalysts, ranging in size from 2 to 3 nm. The catalysts were investigated in the gas phase hydrodechlorination (HDC) of chlorodifluoromethane (R-22). In this environmentally relevant reaction, both the ex-chloride and ex-acetylacetonate Pd–Pt/C catalysts exhibited better HDC activity than the monometallic catalysts, which is consistent with the previous results of HDC for other chlorine-containing compounds. This effect, understood at first glance as a synergistic effect, could be attributed to the electron charge transfer from platinum to palladium. However, no synergy was observed for product selectivity, as it changed regularly with Pd-Pt alloy composition, from 70-80% to CH_2F_2 for Pd/C to the selective formation of CH_4 for Pt/C (60–70%). An additionally adopted catalyst oxidation at 350-400 °C produced nearly an order of magnitude increase in the turnover frequency of Pd/C, from 4.1×10^{-4} to 2.63×10^{-3} s^{-1}. This increase is not caused by changes in metal dispersion or possible decontamination of the Pd surface from superficial carbon, but rather by unlocking the active surface, originally inaccessible in metal particles tightly packed in the pores of carbon. Burning carbon from the pore walls attached to the metal changes the pore structure, providing easier access for the reactants to the entire palladium surface. Calcination of Pt/C and Pd-Pt/C catalysts results in much smaller evolution of catalytic activity than that observed for Pd/C. This shapes the relationship between TOF and alloy composition, which now does not confirm the Pd-Pt synergy invoked in the previous work. The use of even higher-preheated carbon (1800 °C), completely free of micropores, results in a Pd/C catalyst that does not need to be oxidized to achieve high activity and excellent selectivity to CH_2F_2.

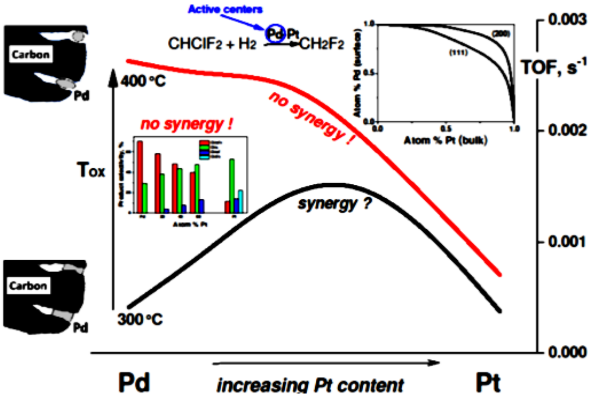

Fig 1. Changes in the catalytic behavior of Pd-Pt/Norit1600 catalysts in $CHClF_2$ hydrodechlorination caused by catalyst precalcination. Inset: the relation between surface and bulk composition of Pd-Pt alloys.

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O-7

. Popioły z sektora energetycznego jako materiały wyjściowe do syntezy katalizatorów

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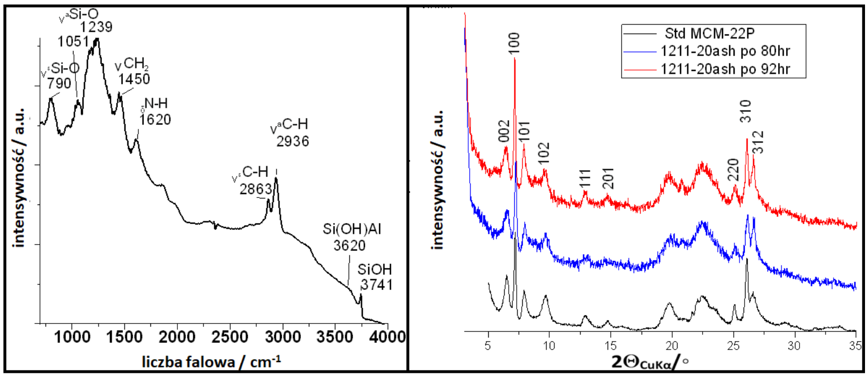
Wytwarzanie energii jest niewątpliwie jednym z najistotniejszych sektorów gospodarki. Ciągle rosnące zapotrzebowanie na energię elektryczną wymaga stałego rozwoju technologii jej produkcji. Uzasadniona troska o środowisko naturalne a także nagląca konieczność zapobieżenia postępującym zmianom klimatu stwarzają przestrzeń do poszukiwania alternatywnych źródeł energii. Źródła konwencjonalne wciąż jednak mają bardzo istotny wkład w produkcję energii, w związku z tym uzasadnione są działania zmierzające do minimalizacji ich negatywnego oddziaływania na środowisko. Jednym z możliwych wektorów aktywności innowacyjnej w tym zakresie jest dbałość o maksymalne zagospodarowanie odpadów generowanych przez sektor energetyczny. W nurt ten wpisuje się obecna propozycja wykorzystania popiołów powstających w trakcie energetycznego spalania paliw kopalnych jako materiałów wyjściowych do syntezy materiałów wykorzystywanych w katalizie.

W niniejszej pracy zaprezentowane zostaną wyniki badań strukturalnych, teksturalnych i funkcjonalnych popiołów pochodzących z sektora energetycznego, generowanych ze spalania dwóch rodzajów paliw kopalnych: ciężkich frakcji naftowych oraz węgla kamiennego. Popioły pochodzące ze wspomnianych źródeł wykazują wyraźne zróżnicowanie właściwości, zarówno pod względem składu chemicznego i fazowego, jak i cech strukturalnych ziaren. Uzyskane przez nas wyniki potwierdzają możliwość wykorzystania tego typu materiałów do syntezy dwojakiego rodzaju układów wykorzystywanych w katalizie: zeolitów i tlenkowych układów nośnikowych. W tym ostatnim przypadku zarówno nośnik, jak i faza naniesiona, zawierająca takie składniki katalitycznie aktywne, jak: wanad, nikiel, żelazo czy miedź, pozyskane zostały z popiołów lotnych. Dla finalnych układów katalitycznych określono skład chemiczny metodą XRF, zbadano skład fazowy metodami XRD i RS, przeanalizowano właściwości teksturalne ziaren metodą SEM/EDS i określono właściwości funkcjonalne metodami DRIFT oraz UV/Vis-DR.



Rys. Cechy funkcjonalne (po lewej) i strukturalne (po prawej) materiałów zeolitowych otrzymanych z popiołów lotnych generowanych ze spalania węgla kamiennego.

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O-8

Aktywność katalityczna ugrupowań N-hydroksyftalimidowych immobilizowanych na nośnikach kopolimerowych i krzemionkowych w aerobowym utlenianiu węglowodorów alkiloaromatycznych

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Reakcje utleniania są powszechnie wykorzystywane w wielu gałęziach przemysłu spożywczego, farmaceutycznego, kosmetycznego i perfumeryjnego jako prosta metoda przekształcania podstawowych związków chemicznych w produkty zawierające ugrupowania tlenowe, takie jak kwasy karboksylowe, alkohole, aldehydy, ketony, epoksydy czy wodoronadtlenki. W aerobowym utlenianiu węglowodorów alkiloaromatycznych w fazie ciekłej jako katalizator homogeniczny szeroko testowany jest N-hydroksyftalimid (NHPI) [1]. Niestety, problemy związane z wydzieleniem NHPI z mieszaniny reakcyjnej znacząco utrudniają jego aplikację w przemyśle. Obiecującą alternatywą jest możliwość unieruchomienia grup NHPI na stałym nośniku. Otrzymywany w ten sposób układ heterogeniczny można łatwo izolować z fazy ciekłej na drodze filtracji i ponownie wykorzystać w procesie utleniania. W niniejszej pracy przedstawiono oryginalne podejście do otrzymywania katalizatorów z grupami NHPI immobilizowanymi na drodze ich włączenia w strukturę usieciowanego kopolimeru poli(winylodiizopropyloftalan-*co*-styren-*co*-diwinylobenzen) lub szczepienia na powierzchni mezoporowatej krzemionki typu SBA-15.

Przygotowano sześć serii kopolimerów zawierających 10-90% mas. monomeru funkcyjnego (prekursor NHPI) o różnej zawartości monomeru sieciującego (1-11% mas.) [2]. Otrzymanie w wyniku kilkuetapowej modyfikacji grup funkcyjnych NHPI w strukturze kopolimerowej potwierdzono przy użyciu spektroskopii FT-IR (odnotowując obecność pików przy 1778 cm^{-1} i 1712 cm^{-1} odpowiadających drganiom cyklicznych grup imidowych) oraz XPS (pik przy 401,6 eV charakterystyczny dla azotu w grupach [$(C=O)_2N-OH$]). Aktywność katalityczną testowano w reakcji utleniania 4-metyloanizolu z dodatkiem Co(II) jako ko-katalizatora w układzie bez udziału rozpuszczalnika. Największą konwersję substratu (23,6%) uzyskano po 6 h dla katalizatorów zawierających od 30 do 60% mas. estru diizopropylo-4-winyloftalowego w zakresie stopnia usieciowania 3-9%, co odpowiada zawartości 1,66-3,78 mmol grup NHPI na 1 g polimeru.

Immobilizację grup NHPI na nośniku SBA-15 przeprowadzono na drodze graftingu bezwodnika 4-chlorodimetylosililoftalowego (prekursor NHPI) na powierzchniowych grupach silanolowych i następczej aktywacji w reakcji z chlorowodorkiem hydroksyloaminy. Otrzymane katalizatory NHPI/SBA-15 scharakteryzowano pod kątem składu oraz struktury powierzchniowej. Potwierdzono wprowadzenie do 14% mas. modyfikatora organicznego. Badania katalityczne w aerobowym utlenianiu p-ksylenu przeprowadzono z dodatkiem Co(II) w układzie bezrozpuszczalnikowym w aparaturze gazometrycznej. Największą konwersję substratu aromatycznego (38,1%) odnotowano po 24 h w obecności katalizatora zawierającego 0,53 mmol grup NHPI na 1 g krzemionki.

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O-9

Nanomateriały Cu-heteropolikwas-TiO_2 w roli fototermokatalizatorów

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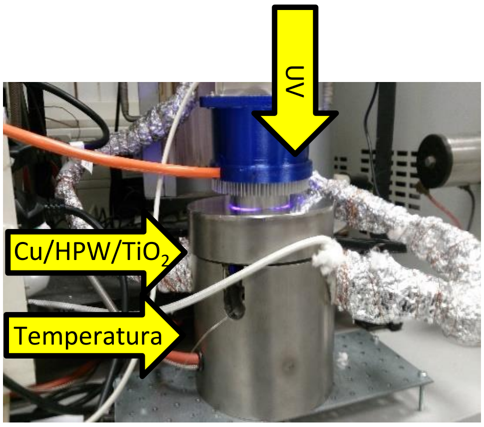
Tlenek tytanu(IV) jest najpopularniejszym materiałem o właściwościach fotokatalitycznych. Z powodzeniem jest używany także w katalizie, jako tani materiał nośnikowy dla fazy aktywnej, materiał o wysokiej stabilności termicznej i chemicznej. W związku z tym faktem postanowiono zsyntetyzować katalizator zawierający TiO_2, w których tlenek pełniłby zarówno funkcję nośnika katalizatora jak i funkcję fotokatalizatora. Temperatura w reakcji katalitycznej jest istotnym czynnikiem kontrolującym kinetykę i termodynamikę tej reakcji, natomiast jej wpływ na efekty fotokatalityczne jest słabo przebadany. Dotychczasowe badania wykazały, że rejestrowany efekt foto-termo-katalityczny (F-T-K) nie jest prostą sumą efektu termokatalitycznego i fotokatalitycznego. Dane literaturowe dotyczące zjawiska F-T-K głównie opisują jego zastosowanie do usuwania lotnych związków organicznych [1].

W ramach badań statutowych zsyntetyzowaliśmy serię potencjalnych materiałów fotokatalitycznych Cu-HPW-TiO_2, zawierających miedź, heteropolikwas $H_3PW_{12}O_{40}$ (HPW) i TiO_2 jako nośnik. Zawartości Cu i HPW w każdym materiale wyniosły odpowiednio 5 % wag. i 10 % wag. Celem naszych badań było określenie wpływu poszczególnych parametrów strukturalnych katalizatorów Cu-HPW-TiO_2 (porowatości, rozwinięcia powierzchni właściwej, rodzaju fazy miedziowej i jej krystaliczności) oraz wpływu charakteru nośnika TiO_2 na aktywność katalizatorów miedziowych w reakcji testowej - konwersji n-butanolu w fazie gazowej. Różnice w parametrach strukturalnych miedziowych katalizatorów wynikały z zastosowania różnych metod ich syntezy: metody mokrej impregnacji lub metody kapilarnej impregnacji. Wybrana reakcja testowa umożliwiła badania właściwości kwasowych jak i redoksowych katalizatorów. W wyniku dehydratacji n-butanolu zarejestrowano następujące produkty: cis-buten, trans-buten, butanal i eter di-n-butylowy. Przeprowadzono testy termokatalityczne (grzanie reaktora, bez światła) oraz testy foto-termo-katalityczne (z równoczesnych grzaniem i naświetlaniem reaktora lampą LED). Porównano aktywności katalizatorów w obu warunkach prowadzenia testów termicznych (bez lampy i z lampą).



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O-10

Thermal inactivation and aggregation of (R)-1-(4-hydroxyphenyl)-ethanol dehydrogenase from *A. aromaticum*

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R-specific 1-(4-hydroxyphenyl)-ethanol dehydrogenase (R-HPED) is an enzyme coming from denitrifying bacterium *Aromatoleum aromaticum* (*Azoarcus sp*.). The physiological R-HPED's function is to catalyse the NAD^+-dependent stereospecific oxidation of R-1-(4-hydroxyphenyl)-ethanol to 4-hydroxyacetophenone. However, R-HPED is also capable of catalysing the industrially important reverse reactions: NADH-dependent enantioselective reductions of acetophenone and other prochiral ketones to R-alcohols with 100% enantioselectivity [1,2]. The presented research focuses on the basic factors that improve the stability of non-immobilized R-HPED as well as on the identification of the thermal inactivation model of this enzyme. Indication of factors that affect the stability of R-HPED activity combined with its high enantioselectivity and availability of overexpression system can make R-HPED a powerful bio-tool for the production of homochiral R-alcohols.

At the first stage of research we searched for the appropriate pH conditions, where inactivation rate and aggregation rate were relatively slow. Inactivation experiments were carried out in the temperature range of 47.5 – 60.0 °C at two conditions: i) 0.1M Tris/HCl buffer pH 8.5 without additives and ii) 0.1M Tris/HCl buffer pH 8.5 enriched with 1.5M glucose. The analysis of the dynamics of the enzyme inactivation process was carried out using the isothermal and multitemperature evaluation of experimental data [3]. The obtained results combined with the measurements of protein aggregation indicated that the enzyme is inactivated according to the irreversible one-step mechanism, while the observed protein aggregation is a secondary process taking place for already inactivated biocatalyst molecules. Moreover, the courses of the inactivation curves under various conditions indicated that glucose causes a significant improvement in the stability of R-HPED activity.

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O-11

A tungsten enzyme is a hydrogenase, reducing carboxylic acid with electron bifurcation

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The W-dependent aldehyde oxidoreductase from the *Betaproteobacterium Aromatoleum aromaticum* (AOR_{Aa}) catalyses the oxidation of aldehydes to carboxylic acids and the respective reverse reaction, reduction of non-activated carboxylic acids to aldehydes. The enzyme contains a tungsten-*bis*-metallopterin cofactor in its active site which is connected with a FAD in a γ subunit by a chain of FeS clusters localized in the α and β subunits. The oxidation of aldehydes can be coupled either to NAD^+ or benzyl viologen reduction. Notably, the AOR_{Aa} is more resistant to air exposure and inactivation by O_2, than the AORs from Archaea such as *Pyroccocus furiosus*, with a half-life time of 1h for the purified enzyme [1].

Although known AORs were reported to exhibit activity in the reduction of carboxylic acids to aldehydes when coupled to strong reducing agents (such as methyl viologen or Ti(III) or Eu(II) complexes) [2], unexpectedly, the AOR from *A. aromaticum* turned out to be also a hydrogenase, which efficiently utilizes electrons from H_2 oxidation for the reduction of carboxylic acids. Furthermore, the enzyme can be employed as a new NADH-recycling system when the hydrogenase activity is employed to reduce NAD^+ to NADH.

In the study, we used the recombinant AOR_{Aa} overproduced in the novel overexpression system in *Aromatoleum evansii*. We have characterized its structure via the Cryo-EM technique with an average resolution of 3.3 Å. This allowed us to build a model of the protein and localize the position of all metal cofactors while more detailed structural characteristics of the tungsten cofactor were obtained based on QM calculations and reinterpretation of the electron density of AOR from the X-ray structure of AOR from *P. furiosus*.

We have characterized the catalytic properties of the enzyme acting in both directions, i.e. oxidation of aldehydes coupled to NAD^+ or benzyl viologen and reduction of carboxylic acids coupled to H_2. The AOR_{Aa} reduced a wide range of substrates i.e., aromatic, heterocyclic, alkylaromatic and aliphatic carboxylic acids. The reactions were conducted under inert gas atmospheres containing H_2 (0.1%-100%) or syngas mixtures (CO, N_2, H_2 59/40/1 v/v) The applicability of AOR in NADH recycling was demonstrated by reducing acetophenone to (*R*)-1-phenylethanol by appropriate stereoselective alcohol dehydrogenase. Interestingly, we observed accelerated reduction rates in reactions with NAD^+ and carboxylic acids together than in those with NAD^+ or carboxylic acids separately. This result suggests that AOR_{Aa} is a new type of electron bifurcating enzyme.

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O-12

Structural, textural and functional features of copper-based catalysts for CO_2 hydrogenation obtained via modified synthetic route

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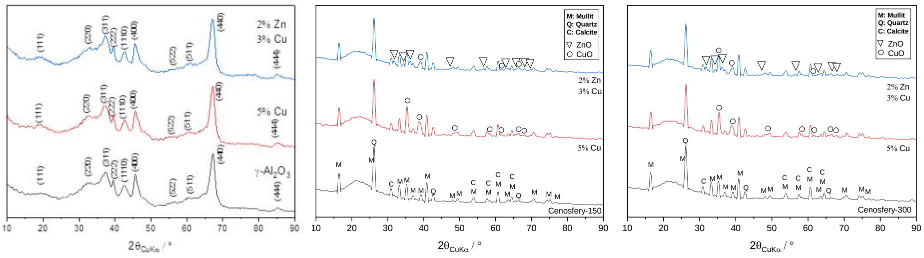
It is generally accepted, that carbon dioxide is a powerful greenhouse gas which has been increasing in emissions, substantially contributing to anthropogenic climate change. There is a necessity in not only reducing emissions of CO_2, but also removing CO_2 from the atmosphere to decrease the risks associated with the observed climate changes. Of the various methods of carbon dioxide utilization, catalytic valorization of CO_2 has numerous benefits including its efficiency, applicational potential, and an attractive possibility to convert CO_2 to many valuable products, including methanol, synthesis gas, dimethyl ether, low hydrocarbons etc. Many of them can be considered as components of synthetic fuels.

This paper is focused on oxide catalysts for CO_2 hydrogenation to methanol. For at least a decade copper-based systems are known to be active in this reaction, however the conventional catalysts tested in several laboratories, contained the mixture of copper, zinc and aluminum oxides and were usually synthesized via the simplest coprecipitation method. In our case two series of γ-Al_2O_3-supported catalysts containing copper and zinc as active components were synthesized via impregnation method, giving us a possibility to control surface architecture of our catalysts more precisely. Our goal was to check whether all crucial structural, textural and functional parameters controlling catalytic activity of the supported catalysts are similar to those determined for bare coprecipitated samples. Additionally, the effect of support was elucidated, because apart from the γ-Al_2O_3-supported samples also those supported on commercial cenospheres of various granulation were synthesized.



a b c

Figure: Series of XRD patterns collected for the investigated samples supported on γ-Al_2O_3 a) and those supported on commercial cenospheres: Cen-150 b) i Cen-300 c).

All series of the synthesized catalysts have been comparatively characterized by XRD, RS, SEM/EDS, porosimetry, DRIFT and UV/Vis-DR. The obtained results clearly show that calcination, nature of the support and the presence of zinc additives strongly influence the speciation of copper surface sites and can be decisive for both catalytic performance and a stability of the studied catalysts. Regardless their granulation, cenospheres used as catalytic supports favor stabilization of nanocrystalline CuO and ZnO surface forms, whereas γ-Al_2O_3 support facilitates higher dispersion of the deposited active components.

O-13

NO, O_2 and H_2O interaction with dual Cu—Cu sites of SSZ-13–Cu zeolite – DFT QChM simulations and first principles thermodynamics

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Removal of the nitrogen oxide contaminants is one of the prime challenges for environmental catalysis. The most important processes for NO_x removal is selective catalytic reduction (SCR) of NO_x by using NH_3 or various hydrocarbon molecules which is accelerated significantly by oxidation of NO into NO_2. SSZ-13-Cu zeolite is regarded as a very effective catalyst for NO oxidation even at low temperatures and high space velocities. It typically contain two types of Cu sites (depending on Al distribution within zeolite framework) mono-Cu and dual-Cu. With regards to the fact that an in-depth molecular-level description of the reaction of nitrogen oxides with the zeolite Cu–Cu dual active sites is still lacking, we performed comprehensive DFT, atomistic thermodynamic investigations of their interaction with gaseous NO, O_2 and H_2O.

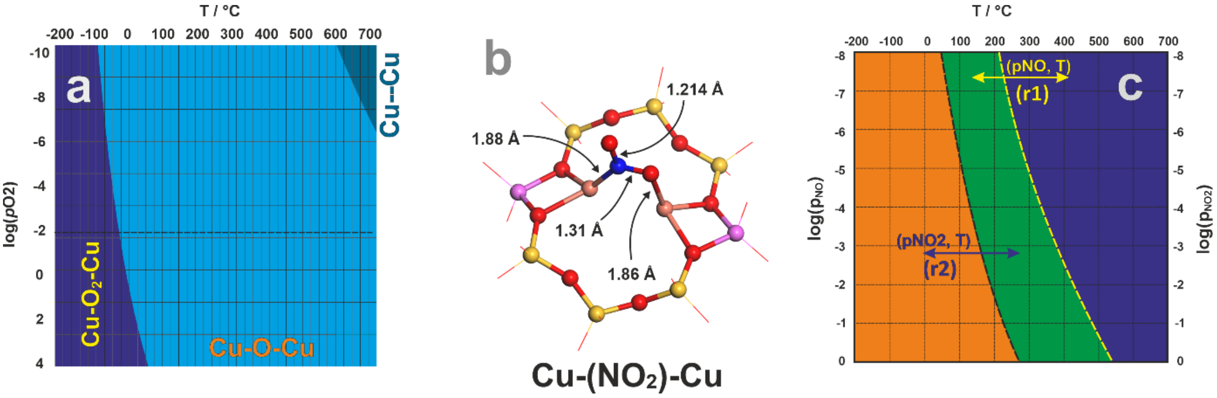

Fig.1: Ab initio thermodynamic diagram of O_2 adsorption on dual Cu-Cu sites (a). NO adsorption on Cu-O-Cu site resulting in Cu-NO_2-Cu formation (b). Thermodynamic diagram of NO_2 release.

We found that interaction of oxygen lead to facile formation bridging structures of Cu-O-Cu, and Cu-O_2-Cu character (Fig. 1a) depending on temperature and O_2 pressure (the former is stable in typical catalytic conditions), whereas bare Cu-Cu site is highly unstable. Addition of NO results in formation of NO_2 and NO_3 adspecies with inclusion of bridging oxygen moieties (Fig. 1b). Presence of water do not disturb this observations, however, water may be responsible for formation of mobile hydroxyl groups witch in turn may be converted into new Cu-O-Cu sites. The gaseous NO_2 is released in medium temperatures (200 °C) leaving rather Cu-O-Cu bridges than bare Cu-Cu (Fig. 1c).

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O-14

Modyfikacja receptury i formy ziarna a efektywność katalizatorów parowej konwersji tlenku węgla

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Wzrastające zainteresowanie wydajnymi a jednocześnie ekologicznymi technologiami wytwarzania wodoru jest motorem do stałego doskonalenia układów katalitycznych. Stwierdzenie to w dużej mierze dotyczy katalizatorów parowej konwersji tlenku węgla (LT-WGS) tj. kluczowej reakcji wzbogacania w wodór produktów parowego reformingu, gazów koksowniczych czy też gazów pochodzących z procesów zgazowania [1]. Reakcja LT-WGS jest słabo egzotermiczna, przez co zwiększeniu stopnia konwersji sprzyja obniżenie temperatury. Znanym jest, że układy Cu/ZnO stosowane w przedmiotowej reakcji są wrażliwe na trucizny (związki siarki i/lub chloru) lecz także podatne na rekrystalizację, co sprawia, że łatwo ulegają dezaktywacji generując istotne problemy technologiczne w wytwórniach gazów syntezowych lub wodoru [2].

Praca skupia się na zagadnieniu możliwości zwiększenia aktywności i termostabilności miedziowych katalizatorów LT-WGS szczególnie w zakresie temperatur 180–190 °C, poprzez domieszkowanie układów $Cu/ZnO/Al_2O_3$ tlenkami o stosunkowo wysokiej temperaturze topnienia (La lub Zr). Istotnym obszarem prac było także określenie możliwości formowania materiału katalitycznego w kształtki o wysokiej powierzchni geometrycznej na jednostkę objętości złoża.

Techniką współstrącania i obróbki termicznej spreparowano serię hydroksywęglanowych prekursorów i tlenkowych form katalizatorów, które poddano wszechstronnym badaniom technikami XRD, sorpcji N_2, chemisorpcji N_2O, H_2-TPR. Dla otrzymanych katalizatorów wyznaczono stałe szybkości reakcji LT-WGS (p=2.5 MPa) w obszarze kinetycznym (przed i po symulowanym starzeniu w warunkach reakcji) przy użyciu różniczkowego reaktora ze złożem stałym. Techniką prasowania uzyskano zróżnicowaną pod względem wielkości i geometrii ziarna finalną postać katalizatora. Wyznaczono parametry hydrodynamiczne złóż kształtek o zróżnicowanej wielkości i geometrii.

Wykazano, że wysokomiedziowe katalizatory domieszkowane La lub Zr są układami mezo- i makroporowatymi o stosunkowo wysokim rozwinięciu powierzchni właściwej. Uzyskiwaniu wysokiej porowatości i wyższych S_{BET} sprzyja prowadzenie syntezy prekursora przy wyższym stosunku $Na_2CO_3/NaOH$. Nieco wyższe rozwinięcie powierzchni właściwej i powierzchni aktywnej uzyskano dla katalizatorów domieszkowanych Zr. Modyfikacja układu $Cu/ZnO/Al_2O_3$ tlenkiem La lub Zr prowadzi do zwiększenia aktywności, przy czym zależność aktywności od rodzaju i ilości modyfikatora okazała się niejednoznaczna. Obecność La lub Zr skutkuje zwiększeniem termostabilności katalizatora w warunkach LT-WGS.

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O-15

Polymers based on fluorinated methylstyrenes and styrene units modified with sulfonic species as effective heterogeneous catalysts for esterification

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Esterification of carboxylic acids with alcohols is the well-known liquid-phase reaction of industrial interest due to the importance of esters. Generally, esterification proceeds both, in the absence and in the presence of an added catalyst. However, in the absence of catalyst, the reaction is extremely slow. Therefore, in order to obtain satisfactory yields of esterification, it is carried out in the presence of an acid catalyst. The catalysts commonly used in such reaction are strong mineral acids. However, due to the environmental and safety issues related to the use of mineral acids, the use of solid acid catalysts in esterification has gained an increasing interest over the last decades.

The aim of this work was the synthesis and characterization of polymers with different morphology, which can be act as the effective heterogeneous catalysts in esterification. Thus, the sulfonic-acid-functionalized poly(F-STs-*co*-ST) copolymers based on fluorinated methylstyrenes and styrene were successfully synthesized via post-sulfonation method using chlorosulfonic acid (HSO_3Cl) as a sulfonating agent. The as-prepared solid acid catalysts were fully characterized by FTIR, elemental analysis, TGA, DSC, acidimetric titration and XPS. Catalytic activity of the materials was examined in esterification of acetic acid with *n*-butanol in different reaction conditions.

The obtained results indicated that the molar mass (M_n) of polymers influenced on homogeneity/heterogeneity of catalysts. The polymers with M_n up to 23 700 g mol^{-1} exhibited homogeneous properties, while that with M_n up to 65 000 g mol^{-1} could be used as heterogeneous catalysts. The presence of fluorinated methylstyrene units incorporated into polystyrene structure promoted an increase in glass transition temperature value (up to 165 °C for **sFAP6**) compared to that of the unhalogenated commercial **Dowex-50W** resin. This observation confirmed that the presence of bulky -CF_3 side groups in polystyrene structure may promote the improvement of thermal properties of the resulting fluorinated catalysts. The new acidic solid catalysts (**sFAP5** and **sFAP6**) showed high catalytic activity (ca. 85%) in *n*-butyl acetate formation in the esterification of acetic acid with *n*-butanol. The TOF values for **sFAP5** and **sFAP6** catalysts were higher than that obtained for the commercial **Dowex-50W** resin. The higher catalytic activity of **sFAP5** and **sFAP6** relative to that of the **Dowex-50W,** results from the presence of fluorine-containing substituents in the polymer structure. On the one hand, the strongly electron-withdrawing properties of the fluorinated methyl moieties may reduce the electron density of aromatic rings in the polymer chains and increase the acidity of the sulfonic acid groups located in the neighborhood of fluorinated ones. On the other hand, the direct vicinity of fluorinated methyl moieties and -SO_3H groups in the side chains of polymers caused self-organization of the macromolecules in the esterification conditions. The resulting aggregate improved the accessibility of -SO_3H groups, promoting higher efficiency of the esterification reaction. Finally, the fluorinated catalysts showed good recyclability and maintained high activity even after five cycles of consecutive runs. Prospectively, such new fluorinated polymers could be used as efficient solid acids in other heterogeneous catalytic reactions that require active sites of this type.

O-16

DFT and *ab initio* thermodynamics studies of morphology and surface structure stability of cryptomelane nanorod catalyst for soot oxidation in various redox conditions

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By means of periodical DFT+ U and *ab initio* thermodynamic modeling the morphology and surface stability of the cryptomelane (KMn_8O_{16}) nanorod catalyst in various redox conditions were analyzed. DFT calculations were performed with the VASP code (PAW method, PBE exchange-functional, Hubbard parameter U = 2.5 eV). The Monkhorst-Pack grid with the 3×3×5 sampling mesh for bulk calculations with the cutoff energy of 400 eV were applied. The most abundant surfaces of he cryptomelane nanorods, i.e. (100) and (110) were reveald by TEM imaging joined with the reverse Wulff construction. For examination of the surface stability in various redox conditions the (100) and (110) slab models with the 3×3×1 sampling mesh and 400 eV cutoff energy were used. Each slab had ~16 Å thickness containing 13 atomic layers, whereas the vacuum separation was set to 15 Å.

To determine the defect structure of the selected surfaces at various *T*, p_{O2} conditions the free energy, γ, of the surface containing N_O oxygen atoms and N_{Mn} manganese atoms relative to the bulk KMn_8O_{16} was calculated as:

$$\gamma(T, p_{O2}) = \frac{1}{2A}\left[G^{slab}_{\mathrm{KMn_xO_y}}(T, p_{O2}, N_{Mn}, N_O) - N_{Mn} G^{bulk}_{\mathrm{KMn_8O_{16}}}(T, p_{O2}) - (N_O - 2N_{Mn})\mu_{\mathrm{O}}(T, p_{O2})\right]$$

where: A - slab surface area. $\mathrm{G^{slab}_{KMn_xO_y}}$ and $\mathrm{G^{bulk}_{KMn_8O_{16}}}$ stands for slab and bulk free energy, respectively, normalized to a formula unit (KMn_8O_{16}). The entropic vibrational contributions to the Gibbs free energies were approximated by the corresponding DFT energies. $\mu_{\mathrm{O}}(T, p_{O2})$ is the O_2 chemical potential, factored into the electronic energy $(\frac{1}{2}E^{tot}_{O_2})$ togethre with temperature and preasure dependent contributions:

$$\mu_O(T, p_{O2}) = \frac{1}{2}E^{tot}_{O_2} + \mu'_O(T, p^0_{O2}) + \mathrm{k}T\ln\left(\frac{p_{O2}}{p^0}\right)$$

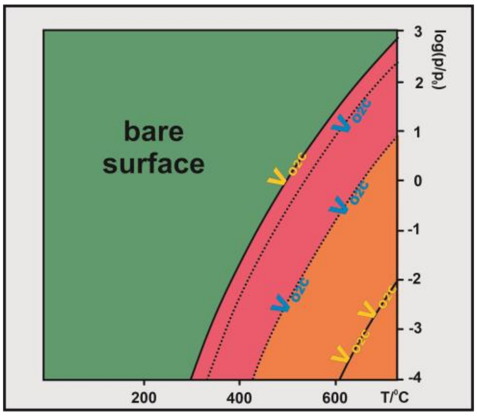

Fig 1. Stability of different vacancies at various T, p_{O2} conditions. Vacancies on (100) and (110) surfaces are marked by yellow and blue, respectively

The performed calculations reveald that both (100) and (110) terminations exhibit the same kind of the surface O^{2-}_{2c} and O^{2-}_{3c} anions which can form different forms of surface vacancies. They may further diffuse toward the bulk of the cryptomelane catalyst, where they are more stable. The suprafacial ROS species produced upon interaction of dioxygen with the catalyst surface are quite softly bounded and the diffusion barriers are rather small. As a result they may participate in the soot combustion hopping from the catalyst surface directly onto the soot particles in the catalyst-soot particles interface regions, justifying the particular role of the surface di – (O_{2c}) and tri-coordinated (O_{3c}) oxygen anions, located on the (100) and (110) planes of the cryptomelane nanorods in the soot ignition process.

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O-17

Gold catalysts supported on 2D and 3D zeolites – characterization and application in base-free glucose oxidation

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Glucose is an example of biorenewable feedstock that can be transformed into an array of valuable chemicals such as sugar acids commonly used in the food, cosmetics, and pharmaceutical industries [1]. In recent years, much attention has been paid to the catalytic oxidation of glucose. Hitherto, it has been documented that gold nanoparticles (Au NPs) deposited on various supports are attractive catalysts of this reaction [1-4]. Literature provides examples of aerobic glucose oxidation carried out in a batch reactor under elevated oxygen or air pressure [1,2], as well as microwave-assisted oxidation with the use of hydrogen peroxide [3,4]. The latter approach permits an extreme reduction in the reaction time (from hours to minutes) without much loss in activity and selectivity, when compared to those of the former ones [3]. However, in a large number of these reports glucose oxidation has been performed in an alkaline medium [2,3]. Since base addition can be undesirable because of the risk of salts instead of acids formation [1,4], it would be desirable to carry out the above-mentioned processes in non-basic media.

The aim of this work was the synthesis of gold catalysts supported on two types of zeolitic supports – the three-dimensional HBeta and the layered two-dimensional MCM-36 – and evaluation of their activity and selectivity in base-free oxidation of glucose with the use of molecular oxygen or hydrogen peroxide as the oxidant. The gold deposition was carried out via the grafting method employing (3-aminopropyl)trimethoxysilane (APMS) as an amino-organosilane modifier with further reduction using $NaBH_4$. Selected samples were subsequently calcined at 500°C for the removal of APMS whereas in the others (non-calcined ones) APMS was left on the zeolite surface. The as-prepared materials were characterized using complementary techniques (XRD, N_2 adsorption-desorption, FTIR combined with pyridine adsorption, DR-UV-Vis, XPS, TEM, ICP-OES and elemental analysis) in order to determine composition, structure/texture properties and acidity of the zeolitic supports as well as size and electronic properties of Au NPs.

It was established that both, the type of zeolitic support and the presence or absence of APMS, affected gold phase properties and consequently also catalytic performance. Gold catalysts based on MCM-36 zeolite exhibited higher glucose conversion than the respective ones supported on HBeta, which was related to the larger porosity and to the higher partial negative charge on Au NPs for the former materials. It was also documented that non-calcined gold catalysts, containing smaller Au NPs and partially protonated amino-organosilane species, revealed a higher catalytic activity in glucose oxidation than calcined ones. Moreover, the differences in rate-determining step depending on the oxidant used (O_2 vs. H_2O_2) were indicated.

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O-18

Wpływ specjacji wanadu w katalizatorach na osnowie fojazytu w reakcji ODH lekkich alkanów

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Olefiny są uznawane za jedne z najważniejszych substratów we współczesnych gałęziach przemysłu, w szczególności są wykorzystywane do produkcji produktów polimerowych. Znane konwencjonalne procesy produkcji alkenów posiadają liczne ograniczenia, które sprawiają, że wdrążone procesy wciąż nie są w pełni selektywne do pożądanych produktów. Znalezienie alternatywnych sposobów produkcji lekkich alkenów ma ogromne znaczenie i potencjał dla badaczy XXI wieku. Jednym z nich jest utleniające odwodornienie alkanów (ODH), w którym alkan jest przekształcany w alken w obecności utleniacza, którym może być tlen, ale także tlenek węgla(IV) czy tlenki azotu. Reakcja jest korzystna ze względu na niskie zużycie energii, mniejszą tendencję do wytwarzania koksu i wyższą selektywność do pożądanego produktu reakcji, w porównaniu z konwencjonalnym procesem odwodornienia. Jednak proces ten jest wciąż w fazie komercjalizacji ze względu na trudności w kontroli selektywności do olefin, która wynika z reakcji nieselektywnego utleniania, powodując powstanie znacznych ilości niepożądanych tlenków węgla (CO_2, CO).

Celem prezentowanych badań jest synteza katalizatorów wanadowych naniesionych na matrycę fojazytu, ich charakterystyka fizykochemiczna oraz badanie aktywności katalitycznej w reakcji ODH propanu. Badanie specjacji aktywnych centrów wanadowych ma kluczowe znaczenie dla unikania następczych reakcji spalania produktu reakcji ODH do tlenków węgla. Problemem nadal pozostaje rodzaj centrów wanadowych biorących udział w badanej reakcji. Czy są to izolowane, pojedyncze centra wanadowe czy też polimeryczne łańcuchy V-O-V, a może sam wanad w koordynacji tetraedrycznej czy oktaedrycznej. Zeolity, łączą w sobie unikalne cechy teksturalne, kwasowo-zasadowe i redoksowe, umożliwiające aktywację alkanów w stosunkowo niskich temperaturach. Stąd też zsyntezowano wanadowe katalizatory osadzone na zeolicie FAU (Si/Al=31) oraz jego hierarchizowanej formie FAU_{des} (Si/Al=18) oraz zbadano ich aktywność w reakcji ODH lekkich alkanów (propanu i etanu). Badane układy wykazywały aktywność w reakcji ODH w temperaturze 400 – 525 °C oraz wysoką selektywność do pożądanych olefin. Rodzaj specjacji wanadu w katalizatorach ma ogromne znaczenie na powstające produkty w reakcji ODH lekkich alkanów [1].

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O-19

IR spectroscopy studies of the Oxidation of Ethanol in Cu-Faujasites

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In the undertaken research, IR studies of the coadsorption of ethanol and CO on Cu^+ cations indicated the transfer of electrons from ethanol to Cu^+, which led to the lowering of the frequency of the band assigned to CO bonded to the same Cu^+ cation due to the more effective π back donation of d-electrons of Cu to antibonding π* orbitals of CO. The reaction between ethanol and acid sites in zeolite HFAU above 370 K resulted in the production of water and ethene, which was followed by the polymerization of ethene to polyethylene. The adsorption of ethanol adsorbed on zeolite Cu(2)HFAU containing acid sites and Cu^+_{exch} also resulted in the production of ethene, but in this case without the polimerization. C=C stretching (being IR non-active in the free ethene molecule), became IR active, thus the appearance of a weak band at 1538 cm^{-1} took place. The reaction of ethanol above 370 K in Cu(5)NaFAU zeolite (containing small amounts of Cu^+_{exch} and bigger amounts of Cu^+_{ox}, Cu^{2+}_{exch} and CuO) led to the production of acetaldehyde, which underwent further oxidation to the acetate species (CH_3COO^-). It was found that the Cu species present in our zeolite played a role of the donors of oxygen. The CO and NO adsorption experiments conducted in Cu-zeolite before and after ethanol reaction indicated that both Cu^+_{ox} and Cu^{2+} (Cu^{2+}_{exch} and CuO) were consumed by the ethanol oxidation reaction. Additionally, the oxidation of ethanol was carried out on zeolites, in which the proportion between the Cu^+_{ox} and Cu^{2+}_{ox} contents was altered by various treatments. Based on all these experiments, as well as the reaction of ethanol over bulk CuO and Cu_2O, it may be concluded that ethanol was oxidized to acetaldehyde by Cu^{2+}_{ox} and probably also by Cu^+_{ox}, whereas Cu^+_{ox} was responsible for the further oxidation of acetaldehyde to the acetate species.

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O-20

Studies on the synthesis of the porous carbon materials derived from biomass

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In this work, microporous spherical carbon materials from biomass were obtained by the hydrothermal method connected with chemical activation with KOH solution. The citrus peels solution (with different concentration) was placed in an autoclave for 12 h at 200 °C. After completing the hydrothermal synthesis, the sample was removed from the autoclave, rinsed with deionized water until it was neutral, and then dried at 110 °C. The morphology of the obtained carbon materials was examined with the Hitachi SU 8200 field emission scanning electron microscope. It was evidenced that the grains were spherical, slightly deformed, and their diameters range from 6 - 10 nm. After drying, the material obtained from a hydrothermal synthesis was modified with a KOH solution for 3 h. The material was heated at a temperature of 750 °C. The annealing process was carried out in a nitrogen atmosphere (flow 20 dm^3/h). The obtained activated carbon-containing decomposition products of potassium hydroxide were rinsed with distilled water until the reaction was neutral. Then, the sample of carbonaceous material was flooded with HCl solution with a concentration of 1 mol/dm^3 and left for 20 h. The obtained carbon material was washed with distilled water until the pH was neutral. In the final stage, the material was dried at 110 °C for 20 h to obtain the desired carbon material.

The textural characterization of the carbon materials was performed using the Quantachrome Instruments Quadrasorb Evo apparatus. Measurements of low-temperature N_2 adsorption isotherms at -196 °C were performed. Before measuring the adsorption, to remove impurities, samples of carbon materials were heated at the temperature of 250 °C for 12 h under reduced pressure, using a MasterPrep apparatus coupled with a computer. Based on the measurements of N_2 adsorption, the following was determined:

-- specific surface area (S_{BET}), which was calculated from the BET equation (Brunauer-Emmet-Teller) in the partial pressure range $p/p_0 = 0.05$-0.2 (p – N_2 pressure, $p_0 = 760$ mmHg);
-- total pore volume (V_{por}), based on the maximum nitrogen vapor adsorption for $p/p_0 = 0.99$;
-- pores in the range of micropores ($V_{mic,N2}$) and mesopores were determined using the nonlinear method of Density Functional Theory (DFT);
-- pores with smaller diameters (0.3 - 1.47 nm) were determined using CO_2 at a temperature of 0 °C. The pore size distribution was determined by the DFT method.

CO_2 adsorption studies at 0 °C were also carried out in the Quantachrome Instruments Quadrasorb Evo apparatus. To control the temperature of the measurements, the sample was placed in a bath with a mixture of water and ice. Before analyzing CO_2 adsorption, the samples were annealed at the temperature of 250 °C for 12 h under reduced pressure.

The specific surface area values for the obtained materials were in the following ranges: 920- 1530 m^2/g. It was also evidenced that the total pore volume as well as CO_2 adsorption capacity increase along with increasing concentration of the citrus peels solution. The pore volume determined for the carbons fluctuated in the 0.58-0.85 cm^3/g range, while the CO_2 adsorption capacity changed in the ranges: 5.2-7.4 mmol/g. Therefore, the obtained activated carbons can be successfully used as adsorbents in the CO_2 adsorption process.

Flash oral presentations

FO-1

Crucial parameters determining the structure of surface sites remaining of catalytic importance for selected processes of chemical valorization of CO_2

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Catalytic valorization of carbon dioxide belongs nowadays to the key pro-environmental technologies giving us a chance to systematically reduce the still growing emission of this greenhouse gas, that strongly contributes to anthropogenic climate changes. CO_2 molecule is thermodynamically very stable and its chemical activation, including a catalytic option, is rather difficult and strongly energy demanding. This is an obvious drawback placing chemical CO_2 valorization among rather unpopular industrial large-scale solutions. On the other hand, an applicational potential of the catalytic conversion of CO_2 is very attractive because of many valuable products, including methanol, hydrogen, synthesis gas, dimethyl ether, low hydrocarbons etc., that may be produced. Many of them can also be considered as synthetic fuels or their important components.

In this paper our attention is focused on two possible pathways of CO_2 conversion: dry methane reforming (DMR) to synthesis gas (occurring in the presence of CO_2 as a co-reactant) and direct CO_2 hydrogenation to methanol. Both reactions can be successfully implemented with using nickel- and copper-based catalysts, respectively. The efficiency of these reactions is strongly dependent on the ability to design, to control and to prevent from deactivation catalytically active sites in such relatively complex systems as e.g., NiO_x/CeO_2-ZrO_2 or CuO_x-ZnO_x/γ-Al_2O_3. As it was mentioned above, the first catalyst is dedicated to DMR and the second one to CO_2 hydrogenation. The status and possible evolution of transition metal centers are crucial for both catalytic performance and stability of the catalytic systems mentioned above. On the other hand, as it was confirmed in our studies, there is a strong effect of supports, presence of additives and calcination temperature on both speciation and stability of the investigated nickel and copper active sites.

The studied samples have been characterized by XRD, RS, SEM/EDS, porosimetry, XPS, DRIFT and UV/Vis-DR to elucidate and to understand in more detail the relationship between the nature of the exposed active sites and key structural, textural and functional features of the investigated samples.

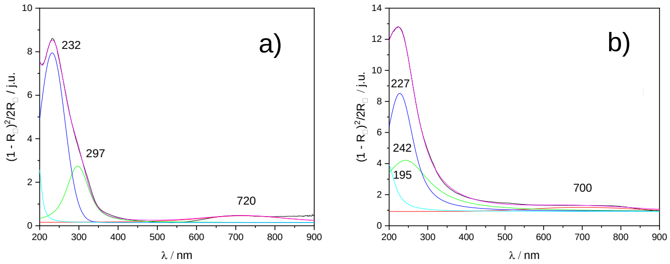

Figure: Deconvoluted UV/Vis-DR spectra of the supported copper-based samples,
illustrating the differences in Cu speciation between a) uncalcined samples and b) calcined at 400°/4h.

Acknowledgements: This work was partially carried on in the framework of the NiCe ERANet RUS Plus – S&T project, financially supported by the National Centre for Research and Development (Agreement No. DZP/RUSPLUS/ S&T/270/2016).

FO-2

Physicochemical characterization of montmorillonite composites with TiO_2 nanoparticles prepared by inverse microemulsion method

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The aim of the work was to obtain TiO_2/clay composites according to a novel design, based on combining the synthetic chemistry involved in the preparation of organoclays with the inverse micellar route of producing oxide nanoparticles in an organic medium.

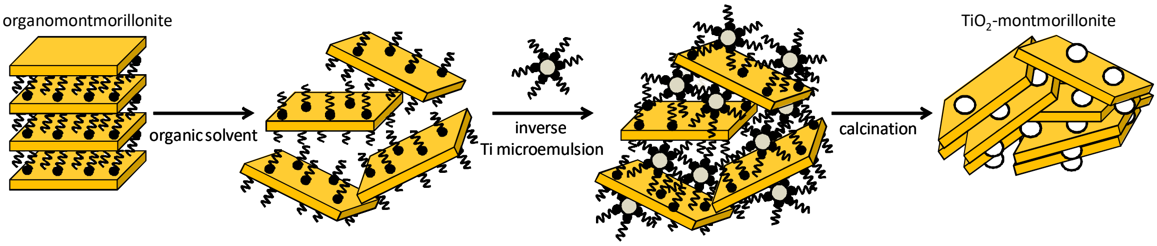

Fig. 1. Synthesis of TiO_2/clay composite from organomontmorillonite and inverse Ti micelles.

Inverse micelles are spheroidal water in oil droplets, formed when aqueous solutions of surfactants are added to organic solvents. Such systems are referred to as inverse microemulsions. Upon collision, micelles may exchange their water content, which makes possible coprecipitation of reactants dissolved in aqueous droplets, to yield, for instance, metal hydroxides. The size of synthesized particles is determined by the dimensions of the micellar core.

Ti pillaring solution from $TiCl_4$ precursor was used for preparation of inverse Ti-microemulsion, using 1-hexanol as an oil phase and cetyltrimethylammonium bromide as a surfactant. The microemulsion was added to the organomontmorillonite dispersion in 1-hexanol, and neutralized by addition of NaOH or NH_3 (aq). The recovered precipitates were calcined at 600°C and termed Ti-IMEC. For comparison, conventionally pillared montmorillonite Ti-PILC was also obtained. The composites were characterized with XRD, SEM, TG/DSC and N_2 adsorption/desorption isotherms.

XRD patterns showed that Ti-IMEC has a disordered house of cards structure, in contrast to ordered layered structure of Ti-PILC. Titania part of composites shows reflections assignable to the anatase modification, but in Ti-IMEC they are more pronounced than in Ti-PILC, which points to the better crystallinity of TiO_2 particles in the former. The pore size distribution profile of Ti-IMEC is more homogeneous than that characteristic of Ti-PILC, with maximum shifted to about 6.7 nm, in comparison to ca. 2.5 nm displayed by Ti-PILC. This indicates a more open, mesoporous network, which should facilitate diffusion of reagents. Anatase crystal size in the novel composites, estimated from XRD data, is around 7 nm, which corresponds well with the pore size maximum and suggests that uniform dimensions of TiO_2 grains formed within inverse micelles are the chief factor determining mesoporosity of composites prepared via inverse micellar route.

Acknowledgements: This research received financial support from National Science Foundation within project OPUS nr UMO-2018/31/B/ST5/03292.

FO-3

The Role of Water in the Confinement of Ibuprofen in SBA-15

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Ibuprofen is one the most widely used nonsteroidal anti-inflammatory drugs (NSAID). It is a perfect candidate for a controlled release by incorporation into various drug delivery systems. When confined into mesoporous silica-based materials, ibuprofen does not form crystals but exists in a glassy state characterized by high mobility of the molecules[1]. ^{1}H MAS NMR spectra of such systems exhibit narrow signals from ibuprofen located inside mesopores[2,3]. This phenomenon is not fully understood and the main reason for this behavior is still a matter of discussion.

The impact of water molecules on the dynamic behavior of ibuprofen in confinement was analyzed. Series of samples have been prepared with varying content of ibuprofen. Then, the samples have been dehydrated using thermal treatments in an oven or in vacuum. Preparation of samples in a water-free environment has also been performed. The impact of hydration of samples on the release properties and the toxicity of the samples have also been examined. The samples were characterized by XRD, TG, DSC, TEM, and 1D (^{1}H, ^{13}C HPDEC, ^{13}C CP MAS) and 2D (^{1}H-^{1}H NOESY) MAS NMR spectroscopy.

The samples of SBA-15 material contained from 9 to 33% of ibuprofen. The samples were not toxic to mouse monocyte-macrophage cells and do not stimulate a pro-inflammatory response. The sample with 25% of the drug showed no crystalline ibuprofen and almost filled mesopores, while the sample with 33% showed a total filling of the mesopores with some crystalline ibuprofen present. ^{1}H and ^{13}C MAS NMR results show that water has an impact on the mobility of ibuprofen molecules and their location within the sample (outside or inside mesopores). In dehydrated samples, water signals from ^{1}H MAS NMR spectra disappear, and simultaneously, signals from ibuprofen are broadened, which implies lower mobility of organic molecules. ^{1}H-^{1}H NOESY MAS NMR spectroscopy showed that water coexists with ibuprofen in mesopores. ^{13}C MAS NMR spectra show that when water co-existing with ibuprofen in mesopores is evacuated, ibuprofen located outside mesopores enter these voids. After rehydration of the sample, ibuprofen is removed by water from mesopores. The thermal treatment in vacuum evacuates the ibuprofen located outside mesopores out of the samples. Studies in dehydrated state show for the first time that high mobility of ibuprofen in mesopores is directly connected to the presence of water. Dehydrated samples show slightly slower release rates to simulated body fluids (SBF) in comparison to hydrated counterparts.

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FO-4

Deeper insight into the role of synthetic variables determining the formation of β-TiO_2 nanocrystals

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Designing effective photocatalysts, that can exhibit outstanding performance in such organic oxidation reactions as e.g. oxidation of terephthalic acid (TA), remains currently a real challenge. Herein, we propose a system based on β-TiO_2 nanocrystals for synthesis of hydroxyterephthalic acid (TAOH) under visible light. A series of samples containing a majority β-TiO_2 phase was successfully synthesized by hydrothermal method using the anatase TiO_2 phase as a precursor. Another series was synthesized via microwave assisted hydrothermal method.

The presence of metastable monoclinic β-TiO_2 was confirmed in the obtain preparation by XRD (see Figure below). It was shown in catalytic tests that β-TiO_2 demonstrates a satisfactory photocatalytic performance under visible light, which is higher than that reported by both anatase TiO_2 and P-25. Our approach can be considered as a facile route to obtain promising and efficient photocatalysts tailored for synthesis of selected organic compounds. In this paper the role of main synthetic variables controlling the formation of β-TiO_2 will be discussed in detail.

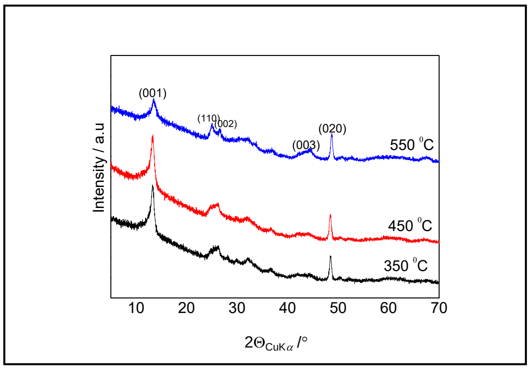

Fig. XRD patterns of the synthesized samples at various calcination temperatures.

Acknowledgements: H. Hamad gratefully thanks the Coimbra Group Universities for the financial support of his stay at the Jagiellonian University in Krakow in the framework of Scholarship Programme for Young Researchers from European Neighbouring Countries.

FO-5

Epoxidation of propane with oxygen and/or nitrous oxide over V-SBA-3

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Propylene oxide (PO), the third largest propene derivative, is a widely used high value-added intermediate and its annual worldwide production capacity exceeds 7.5 million tons. Currently used PO production technologies (mainly chlorhydrine method and process based on organic peroxides) are multi-stage processes and fabricate a large amount of by-products and cause environmental problems. Therefore, the direct synthesis of PO is one of the most desirable reactions. Recently, vanadium-supported silica catalysts have been reported as an attractive catalytic system for propene to PO oxidation with nitrous oxide as an oxidant [1]. Furthermore, the V-SBA-3 catalyst with nitrous oxide show also relatively high initial activity in direct propane epoxidation, however fast deactivation of catalysts was observed [2]. Rozanska et al. [3] indicated that vanadium reduction was considered as a reason of catalyst deactivation since N_2O ability to reoxidise of reduced V-species is much lower than that of molecular oxygen.

Considering the above statement, in the presented paper the mixed oxidants (N_2O with oxygen) were applied in the reaction of propane to propylene oxide direct transformation performed over V-SBA-3 catalyst in the temperature range of 673 – 743 K.

The influence of different oxidants (oxygen, N_2O or a mixture of N_2O with O_2) on the vanadium oxidation state, and, in a consequence, on propane to propylene oxide processing has been explored. Various technics: ESR, FTIR, UV-vis, and XPS spectroscopies and also XRD, H_2-TPR, and low temperature N_2 adsorption/desorption were applied for characterization of fresh and spent catalyst.

The catalytic activity tests in direct propane epoxidation evidenced that the use of mixed oxidants, comprising nitrous oxide and oxygen allows to stabilize the vanadium valence on a high level (near V^{5+}) and to obtain a high and relatively stable activity in the studied reaction. If oxygen was applied as the only oxidant of propane, CO_2 was a main product. In turn, the use of exclusively nitrous oxide as an oxidant brought about visible vanadium reduction and in a consequence, resulted in a very fast deactivation of catalyst. The introduction of molecular oxygen into the oxidative mixture, significantly improved reoxidation of vanadium species and brought about relatively high and stable activity. In the presented studies propane conversion of 40%, propylene selectivity of 45%, and propylene oxide selectivity of 11%, corresponding to a STY of propylene oxide of about 15 g kg_{cat}^{-1} h^{-1} have been obtained. These values are comparable to literature data calculated for only propylene epoxidation, however, the use of propane as a regent eliminates the additional stage of propylene production. On the basis of the obtained results the tentative reaction pathways of one-step propane epoxidation with N_2O/O_2 mixture on V-SBA-3 have also been proposed.

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FO-6

Modified silicalite-1 as acid catalysts and catalytic supports

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Silicalite-1 (MFI structure) shows very low acidity, which limits their use as acid catalysts. The role of acidic active sites play silanols groups on its surface. It was shown that treatment of silicalite of MFI structure, with an aqueous solution of ammonium salts and at least one basic compound generates additional acid sites in form of H-bonded silanol defect groups of a different kind causing increasing in the activity [1].

Regarding the above, in the presented study we modified silicalite-1 with solutions of ammonium compounds (NH_4NO_3, NH_4Cl, NH_4F, NH_4OH) without any additional alkaline agent in order to generate additional acidic sites. The influence of the nature of anion in the applied ammonium salt on the number and strength of resulting acid sites was investigated. The obtained materials were examined as catalysts for acetalization of glycerol with acetone to produce solketal. Selected samples were also used as supports of iridium catalysts and tested in toluene hydrogenation. The influence of acidity of the support on the activity of iridium catalysts was studied. The modified silicalite-1 materials as well as iridium catalysts were characterized by XRD, SEM, TEM, BET, NH_3-TPD, FTIR TPR-H_2, H_2 chemisorption.

The treatment of silicalite-1 with ammonium salt solutions at elevated temperature results in a change in its textural properties (increase in specific surface area and the pore volume, especially for samples modified with NH_4OH and NH_4F). The N_2 adsorption measurements confirmed formation of framework defects and generation of mesopores upon the modification. The acidic nature and the strength of OH groups in the modified samples have been confirmed by means of NH_3-TPD measurements and the IR spectra of adsorbed pyridine (Py). All the modified silicalites of the MFI structure showed considerable activity for glycerol acetalization with acetone with high selectivity to solketal. The activity of the studied catalysts increases simultaneously with the growth of their acidity.

The selected samples (pristine silicalite-1 and modified with NH_4OH and NH_4F) were used as supports for iridium catalysts. The impregnation did not change the crystallinity, textural properties, and acidity of the supports (XRD, low-temperature N_2 adsorption, and NH_3-TPD). The results of H_2 chemisorption measurements indicate that using of the modified silicalite-1 supports with mesoporous structure allows to attain higher dispersion and lower particle size compared to iridium catalysts supported on pristine silicalite-1 support. The highest dispersion and the smallest iridium particles were observed for Ir/Sil-1_OH catalyst with the highest surface area and pores size as well as with high acidity of medium strength. Such acid sites interact weaker with iridium precursor causing the formation of smaller Ir particles. The obtained catalysts show considerable activity in the hydrogenation of toluene. The highest activity shows iridium supported on silicalite-1 treated with NH_4OH (higher porosity of support, presence of weak Lewis acid sites, better dispersion of active phase).

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Acknowledgements: Monika Kot acknowledges the financial support from the National Science Center (Poland), grant PRELUDIUM UMO-2017/27/N/ST5/02042.

FO-7

Baeyer-Villiger oxidation of cyclohexanone over Mg-Al hydrotalcite catalysts precipitated with different bases

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Baeyer-Villiger (BV) oxidation is an important oxidative transformation which enables conversion of linear and cyclic ketones into respective esters and lactones. BV oxidation of cyclohexanone leads to formation of ε-caprolactone – an important building block for biocompatible and biodegradable polymer. In the presence of Mg-Al hydrotalcite (Htlc) solid base catalyst the monomer can be obtained with H_2O_2 as an oxidant. It is known that the catalytic performance depends on the Htlc Mg/Al ratio, crystal size, surface area, etc. [1, 2] This work aimed to explore the effect of different organic and inorganic precipitating bases.

Mg-Al Htlc solids, synthesized using NaOH, NH_3aq, TBA-OH and choline as precipitating agents, were characterized by means of chemical analysis, PXRD, FTIR, SEM, and surface basicity determination. The materials were tested as catalysts in the BV oxidation of cyclohexanone with the H_2O_2/acetonitrile system.

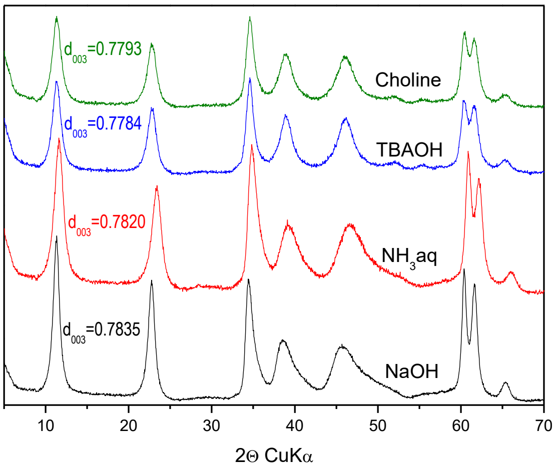

Fig. 1. PXRD Patterns of prepared samples.

PXRD confirmed that pure Htlc phases were obtained (Fig. 1). Their catalytic activity, expressed as ε-caprolactone yield after 3h of reaction, followed the order: choline > TBAOH > NH3aq > NaOH, pointing to the superior properties of organic bases as precipitants.

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FO-8

Selective catalytic hydrogenation of nitrocyclohexane in a flow reactor

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The chemical industry is a leading supplier of materials for modern civilization. Hence, even a tiny improvement introduced into any manufacturing process may significantly affect numerous strategic areas. For example, switch from batch to flow conditions is one of the most mentioned priorities for sustainable manufacture in the fine chemical sector.

Catalytic hydrogenation of nitrocyclohexane remains an underappreciated technological solution, so far studied mainly in batch conditions at high temperature and pressure [1-2]. This process could be challenging due to the follow-up hydrogenation and competing reactions (Fig. 1). However, selective hydrogenation of nitrocyclohexane could be an excellent source of various significant chemical compounds: cyclohexylamine (a building block for pharmaceuticals), dicyclohexylamine (rubber production), cyclohexanol, cyclohexanone and cyclohexanone oxime (all used in the production of nylons).

In our studies we decided to investigate the catalytic performance of metal-support catalysts in the reactions conducted in the liquid flow conditions at various temperatures and pressures. The application of the continuous-flow reactor distinguishes our studies in this field.

Catalysts based on low-cost transition metals (Cu, Zn, Al) proved to be active and selective in the hydrogenation of nitrocyclohexane. Their catalytic behaviour correlates with their structure and the applied reaction conditions. The obtained results allowed us to determine further steps for our studies in this promising field.

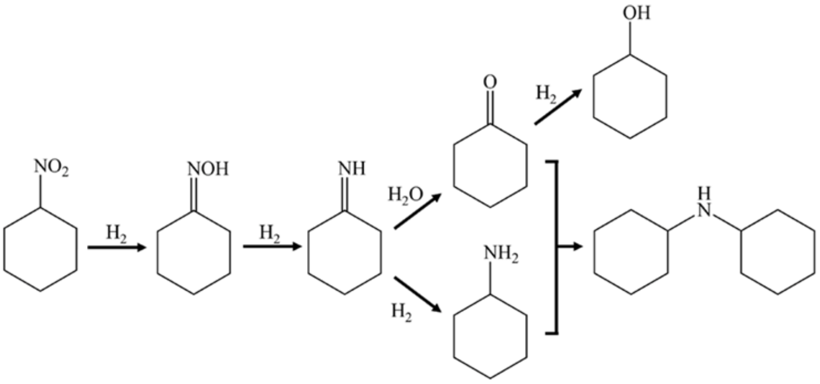

Fig. 1. Mechanism of nitrocyclohexane hydrogenation [3]

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FO-9

Sonochemical-assisted preparation of Co-Ce/γ-Al_2O_3 as catalysts for cyclohexene oxidation

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Metal-loaded alumina can be used as catalyst in many chemical processes, in which the contribution of red-ox active sites is required [1]. One of the methods of the deposition of metal active phase over alumina support is the ultrasonic-assisted impregnation. This technique causes the production of the oxide systems with enhanced dispersion of active phase over the carrier surface in comparison with analogues prepared via conventional methods (e.g. co-precipitation, impregnation, hydrothermal or solvothermal treatment) [2].

In the present paper, we reported the synthesis and characterization of Co and/or Ce loaded γ-Al_2O_3 as active catalysts for the oxidation of cyclohexene. Gamma alumina support was impregnated with aqueous solutions containing cobalt and/or cerium active phase. The impregnating solution underwent the ultrasonic irradiation pretreatment (sonochemical method) or not (classical procedure). The physicochemical and catalytic properties of the Co,Ce/γ-Al_2O_3 materials prepared using the ultrasonic-assisted procedure were compared with analogues synthesized using the conventional impregnation method.

Analysis of physicochemical properties of prepared catalysts led to the conclusion that the use of ultrasonic irradiation during synthesis procedure resulted in significantly higher distribution of Co and Ce over γ-Al_2O_3, as well as smaller crystallites and grains in relation to the samples prepared conventionally. Furthermore, the sonochemically prepared catalysts revealed a smaller both pore size and pore volume with simultaneous higher surface area in respect to the samples prepared via standard procedure. In the studied materials, Co was found in the form of both Co_3O_4 and $CoAl_2O_4$ spinel, while Ce was detected as CeO_2.

All studied catalysts were active in the oxidation of cyclohexene. The conversion of cyclohexene was in the range of 61-84%. In turn, the selectivity to 2-cyclohexene-1-ol, 2-cyclohexene-1-one and trans-cyclohexane-1,2-diol was 18-30%, 18-39% and 17-50%, respectively. The catalysts prepared via the sonochemical route indicated different catalytic properties from the catalyst synthesized conventionally, however, an unambiguous impact of ultrasonic irradiation on catalytic properties in the studied reaction was not found.

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FO-10

Copper based catalysts for ethanol steam reforming

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The influence of $CuO/ZrO_2/ZnO$ (Cu/Zr/Zn) catalyst modification with Mn, Ni, Ga on the physicochemical properties and activity toward hydrogen production in steam reforming of ethanol (SRE) reaction has been evaluated. The copper based catalysts were synthesised by co-precipitation method using Na_2CO_3 at constant pH = 7 and fixed (wt.%) CuO/ZrO_2 = 2.3. The catalysts were characterized by means of N_2 physisorption, temperature programmed reduction (H_2-TPR), N_2O dissociative chemisorption, X-ray diffraction (XRD), CO_2 temperature programmed desorption (CO_2-TPD), μRaman spectroscopy and X-ray photoelectron spectroscopy (XPS).

The modification of Cu/Zr/Zn catalyst with dopants resulted in increase of BET surface area, copper dispersion and in change in the distribution of surface basic sites. The highest yield to hydrogen is observed for Cu/Zr catalyst modified with Ga (Y_{H2} = 66 %) and Mn (Y_{H2} = 67 %). For these both catalysts, the primary source of hydrogen is acetone formation reaction which undergoes during SRE. On the other hand vast deactivation of Cu/Zr/Zn/Ni catalyst is observed which leads to decrease in ethanol conversion (X_{EtOH} = 67 %) and hydrogen yield (Y_{H2} = 34 %) in comparison with Cu/Zr/Zn catalyst. This is caused by formation of carbon deposit and adsorption of organic by-products at the catalyst surface as indicated by XPS and μRaman spectroscopy. In the case of this catalyst, hydrogen is produced mainly upon ethanol dehydrogenation to acetaldehyde, which results from the highest surface basicity.

The physicochemical characterisation of spent catalysts revealed changes in catalysts phase compositions and reducibility. In the case of Cu/Zr/Zn, Cu/Zr/Zn/Ni and Cu/Zr/Zn/Ga catalysts, the CuO phase was reduced to metallic phase and Cu_2O according to XRD and XPS analysis. Therefore, these spent catalysts exhibited lower reduction degree in comparison with fresh catalysts. On the other hand, the addition of Mn preserved the copper on +2 oxidation state during SRE reaction, which was confirmed by XRD and XPS.

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FO-11

Sorption properties of Laponite-derived nanocomposites triggered by chemical and hydrothermal treatment

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Environmental pollution is one of the main harmful side aspects of the development of modern civilization. Progressing industrialization, exploitation of fossil deposits, development of new technologies, are not inert to the environment in which we live. Accumulating evidence indicates that industrial combustion of fossil fuels has raised the greenhouse gas emission, predominantly CO_2. The harmful influence of CO_2 on climate is generally recognized. The new solutions enable to minimize the level of CO_2 emission are being sought. Nowadays, two strategies to deal with the problem are proposed: CCS – CO_2 Capture and Storage and CCU – CO_2 Capture and Utilization. CO_2 capture and sequestration (CCS), especially from post-combustion effluents, using solid sorbents has been proposed as a very promising technology. Consequently, the development of efficient materials with high sorption properties for CCS has increased. The high demand for efficient, stable, and cheap CCS nanosorbents has drawn our attention to the clay minerals, attractive from the point of view of sorption properties and belonging to the major components of soil. The inherent features in composition, structure and ion exchange properties predispose them to be engineered into various functional solids using various techniques, either directly as raw materials or after suitable modification of their surface or structure. Some modification methods lead to the enlarging of specific surface area, another allow for enrichment of the surface into ions or nanostructures enhancing the sorption affinity. Due to CO_2 affinity to alkali doped catalysts or basic metal oxides, exploration of high efficiency CO_2 sorption catalysts, prompted us to perform study focused on modification of the structure of clay minerals, specifically those belonging to the smectites group, with the aim to develop the surface basicity in highly porous systems, and consequently to increase the sorption properties for CCS process.

In the frame of the project the series of potential materials for CO_2 sorption was synthesized. Synthetic clay mineral Laponite - the hydrous magnesium silicate - consisting of octahedral sheet (occupied by Mg^{II}) sandwiched between two tetrahedral sheets (occupied by Si atoms) was used to obtain highly porous heterostructured nanocomposites (PCH), merging the properties of crystalline layered clay mineral and mesoporous silica. The chemical, sonochemical and hydrothermal activation of pure Laponite and Laponite derived PCH were applied to force the migration of Mg cations from octahedral sheets of used clay mineral and enriched the surface of composites into base properties.

It was stated that the precursor approach influenced the Mg content exhibited to the surface. The detailed characterization of surface species with the use of X-ray diffraction (XRD) method, scanning electron microscopy (SEM), advanced X-ray photoelectron spectroscopy (XPS), FTIR techniques in MIR and NIR regions and temperature programmed CO_2 sorption allowed to distinguish the distribution of Mg moieties and establish their contribution in the sorption properties.

FO-12

Physicochemical characterisation of mechanochemically and alkali activated talc

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Talc, a natural mineral, is a 2:1 layered silicate, with structure built of layers consisting of octahedral Mg-based sheet sandwiched between two tetrahedral Si-based sheets. Being a magnesium silicate, talc can be considered as a potential base catalyst. Solid bases, that can be industrially utilized as catalysts or sorbents, gained attention in recent years, due to the growing need of developing environmentally friendly materials for industrial purposes. However, pristine talc is characterized by low specific surface area (SSA) and low basicity per mass of mineral. It is known that appropriate grinding of talc results in an increased SSA, but the effect of milling on talc's basicity has not been addressed in the literature. This aspect has been investigated in the present work. The study encompassed also activation of ground talc with alkaline solution, aiming at further enhancement of basicity.

Talc was activated by grinding in a planetary mill (for 10, 30 and 60 min) and subsequently treated with 2M NaOH solution (at 90^{o}C, for 3 and 20 h). Physicochemical characterization (XRD, FTIR, Raman, N_2 sorption/desorption isotherms, benzoic acid adsorption) of obtained materials proved, that grinding combined with alkali treatment led to significantly increased SSA, along with increased basicity (Fig. 1). The former effect was ascribed to the formation of magnesium silicate hydrate (MSH) phase that evolved as a result of reaction between the amorphous silica generated by grinding and crystalline magnesium hydroxide produced during leaching of talc with alkaline solution. In the base-catalysed aldol condensation of acetone the mechanochemically and alkali activated talc sample with the highest SSA and basicity proved 50-times more active than the parent talc.

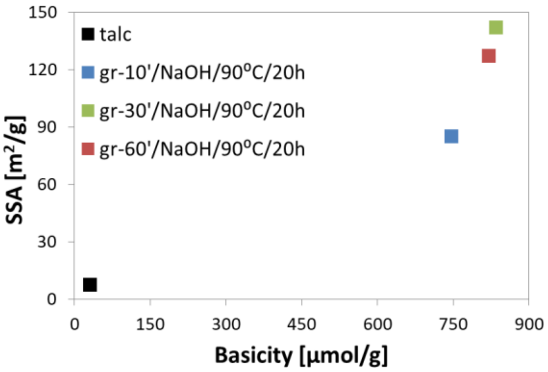

Fig. 1. Specific surface area of investigated talc samples vs. basicity measured by benzoic acid adsorption

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FO-13

The effect of cobalt doping on properties of Co-containing siliceous BEA zeolite

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The liquid phase oxidation of hydrocarbons in the presence of transition metal complexes as catalysts was of interest to researchers for many years [1]. This reaction is widely used in chemical industry for the synthesis of important large-scale products (e.g. polyamide, polycaprolactone) as well as for the production of fine chemicals [2]. In particular, oxyfunctionalization of cycloalkanes in biomimetic system with molecular oxygen in the presence of transition metal complexes as catalysts is a continuous challenge to chemists. One of the aspects of interest is the design of a novel catalytic system which would modify the reaction characteristics.

In the present communication we report on the application of single-site cobalt BEA zeolites with cobalt content varying from 1.0 to 9.0 wt % as catalysts in the selective oxidation of cyclooctane with molecular oxygen. Co_xSiBEA zeolites were synthesized, physico-chemically characterized by NMR, XPS, FTIR and UV-Vis spectroscopy as well as by XRD. A series of Co_xSiBEA zeolites were compared with the parent SiBEA zeolite. The main products of cyclooctane oxidation with molecular oxygen were cyclooctanone and cyclooctanol.

The incorporation of cobalt cations into the SiBEA framework was evidenced by FTIR and NMR spectroscopy. To distinguish between the framework and non-framework positions of cobalt cations in SiBEA zeolite DR UV-Vis and XPS measurements were performed.

The catalytic study revealed that an efficient transformation of cyclooctane to cyclooctanone and cyclooctanol in the oxidation reaction depends on the cobalt oxidation state and its environment. The yield of oxygenates gradually increases with the increase of cobalt content up to 3.0 wt % in Co_xSiBEA zeolites. However, for a higher content of cobalt in SiBEA structure, namely for Co_5SiBEA and Co_9SiBEA, the catalytic activity gradually drops.

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FO-14

DFT and MD studies of hydrocarbon adsorption on zeolites

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Zeolite-based systems are widely used as catalysts for hydrocarbons transformations. These microporous and mesoporous materials, often used as supports for metallic active centres, are promising catalysts due to their ability to combine unique textural and acid-base properties, which allow for the activation of alkanes at relatively low temperatures. In addition, their high specific surface area allows preparing catalysts with well-dispersed active sites.

In the present studies we focus mostly on vanadium-based systems which are used for oxidative dehydrogenation (ODH) of light alkanes. In this process unreactive alkanes are transformed into olefins, which are considered valuable substrates for production of fuels and chemicals.

The aim of the present theoretical studies is to study the speciation of vanadium ions introduced into zeolitic materials and to gain insight into the nature of the interaction between hydrocarbon (methane, etane, propane) molecules and active sites present in zeolitic materials (both acid sites and transition-metal ones), mostly in BEA and ZSM-5.

The theoretical investigations were performed within Density Functional Theory (DFT) within cluster and periodic approaches with Perdew-Burke-Ernzerhof (PBE) functional. Calculations were done with Turbomole and Scigress program packages.

The present DFT calculations suggest that vanadium could substitute T atoms in all available nine crystallographic positions in BEA. As the V–OH group, vanadium center is bound preferentially in the T2 position. Vanadium could be present as the V=O moiety in T2 or T3 positions, but the energy difference between the two is too low to draw any definite conclusions regarding the preference as to its sitting. The introduction of the V=O center generates an additional acidic site in its proximity, which may act as an anchor for reagents. The most energetically favored position for the V(=O)(–OH) group is T3. The analysis of Mulliken charges accumulated on oxo and hydroxyl centers indicates their nucleophilic character. Their dominance in the valence band (as revealed by DOS plots) points out that both oxygen species may play an active role in catalysis, in particular in redox processes.

MD simulations show that all studied alkanes can easily diffuse inside relatively large zeolitic pores present in BEA, the diffusion is somewhat limited inside ZSM-5 channels.

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FO-15

Wpływ dotacji potasem na zeolit Y modyfikowany kobaltem (CoY). Specjacja potasu a reaktywność układu w reakcji reformingu parowego etanolu.

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Obecnie znaczna część światowego zapotrzebowania na energię zaspokajana jest przez szkodliwe dla środowiska, nieodnawialne paliwa kopalne. Zwiększone zapotrzebowanie na energię na przestrzeni ostatnich lat, prowadzi do poszukiwania jej alternatywnych źródeł. Wodór, nieszkodliwe dla środowiska źródło energii, jest obiecującym rozwiązaniem światowego problemu energetycznego. Procesem, który pozwala na jego wydajne i efektywne pozyskanie na skalę przemysłową jest reforming parowy etanolu (ESR). Katalizatory na bazie metali szlachetnych charakteryzują się wysoką aktywnością w ESR, jednak ze względu na wysokie koszty, dużym zainteresowaniem cieszą się także układy wykorzystujące metale przejściowe, w tym kobalt [1]. Z kolei obiecującymi materiałami do zastosowania w roli nośnika fazy metalicznej są zeolity o rozwiniętej powierzchni [2].

W pracy przygotowano serię próbek na bazie zeolitu Y (Si/Al = 31) modyfikowanego kobaltem (10% wag. fazy kobaltowej) dotowanych potasem w zakresie 0 – 4% wag. Dodatkowo otrzymano próbkę Co(K)Y, nanosząc fazę kobaltową na zeolit Y uprzednio zmodyfikowany potasem na drodze wymiany jonowej. Otrzymane próbki scharakteryzowano pod kątem składu fazowego i chemicznego, morfologii, tekstury oraz redukowalności z wykorzystaniem metod XRD, ICP, STEM/EDX niskotemperaturowej adsorpcji N_2 i H_2-TPR. Kwasowość katalizatorów zbadano z zastosowaniem metody spektroskopii w podczerwieni FT-IR, z użyciem cząsteczek sond tj. pirydyna oraz CO. Testy katalityczne przeprowadzono w temperaturze 500°C dla stosunku molowego EtOH:H_2O 1:4 oraz 1:12.

Stwierdzono, że obecność potasu w układzie CoY skutkuje nieznacznym zmniejszeniem się porowatości układu oraz pogorszeniem dyspersji kobaltu na nośniku zeolitowym, co więcej potas spowodował wyraźne obniżenie stężenia centrów kwasowych na powierzchni katalizatora. Obserwowane efekty silnie zależą od natury K w katalizatorze i znajdują odzwierciedlenie w działaniu katalizatora w procesie ESR. Mianowicie, 100% konwersja etanolu dla CoY ulega obniżeniu: do wartości 75-80% w wyniku wprowadzenia potasu w pozycje jonowymienne oraz nawet do 5-10% w wyniku wprowadzenia K na zewnętrzną powierzchnię układu. Co istotne, wprowadzenie K zdecydowanie obniżyło selektywność do wysoce niepożądanego produktu procesu ESR – C_2H_4. Selektywność do C_2H_4 z wartości 65-70% zmniejszyła się do 45-55 % dla próbki z K w pozycjach jonowymiennych oraz do 0-5% dla próbki zawierającej K na powierzchni zewnętrznej katalizatora.

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FO-16

Exploration of unknown biochemical role of selenocysteine in enzymes

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The biochemical role of selenium has only been recognized in the 1950s, therefore it is sometimes called ‘the youngest’ bioelement. Biological activity of selenium is mostly due to its presence in selenoproteins in form of selenocysteine (Sec) residues. Sec is the 21st naturally occurring amino acid and structurally is similar to cysteine (Cys) residue with only one sulfur atom replaced with selenium. The slight differences between these two elements determine significant biochemical dissimilarities among Sec- and Cys-proteins (lower pK_a value in comparison to Cys, higher nucleophilicity, higher reaction rates with electrophiles).

The question why nature has chosen selenium as suitable for biological purposes remains unanswered. It seems likely that the presence of selenium atom in enzymes renders unique features and explains the existence of Sec in proteins. In recent years, huge development in selenium enzymes structures and properties recognition have been made. Some of the latest papers connecting with selenoproteins deal with the incorporation of selenocysteine in place of cysteine residue. This replacement should have a significant influence on many features of enzyme i.e. stability and redox potential and therefore may lead to improvement of selected enzyme properties. However, the development of this method is very restricted due to many inconveniences in application of such technique (complex incorporation of Sec, highly difficult expression of selenoprotein in popular microbial hosts, low yield of Sec-enzyme production).

Conducted studies aim to elucidate some aspects of the importance of Sec in proteins and to increase our knowledge about the role of selenium and selenocysteine in living organisms. The research is based on the incorporation of selenocysteine in place of cysteine in selected enzymes using a recently established molecular biological system of efficient Sec-insertion in *E. coli* [1]. Generation of Sec-analogues of proteins with a Cys in the active site or involved in binding of cofactors will allow us to determine the influence of sulphur-to-selenium exchanges on enzyme features such as structure, stability of enzymes. The research includes: preparation of DNA constructs containing Sec-coding enzymes, testing and optimization of the Sec-expression system in *E. coli*, biochemical and catalytic characterization of obtained enzymes. The obtained results for modified proteins (i. e. for phenylacetaldehyde dehydrogenase) will be presented.

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FO-17

TOF-SIMS study of Fe(111) surface wetting with potassium, calcium and aluminum oxides

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The high activity and thermodynamic stability of the fused iron catalyst used in the synthesis of ammonia is due to the presence of promoters in its structure, but their role has not been clarified unambiguously so far.

In this study, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to analyze the wetting by potassium, calcium and aluminum oxides the (111)-oriented surface of monocrystalline iron selected as a model system of fused iron catalyst. The choice of this technique is related to the fact that it provides direct evidence for the presence of promoters on the catalyst surface. Moreover, TOF-SIMS allows obtaining information concerning the interaction of promoters with the iron surface.

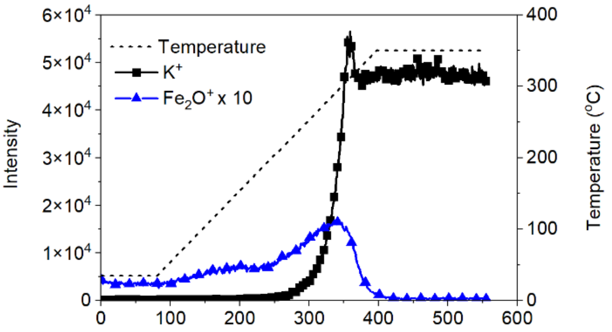

Fig. 1. Temperature programmed TOF-SIMS profile of the potassium concentration on the surface of the iron sample.

It was shown that efficient diffusion of potassium on the iron surface occurs already at a temperature of about 230°C. An exemplary TOF-SIMS profile for iron surface wetting by potassium oxide is presented in Figure 1. The emission of Fe_2O^+ ions from the sample surface indicates that surface of the iron that is wetted with potassium contains oxygen.

Calcium diffusion on the iron surface occurred at a similar temperature. In the range of sample temperatures up to 350°C, no surface diffusion of aluminum was observed.

Efficient diffusion of potassium on the iron surface was also found to occur when trace amounts of potassium are present on the sample surface in the presence of calcium and aluminum.

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FO-18

Cenosfery jako nośnik faz tlenkowych aktywnych w reakcjach katalitycznych o znaczeniu środowiskowym

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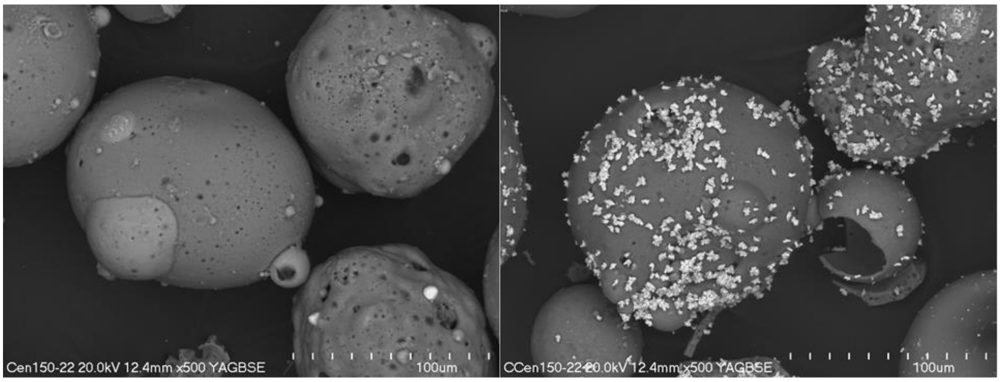
Zgodnie z zasadami gospodarki o obiegu zamkniętym poszukiwane są nowe metody wykorzystania produktów ubocznych procesów technologicznych. Przykładem takich materiałów są cenosfery, stanowiące jeden z typów ziaren obecnych w popiołach lotnych, czyli ubocznych produktach energetycznego spalania paliw. Cenosfery są materiałem o interesujących właściwościach fizykochemicznych wskazujących na szeroki wachlarz możliwości ich efektywnego zagospodarowania. Cenosfery powstają w temperaturze przekraczającej 1200^{o}C ze składników niepalnych zawartych w węglu. Po spaleniu części organicznej materiał pozostający w komorze spalania ulega stopieniu i zostaje wzbogacony głównie w krzem, glin, żelazo oraz pierwiastki alkaliczne. W takich warunkach, pod wpływem uwalnianych podczas spalania gazów, formowane są sferyczne ziarna cenosfer. Ziarna te charakteryzujące się m.in. niską gęstością oraz wysoką odpornością mechaniczną oraz chemiczną. Znaczny udział mullitu oraz innych faz glinokrzemianowych w strukturze cenosfer zapewnia ich wysoką stabilność termiczną. Wspomniane właściwości sugerują wysoki potencjał wykorzystania cenosfer jako nośników katalitycznych.

W niniejszej pracy zaprezentowane zostaną wyniki badań nad wykorzystaniem jako nośników katalitycznych komercyjnych cenosfer. I tak, przebadane zostały dwa rodzaje próbek różniące się uziarnieniem. W toku badań naniesiono na cenosfery metodą suchej impregnacji fazę aktywną zawierającą miedź oraz cynk. Skład chemiczny powierzchni uzyskanych próbek został określony przy pomocy pomiarów EDS, skład mineralny oraz fazowy - za pomocą technik XRD oraz RS, właściwości teksturalne, w tym wielkość powierzchni właściwej przy wykorzystaniu niskotemperaturowej sorpcji azotu, zaś wielkość i morfologia ziaren na podstawie analizy obrazów SEM. Właściwości funkcjonalne określono na podstawie pomiarów DRIFT oraz UV-Vis DR. Przeprowadzone badania potwierdziły korzystny wpływ cenosfer na strukturę i stabilność fazy naniesionej oraz jej korzystne parametry funkcjonalne, pozwalające na wykorzystanie uzyskanych układów jako katalizatorów uwodornienia CO_2.



Rys. Obrazy SEM cenosfer przed (lewy) oraz po (prawy) impregnacji fazą aktywną.

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FO-19

Adsorpcyjno-fotokatalityczne oczyszczanie wody z zanieczyszczeń organicznych z użyciem układów rdzeniowo-powłokowych C@TiO$_2$

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Tlenek tytanu(IV) jest szeroko wykorzystywany w licznych aplikacjach środowiskowych ze względu na wysoką efektywność działania w procesach fotokatalitycznych. Najnowsze doniesienia sugerują jednak, że nanometryczne ziarna TiO$_2$ wykazują tendencję do kumulacji w takich narządach, jak wątroba, śledziona czy płuca [1]. Kluczowe wydaje się zatem opracowanie na bazie TiO$_2$ materiałów, które przy zachowanej fotoaktywności byłyby jednocześnie zabezpieczone przed niekontrolowanym przenikaniem do środowiska naturalnego. Jednym z proponowanych rozwiązań jest konstrukcja układów kompozytowych, których przykładem są struktury rdzeniowo-powłokowe. W prezentowanej pracy zsyntetyzowano materiały C@TiO$_2$ zawierające węglowy rdzeń, którego zadaniem jest usuwanie zanieczyszczeń organicznych na drodze adsorpcyjnej, oraz otoczkę (powłokę) wytworzoną ze zagregowanego, fotoaktywnego TiO$_2$. Głównym celem przeprowadzonych badań było przetestowanie opracowanych układów C@TiO$_2$ w roli efektywnych adsorbentów i fotokatalizatorów do usuwania wybranych polutantów organicznych zawartych w wodzie.

Syntezę kompozytów przeprowadzono stosując strategię *bottom-up*. W pierwszym etapie uzyskano sferyczne ziarna na bazie żywicy rezorcynowo-formaldehydowej, które po karbonizacji wykazywały strukturę mikroporowatą o rozwiniętej powierzchni właściwej [2]. Otrzymane materiały węglowe prezentowały pojemność adsorpcyjną wobec zanieczyszczeń fenolowych bez dodatkowej aktywacji powierzchni, co potwierdziły testy adsorpcyjne fenolu z fazy wodnej (Q_{max} = 150 mg/g) [2]. Finalny materiał kompozytowy ze zdeponowaną warstwą tlenkową uzyskiwał, obok mikroporowatości specyficznej dla rdzenia węglowego, również mezoporowatość wynikającą z obecności otoczki TiO$_2$. Pozwoliło to na utrzymanie dużej powierzchni właściwej materiałów C@TiO$_2$ (rzędu 400 m^2/g). Dowiedziono, iż rdzeń węglowy stanowi rusztowanie dla zdeponowanej fazy TiO$_2$, po którego usunięciu struktura sferyczna otoczki ulegała destrukcji. Aktywność fotokatalityczną powłoki TiO$_2$ zweryfikowano na podstawie testów fotodegradacji 4-nitrofenolu w fazie wodnej (pH = 7) oraz niejonowego związku powierzchniowo czynnego Triton X-100 (pH = 4). Sprawdzono jak skład fazowy otoczki (stosunek anatazu do rutylu) wpływa na efektywność usuwania wybranych zanieczyszczeń organicznych. Dodatkowo, w przypadku eliminacji Tritonu X-100, przetestowano działanie materiałów C@TiO$_2$ w układzie rzeczywistym (woda rzeczna – rzeka Wkra).

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FO-20

Nowe perokso- oraz poliokso- związki Mo(VI). Synteza, badania strukturalne i zastosowania w procesach utleniania.

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Testując szeroki zakres warunków syntez w roztworach wodnych [1,2], otrzymano kilka nowych związków z grupy hybrydowych polioksomolibdenianów jak i kilka nowych peroksomolibdenianów sodu zawierających molekuły kwasów karboksyprirydynowych wbudowanych w grupę anionową. Molekuły organiczne wpływają na stabilność połączeń. Mogą też modyfikować własności fizykochemiczne i farmakologiczne.

Czystość produktów reakcji badano metodami dyfrakcji proszkowej (xrpd). Badania struktur krystalicznych prowadzono metodami dyfrakcji monokryształów (xrd). W przypadku braku monokryształów, badania strukturalne stosowano techniki xrpd przy użyciu metod bezpośrednich oraz metod przestrzeni rzeczywistej.

Dla uzyskanych połączeń planowane są testy katalityczne w reakcjach utlenienia cyklooktanu oraz w reakcji Baeyera-Villigera. Otrzymane peroksomolideniany sodu będą też testowane jako środki przeciw nowotworowe na wybranych liniach komórkowych.

Opis otrzymanych związków.

Nr, Nazwa/skład, technika badawcza, układ krystalograficzny, opis struktury.

1) (MoO_3)1,2-diaminocykloheksan, xrpd, ukł. rombowy, polimeryczny hybrydowy MoO_3
2) Na($MoO(O_2)_2$)kwas izonikotynowy, xrd, ukł. jednoskośny, polimeryczny łańcuch bipiramid MoO_7 i molekuł organicznych
3) Na($MoO(O_2)_2$)kwas 35-dikarboksypirydynowy, xrpd, ukł. jednoskośny, cykliczne, centrosymetryczne dimery utworzone z dwóch bipiramid MoO_7 i dwóch molekuł organicznych.

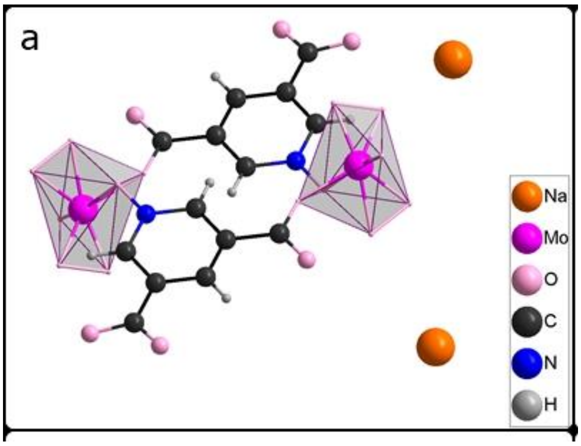

Fig. 1. Anion związku 3); Na($MoO(O_2)_2$)kwas 35-dikarboksypirydynowy.

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FO-21

In search for the best bifunctional catalysts, based on MnSBA-15 and modified with Cu or Au, addressed to oxydehydration of glycerol

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One of important transformations of glycerol into valuable compounds is the formation of acrylic acid via dehydration - oxidation process [1]. This two-step reaction requires bifunctional catalyst, because acidic and redox sites are involved in the dehydration of alcohol to acrolein and its oxidation to acrylic acid, respectively. Catalyst addressed to this reaction should contain not too strong acidic centers on the outside surface and effective redox centers located in the subsurface layer. Metal containing mesoporous silica SBA-15 has been selected as material that allows the separation of acid (in the framework) and redox (in pores) centers as needed.

The aim of this study was the preparation and characterization of bifunctional catalysts containing redox and acid centers supported on SBA-15 matrix and to select the best one for the catalytic oxydehydration of glycerol.

The idea was to generate acid centers by introduction of Mn into the structure of SBA-15 during the synthesis, and redox centers by post synthesis modification of MnSBA-15 with gold or copper (2 wt.% of Au or Cu). Two kinds of the sources of Mn has been used: manganese acetate (mixed with TEOS - AT) and manganese nitrate (in TEOS and water mixture – NTW). The physicochemical properties of the catalysts were investigated by means of XRD, N_2 ads./des., TEM, UV-Vis, XPS, FTIR with pyridine adsorption and 2-propanol decomposition test reaction.

It has been found that the source of metal and method of its introduction during the synthesis of SBA-15 determine the loading and location of manganese species in the silica structure. The use of manganese acetate led to location of the metal in the form of manganese oxides in extra-framework positions in MnSBA-15-AT, while MnSBA-15-NTW synthesized with the use of $Mn(NO_3)_2$ contained manganese localized mainly in the framework. Moreover, the support synthesized with manganese nitrate was characterized by a significantly higher metal loading (0.5 and 0.2 wt.%, respectively).

Using the test reaction of 2-propanol decomposition, it has been documented that MnSBA-15-AT showed relatively high acidity (43% of alcohol conversion at 573 K) due to the presence of extra-framework forms of manganese which act as Lewis acid centers. The introduction of gold or copper reduced the acidity of this support as a result of the removal of manganese oxides, simultaneously the generation of basic/redox properties of the surface was observed. The acidity of MnSBA-15-NTW with Mn in the framework was much lower (8% of conversion). Among bifunctional catalysts, the highest basic/redox properties (ca. 60% of selectivity to acetone at 573 K) was observed for Au-MnSBA-15-NTW and Au-MnSBA-15-AT. The source of basicity in gold containing samples is the negatively charged metallic gold $(Au^0)^{\delta-}$ playing also the role of redox centers. On the other hand, the high selectivity to propene (ca. 60 % at 573 K) was found for copper-MnSBA-15 materials, indicating the domination of acidic properties in these catalysts.

The full characterization of the catalysts obtained and the effect of modification with metals on the activity and selectivity of bifunctional (Au or Cu)MnSBA-15 samples in oxidative dehydration of glycerol with H_2O_2 as oxidant will be reported in the full contribution.

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FO-22

Determinants for substrate recognition in benzylsuccinate synthase from *Thauera aromatica* - targeted mutagenesis and MD simulations

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Anaerobic toluene degradation is initiated by a remarkable and energetically challenging free radical reaction - toluene addition to fumarate catalyzed by the glycyl radical enzyme (GRE) benzylsuccinate synthase (BSS). This reaction allows anaerobic activation of toluene and various other hydrocarbons, providing carbon sources for many anaerobic chemotrophic bacteria. BSS from *Thauera aromatica* is a heterohexameric (α2β2γ2) enzyme with a Gly828 and Cys492 catalytic dyad in the □ subunit [1]. Thanks to a recently developed recombinant production system producing active BSS we were able to generate several active-site mutants that modified the substrate specificity of the enzyme. A single substitution of Ile617 to Val inside a hydrophobic pocket of the active site led to an extension of the substrate range of the mutated variant, which includes conversion of *m*-xylene, but not of *o*- or *p*-xylene. Mutation of Arg508Lys enabled the enzyme to bind 3-acetylacrylate in addition to fumarate which resulted in the production of a small amount of 3-benzyl-4-ketopentanoate [2].

We applied MD simulation for wild-type and mutant variants of BSS to understand the observed phenomena and gain additional insight into factors imposing enzyme selectivity. The distribution of the distance between the methyl group of the substrate and the S atom of the Cys492 turned out to be a good predictor of the enzyme's activity with the particular substrate. Analysis of substrates behavior in the active site allowed us to pinpoint molecular interactions that ensure substrate selectivity, such as steric interaction with Ile617, which prevents the effective binding of *m*-xylene or Leu391, 482, Val704 restricting access of *o*-xylene. We have also shown that *p*-xylene binds perpendicularly to the usual toluene pose which results in a catalytically non-active arrangement. Furthermore, careful analysis of MD trajectories allowed identification of several important H-bond interactions involved in binding and positioning of fumarate or 3-acetylacrylate, which becomes a substrate in the Arg508Lys mutant.

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FO-23

Tuning metathesis activity of molybdenum catalyst by high temperature pretreatment procedure

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Molybdenum oxide deposited on porous supports (e.g., silica, alumina and silica-alumina) are important metathesis catalysts. It is generally accepted that metathesis reaction is catalysed according to the metallacyclobutane intermediate mechanism [1]. This mechanism assumes that during induction steps of metathesis alkylidene active sites are formed on the surface of oxide-based catalysts (Me = CHR, where Me is a metal atom, e.g., Mo or W, and R is a hydrogen atom or an alkyl group). The number of active alkylidene species in these catalysts is at most 2% of the total metal content [2–4]. The concentration of the active sites can be increased by modifications in preparation steps or catalysts pretreatment before metathesis reaction. To the latter, one can include room-temperature photoreduction with carbon monoxide [5], high temperature pretreatment in olefins (ethene, propene) [6] or methane [7].

Silica-alumina supports have been suggested to provide a higher dispersion of molybdenum oxide [8].

SBA-1 supported molybdenum oxide were investigated in a low-temperature metathesis reaction. Effect of support acidity as well as high-temperature pretreatment of catalysts before metathesis was evaluated. 5 wt. % of Mo was deposited on pure and Al-doped supports by incipient wetness impregnation. A correlation between the acidity of the supports and catalytic results were found. Furthermore, the effect of high-temperature pretreatment of catalysts on their metathesis performance was investigated. Molybdenum oxide-based catalysts supported on pure SBA-1 was pretreated in the flow of inert gas, hydrogen, carbon monoxide and hydrocarbons (ethane and propane) at 650 °C.

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FO-24

3D printed monolithic catalysts in DLP technology dedicated to oxidative coupling of methane

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The importance of monoliths has increased in the last few decades. They were used in the automotive industry as catalysts. Today, they are also used for the removal of volatile organic compounds (VOCs), or for selective catalytic reduction (SCR) of NOx [1,2]. One of the promising technologies to obtain monoliths is the 3D printing, where monolithic structures are obtained using various additive methods such as Selective Laser Sintering (SLS), Fused Deposition Modeling (FDM) or Stereolithography (SLA). However, a simple but also perspective technology for obtaining ceramic monoliths, in addition to the SLA technique, is the Digital Light Processing (DLP) method, where a photopolymer resin is cured using a light source (projector). In these techniques, two additional methods are used: indirect, where by designing and printing a template of polymer resin, filling it with an appropriate mixture and finally firing it, and direct, where instead of pure polymer resin, its mixture with various ceramic components such as alumina, silica powder, hydroxyapatite or zirconia is used. The basic ingredients included in the ceramic resin, in addition to the ceramic components, are a solvent, photoinitiator, dispersant, absorber, and mono – or bifunctional acrylates [3 – 5].

Here, we present the method to obtain ceramic monoliths by direct 3D printing in Digital Light Processing (DLP) method using ceramic resin containing α – Al_2O_3 and/or kaolin will be discussed. Additionally the resulting monoliths were initially characterized by XRF, XRD, DTA/TG, SEM with EDS and mechanical tests. The method was developed to prepare a series of monoliths with different ceramic part content in the resin mass. The ceramic resin contained 45 or 55% ceramic part and the residue was the base resin containing poly(ethylene glycol) diacrylate (PEGDA), photoinitiator, solvent and dye. After printing and firing, the active phase was applied to monoliths and the oxidative coupling of methane reaction were performed on them. The method of direct 3D printing using the developed new resin allowed obtaining ceramic monoliths with high resolution and good mechanical properties suitable for different applications including high – temperature catalytic processes.

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FO-25

Lantan jako ochroniarz podłoża węglowego w katalizatorach Ru/C do metanizacji tlenku węgla

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Metanizacja tlenku węgla należy do procesów katalitycznych wykorzystywanych w przemyśle na szeroką skalę do oczyszczania gazu przeznaczonego do zasilania ogniw paliwowych, bowiem CO jest trucizną dla anody takiego ogniwa. Służy także oczyszczaniu gazu do syntezy amoniaku, ponieważ nawet niewielkie ilości związków tlenowych stanowią zagrożenie dla katalizatora żelazowego stosowanego w syntezie NH_3. W przemysłowych instalacjach metanizacji zwykle stosowany jest katalizator typu Ni/Al_2O_3, jednak inny metal - ruten wykazuje aktywność wyższą od powszechnie stosowanego niklu. Ponadto przegląd literatury wskazuje, że dodatek lantanu istotnie zwiększa aktywność katalizatorów w reakcji metanizacji CO_x [1].

Obok popularnych nośników tlenkowych (tlenek glinu, tytanu czy krzemionka), na uwagę zasługują materiały węglowe, których odpowiednia modyfikacja pozwala otrzymać nośniki o dużej czystości, pożądanym rozkładzie porów i bardzo rozwiniętej powierzchni. Jednak w literaturze dotyczącej wykorzystania nośników węglowych często zupełnie pomijane jest ryzyko ich metanizacji, a w konsekwencji- destrukcji podłoża. Wprowadzenie odpowiednich modyfikatorów może znacznie obniżyć to ryzyko.

Celem pracy było dotowanie materiałów Ru(10% wag.)/C niewielkimi ilościami lantanu (0,005-0,04 mmol La/g_{C+Ru}), jako potencjalny sposób obniżenia stopnia niepożądanej metanizacji podłoża w warunkach procesu przy jednoczesnej wysokiej aktywności katalitycznej. Przeprowadzono szeroką charakteryzację uzyskanych materiałów.

Stwierdzono, że w opracowanych układach lantan jest dobrze zdyspergowany, a przy optymalnej zawartości powoduje wzrost aktywności katalitycznej układu Ru/C. Niepożądane zjawisko metanizacji nośnika węglowego może być hamowane poprzez odpowiedni dodatek promotora lantanowego.

Tabela 1. Katalizatory Ru/C dotowane lantanem: stopień przemiany CO do CH_4 w temp. 240°C (1% obj. CO/H_2) oraz względna powierzchnia piku CH_4 (m/z=15) wydzielającego się przy ogrzewaniu próbki przez 2 h w temp. 600°C (H_2/Ar=1:1; badanie TG-MS)

Symbol próbki*	$X_{CO \rightarrow CH4}$ (240°C) [%]	Pow. piku CH_4 (m/z=15) [j. u.]
Ru/C	22,9	4,51
La(0,005)-Ru/C	25,5	2,88
La(0,01)-Ru/C	32,2	2,87
La(0,015)-Ru/C	29,1	4,34
La(0,02)-Ru/C	26,2	4,64

*Zawartości lantanu podane w nawiasach w mmol La/ g_{C+Ru}.

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FO-26

Fumarate-adding enzymes: activity of the new BSS and NMS mutants

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Fumarate-adding enzymes, including the benzylsuccinate synthase (BSS) and naphthyl-2-methyl-succinate synthase (NMS) belong to the glycyl radical enzyme family. Their function is the involvement in the arenes anaerobic biodegradation pathway. FAE are characterized by an extreme oxygen sensitivity and the stereospecifity of the catalysed reactions [1].

The aim of this experiment is to examine whether BSS remains active after the introduction of the single point mutations in the active site. Another objective is to perform the first activity tests with NMS in *Aromatoleum evansii* as well as to study the effect of various reaction conditions (such as presence of the protective factors against the oxygen) on the potential substrate turnover efficiency.

In this research, pASG3' plasmids with an insert containing genes for BSS mutants and NMS, fused with a Strep-Tag® will be introduced into *Escherichia coli* strain WM3064. After that, a facultative anaerobe, *A. evansii* will be transformed through conjugation with *E. coli* WM3064 mutants to produce new variants of BSS and a Wild-Type NMS.

In the described experiment, four new mutants of BSS: Trp613→Phe, Trp613→His, Gln707→Glu and Gln707→Asn will be investigated. Effect of the introduced mutations on FAE activity is going to be compared in a series of experiments, including the enzyme assays performed on the whole-cell systems and crude extract. Protein purification by an affinity chromatography is also planned. Potential product identification and quantification will be determined with HPLC. Same approach will be applied for the Wild-Type NMS enzyme.

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FO-27

Spherical silica modified with magnesium and ruthenium – synthesis, characterization and catalytic properties

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Porous materials with a large surface area are of great interest in the field of heterogeneous catalysis as they enable easier diffusion of reactants in order to access active sites. Large surface area provides also a high dispersion of active phase. Silica is one of the most frequently chosen material for pores generation since it is easy to synthesize and further to submit to modification. Here we present the layered silica nanospheres with separated two metals. The bifunctional catalyst with alkali metal (magnesium) introduced into primary nanoporous silica is modified with another layer of silica impregnated with ruthenium source.

Porous silica nanospheres (NS) were prepared by etching of synthesized nonporous silica. Next the material was modified by wetness impregnation of magnesium acetate with three different loadings of metal: 5, 10 and 15 weight %. As-obtained solids were further covered with silica layer and in the final step impregnated with the same amount of ruthenium in each sample (using ruthenium(III) chloride). The solids were calcined at 500˚C. Finally, three samples were obtained, namely Ru/NS/5Mg/NS, Ru/NS/10Mg/NS, Ru/NS/15Mg/NS. Additionally porous silica nanospheres impregnated directly with magnesium (5 wt.%) and ruthenium (Ru/5Mg/NS) or only ruthenium (Ru/NS) were obtained and used as reference materials.

The samples were characterized with the use of low-temperature nitrogen adsorption/desorption, SEM, XRD, ICP. The activity of catalysts was measured in the test reactions, i.e. dehydrogenation and dehydration of 2-propanol and hydrogenation of levulinic acid.

Pristine porous silica possessed a high surface area (505 m^2/g) which gradually decreased with increasing amount of impregnated magnesium and ruthenium. The pore size of samples was ca. 3.3 nm. The XRD patterns showed intense peaks coming from RuO_2 phase while there was no signal related to crystalline magnesium species. The catalytic testing revealed that the smallest amount of magnesium contributed to the highest activity (Ru/NS/5Mg/NS). The reference samples, i.e. Ru/NS and Ru/5Mg/NS were not as active as Ru/NS/5Mg/NS. The transformation of 2-propanol over the catalyst obtained led mainly to the acetone production proving redox properties of the samples. As for levulinic acid hydrogenation the catalytic performance trend was similar to the results of 2-propanol transformation and Ru/NS/5Mg/NS was the most promising catalyst.

The catalysts synthesized represents interesting concept of combining porosity with morphology and functionality of material. The magnesium phase was separated in the inner part of the catalyst and ruthenium loaded onto external layer. It was proven that materials prepared in this way were more catalytically effective than reference samples.

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Nowe techniki i metody analizy własności powierzchni.

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Jako firma działająca w branży wyspecjalizowanej aparatury naukowo-badawczej od ponad 20 lat obserwujemy ciągły rozwój i doskonalenie metod przeznaczonych do badań własności powierzchni. Tradycyjnie najbardziej innowacyjną techniką badawczą jest mikroskopia, która jest ważnym narzędziem dla nanotechnologii. Obecne metody obserwacji obiektów metodami SEM, TEM czy AFM osiągnęły wysoki poziom zaawansowania a dodatkowo postępuje intensywna integracja różnych technik obrazowania oraz łączenie ich z metodami analitycznymi. Przykładem mogą być produkowane przez firmę Tescan wyspecjalizowane systemy mikroskopii korelacyjnej, mikroskopy SEM-AFM, SEM-TOF-SIMS, SEM-RAMAN czy zintegrowane z SEM analizatory elementarne o coraz lepszej czułości i dokładności.

Kolejną, intensywnie rozwijaną grupą aparaturową są urządzenia przeznaczone do badania własności sorbentów. Nowoczesne analizatory sorpcji dynamicznej serii MixSorb firmy 3P Instruments są doskonałym narzędziem - zwłaszcza dla grup badawczych pracujących nad wdrożeniami - zapewniając możliwość szybkiej kontroli własności nowych, syntetyzowanych materiałów za pomocą złożonych procesów dynamicznej sorpcji mieszanin gazów oraz gazów i par a także doboru parametrów pomiaru takich jak: ciśnienie i temperatura gazu, czas przepływu i ilość testów cyklicznych.

Metody dynamicznego przepływu gazu stosuje się także w analizie chemisorpcji – szczególnie istotnej dla oceny własności katalizatorów. Najważniejszym celem tych pomiarów jest wyznaczenie chemicznie aktywnej części powierzchni. W grupie aparatów przeznaczonych do analizy chemisorpcji na szczególną uwagę zasługują urządzenia produkowane przez firmę Altamira z uwagi na szeroką gamę dostępnych modeli i opcjonalnego wyposażenia. Altamira od kilkudziesięciu lat produkuje zaawansowane technicznie i niezawodne urządzenia oraz dedykowane systemy pomiarowe.

Rys. 1. Urządzenia do pomiarów dynamicznych: sorpcji chemicznej (Altamira AMI – z lewej strony) oraz analizy sorpcji mieszanin gazów i par (mixSorb S firmy 3P Instruments – z prawej strony).

Referencje:

1. Tescan: www.tescan.com
2. 3P Instruments: http://www.dynamicsorption.com/
3. Altamira Instruments: http://www.altamirainstruments.com/

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