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Polski Klub Katalizy
Komitet Chemii PAN
European Research Institute of Catalysis

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PL-1

Tailoring materials with catalytic properties dedicated for chemical and biochemical processes

Anna Chrobok

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Environmental regulations forced the modification of a number of chemical processes toward circular economy with low waste production and low energy consumption, in which the challenge for both academia and industry is to generate economically sustainable consensus. In this presentation the research on the development of new, specialized catalysts required for the design of clean, environmentally friendly technologies dedicated for the production of fine chemicals will be demonstrated.

This goal is achieved by designing catalysts based on innovative nanomaterials and ionic liquids (ILs). The resulting hybrid materials are based on carbon nanostructures with exceptional mechanical, magnetic, thermal and electronic properties, as well as non-volatile ILs as "green" media, combine the unique properties of both materials. ILs can be adsorbed on the surface of the solid material or attached by a chemical bond (Fig. 1). Novel ILs with acidic properties of both Brønsted and Lewis acids will be presented. Additionally, ILs based on renewable raw materials, mainly D-glucose, which are a favorable environment for enzymatic reactions, will be discussed. The developed catalytic materials are characterized by high activity, selectivity and stability in following chemical processes: esterification, alkylation, oxidation, cycloaddition, including the processes of biomass valorization and others [1-3].

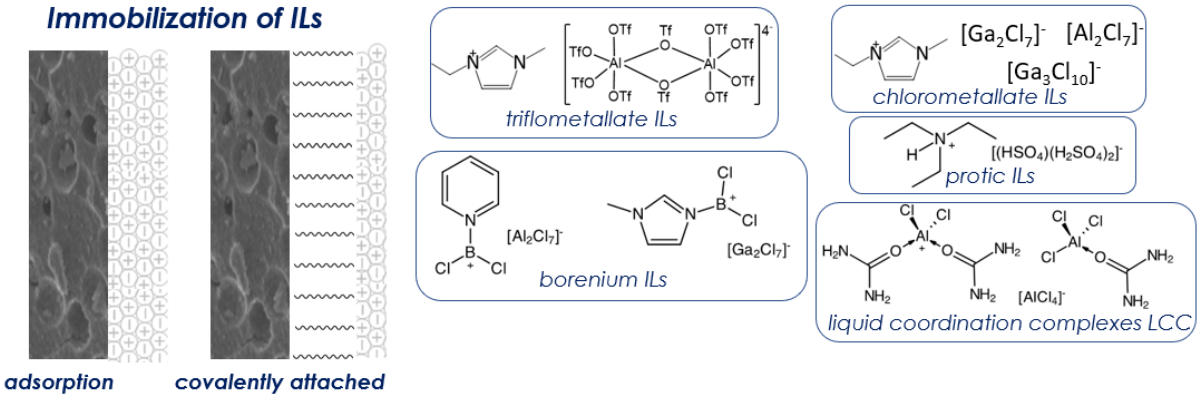

Fig. 1. Methods of immobilization of ILs on the surface of solid materials.

In this presentation, taking the advantage of environmental sustainability of biocatalysis, the following biotransformations will be also presented: synthesis of alkyl levulinates from α-angelica lactone, the synthesis of lactones via chemo-enzymatic Baeyer-Villiger reaction and the synthesis of diester plasticizers in esterification of dicarboxylic acids. Special emphasis will be placed on the improving of lipases activity, selectivity as well as stability in the organic environments. The surface of nanomaterials can be modified with ILs, PTFE as a hybrid platform for lipases. Generally, a clear improvements was archived: the reaction times were drastically shortened, high stability of proposed biocatalysts enabled a multiple recycling of catalyst or used of flow reactor, the high yield and selectivity of products were noted [4-6].

Easy separation of the catalyst from the post-reaction mixture, the possibility of its multiple recycling to the new reaction cycles and economic availability make the developed technologies attractive for industrial applications.

In summary, the designing of a high-performance and recyclable catalysts and biocatalysts dedicated for the synthesis of fine chemicals will be presented. A generic approach to nanobiocatalysis as an industrially relevant process in which the challenge is to generate both environmentally and economically sustainable processes will be proposed.

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PL-2

Understanding and optimizing Keggin based catalysts at work in alcohols dehydration : the cases of MeOH and ButOH

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Being a promising renewable fuel, the production of dimethylether (DME) via the gas phase condensation of methanol nowadays attracts growing interest. Because of their exceptionally high Brönsted super-acidity, heteropolyacids (HPAs) deserve to be explored in this context.

The Keggin $H_3PW_{12}O_{40}$ HPA indeed allows reaching high methanol conversions at much lower temperatures than conventional acid catalysts and leads to much better selectivity to DME. However, bulk $H_3PW_{12}O_{40}$ displays low surface area which might limit its overall performance.

To begin, the communication will report on the two strategies we have followed to solve this issue.

The first strategy is to exploit the capability of HPAs to catalyze reactions in the pseudo-liquid way, precisely to perform the condensation of methanol not only at the surface of HPA crystals but also within their bulk, so exploiting all the protons located therein. This behavior has already been evoked in the past [1] but yet not efficiently exploited. Thanks to a Raman *operando* approach, we will show how to succeed this. Precisely, we will enlighten the pretreatment conditions allowing $H_3PW_{12}O_{40}$ to have its bulk simultaneously accessible for methanol and catalytically active [2].

The second strategy is to disperse HPAs on supports. TiO_2 is often claimed as an excellent choice... but we will show it is actually not. If HPAs indeed disperse well on TiO_2, their strong interaction with it markedly lowers their acid strength, with correspondingly a lowered efficiency to convert methanol. In this context, we will point hexagonal boron nitride as a much better support [3].

At the end of this approach, an 8-fold improvement of the DME yield was reached.

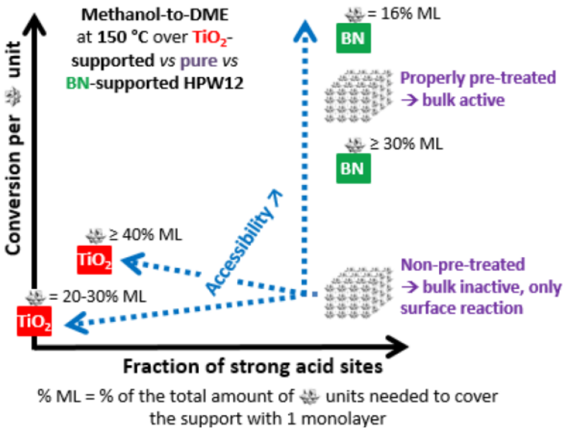
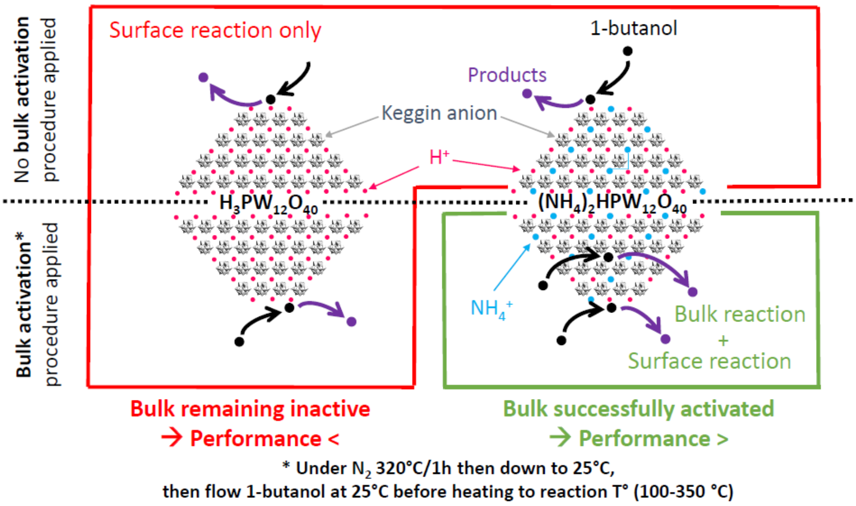


Fig. 1. Semi-quantitative comparison of methanol conversion on the different catalysts evoked, and correlation with their acid strength. Selectivity to DME is 100% in all cases. (reproduced from [3]).

PL-2

The second part of the communication will report on our subsequent exploration of the behaviour of $H_3PW_{12}O_{40}$ in the transformation of 1-butanol. Rapidly, *operando* Raman characterization of the catalyst at work revealed that the pretreatment procedure established with methanol to have the pseudo-liquid behavior of the HPA activated is no more operational with 1-butanol, and only leads to poor performance. This is interpreted as due to the fact that 1-butanol is bigger and more hydrophobic than methanol and thus cannot infiltrate the bulk of the HPA crystal even when the later is properly dehydrated and exposed to the alcohol. We will demonstrate how a partial substitution of the protons of the pristine HPA by ammonium, leading to $(NH_4)_xH_{3-x}PW_{12}O_{40}$, allows to solve the issue. The best catalyst is when x = 2 [4].



* Under N_2 320°C/1h then down to 25°C,
then flow 1-butanol at 25°C before heating to reaction T° (100-350 °C)

Fig. 2. Comparison of the behaviour of $H_3PW_{12}O_{40}$ and $(NH_4)_xH_{3-x}PW_{12}O_{40}$, with and without bulk activation procedure applied, in the transformation of 1-butanol. (reproduced from [4]).

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PL-3

Ab initio predictions for elementary adsorption and reaction steps in heterogeneous catalysis

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Experimental kinetic studies deal with complex reaction networks, whereas computational studies can provide energy barriers, reaction energies and pre-exponentials for individual reaction and adsorption steps. If made with sufficient, i.e. chemical, accuracy, computational predictions are very useful to check critical steps in microkinetic models.

The availability rigorous methods made it possible to revise the well-established "Lunsford" mechanism for the oxidative coupling of methane on Li-doped MgO and to predict an alternative one that stimulated new experiments.

Our hybrid high level QM:low level QM method[1] has been demonstrated to yield chemical accuracy (4 kJ/mol for energies and one order of magnitude for rate constants) for the methylation of ethene, propene and butene in H-ZSM-5.

We demonstrate the importance of accurate predictions for the heat of adsorption and intrinsic barriers for understanding hydrocarbon activation by acidic zeolites, in particular proton exchange and cracking of alkanes as well as the formation of p-complexes, alkoxides, and carbenium ions from alkenes.

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PL-4

Ammonia synthesis using metal nitrides

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Industrial scale ammonia synthesis, as accomplished through the Haber Bosch Process, is of pivotal importance for mankind. Through provision of an accessible route to synthetic fertiliser, it can be credited with sustenance of 40% of the global population. However, this comes with a penalty. When considered in its entirety, including the generation of feedstock hydrogen from fossil based reserves, it accounts for 1-2% of global energy demand and accounts for ca 1.6% of manmade CO2 emissions. Accordingly, there is much interest in the development of alternative routes based on the use of sustainably derived hydrogen. Furthermore, the application of such routes on a localised scale whereby ammonia could be generated close to its point of application, such as on a farm, is a highly desirable contemporary target.

The development of sustainable, localised ammonia synthesis requires a step change in relation to the catalysts employed which should be active under much more moderate conditions than the industrial scale Haber Bosch Processes. In this presentation, our experimental and computational modelling studies investigating the possibility of the development of metal nitride catalysts operating via the Mars-van Krevelen mechanism will be outlined, with particular attention being paid to Co_3Mo_3N for which the reduced Co_6Mo_6N phase was discovered and the possibility of an associative N_2 activation pathway is suggested. The development of nitrogen looping systems based on metal nitrides will also be discussed.

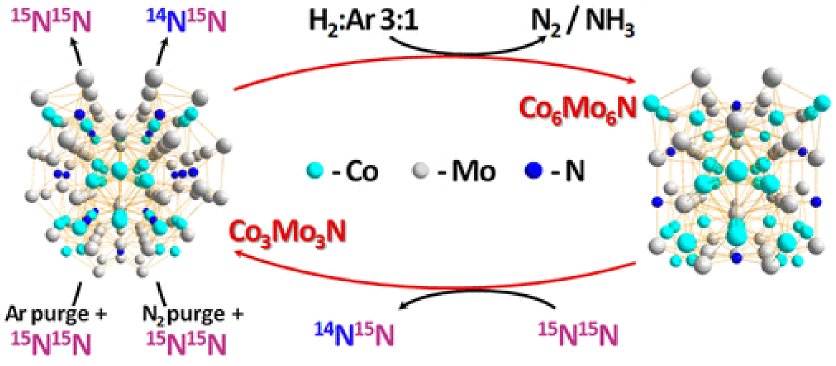

Fig. 1. Isotopic nitrogen exchange over Co_3Mo_3N and Co_6Mo_6N [1].

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Komunikaty ustne
Oral communications

O-1

Cenospheres from fly ashes as an interesting alternative to oxide catalytic supports

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As it can be inferred basing on many representative examples, cenosphers extracted from fly ashes (generated in mass scale by energy sector) can be efficiently used in catalysis as supports or, after appropriate functionalization, as composite catalytic materials. Their use remains in agreement with principles of circular economy, where waste material from one industrial process can be successfully utilized (directly or after necessary modification) as valuable material in another process.

Cenospheres exhibit several features making them particularly interesting as catalytic supports. First of all, they are thermally stable as they were formed at temperatures exceeding 1200°C from non-flammable mineral components naturally occurring in coal. Cenospheres are rich in silicon, aluminum, iron, and alkali elements. Such composition favors specific interactions with various deposited phases, playing a role of catalytically active components. Moreover, strong interaction occurring at the contact interface may, to some extent, determine surface architecture of the deposited phases and in some favorable cases even activate them. Spherical shapes of cenospheres and low density can substantially strengthen their mechanical stability. Another advantage can be associated with high resistance of the cenospheres to chemical corrosion, which might be vital in the case of catalytic high-temperature redox reactions.

In the framework of current studies the results of structural (XRD, RS), textural (SEM, porosimetry) and functional (DRIFT, UV-Vis/DR) characterization of cenosphere-supported oxide systems containing copper and zinc as active components have been obtained.

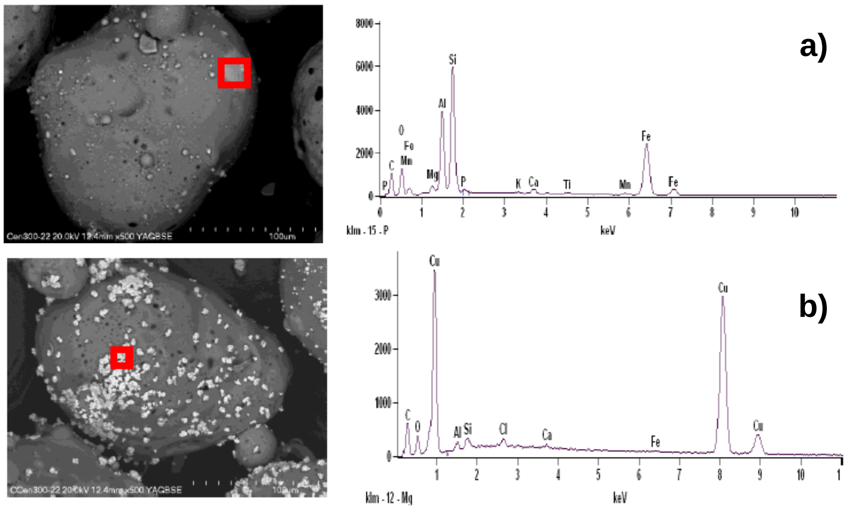

Fig. SEM/EDS images of CEN-300 cenospheres : a) before and b) after their impregnation with an active phase containing copper precursor and subsequent calcination at 400°C for 6 hours.

Cenospheres of 150 and 300 mm in diameter have been impregnated with appropriate amounts of aqueous solutions of copper and/or zinc nitrates and then calcined at 400°C for 6 hours to obtain final catalysts.

The strong influence of supports on both architecture and catalytically relevant properties of the deposited Cu- and Zn-containing phases has been confirmed, suggesting high potential of the obtained samples as catalysts for the efficient CO_2 valorization. .

O-2

CO_2 methanation in the presence of cerium promoted alumina supported nickel catalysts

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The increase in CO_2 emission resulting from the massive consumption of fossil fuels is widely regarded as a major contributor to global warming. Waste carbon dioxide can be captured and further utilized to the production of valuable chemicals and energy carriers, such as methane using renewable hydrogen. The development of CO2 methanation catalysts that show high activity at low temperatures, resistance to sintering at high temperatures and sufficient durability in the presence of impurities in the feed stream such as sulphur compounds is still a challenge.

The aim of the present work was to determine the effect of small amounts of cerium introduced into alumina supported nickel catalysts on their physicochemical and catalytic properties in the CO_2 methanation reaction.

The catalysts containing ca. 20 and 40 wt.% Ni and 1-5 wt.% Ce were prepared by the co-impregnation method using γ-Al_2O_3 as support [1-3]. Nitrogen low-temperature adsorption, temperature-programmed reduction, hydrogen desorption, transmission electron microscopy, X-ray diffraction, Raman spectroscopy and in-situ DRIFTS studies were used for characterization of catalysts. The activity, selectivity and durability tests in CO_2 methanation reaction were carried out by the application of PID Eng & Tech reaction system with fixed-bed continuous-flow quartz reactor [1-3].

It was found that the activity of alumina supported nickel catalysts in CO_2 methanation reaction can be improved by the increase in nickel loading and introduction of cerium promoter. The increase in CO_2 conversion at low-reaction temperatures was attributed to the increase in the active surface area and changes in redox properties of catalysts.

The catalysts showed high resistance towards sintering and coking. It was found that an introduction of H_2S to the feed stream led to decrease in CO_2 conversion and simultaneously methane selectivity. An in-situ DRIFTS studies indicated that deactivation of catalysts by H_2S was associated with successive blocking of nickel active sites, which limited H_2 activation and successive transformation of CO_2 to carbonyl and formate species.

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O-3

Production of pharmaceutical intermediates through continuous flow selective hydrogenation using Cu catalysts

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Catalytic research is focused on achieving the desired products with high selectivity, which is essential in many fields of chemical production, especially in the pharmaceutical industry. Production of medicines and vitamins requires performing a specific and selective chemical transformation, suppressing side reaction paths while being specific to desired functional groups [1]. It can be achieved by implementing catalytic reactions, which detain the undesired products formation, causing a reduction of production costs and reducing the amount of generated waste that could be released into the environment or would need to be disposed of, causing additional costs [1].

Applying a continuous flow system to the catalytic reactions can improve their performance. The main advantages compared to batch setup are better temperature control, ability to manage the process in higher pressure, safer system due to performing reactions in lower volumes, and allowing users to precise control contact time between catalyst and reaction mixture, which may result in selectivity improved [2]. Furthermore, the of the continuous flow hydrogenation application may significantly reduce the high E-factor, which means the relation between the mass of generated wastes to the mass of obtained products, which is a key aspect of the fine chemical sector [3].

The compounds analysed as part of our research can be classified as fine chemicals. They are 2-methyl-3-butyn-2-ol (MBY), 2-methyl-2-pentenal (MPEA) and 2-butyne-1,4-diol (BYD). They can take an important role in the fast-growing pharmaceutical industry sector. Hydrogenation product of 2-methyl-3-butyn-2-ol related to transformation triple to C=C bond allowing to obtain 2-methyl-3-butene-2-ol which is an important intermediate for the synthesis of vitamins (A, E) or can be used in perfumes production [4]. The chemoselective hydrogenation of unsaturated aldehyde, 2-methyl-2-pentenal, can lead to the formation of 2-methylpentanal used to synthesize dyes, resins and sedative drug meprobamate [5]. From an industrial point of view, a product of semi-hydrogenation of 2-butyne-1,4,diol – 2-butene-1,4-diol has many applications and has an important role in the synthesis of vitamins A and B6 or insecticides [6].

Our studies present the continuous flow catalytic hydrogenation of selected compounds MBY, MPEA and BYD. Non-noble metal was selected as an active phase in catalysts due to cheaper replacements for well-used but expensive palladium catalysts [7]. Catalytic systems based on active carbon - supported copper with different loading were analysed in continuous flow hydrogenation in a wide range of pressure and temperature. Results allow us to obtain the desired products with high selectivity, giving the fine chemical sector an attractive alternative to current solutions.

O-3

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O-4

DFT and *ab initio* thermodynamic investigations into structure and stability of the (1-10) surface of $Na_2Mn_3O_7$ nanoplates in various redox conditions

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By means of periodical DFT+ U and *ab initio* thermodynamic modeling the strucutre and stability of the (1-10) surface of $Na_2Mn_3O_7$ nanoplates in various redox conditions were analyzed. DFT calculations were performed with the VASP code (PAW method, PBE exchange-functional, Hubbard parameter U = 3.9 eV). The Monkhorst-Pack grid with the 6×6×6 sampling mesh for the bulk calculations, and the cutoff energy of 420 eV were applied. As it was revealed by HR TEM image analysis supported by image simulations the $Na_2Mn_3O_7$ nanoplates expose the (1-10) surface only. For examination of the surface stability in various redox conditions the (1-10) slab model with the 3×3×1 sampling mesh and 420 eV cutoff energy was used. Each slab model had ~16 Å thickness containing 6 Mn_3O_7 atomic layers, separated by sodium ions. In order to preserve correct stoichiometry, the sodium ions were also located at the top and at the bottom of the model. 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 of $Na_2Mn_3O_7$ was calculated as:

$$\gamma(T,p_{O_2}) = \frac{1}{A}\left[G(T,p_{O_2},N_O,N_{Mn}) - \frac{N_{Mn}}{3}g^{bulk} + \left(\frac{7}{3}N_{Mn} - N_O\right)\mu_O(T,p_{O_2})\right]$$

where: A - slab surface area G and g^{bulk} stands for slab and bulk free energy, respectively, normalized to a formula unit ($Na_2Mn_3O_7$). The entropic vibrational contributions to the Gibbs free energies were approximated by the corresponding DFT energies. $\mu_O(T,p_{O2})$ is the O_2 chemical potential, factored into the electronic energy ($\frac{1}{2}E_{O_2}^{tot}$) together with temperature and preasure dependent contributions:

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

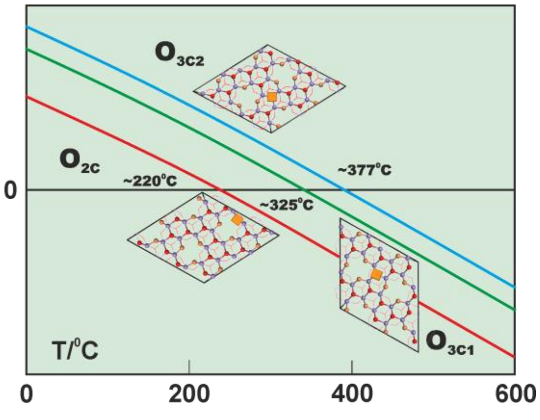

Fig 1. Stability of different vacancies (marked in orange) on (1-10) surface of $Na_2Mn_3O_7$ at various T, p_{O2} conditions.

The performed calculations reveald that the (1-10) termination exhibit surface O^{2-}_{2C} and O^{2-}_{3C1} and O^{2-}_{3C2} anions which can form different forms of surface vacancies. According to atomistic thermodynamic calculations, due to the relatively low formation energy, this vacations (especially O_{2C}) can be easilly formed on the surface (Fig 1). Furthermore, the analysis of different suprafacial ROS species produced upon interaction of dioxygen with the catalyst surface revealed the presence of softly bounded oxygen adspecies with rather small diffusion barriers. The obtained results will be incorporated into an analysis of the mechanism of soot combustion process on the (1-10) surface on $Na_2Mn_3O_7$ catalyst.

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O-5

Mg-Al hydrotalcite catalysts precipitated with inorganic and organic bases – effect of starch biotemplate

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Synthetic Mg-Al hydrotalcites are used in many important applications such as catalysts, catalyst supports and sorbents, due to their basic properties, high surface area and low environmental burden [1]. Their catalytic properties in base-catalysed Baeyer-Villiger oxidation reaction of cyclohexanone to ε-caprolactone with hydrogen peroxide/nitrile system are governed by two major factors: 1) composition – Mg/Al ratio, which also control their basicity, and 2) their crystal size [2, 3]. This work aims to explore the influence of synthesis conditions such as the nature of precipitating base and the presence of biotemplate (starch) on the catalytic properties.

Mg-Al materials were prepared using co-precipitation at pH = 10 with inorganic (NH_{3aq}, NaOH) and organic (choline hydroxide and tetrabutylammonium hydroxide) precipitating agents. Two series of samples were prepared – one using water and one using gelatinous aqueous starch solution as medium for synthesis.

Prepared solids were characterized with chemical analysis, XRD, SEM, and FTIR. Results of analyses confirmed preparation of Mg-Al-CO_3 synthetic hydrotalcites, possessing Mg/Al ratio close to 3, both in the absence and the presence of starch, but the obtained materials displayed different grain morphology and crystallinity. SEM showed that catalysts prepared using aqueous starch solution possessed smaller platelets than their equivalents prepared without biotemplate. Similar observation was made when comparing crystallite sizes calculated from XRD patterns using Scherrer equation – samples precipitated in starch solution possessed finer crystallites. The synthesized hydrotalcites were tested as a catalyst in liquid phase B-V oxidation of cyclohexanone to ε-caprolactone. All materials proved active in the test reaction. In general, in both series of samples, organic-precipitated catalysts displayed slightly higher activity than their counterparts prepared with inorganic bases. Hydrotalcites obtained in the presence of starch produced more ε-caprolactone than materials prepared without starch, the effect attributed to finer crystallinity of the former.

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O-6

Preferential Carbon Monoxide Oxidation (CO-PROX) on Mixed Spinels – Catalytic Performance and Mechanistic Account

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Preferential carbon monoxide oxidation in hydrogen rich streams (CO-PROX) belongs to the promising and economically appealing technologies for purification of H_2 down to the level below 100 ppm[1–2]. Development of highly active, selective and stable CO-PROX catalysts, is then an intensively explored research field of the recent catalytic chemistry[3]. The aim of presented studies was to develop a mechanistic understanding of the reaction course that controls the activity and selectivity of the mixed spinel catalysts.

For this purpose a series of mixed cobalt- spinel catalysts ($M_xCo_{3-x}O_4$ (M = Cr, Fe, Mn, Ni, Cu, Zn) was synthetized and characterized by XRF, XRD, XPS, Raman, IR Spectroscopies, and by TEM/STEM/EDX along with SEM microscopic techniques. The evaluation of redox -related electronic properties was tested by means of the work function measurements. The obtained series of catalysts were tested in the CO-PROX reaction (with $^{16}O_2$ and $^{18}O_2$), and in the reference sole CO and H_2 oxidation processes.

Depending on the oxygen *u* parameter value, revealed by Rietveld refinement of the XRD pattersn, two types of the mixed spaniel catalyst of distinctly different catalytic behavior in the CO-PROX reaction were distinguished. The **A**-type spinels (Co, Ni, Cu) with *u* ~0.2625 exhibit overall higher activity in CO and H_2 oxidation, and lower selectivity in the high temperature range ($T > 180^oC$), whereas **B**-type spinels (Cr, Fe, Mn) with $u < 0.2625$ are less active, yet more selective in the high temperature range. The work function of the spinel catalysts was found to be a useful concise parameter in accounting for their CO-PROX performance, supporting also the proposed categorization of the mixed spinels. Two heuristic descriptors, $E_{O2p} + k\Delta|<\chi_M> - \chi_O|$ and $\Delta E_{M-O} = (E_{M3d} - E_{O2p})$, based on the position of the oxygen 2p (E_{O2p}) and the metal 3d (E_{M3d}) bands centers, and on the average metal $<\chi_M>$ and oxygen (χ_O) electronegativity difference, were proposed for rationalization the mixed spinels performance in terms of their intrinsic electronic properties. It was established that activity depends in the volcano-fashion of the ΔE_{M-O} values, whereas the selectivity is correlated in the monotonous way with the $E_{O2p} + k\Delta|<\chi_M> - \chi_O|$ parameter (Fig.1a). The unique behavior of the Zn-Co spinel results from lifting of the O2p center above the 3d band center of the redox Co^{3+} cations, in contrast to the remaining mixed spinel catalysts[4].

More accurate elucidation of the mechanistic aspects of the CO-PROX processes, occurring on the spinel-type catalysts, was possible after examining the catalytic performance with the isotopically labelled reactants and the catalysts. The developed heuristic approach, where the prototype isotopic compositions of the reaction products ($C^{16}O^{18}O$, $C^{16}O_2$, $C^{18}O_2$, $H_2{}^{16}O$ and $H_2{}^{18}O$), inferred from a conceivable molecular course of the postulated catalytic scenarios, are confronted with the experimental data, for delineation of the CO-PROX reaction mechanism (Fig 1b). It was shown that the catalytic turnovers of CO and H_2 result from various combinations of the generic intrafacial Mars van Krevelen and suprafacial Langmuir-Hinshelwood/Eley-Rideal patterns, where the formation of surface carbonates as a common key intermediate allows for successful reproduction of the observed variation of the isotopic composition of CO_2 and H_2O with the selectivity[5-6]. The mechanistic proposals were substantiated by DFT+U and ab initio thermodynamic modeling, corroborated by IR studies, which provided the requisite theoretical background for the dual role of the carbonate species as intermediates or spectators in the CO-PROX reaction, depending on their mode of attachment on the catalyst surface.

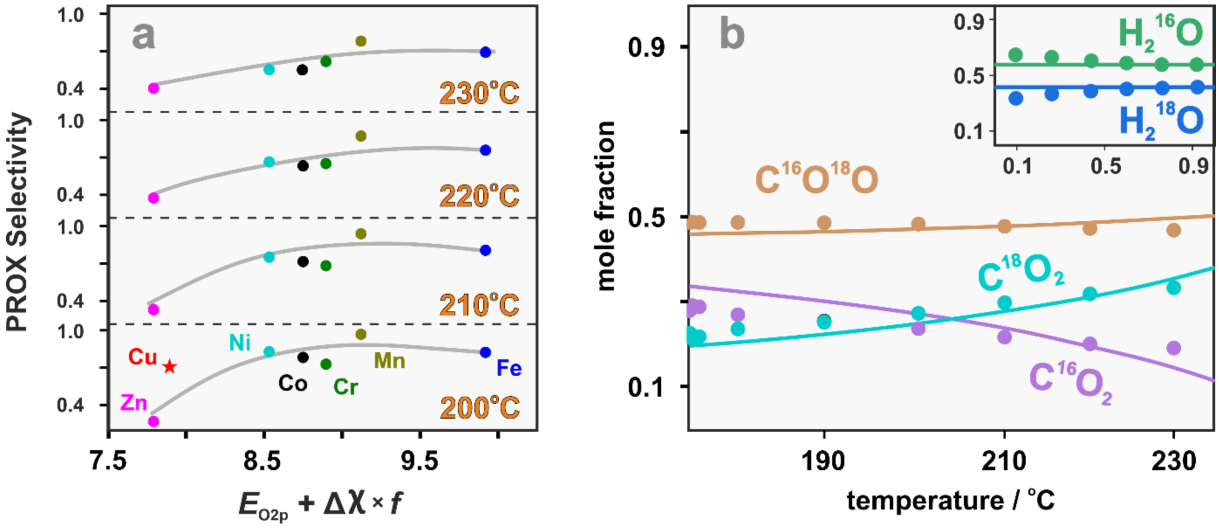

Fig. 1. Catalysts selectivity versus the modified E_{O2p} (a) and temperature dependence of experimental isotopic mole fractions (dots) with fitted profiles representing combination of LH and MvK mechanisms (lines) (b).

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O-7

The active site of 3-ketosteroid dehydrogenase – point mutations, kinetics and modelling

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The chemical and biotechnological modification of steroids is of utmost importance for the development of new functionalities of steroid drugs. One of such modifications is the Δ^1-dehydrogenation of the ring A of the steroid core which increases the potency and selectivity of steroid drugs. The reaction is catalyzed by a microbial flavine enzyme, 3-ketosteroid Δ^1-dehydrogenase. Recently, we reported on the mechanism of Δ^1-dehydrogenation confirming the classical two-step reaction mechanism i.e., enantioselective deprotonation at the C2 atom followed by hydride transfer from C1 to the flavine, the release of the product and reoxidation of the FADH by electron acceptor [1]. We also were able to determine the crystal structure of -ketosteroid Δ^1-dehydrogenase from *Sterolibacterium denitrificans* (AcmB, PDB code 7P18) which is more representative of the majority of known KstD sequences due to the presence of the additional 40 amino acid domain. Based on the obtained structure we were able to study the role of residues involved in the catalytic process using point mutation, QMMM MD modelling and kinetic experiments.

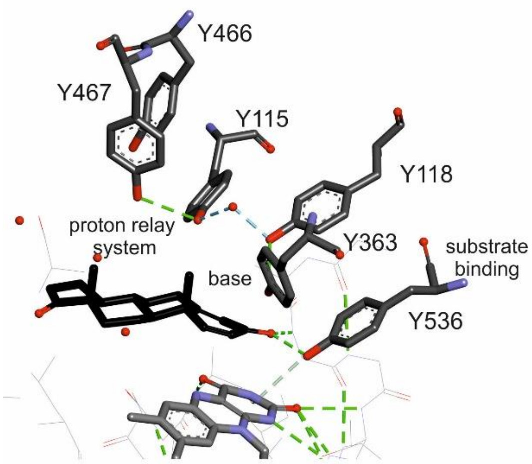

Fig. 1. The active site of AcmB

The examination of the AcmB structure revealed that the active site contains six conserved tyrosine residues: Y115, Y118, Y363, Y466, Y467 and Y536. Y363 is a position close to C2 of the steroid and can act as a catalytic base in substrate activation as it is assumed to be in the ionized tyrosyl form. It is accompanied by Y118 which forms H-bond with Y363. Y536 is involved in substrate binding, forming H-bond with a 3-keto group while Y115, Y466 and Y467 are a part of the proton relay system formed together with water molecules (Fig. 1)

We have measured specific activity for the following mutants of Y115F, Y118F, Y363F, Y467F and Y536F and QMMM MD method to obtain the free energy surfaces in terms of potentials of mean force for catalytically capable variants i.e., Y115F, Y118F, Y467F and Y536F. As a result, we gained insight into the role of these residues in the stabilization of the transition state and intermediate during the reductive half-cycle of the reaction.

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O-8

Ultrasonic assisted well-coated microreactor: A versatile tool for photocatalytic selective oxidation

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The high variability of lignin, a significant by-product from paper and pulp industries and bio-refineries, is a challenge in the development of a photocatalytic system for it's valorization [1]. Microreactor is a superior approach towards photocatalysis because of advantages like improved irradiation profile, sizeable surface-to-volume ratio, enhanced mass transfer characteristics, on-site/on-demand production, higher spatial illumination homogeneity, and better light penetration through the entire reactor depth compared to conventional batch [2]. Recently, fluoropolymer-based microreactors have been shown to be a better option in designing the photo-microreactor due to its excellent light transmission and high chemical stability [3]. In addition, the photocatalytic conversion of lignin model compounds especially aromatic alcohol, into its aldehyde has attracted considerable attention due to its fundamental interest and potential applications [4].

The current work focuses on the selective photocatalytic oxidation of the lignin-based model compound (benzyl, coniferyl, cinnamyl and vanillin alcohol) in a catalyst deposited polymer-based (Perfluoroalkoxy alkane, PFA) microfluidic photoreactor. Photocatalysis-based selective oxidation of aromatic alcohol has been carried out using commercially available, sol-gel synthesized TiO_2, monometallic TiO_2, and bimetallic (e.g., Au/Fe) TiO_2 photocatalysts. Incorporation of various noble metals on different photoactive catalyst supports has been reported to achieve improved activities even under visible light conditions [5]. Alloying of multiple metals tends to enhance the reaction rate and also prevent photocatalytic deactivation. The development of bimetallic catalyst was proposed to increase the activity of the sol-gel synthesized catalyst. The TiO_2 modified by bimetallic gold (Au) NPs have been synthesized by following a simple sol-gel method and further the photocatalytic activity in microflow system was studied.

A PFA microtube (microcapillary of 0.8 mm ID), pure from the market, after a cleaning process used for catalyst deposition. An ultrasonic bath (Sonorex-digital RC, 37 kHz, 100% amplitude) was used in sweep mode. The tube was placed in the ultrasonic bath. The catalyst suspension was passed through a cleaned PFA microtube under the influence of ultrasound using a syringe pump (Fig. 1). Evaluation of the photocatalytic activity of these micro capillaries carried out for selective conversion of aromatic alcohol to its aldehyde under UV light (375 nm wavelength) [6,7]. The sol-gel synthesized catalysts were analyzed by X-ray diffraction (XRD), UV-Vis DRS, Scanning Electron Microscopy (SEM), and nitrogen physisorption. Surface area of sol-gel synthesized TiO_2 was found to be 284 m^2/ g, whereas 0.5 at% Fe-TiO_2 showed 161 m^2/ g. From XRD analysis. Among all monometallic TiO_2 catalysts, 0.5 at% Fe-TiO_2 showed better BnOH conversion. Though the surface area was increased, crystallinity loss was observed by modifying the catalysts with monometals (Cu, Co) whereas 0.5 at% Fe-TiO_2 showed anatase: brookite phase ratio 66:34.

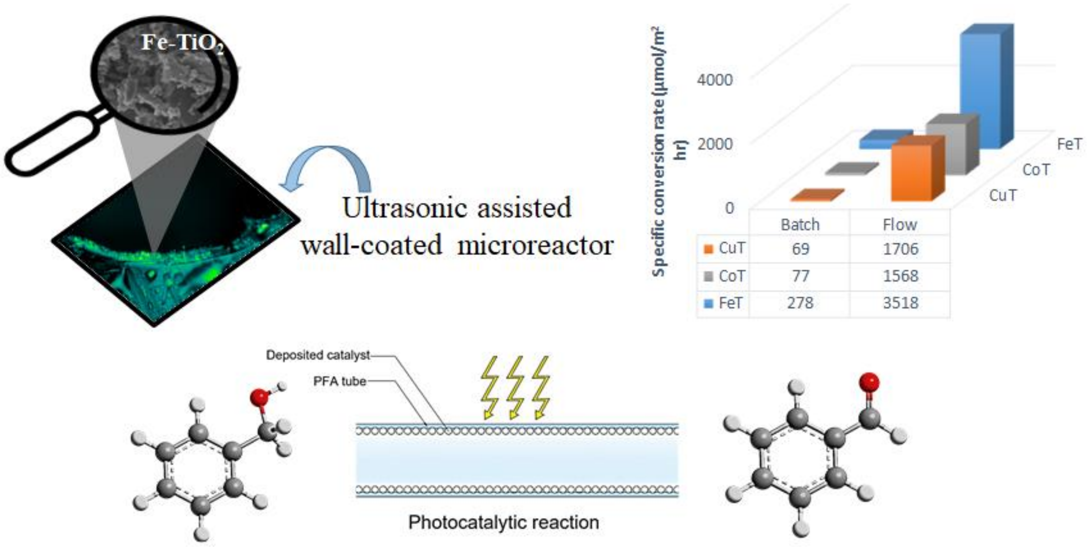

Fig. 1. Catalyst deposited PFA microtube and photocatalytic activity of the catalysts. (Sol-gel synthesized TiO_2 (SOLT), 0.5 at% Cu-TiO_2 (CuT), 0.25 at% Co-TiO_2 (CoT), and 0.5 at% Fe-TiO_2 (FeT))

The metal-containing TiO_2 showed higher photocatalytic activity under UV irradiation than the synthesized TiO_2 in the batch system. Among all the metal-containing TiO_2 samples, the 0.5 at% Fe-TiO_2 (both iron and titanium, as cheap, safe, and abundant metals) photocatalyst exhibited the highest BnOH conversion (29%) compared to other catalysts under visible light (515 nm) in a microflow system [8]. This could be explained by the higher crystallite size observed in XRD analysis, high porosity, and flake-like morphology. The utilization of ultrasonication (US) during the deposition process plays a vital role, which leads to an enhanced mass deposition.

The utilization of nano-engineered microreactors as an additive-free system makes it an eco-friendly approach for the selective oxidation of biomass-derived compounds.

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O-9

Activation and formation of N-O, C-O, C-H, H-H and O-H bonds on spinel surfaces – relevance for CO-PROX, CH_4, and NO oxidation processes

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Spinel oxides are an excellent redox-tunable model catalytic materials of widespread fundamental and practical interest. In particular, they have been found to be active in many oxidation reactions (involving NO and CH_4) and in preferential oxidation of CO in the presence of bulk H_2 (CO-PROX) process. All these reactions may be divided into several mechanistic steps including: (1) substrate adsorption, (2) CO, H-H, C-H, N-O bond activation, (3) formation of new O-X bonds (N-O, C-O, O-H) and final desorption of the products. The reaction steps sequence may follow suprafacial (Hinshelwood-Langmuir, Eley-Rideal) or interfacial (Mars van Krevelen) routes. However, only the optimal cooperation of all these routes leads to efficient and selective action of the catalyst, and their cooperation is primarily controlled by the catalyst redox properties. The latter influence the ability of the catalysts to stabilize surface oxygen species and/or oxygen vacancies, and depend on the catalyst stoichiometry, morphology (termination exposed) and thermodynamic conditions (*T*, *p*).[1] The atomic scale understanding of above defined elementary steps makes it possible to determine the most important features of the spinel oxides that controls the catalyst performance, and enables the optimization of the catalytic system for application in a given oxidation processes.

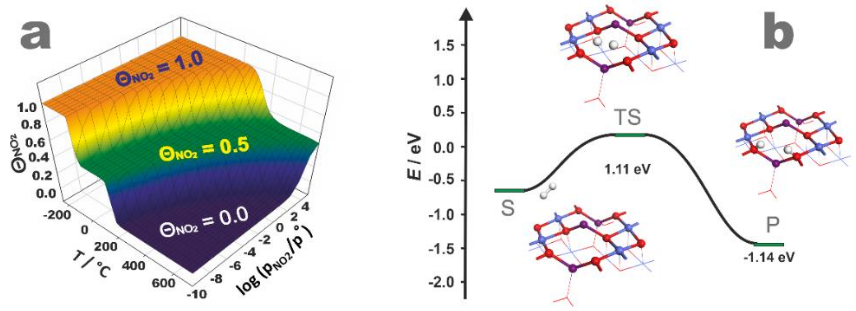

Fig. 1. NO_2 coverage as a function of T and p (**a**). Energy profile of H_2 activation on Co_3O_4 (**b**)

This paper presents the results of molecular modeling and of atomistic thermodynamics simulations which allow for atomic sale insight into formation and activation of N-O, C-O, C-H, H-H on spinel surfaces. Adsorption of substrates (of O_2, NO, CO, H_2, CH_4) and desorption of products (NO_2, H_2O, CO_2) are modeled in real thermodynamic conditions (**Figure 1a**), and all relevant on-surface steps are discussed, taking into account their activation barriers (**Figure 1b**). The obtained results reveal that for the optimal performance of the catalyst, the exposed termination is of great importance in the harmonization of the adsorption and desorption energies, whereas catalyst redox state, being responsible for stabilization of ROS and oxygen vacancies, is crucial in the process of activation and formation of new bonds.

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O-10

Zeolites Ga(Nb,Ta)SiBEA: Acid-base characteristics and catalytic performance in the oxidative dehydrogenation of propane to propylene with CO_2

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Catalytic propane dehydrogenation with CO_2 (PDH-CO_2) is of particular interest to researchers [1]. To improve the performance of the oxidative dehydrogenation process, the improvement of known catalysts or development new catalytic systems are necessary [2]. Zeolite catalysts with incorporating heteroelement ions in the framework allow to targeted control of their acid–base and redox characteristics that possible even at the synthesis step. For example, the effective catalysts for PDH were prepared by chromium [3] or vanadium [4] incorporation in siliceous SiBEA using the two-step postsynthesis procedure. Ga-containing dehydrogenation catalysts have been the target of renewed attention in recent years. The exact nature of the active sites in the catalysts is still under debate. In the case of Ga/H-MFI, the presence of three different types of acid sites over surface were indicated: one type of BAS and two types of LAS (gallium cations and Ga_xO_y) respectively. The activity and selectivity of Ga_2O_3-containing catalysts in the PODH-CO_2 process is determined by the acid-base properties of their surface, both Lewis (LAS) and Brønsted (BAS) acid sites present in Ga_2O_3/H-ZSM-5 take part in the propane dehydrogenation reaction [5].

In this work, we have investigated the influence of the nature of heteroelements (Ga, Ta, Nb) incorporated into the framework of siliceous SiBEA zeolite on their acid-base characteristics and catalytic performance in the propylene production in the catalytic propane dehydrogenation with CO_2.

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O-11

Non traditional aspects of catalysis over semiconductors

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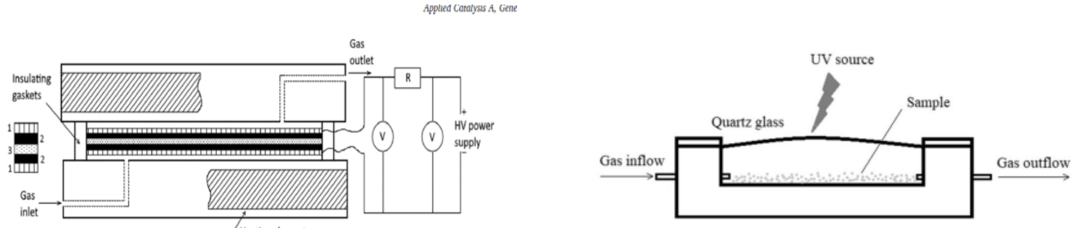
Catalytic properties of semiconductors are commonly explained by the extent of the formation and separation of electron-hole pairs. Those processes can be initiated by both high energy electromagnetic radiation (UV light) and the effect of applied electric field.

In our work we investigated the behaviour of modified semiconductor oxides (TiO_2, Fe_2O_3, Al_2O_3, SiO_2) in the model reaction of reduction of carbon dioxide with water vapor under the influence of UV radiation or electric field. Selection of oxides was performed on the basis of the differences in their band gaps. All experiments were permed in continuous flow reactors (Figure 1).



[1] [2]

Figure 1 Experimental setups for CO_2 reduction by water vapour under the influence of electric filed (1) and UV radiation (2).

The results of catalytic measurements are presented on a Figure below.

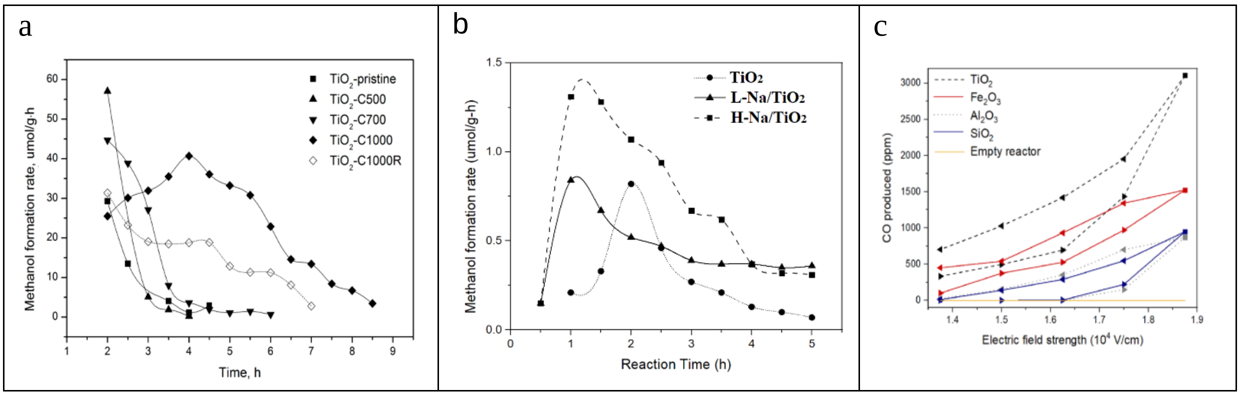


Fig 2 Catalytic activity of: a) TiO_2 under UV radiation b) Na modified TiO_2 under ViS radiation c) different semiconductors under the influence of applied electric field

During experiments it was proven that:

1. Photocatalytic CO_2 reduction leads mainly to the formation of organic compounds (methane and methanol) and trace amounts of carbon monoxide. During reduction process rapid deactivation of catalysts was observed. This phenomena is caused by the slow desorption of reaction products.
2. Reduction of CO_2 in the presence of electric field leads to the formation of CO as a main product, only traces amounts of organic were registered. Deactivation of catalysts was not observed.

3. Despite of the differences between such processes, they both had the similar mechanism. More particularly, the electrons activated the adsorbed carbon dioxide forming negative $CO_2^{\cdot -}$ species while the holes took participation in the splitting of water to yield protons and oxygen. Next, the CO was formed by protonation and reduction of the formed $CO_2^{\cdot -}$. The activation of semiconductors in the presence of electric field is more efficient in terms of energy utilization and the amount of products formed.

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O-12

Designing of supported ionic liquid phase catalysts dedicated for aminolysis of epoxides in continuous flow synthesis

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Continuous-flow synthesis started to be a key technology in the synthesis of high added value chemicals. Continuous synthesis provides many advantages over batch reactions. These processes are more efficient, sustainable, safer and cheaper. The most promising solution is the use of heterogeneous catalyst with column-type fixed-bed reactor. The advantages of the use of heterogeneous catalyst in the continuous flow reactor are the physical separation of the product and catalyst as well as the reduction in activation and loss of the catalyst.

The state of the art of the use of heterogeneous catalysts in the flow systems compered to the homogenous ones remains still open. The lifetime of heterogeneous catalysts is a significant hurdle to realize sustainable flow synthesis. To achieve this goal, more efficient heterogeneous catalysts should be developed characterized by high catalytic activity and stability.

Developed in our group ionic liquids based of triflate anion and aluminum triflate have been used as the efficient acid catalysts in a solvent-free, one-pot syntheses of chromane and levulinic acid esters. It was found that immobilization of trifloaluminate ionic liquids onto multi-wall carbon nanotubes (MWCNTs) to form a supported ionic liquid phase (SILP) offered numerous advantages in terms of product separation, catalyst stability, and recycling in batch systems (Fig. 1) [1], [2].

In this work, the developed ionic liquids were immobilized on the inorganic oxide materials or nanocarbon supports and used as highly active and stabile catalysts in flow system for aminolysis of epoxides to 1,2-amino alcohols which are important molecules in organic synthesis and medicinal chemistry [3].

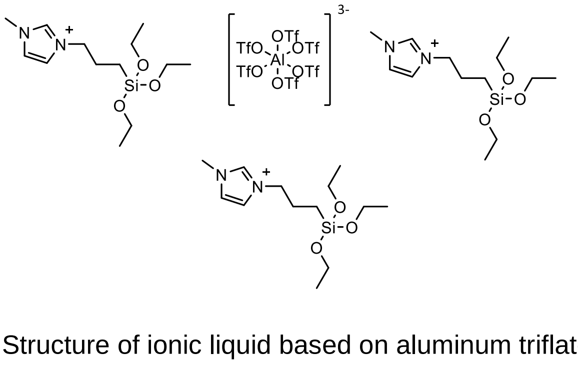

Fig. 1. Structure of ionic liquid based on aluminum triflate anion.

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O-13

Unexpected role of reactive oxygen species in adsorption and degradation of antibiotics – the case of ciprofloxacin and Nb_2O_5

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One of the most effective methods for elimination of antibiotics from wastewater are sorption processes leading to immobilization of the molecules of a pollutant on the surface of various adsorbents (e.g. activated carbons, mineral clays, silica or zeolites). Efficiency of the sorption processes is strongly affected not only by properties of the target pollutant and parameters of the wastewater (temperature, pH, presence of other pollutants), but also by physicochemical characteristic of the adsorbents (e.g. surface area, surface acidity, isoelectric point of the solids, etc.). From among other highly efficient and promising methods for detoxication of wastewater, particular attention is paid to advanced oxidation processes (AOPs) (e.g. photocatalytic degradation, Fenton and Fenton-like reactions or ozonation). In all these processes the antibiotic molecules are degraded/mineralized by highly oxidizing reactive oxygen species (ROS) formed in-situ in reaction media.

In this work, the contribution of adsorption and degradation processes to the removal of ciprofloxacin by amorphous niobium pentoxide was analyzed. ROS were formed in-situ or ex-situ upon treatment of Nb_2O_5 with H_2O_2. The formation of ROS was confirmed by EPR and Raman spectroscopy (Fig. 1a). Modification of niobia surface charge by ROS was monitored with zeta potential measurements. Kinetics of CIP removal was followed with UV-vis spectroscopy, whereas identification of CIP degradation products and evaluation of their cytotoxicity were obtained with liquid chromatography hyphenated with mass spectrometry (LC-MS) and microbiological studies, respectively.

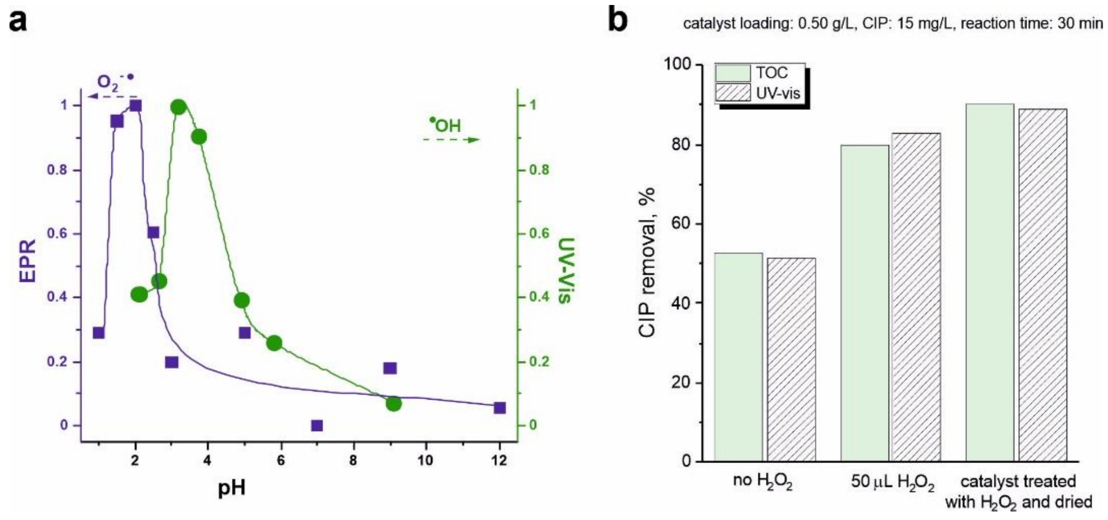

Fig. 1. The relative concentration of $^\bullet OH$ and $O_2^{-\bullet}$ radicals formed during interaction of H_2O_2 with parent amorphous Nb_2O_5 with respect to the pH value (a) and comparison of CIP removal determined with UV-vis and TOC analysis (b).

O-13

It was found that superoxo and peroxo species enhanced significantly the efficiency of CIP adsorption on Nb_2O_5 by modification of its surface charge (Fig. 1b). At low catalyst loadings and with a short reaction time, adsorption was the main process responsible for the enhanced CIP elimination, while the contribution of the degradation by ROS was negligible. This unexpected role of ROS stabilized on the Nb_2O_5 surface needs to be emphasized because in many studies devoted to the removal of environmental pollutants with the use of niobia-based catalysts, the analysis of the adsorption contribution, which may be dominant in short reaction times, has been neglected. Instead, only oxidative degradation of organic compounds has been taken into account, which can lead to misinterpretation of the kinetic results and wrong conclusions about the reactivity of ROS in degradation processes. The highest efficiency of CIP adsorption was observed under neutral conditions at which the antibiotic was present in zwitterion form. The enhanced adsorption of CIP was confirmed by IR-ATR, TOC and elemental analysis. The products of partial degradation of CIP were analyzed with LC-MS technique. The latter analysis, in combination with the results obtained from the elemental analysis and TOC measurements, allowed us to conclude that the piperazine moiety was probably responsible for the efficient adsorption of CIP on the Nb_2O_5 surface. Upon degradation of this functional group, the formed organic pollutants were desorbed from the metal oxide, leading to regeneration of the spent catalysts. Furthermore, apart from being a versatile catalytic material active in the adsorptive removal of CIP, Nb_2O_5 oxide can be easily regenerated by environmentally benign UV light treatment in the presence of H_2O_2.

Acknowledgements: This work was financially supported by the National Science Center, Poland (NCN), grants Sonata Bis 2017/26/E/ST4/00794 and Sonatina2 2018/28/C/ST5/00255.

O-14

Titania-based photocatalytic selective cleavage of C–C bond of a lignin based model compounds

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Biomass shows a potential candidate as a renewable abundant source for the production of various aromatic organic chemicals and hence the research attention in academia and industries as well is attracted. Woody biomass contains three major components cellulose, hemicellulose, and lignin [1]. Lignin is by far the largest, by volume, renewable source of aromatic chemicals in the nature. It is the only component of biomass which contains aromatic moieties linked to each other through C-O-C or C-C bond/bridges. The selective transformation of lignin-based compounds into high-value products is highly desirable towards sustainability and (bio)curricular economy. However, lignin is a three-dimensional amorphous macromolecule and possesses a complex structure which makes its selective transformation a challenging task [2].

Various research approaches for the oxidative cleavage of lignin-based model compounds or even of actual lignin have been adopted [3]. Catalytic oxidation of lignin is one of the most promising approaches to obtaining the high-value aromatic compounds through the cleavage of inter-unit linkages/bridges of lignin [1]. Heterogeneous photocatalysis using metal oxide semiconductors gains a continual increment of interest, especially for lignin valorization. Beside from the catalytic performance aspect, the recovery of catalyst after photocatalytic activity and formation of less waste is more beneficial which is very important for the industrial applications [4]. Titanium dioxide (TiO_2) is considered a promising candidate for heterogeneous catalysis due to specific unique physicochemical properties [5].

Various synthesis methods such as solvothermal, sol-gel and hydrothermal etc., are being adopted for the synthesis of TiO_2, but precipitation based method show the more advantangs due to possing the ability to tune the featues such as particle size and pore size distribution [6]. The use of mechanochemical forces as a synthetic tool, and specially sonochemistry gained a great interst due to various advantages such as of being greener, environment-friendly, energy-efficient, with shorter reaction duration, etc. The major derived effect upon ultrasonication are enhanced mass transformation and formation of acoustic cavitation and hot spots, and by tuning the frequency and power it is feasible to manipulate the physicochemical features of synthesized materials [7].

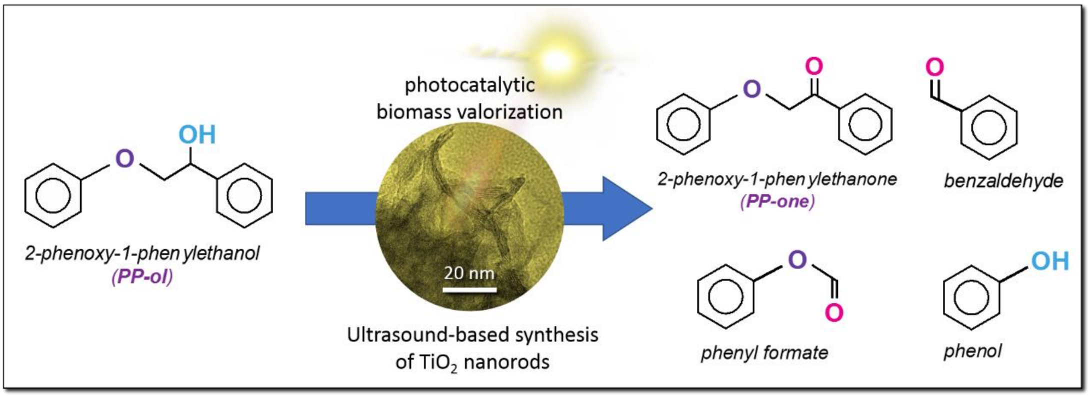

Figure 1. Photocatalytic oxidation of Lignin model compound (PP-ol) by using TiO_2

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In this research work, the ultrasound-assisted precipitations approach was used for the synthesis of TiO_2 catalysts [6]. Low-frequency ultrasound (US) 22 kHz with varying the power (such as 8, 24, 40, 56 and 72 W) was used during the synthesis. The sample was labelled as US22kHz-xW. In order to study the overall effect of US irradiation on the final physicochemical properties of synthesized materials, a sample of TiO_2 was also synthesized by using magnetic stirring instead of US, referred to as MagS. A commercially available TiO_2 catalyst (P25) was also used for the sake of comparison. Regarding the physicochemical features, US22kHz-24W showed the highest specific surface area (319 m^2/g) and total pore volume (0.339 cm^3/g) between all the herein studied catalysts. Electron microscopy analysis revealed that the use of ultrasonication during the synthesis led to the formation of nanorods. XPS analysis showed the presence of some reduced Ti sites on the ultrasound-assisted TiO_2 compared to MagS, while MagS possess a higher amount of sodium than US22kHz-24W.

The photocatalytic performance was pre-screened by evaluating the partial selective oxidation of benzyl alcohol to benzyl aldehyde under the UV (365 nm) light irradiation. The US22kHz-24W catalyst showed the highest conversion of BnOH (75%), and yield of benzyl aldehyde (68%) as compared to all other US assisted synthesized TiO_2 catalysts. Hence, it was selected among all other US assisted synthesized TiO_2 samples along with MagS and P25 for studying the photocatalytic selective oxidation of lignin-based model compound such as 2-phenoxy-1-phenylethanol (PP-ol) to the corresponding products. The results showed that all the targeted catalysts were found active for the selective cleavage of C-C of the PP-ol to the benzyl aldehyde, phenyl formate, phenol and 2-phenoxy-1-phenylethanone (figure 1). P25 showed the highest conversion (62%) of PP-ol with the 32% yield of the benzyl aldehyde, which is the desired product, whereas as US22kHz-24W showed lower conversion (47%) of PP-ol but a higher yield (45%) of benzyl aldehyde. MagS showed a PP-ol conversion of 19 %, which is lower than US22kHz-24W and P25. This research work showed that optimizing not only the frequency but also the power of the sonication play a key role on the synthesis of metal oxide-based catalysts and hence the physicochemical features as well as the photocatalytic performance of synthesized catalysts can be tuned accordingly.

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O-15

Reforming parowy etanolu na katalizatorach zeolitowych zawierających kobalt. Modyfikacja właściwości katalizatora w kierunku zwiększenia wydajności

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Wodór, okrzyknięty paliwem przyszłości, postrzegany jest obecnie jako alternatywa do istniejących technologii opartych na paliwach kopalnych o negatywnym wpływie na środowisko. Wodór można wytwarzać z etanolu (docelowo bioetanolu) w procesie katalitycznego reformingu parowego (ESR). W roli potencjalnych katalizatorów tego procesu zbadano szeroki zakres układów opartych zarówno na szlachetnych, jak i nieszlachetnych metalach przejściowych. Obecnie najczęściej stosowane katalizatory oparte są na niklu lub kobalcie – pierwiastkach znacznie tańszych i szerzej dostępnych niż metale szlachetne. Aktywna faza (nanocząstki kobaltu) jest zwykle zdyspergowana na nośniku, głównie materiałach tlenkowych takich jak Al_2O_3, CeO_2 czy SiO_2. Zeolity o dużej porowatości i dużej powierzchni właściwej również wydają się być interesujące do zastosowania w roli nośników kobaltowych faz aktywnych. Dotychczasowe stosunkowo małe zainteresowanie tymi materiałami w kontekście procesu ESR wynika z wysokiej selektywności do niepożądanego produktu - C_2H_4, powstającego na drodze odwadniania etanolu. Niemiej jednak możliwe jest znaczne ograniczenie lub nawet wyeliminowanie produkcji niepożądanego produktu - etenu poprzez kontrolowaną modyfikację właściwości zeolitu [1, 2].

Kwasowość katalizatorów zeolitowych, odpowiedzialna głównie za odwadnianie etanolu, może być modyfikowana w szerokim zakresie zarówno przez domieszkowanie alkaliami [3], jak i przez zmniejszenie (lub nawet wyeliminowanie) zawartości glinu w strukturze. W naszych badaniach ocenialiśmy skuteczność obydwu tych ścieżek modyfikacji. Serię katalizatorów kobaltowych na bazie zeolitu Y i ZSM-5 dotowanych potasem szczegółowo scharakteryzowano (ICP, XRD, spektroskopia Ramana, UV-VIS, XPS, TEM/EDX, TG/DTA, TPR, adsorpcja ilościowa Py i CO FT-IR) i przetestowano ich działanie w procesie ESR.

Silny efekt potasu na działanie katalizatora (konwersję etanolu oraz selektywność) wyjaśniono w oparciu o jego wpływ na właściwości powierzchni katalizatora, przede wszystkim stężenie i siłę kwaśnych centrów Lewisa. Ponadto wyniki wskazały na znaczenie specjacji i lokalizacji potasu. Spektakularne wyniki uzyskano natomiast dla katalizatorów na bazie zeolitu ZSM-5 mocno zubożonego w glin lub czystokrzemowego. Wspomniane materiały wykazały znakomite parametry pracy w procesie ESR: 100% konwersję etanolu w temperaturze 500°C, wysoką selektywność do pożądanych produktów (np. $S_{H2} > 90\%$) oraz bardzo wysoką stabilność.

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O-15

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O-16

Talc modified by dry milling and alkali activation: physico-chemical characterization

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As a Mg-rich mineral, talc can be considered as an environmentally friendly material with basic character. For this reason talc constitutes a potential substrate for development of solid base catalysts or sorbents. Pristine talc, however, is characterized by a very low specific surface area, and has to be pre-modified in order to enhance the desired physicochemical features. Dry grinding of talc has been widely researched and is known to cause series of morphological and structural modifications resulting, among others, in an increase of surface area. In contrast, the reports on the effects of talc treatment with bases, either with or without previous grinding, are scarce. The present work aimed at filling this gap by studying evolution of talc structure, morphology, texture, surface basicity and catalytic properties upon combined milling and alkali treatment.

Talc, a natural 2:1 layered silicate mineral, was activated by means of dry grinding in a planetary ball mill (for 10, 30 and 60 minutes) with subsequent treatment of obtained materials with 2M NaOH solution (at 90°C for 3 or 24 h). With aid of number of physicochemical methods (SEM/EDX, AAS, XRD, FTIR, Raman, N_2 sorption/desorption isotherms, ^{29}Si MAS NMR, TG/DSC, measurement of surface basicity by adsorption of benzoic acid) it was possible to identify deep changes that took place in the course of mechanochemical treatment. Thus, dry grinding led to gradual destruction of talc lattice and appearance of an amorphous silica phase. Pristine talc was practically unaffected by alkali treatment, but grinding strongly increased its reactivity towards NaOH. As a result, in most heavily ground samples, a desilicated, strongly amorphized talc co-existed with crystalline $Mg(OH)_2$ and magnesium silicate hydrate (MSH), a solid with poorly ordered structure, recognized recently as a promising cementitious material. Ground and alkali treated talc displayed enhanced concentration of surface basic centres and increased activity in the base-catalysed aldol self-condensation of acetone to diacetone alcohol. Thus, combined mechanical and alkali activation of talc yielded a promising material with potential for a range of versatile uses.

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O-17

Spectroscopic and first principle thermodynamic (FPT) investigations of catalytic NO oxidation over Cu-SSZ-13 zeolites

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The use of copper-exchanged chabazite zeolites has become increasingly widespread as a material for selective catalytic reduction of NO_x with NH_3 (NH_3-SCR). Synthetic Cu-SSZ-13 zeolites exhibit high conversion rates, while maintaining excellent hydrothermal stability [1-2]. Within the mechanistic considerations of the SCR process, formation and thermal evolution of nitrates (or NO_x species in general) on copper is often overlooked, yet its chemistry is immensely complex and perhaps critical toward the entirety of the catalytic cycle.

In this work formation and reactivity of $–NO_x^–$ species on copper active centers (namely nitrites $–NO_2^–$ and nitrates $–NO_3^–$) and copper-nitrosyls have been thoroughly investigated. The use of spectroscopic methods (IR, EPR) allowed the characterization and approximate quantification of different types of Cu^{2+}, Cu^+ and $[CuOH]^+$ species, as well as various copper agglomerates (e.g. $[Cu\text{-}O\text{-}Cu]^{2+}$). Such centers have been then modeled using periodic DFT+U calculations in the Vienna ab-initio Simulation Package (VASP), and on top of the optimized geometries, a varying number of NO and O_2 molecules have been adsorbed. The obtained energetics of adsorption process allowed exploration of the thermodynamic relations between obtained adducts and gas-phase molecules, using the First Principles Thermodynamics model (FPT).

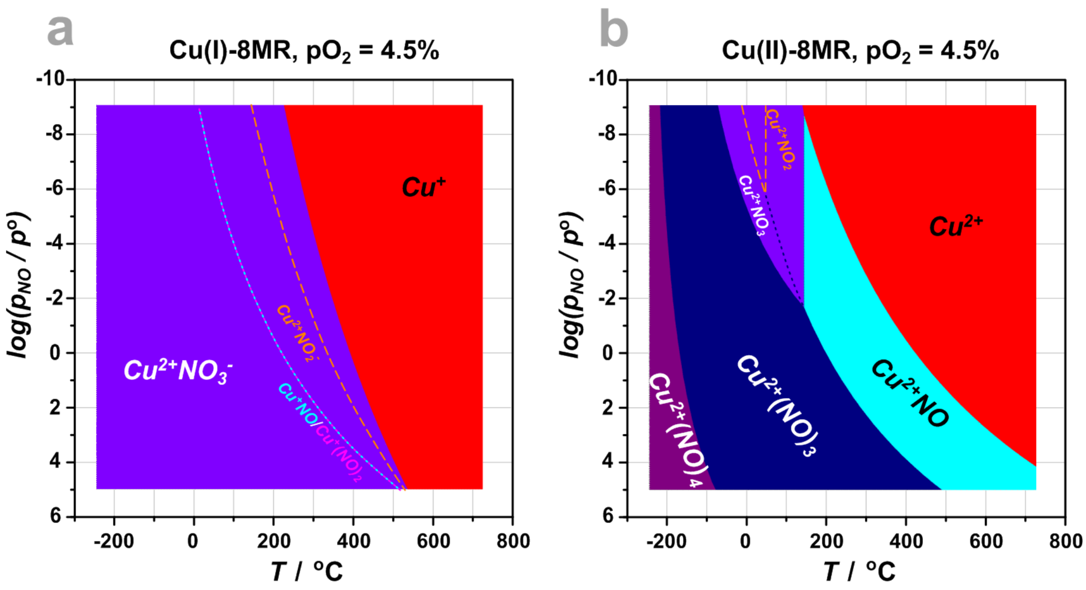

Fig. 1. Projection of the bottom envelope of the Gibbs free energy diagram of the NO_x-O_2 adspecies on Cu^+ (a) and Cu^{2+} (b) located in 8MR of the CHA lattice (p_{O2}/p^0 = 4.5%; p_{H2O}/p^o = 3%).

As seen in Fig. 1a, Cu^+ in the presence of NO forms nitrosyl species at first, which upon interaction with O_2 immediately transform according to the following reaction $Cu^+ + NO + O_2 = Cu^{2+}NO_3^–$. Nitrates remain as the dominant form for the system with reduced copper, formally reoxidizing Cu(I) ions, and acting as an additional stabilizing factor for the system. For the oxidized state that involves copper(II) active centers (Fig. 1b), the resulting nitrates are radicals, are less prominent and compete with nitrosyl-based species.

The FPT analysis of the reactivity of copper nitrate (NO_3^-) revealed the thermodynamic feasibility of the synproportionation reaction with NO ($Cu^{2+}NO_3^- + NO = Cu^{2+}NO_3^- + NO_2$) in the entire temperature range leading to NO_2 oxidant. Furthermore, significant amounts of NO_2 can be formed during the decomposition of nitrites unless this process falls within the region of stability of the nitrates and instability of the nitrites (Fig. 2a). Such a reaction has been confirmed, indeed, by following with QMS and gas-phase IR detection of the products under *operando* conditions.

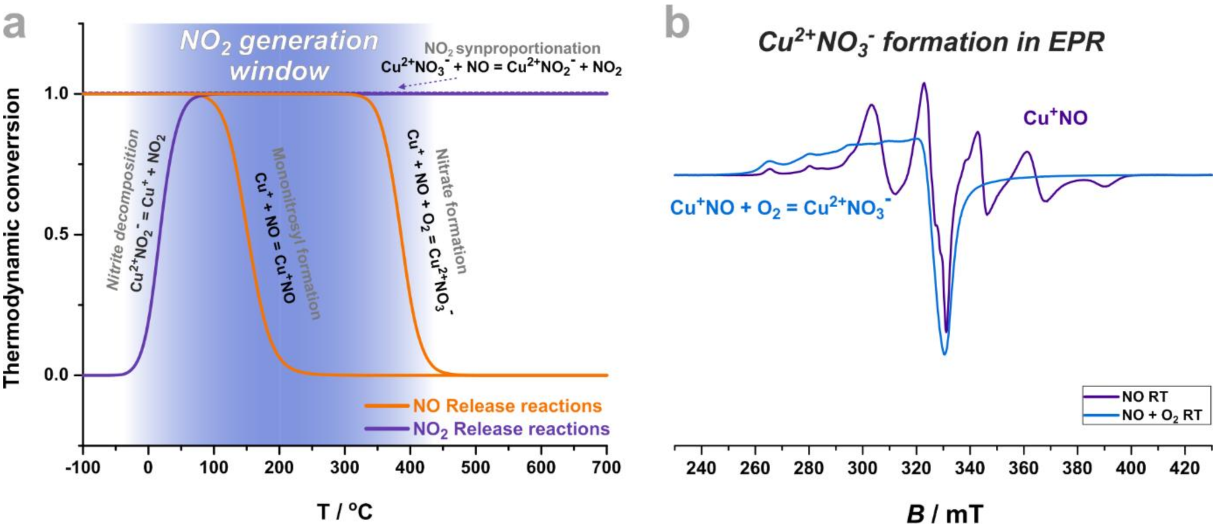

Fig. 2. Thermodynamic conversions of Cu(/$Cu^{2+}NO_3^-$ catalytic cycle with NO and O_2 (a) and EPR spectra of nitrate formation from nitrosyls under in-situ conditions.

Furthermore, the formation of nitrosyls and nitrates has also been confirmed using EPR (Fig. 2b) and IR measurements. The origin of reduced copper species in such a highly oxidative environment has also been resolved. It has been found that the $[CuOH]^+$ species readily react with NO reducing copper and form HONO intermediate (nitrous acid) ($CuOH^+ + NO = Cu^+ + HONO$). It can in turn reduce other Cu^{2+} sites (through proton deposition onto the zeolite lattice) releasing more NO_2. Although HONO cannot be directly observed, its presence is proven by consumption of hydroxyls and generation of Cu(I) even at low temperatures. Moreover, HONO can be considered as the last key intermediate in the formation of N_2 from NO and NH_3, which is crucial for explaining the complete mechanism of NH_3-SCR.

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Flash oral presentations

FO-1

The effect of the impregnation with Ag^+, Ca^{2+} and Co^{2+} ions of Cu and Ag modified K-OMS-2 catalysts on their performance in soot oxidation

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Particulate matter (PM) emitted to the atmosphere as a result of incomplete combustion of fossil fuels is one of the main pollutants affecting the environment.This study aimed to investigate the influence of different metal ions doping on the catalytic activity of K-OMS-2 catalysts in soot oxidation. The parent K-OMS-2 matrix was doped at the synthesis step, with 3 wt. % Cu or Ag. The obtained materials were additionally impregnated with aqueous solutions of Ag^+, Ca^{2+} and Co^{2+} ions in order to obtain bi- and trimetallic systems. The cryptomelane catalysts were characterized by: XRD, RS, XPS, XRF and S/TEM/EDX. The catalysts were subjected to soot oxidation in loose contact mode in various conditions: (i) O_2 in He, (ii) O_2 + NO in He, (iii) O_2 + SO_2 in He, (iv) O_2 + NO + SO_2 in He.

It was found that regardless of the type of metal and the method of doping with metals, the structure of cryptomelane and its morphology did not change. There was a strong effect of dopants on the manganese average oxidation number, the production of NO_2 during the tests of soot combustion in a mixture of gases containing NO, and an increase in catalyst resistance to sulfur poisoning. In addition, it was observed that in the case of bimetallic catalysts containing copper in the support, the presence of sulfur reduces the soot combustion temperature as compared to tests carried out in the presence of oxygen.

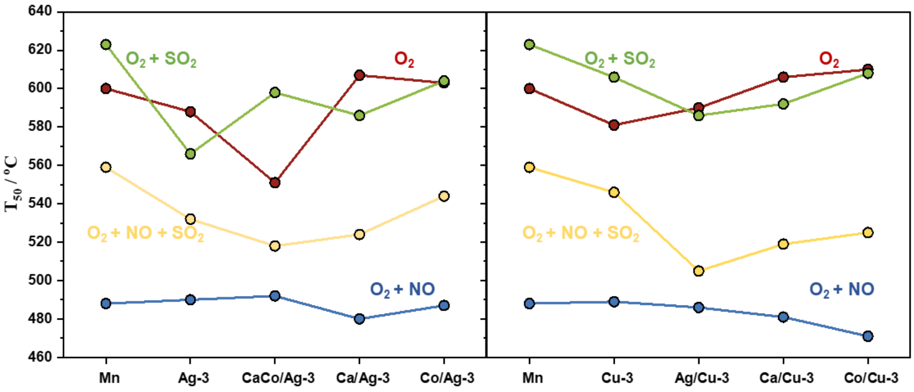

Fig. 1. The temperature of 50 % soot conversion obtained in loose contacts in the presence of: O2 (red line), O_2 + NO (blue line), O_2+ SO_2 (green line) and O_2 + NO + SO_2 (yellow line).

The work was carried out within the MOST program for bilateral collaboration between Poland and China, financially supported by The National Centre for Research and Development, Poland, grant PNOX no. WPC1/PNOX/2019 and from China side by the Project 2017YFE0131200

FO-2

Niskoemisyjne otrzymywanie etanu i etylenu na drodze integracji procesu utleniającego sprzęgania metanu i metanizacji

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Wzrastającemu zapotrzebowaniu na małocząsteczkowe alkeny towarzyszy potrzeba opracowywania selektywnych technologii ich otrzymywania. Szczególnie interesujące są technologie alternatywne bazujące na surowcach innych niż ropa naftowa. Jedną z takich jest utleniające sprzęganie metanu (OCM), które wydaje się być obiecującym źródłem etylenu. Pomimo licznych badań trwających od ponad 30 lat w dalszym ciągu nie udało się w pełni skomercjalizować tego procesu. Jedną z przyczyn jest brak aktywnego, selektywnego i stabilnego katalizatora. Zasadą jest, że ze wzrostem stopnia konwersji metanu zmniejsza się selektywność do węglowodorów C_{2+}. Nawet w przypadku najlepszych katalizatorów osiągi ograniczone są nieformalną regułą, zgodnie z którą suma selektywności do węglowodorów C_{2+} i stopnia konwersji metanu zbliżona jest do 100%. Istotnym problemem są produkty całkowitego spalania (tlenki węgla), które w obecności najefektywniejszych układów katalitycznych powstają z selektywnością 20–30%. Ich redukcja poprzez optymalizację składu katalizatora bądź utylizację w dalszym ciągu pozostaje wyzwaniem.

W niniejszej pracy zaproponowano połączenie utleniającego sprzęgania metanu i metanizacji ubocznie wytwarzanych w nim tlenków węgla w kierunku niskoemisyjnego i selektywnego otrzymywania etanu i etylenu. Proces OCM prowadzono z udziałem katalizatora $Mn–Na_2WO_4/SiO_2$, natomiast metanizację przy zastosowaniu materiałów osnowie niklu.

Określono optymalne warunki integracji przy uwzględnieniu wpływu składu złożonej mieszaniny opuszczającej reaktor utleniającego sprzęgania na przebieg selektywnej i efektywnej konwersji tlenków węgla do metanu realizowanej w obecności układów przygotowanych konwencjonalną metodą preparatyki oraz z wykorzystaniem technologii druku 3D.

FO-3

Synthesis, Characterization and SCR catalytic Activity of $ZnM_2O_4|TiO_2$ (M = Co, Fe, Mn) heterostructures

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Spinel oxide catalysts exhibit promising performance in a wide range of catalytic reactions such as N_2O decomposition, CO, NO and CH_4 oxidation, CO-PROX or SCR processes. Within this contribution we present synthesis, characterization and catalytic activity in the SCR reaction of 3 types of spinel heterostructures $ZnM_2O_4|TiO_2$ (M = Co, Fe, Mn).

Parent zinc spinels of Co, Fe and Mn and titania were synthesized via hydrothermal method. Sonication technique was then used for attaching euhedral spinel nanocrystals to the TiO_2 support. Both parent nanocrystals were dispersed in ethanol solution and sonicated for 10 minutes (1.5s ultrasonic impulses separated by 3s breaks). Finally the mixture of the sonicated oxides was dried and calcinated for 2h in 200^0C.

The morphological, structural and chemical characterisation of the obtained composite catalysts was carried out using high resolution TEM/STEM/EDX, Raman and XRD techniques. XRD measurements were further supplemented by Rietveld analysis. XRD and Raman measurements confirmed presence of the spinel and titania phases only. HAADF STEM imaging confirmed well–developed plates-like morphology of the TiO_2 substrate (Fig. 1.) and euhedral morphology of the spinel nanocrystals (Fig. 2.). Furthermore, the EDX analysis confirmed that the sonication technique followed by sample calcination is sufficient to obtain well developed $ZnM_2O_4|TiO_2$ heterojunctions, which was probably facilitated by the proper morphology of the TiO_2 support.

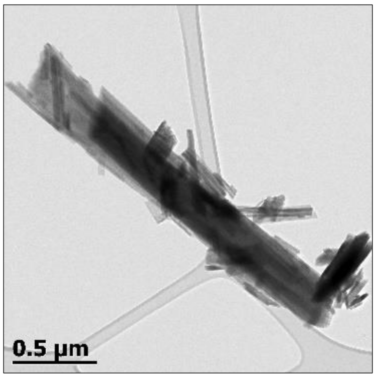

Fig. 1. BF-TEM of titania.

The synthesized composites were then catalytically tested for NH_3-SCR reactions. The obtained results were confronted with the parallel results obtained for bare spinel and titania samples, separately. The obtained preliminary results reveal the effect catalytic of the Fe, Mn and Co cations located in the octahedral sites and the benefits associated with the formation of the $ZnM_2O_4|TiO_2$ (M= Co, Fe, Mn) interfaces. Further in depth analysis of the electronic and atomic structure of the junctions is in progress for full understanding and optimization of their catalysts performance.

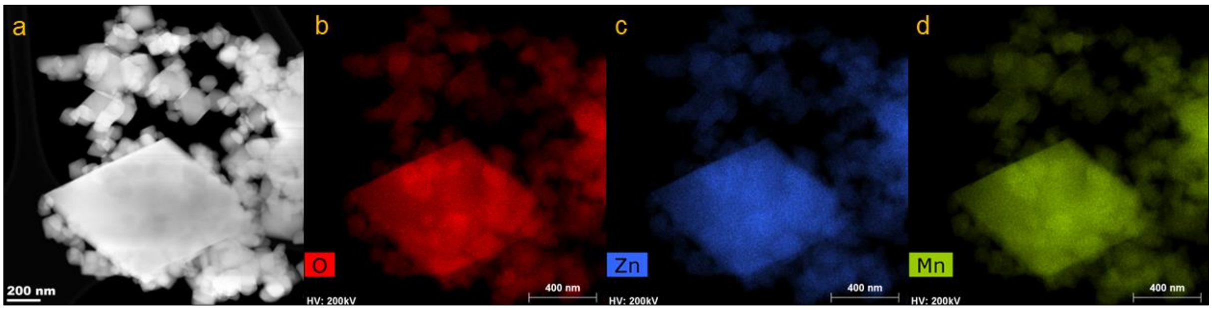

Fig. 2. a) HAADF-STEM and b – d) EDX analysis of $ZnMn_2O_4$ spinel.

Acknowledgements: The project was financed by Polish National Science Centre: Project OPUS, DEC-2011/03/B/ST5/01564

FO-4

Catalytic performance of catalysts based on non-noble metals in the hydrogenation of nitrocyclohexane in flow conditions

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The chemical industry is one of the main sources of compounds for other industrial branches. Hence, even a small improvement in any chemical process may have a tremendous impact on the whole economy. Sustainable Development goals are the directions for further changes. For instance, switch from batch to flow conditions is one of the most mentioned priorities for the modern chemical industry.

Catalytic hydrogenation of nitrocyclohexane seems to be a promising alternative for the synthesis of various useful chemical compounds (**Fig. 1**): cyclohexanone and cyclohexanone oxime used in polyamides production, cyclohexylamine used as a building block for pharmaceuticals, dicyclohexylamine – important in rubber manufacture [1,2]. In contradiction to the currently used methods for the production of these compounds, catalytic hydrogenation of nitrocyclohexane can be performed in one step process, under mild conditions, and without waste formation [4,5].

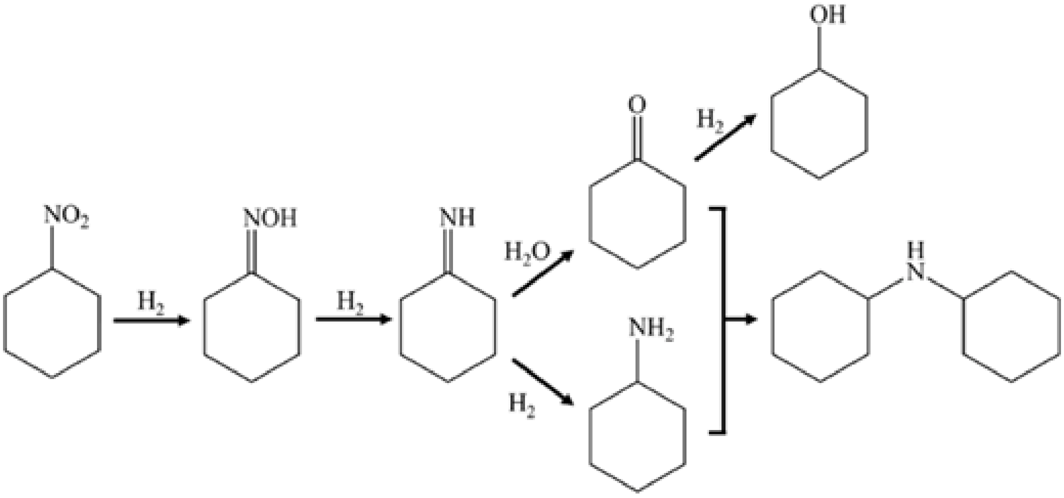

Fig. 1. Mechanism of nitrocyclohexane hydrogenation proposed by Wang et al. [3].

Most of the studies on the hydrogenation of nitrocyclohexane use noble catalysts, batch reactors, and elevated pressure and temperature. In contradiction to these studies, our experiments are conducted in continuous flow reactors with non-noble catalysts based on Ni, Cu and Co.

Due to the small number of results concerning catalytic hydrogenation of nitrocyclohexane in flow conditions published so far, we would like to present the catalytic performance of non-noble metal nanoparticles supported on various materials (Al_2O_3, SiO_2,

CeO_2, active carbon). We believe that such information could be essential for further studies on this topic.

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FO-5

Strukturalny reaktor katalityczny do dopalania metanu

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Dopalanie metanu ze źródeł stacjonarnych, takich jak elektrownie instalowane w biogazowniach, jest ważną kwestią, którą należy rozpatrzyć ze względu na ilość metanu uwalnianą do atmosfery. Metan jest jednym z gazów cieplarnianych, dlatego ograniczenie jego emisji jest kluczowe. W badaniach, zaprojektowano moduł konwertera przeznaczonego do dopalania metanu, do wykorzystania w samodzielnym reaktorze lub w reaktorze dwumodułowym wraz z modułem deNO$_x$. Reaktor oparty został na strukturach krótkokanałowych w postaci siatek metalowych immobilizowanych mieszanym katalizatorem CoPd osadzonym na tlenku glinu typu gamma. Ustrukturyzowane wypełnienie reaktora scharakteryzowano metodami spektroskopowymi i spektrometrycznymi, pod względem składu jakościowego i ilościowego (UV-Vis, EDX, AAS), natomiast morfologia katalizatorów przeanalizowana została techniką mikroskopową SEM. Reaktor przetestowany został w katalitycznej reakcji dopalania metanu pochodzącego z gazów odlotowych w jednoetapowym procesie usuwania metanu, jak również w instalacjach, z obecnością NH_3 stosowanego w procesie deNO$_x$. Wyniki wskazały wysoką aktywność katalityczną dopalania metanu w obu przypadkach, przy zachowaniu mechanicznej odporności katalizatora. Ze względu na uzyskane wyniki, prezentowany reaktor katalityczny jest dobrym przykładem układu do stosowania jako moduł do dopalania metanu w układach katalitycznych stosowanych w kogeneracji z układem do redukcji tlenków azotu w instalacjach ze źródeł stacjonarnych, takich jak małe elektrownie.

Podziękowanie: Badania sfinansowane zostały przez Narodowe Centrum Badań i Rozwoju (LIDER/204/L-6/14/NCBR/2015). Część badań sfinansowana została przez Małopolskie Centrum Biotechnologii ze środków własnych zespołu Interakcji Roślin z Mikroorganizmami.
Autorzy dziękują firmie Spectro-Lab z Łomianek k. Warszawy (http://www.spectro-lab.pl/) za udostępnienie spektrometru masowego do testów katalitycznych jak również firmie Sasol za dostarczenie darmowych próbek Disperal®. Autorzy dziękują również firmie Dynamic Biogas za dostarczenie schematu biogazowni, która może być znaleziona na stronie internetowej https://www.dynamicbiogas.com/en/.

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FO-6

Badanie heterogeniczności kwasowych grup OH w zeolitach metodą spektroskopii w podczerwieni z zastosowaniem azotu jako cząsteczki-sondy

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Zeolity są mikroporowatymi glinokrzemianami, które mogą być zastosowane jako katalizatory m.in. w przemyśle rafineryjnym oraz w wielu procesach "czystej chemii" ze względu na ich właściwości kwasowe, kształtoselektywność, czy też stabilność termiczną [1]. Wiedza dotycząca kwasowości zeolitów jest istotna dla katalizy i powinna uwzględniać zarówno aspekt ilościowy dotyczący stężeń centrów kwasowych Brønsteda i Lewisa jak również charakterystykę mocy kwasowej ze szczególnym uwzględnieniem heterogeniczności kwasowych centrów protonowych [2].

W podjętych badaniach, azot zaproponowany został jako cząsteczka-sonda do badań heterogeniczności kwasowych grup Si-OH–Al w zeolitach metodą spektroskopii w podczerwieni. Zaletą azotu w porównaniu do powszechnie stosowanego CO jest względnie niskie przesunięcie pasma kwasowych grup OH reagujących z azotem poprzez wiązanie wodorowe (70–130 cm^{-1}), dlatego też przesunięte pasma $OH\ldots N_2$ nie nakładają się z pasmami jonów amonowych. Pozwala to na wygodne prowadzenie badań dla zeolitów, dla których amoniak był uprzednio zaadsorbowany a następnie desorbowany w rosnących temperaturach. Przesunięcie położenia pasma $OH\ldots N_2$ w stronę niższych liczb falowych wraz z rosnącą temperaturą desorpcji amoniaku stanowi dowód na heterogeniczność kwasowych grup Si–OH–Al. Jest to spowodowane tym, iż mniej kwasowe hydroksyle w zeolitach (o niższym $\Delta\nu_{OH\ldots N2}$) uwalniają amoniak w niższych temperaturach.

Dla zeolitów NaHY, HMFI oraz HBEA, przesunięcia częstotliwości pasm w podczerwieni zarówno dla wolnych kwasowych grup OH jak również dla hydroksyli związanych z azotem wiązaniem wodorowym wykazały heterogeniczność Si-OH-Al wraz ze wzrostem desorpcji temperatury amoniaku. Z kolei, w przypadku zeolitu HFAU o module krzemowym Si/Al = 31, stwierdzono homogeniczność kwasowych grup OH.

Heterogeniczność Si–OH–Al w zeolicie NaHY wyjaśniona została obecnością hydroksyli charakteryzujących się zróżnicowaną liczbą atomów glinu w bliskim sąsiedztwie. Zgodnie z badaniami ^{29}Si MAS NMR wykryto obecność Si(1Al), Si(2Al) oraz Si(3Al), zaś odpowiadające hydroksyle o zróżnicowanej kwasowości przedstawić można następującymi wzorami: $(SiO)_3Si–OH–Al(OSi)_3$, $(AlO)(SiO)_2Si–OH–Al(OSi)_3$ oraz $(AlO)_2(SiO)Si–OH–Al(OSi)_3$. Natomiast w wysokokrzemowym HFAU stwierdzono obecność jedynie homogenicznych grup $(SiO)_3Si–OH–Al(OSi)_3$.

Heterogeniczność kwasowych grup Si–OH–Al w zeolitach HMFI oraz HBEA może być wyjaśniona zarówno obecnością $(SiO)_3Si–OH–Al(OSi)_3$ oraz małymi ilościami $(AlO)(SiO)_2Si–OH–Al(OSi)_3$ o zróżnicowanych kwasowościach jak również obecnością Si–OH–Al o zróżnicowanej geometrii mostka.

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FO-7

In vitro analysis of cytotoxicity of theranostic polyelectrolyte nanocarriers containing neuroprotective drugs

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Nanotechnology is innovative and fast developing area of science and its growing application in medicine covers diagnosis, imaging and drug delivery. Nowadays, nanoparticles (NPs) have attracted much attention as promising drug carriers that could deliver therapeutics to their specific molecular targets. That could make treatment more accurate and precise and thus may reduce the possible off-target undesired effects. Over the years, various types of nanocarriers (NCs) such as liposomes, polymers, micelles, polymeric nanocapsules and dendrimers have been investigated. Most of them were tested in cancer therapy and diagnosis [1]. Among different kinds of nanocarriers, the multifunctional theranostics NPs that are suitable for both diagnosis and therapy should be highlighted. Therefore, the theranostic drug carriers are able simultaneously to deliver pharmaceutic agents to pathological tissue, but also the delivery may be tracked by imaging technique including computed tomography (CT) or magnetic resonance imaging (MRI) [2].

The aim of this work was to evaluate the cytotoxic effect of the two types of theranostic nanocarriers with encapsulated neuroprotective drugs. For initial tests we have chosen AOT/(PLL/PGA)$_2$-g-PEG and PCL/(PLL/PGA)$_2$-g-PEG nanoparticles. The obtained NCs were characterized by determination of their concentration, zeta potential and hydrodynamic diameter distribution. Moreover, we selected cyclosporine A and tacrolimus (FK506) as neuroprotectants due to their, anti-apoptotic, immunosuppressive and anti-inflammatory properties. Human neuroblastoma SH-SY5Y cells were used to evaluate the potential cytotoxic effect of the theranostic nanocarriers loaded with selected drug. In order to estimate cell membrane integrity, the level of lactate dehydrogenase (LDH) released from damaged cells into culture media was quantified. Furthermore, the WST-1 tetrazolium-based assay was used to determine cell viability. The obtained experimental data on *in vitro* cytotoxicity and cell viability of the tested NCs will be presented.

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FO-8

Copper-based catalysts for methanol synthesis via CO_2 hydrogenation - a sustainable approach

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Catalytic valorization of CO_2 is important from both environmental and technological viewpoints. On one hand, it is crucial for efficient reduction of CO_2 emissions, yet CO_2 conversion can also provide important products, including synthesis gas, hydrogen, methanol, ethanol, dimethyl ether, etc. Some of these products remain of vital market importance and can be used as fuels or fuel components. However, it is important to note, that due to a high thermodynamic stability of CO_2 molecules, their catalytic activation is difficult and strongly energy-demanding. This is an obvious drawback, making chemical CO_2 valorization a rather unpopular industrial larger-scale solutions, though this may change in the future.

In this research our attention is focused on oxide catalysts for CO_2 hydrogenation to methanol. For at least a decade, copper-based systems have been known to be active in this reaction. Most commonly, the conventional catalysts tested in several laboratories contained a mixture of copper, zinc and aluminum oxides, and were usually synthesized via a simple coprecipitation method. In our case, two series of γ-Al_2O_3-supported catalysts containing copper (0.5-10.0 mol.%) or a combination of copper and zinc (0.2-4.0 mol.%) as active components were synthesized via impregnation method. Our goal was to check the effect of copper and zinc concentrations on structural, textural and functional parameters which can control the catalytic activity and selectivity of the supported catalysts. Additionally, the effect of support was elucidated, because in addition to the γ-Al_2O_3-supported series, the corresponding catalysts were also synthesized on commercial cenospheres of 300 μm in diameter. The studied samples have been characterized by XRD, RS, SEM/EDS, porosimetry, DRIFT and UV/Vis-DR.

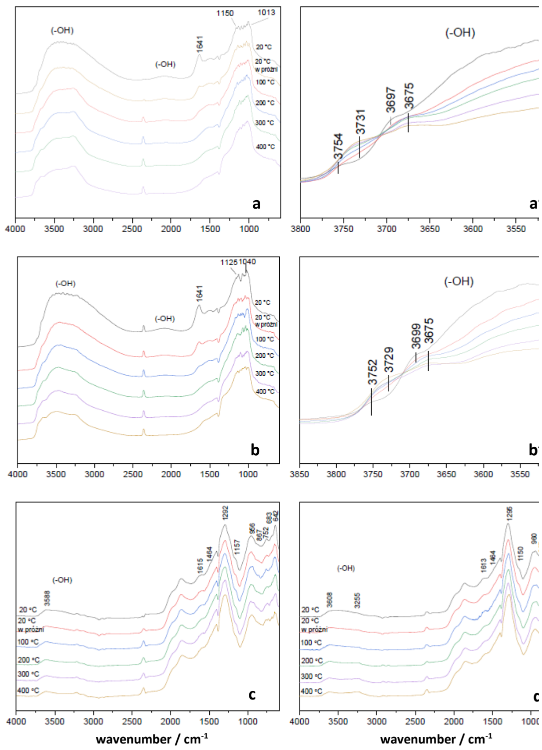

Fig. VT-DRIFT spectra of CuO_x/γ-Al_2O_3 - a, CuO_x-ZnO_x/γ-Al_2O_3 - b, CuO_x/cen-300 - c, CuO_x-ZnO_x/cen-300 - d; corresponding OH region: a' and b'; nominal contents: 3 mol.% of CuO and 2 mol. % of ZnO.

Based on recent studies, we can demonstrate that catalytic hydrogenation of CO_2 towards methanol can be considered not only as a good example of a reasonable chemical pathway of CO_2 emission reduction, but also as a technology providing a valuable market product, while simultaneously meeting favorable conditions required from the perspective of process sustainability.

FO-9

Oxidative Dehydrogenation of Propane over Vanadium-Containing Faujasite Zeolite. Multi-spectroscopic approach to study vanadium sites in desilicated zeolite Y

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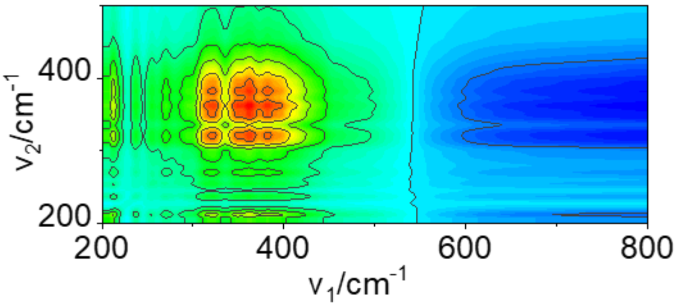
One of the most important classes of the ODH catalysts are vanadium-based systems. Their performance depends strongly on vanadium dispersion, oxidation state, and local coordination [1]. On-going debate on the activity of vanadium centers points to polymeric V-O-V chains as the key-species in the ODH reaction. To precisely address the catalytic activity to peculiar vanadium sites: isolated vanadium in tetrahedral or octahedral coordination or polymeric V-O-V chains, the synthesis of materials with well-defined vanadium centres is required. Zeolites offer a unique opportunity by stabilizing vanadium ions in different locations. The main goal in our work was to study the relationship between the vanadium state and the catalytic activity it offers in the ODH reaction. Vanadium catalysts were obtained by classical impregnation using two types of zeolite Y as supports: HY zeolite with Si/Al ratio of 31 (commercial material modified by steaming and subsequent acid treatment) and desilicated HY_{deSi} zeolite with Si/Al ratio of 18 (zeolite prepared by caustic treatment with NaOH/TBAOH mixture, as described in [2]). The preparation was conducted at acidic environment (pH = 2.5), the final amount of vanadium phase was 6 wt%. The systems were tested for the catalytic activity in the ODH of propane in a gas-flow fixed-bed reactor coupled to GC in temperature range 400-500 ºC [3]. The nature of the introduced vanadium species was determined by a combination of spectroscopic techniques such as ^{51}V NMR, in situ 2D COS DR UV-vis, and in situ FTIR.

Introduction of vanadium slightly affected the crystallinity of the $V\text{-}H_{deSi}$ only. Specific surface area and pore volume were reduced due to location of vanadium species in micropores preferentially. In the fresh samples vanadium exhibited +V oxidation state, which changed during the dehydratation and subsequent reaction with propane, as evidenced by in situ DR UV-vis (Fig. 1). The catalytic tests showed that V-HY system was less selective than the $V\text{-}HY_{deSi}$ counterpart. The products profiles indicated that the reaction proceeds according to the Mars - Van Krevelen mechanism. Our studies showed that the modification of zeolite via caustic treatment can be an effective method of adjusting zeolite surface basicity - a key parameter that plays a particularly important role in the ODH process. The significantly developed mesopore surface ensured the effective attachment of vanadium species to silanol groups and the formation of isolated $(SiO)_2(HO)V{=}O$ and $(SiO)_3V{=}O$ sites or polymeric, highly dispersed forms located inside zeolite micropores. Higher basicity of HY_{deSi}, due to the presence of the Al-rich shell, aids the activation of the C−H bond leading to higher selectivity to propene. The realuminated matrix has also a positive effect on the attachment of the V-species, influencing the reducibility of the catalyst, while the reduced strength of the protonic sites inhibited the polymerization of propene and the formation of coke compounds.



2 COS UV-Vis

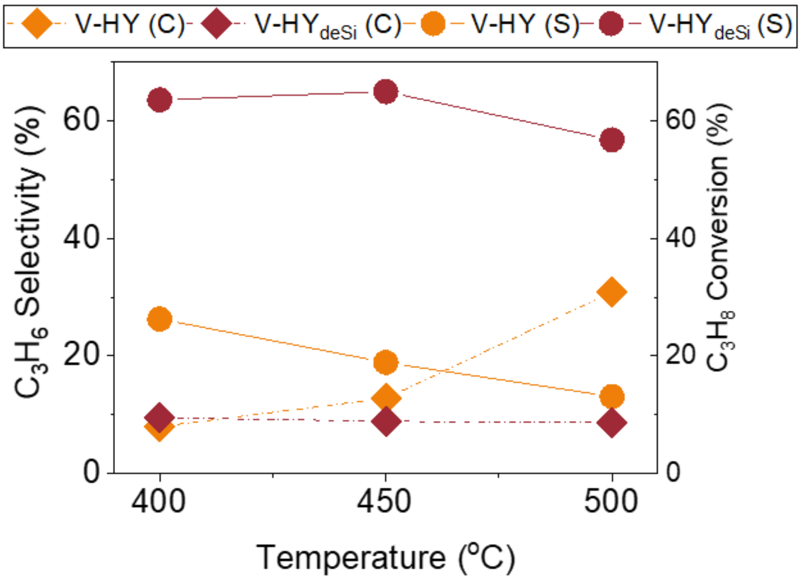


Fig. 1. The catalytic performance of V-HY$_{desi}$ and V-HY faced with 2D COS map indicating V^{5+} to V^{4+} reduction upon the contact of the catalyst with propane at 400 °C.

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FO-10

Nanorurki węglowe dotowane heteroatomami jako katalizatory reakcji redukcji tlenu w środowisku alkalicznym

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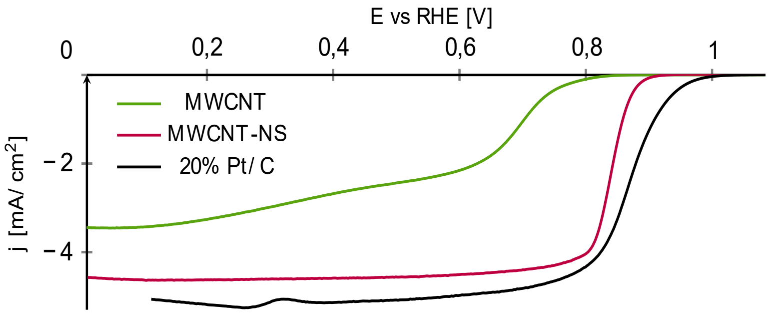
Ogniwa paliwowe z elektrolitem w postaci membran polimerowych stanowią obiecujące źródło energii elektrycznej. Alternatywą dla obecnie stosowanych membran perfluorowanych są membrany anionoprzewodzące, które cechują się znacznie niższymi kosztami produkcji. Alkaliczne środowisko pozwala na stosowanie katalizatorów reakcji redukcji tlenu (*ang.* oxygen reduction reaction, ORR) niezawierających metali szlachetnych [1-2]. Materiały węglowe są szeroko badane pod względem zastosowania jako katalizatory ORR lub ich nośniki, ze względu na swoje wysokie przewodnictwo elektryczne, powierzchnię właściwą oraz możliwość modyfikacji w celu wprowadzenia centrów aktywnych [3].

Nanorurki węglowe zadotowano tlenem poprzez działanie stężonym kwasem azotowym bądź traktowanie plazmą tlenową. W celu wprowadzenia azotu i siarki przeprowadzono pirolizę tiomocznika w atmosferze azotu w temperaturze 850°C. Wbudowanie się heteroatomów do nanorurek potwierdzono z użyciem spektroskopii XPS. oraz analizy elementarnej, a jego równomierność z użyciem mapowania TEM-EDX. Po dotowaniu nanorurki zbadano z użyciem spektroskopii Ramana oraz mikroskopii TEM. Do sprawdzenia aktywności w ORR posłużono się techniką wirującej elektrody dyskowej z pierścieniem (Rys. 1), co pozwoliło na zweryfikowanie selektywności reakcji w kierunku preferowanego mechanizmu czteroelektronowego oraz zbadanie ilości tworzącego się nadtlenku wodoru, mogącego powodować degradację części składowych ogniwa [4]. Dotowanie nanorurek azotem i siarką pozwoliło na zwiększenie potencjału redukcji z 0,80 V vs RHE do 0,89 V, oraz liczby wymienianych elektronów z 3,42 do 3,84.



Rys. 1. Krzywe LSV reakcji redukcji tlenu na dla czystych nanorurek oraz dotowanych N i S

Literatura:

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Plakaty
Posters

P-1

Strategie prewencji konserwatorskiej dla obiektów z poli(chlorku winylu)

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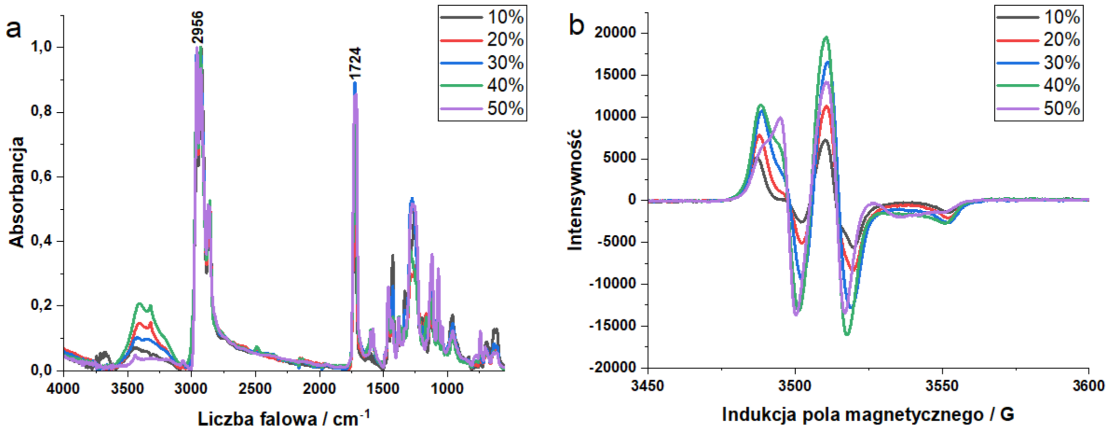
Współcześni artyści tworząc swoje dzieła chętnie sięgają po tworzywa sztuczne. Jednym z takich tworzyw jest polichlorek winylu (PCW). Ulega on degradacji pod wpływem takich czynników fizycznych jak wysoka temperatura, promieniowanie UV czy nawet przechowywania przez dłuższy czas w temperaturze pokojowej. Degradacja polichlorku winylu wizualnie objawia się poprzez przebarwienie lub pękanie elementów [1]. Procesy degradacyjne prowadzą do zaburzenia odbioru wizualnego dzieła sztuki, a w skrajnym przypadku do utraty wykonanych z polichlorku winylu dzieł sztuki. Niestety konserwatorzy nie dysponują jasnymi wytycznymi dotyczącymi ochrony obiektów muzealnych. Dlatego konieczne jest rozpoznanie mechanizmów starzenia się obiektów w warunkach muzealnych i opracowanie metod prewencji konserwatorskiej pozwalających zapobiegać tym niekorzystnym procesom. W niniejszej pracy zostanie przedstawiony mechanizm degradacji modelowych próbek polichlorku winylu o zawartości 10, 20, 30, 40 i $50\%_{wag}$ [2] ftalanu dioktylu (DOP) jako plastyfikatora, oraz stabilizator Tinuvin 770 w ilości i 2% wagi polimeru oraz czystego PCW. Próbki były poddane naturalnemu starzeniu w temperaturze pokojowej oraz przyspieszonej degradacji w temperaturach 80, 120, 160˚C. W temperaturze pokojowej PCW jest twardy a mięknie po osiągnięciu temperatury zeszklenia T_g [3]. Dlatego polimer ten miesza się z plastyfikatorami (pasmo 1724 cm^{-1}, rys. 1a). Pojawienie się sygnału EPR od utlenionego stabilizatora wskazuje, że procesy degradacji nawet w temperaturze pokojowej przebiegają na drodze rodnikowej (Rys. 1b). Zmiany polarności powierzchni próbki śledzono za pomocą pomiaru kąta zwilżania.



Rysunek 1. a) Widma ATR FTIR polichlorku winylu. Pasmo przy 1724 cm^{-1} pochodzi od plastyfikatora ftalanu dioktylu (DOP) b) widma EPR próbek PCW zawierającego Tinuvin 770.

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P-2

The role of rhenium in Ni-Re/Al_2O_3 catalysts in the dry reforming of methane reaction

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Methane reforming with CO_2 is still of great interest due to growing demand creating a continuous need for new hydrogen sources. The main difficulty in this reaction is the deactivation of the catalyst due to the formation of carbon deposits on its surface. Herein, a series of commercial nickel catalysts supported on α-Al_2O_3 and modified with different amounts of rhenium (up to 4 wt%) was investigated. It was revealed that Re addition causes the formation of Ni-Re alloy during high temperature reduction, which was confirmed in deep XRD and STEM studies. The addition of small amounts of rhenium to the nickel catalyst greatly reduces coking in DRM. Unlike other promoters (e.g. K), this does not result in a reduction of catalyst activity. These observations were obtained while simultaneously measuring the activity and rate of coking with the use of an oscillating microbalance (TEOM). The analysis of the reduced catalyst diffraction patterns showed that the increasing amount of rhenium caused the systematic shift of the Ni (111) peak towards smaller diffraction angles. This shift demonstrated the lattice expansion of the Ni unit cell, likely due to the incorporation of Re into the Ni lattice. This indicates the formation of Ni-Re alloy during high temperature reduction. The distribution maps of Ni and Re on the surface of the catalysts obtained by means of STEM-EDS analysis confirmed the alloy formation found in the XRD study. In the range of up to 4 wt.% of rhenium in the active phase of the catalysts, a linear increase of the interplanar distance in Ni-Re alloys was found. XPS tests showed the presence of rhenium surface segregation in Ni-Re catalysts. HRTEM studies proved that the addition of rhenium causes changes in the morphology of the formed carbon deposit. The formation of full carbonaceous filaments and no crystallite deformation of the Ni-Re alloy proves a low carbon nucleation rate. It seems that this may be related to the lower dehydrogenation degree of surface species CH_y on the Ni-Re alloy surface than on the nickel surface. The addition of small amounts of rhenium to the nickel catalyst is sufficient to obtain a good catalyst for methane reforming with CO_2.

Acknowledgements: Research done with a research subsidy awarded by the former Ministry of Science and Higher Education. The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Programme (contract no. POIG.02.01.00-06-024/09 Centre for Functional Nanomaterials).

P-3

DFT studies of (M-porphine)$_2$ dimers (M = Fe, Ni, Mn, Co) as models of binuclear transition metal sites

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Enzymes are Nature’s catalysts to run important chemical processes. Typically, they contain single metal sites, but those bearing two metal centers in proximity (having binuclear active sites) are also known. Enzymes bearing binuclear active sites are responsible for various chemical processes, such as methane oxidation as is observed for particulate methane monooxygenase which contains two copper ions in its active site, or soluble methane monooxygenase containing two iron ions in its active canter.
In the current project, we aim at the exploration of inorganic analogues of the bimetallic sites in enzymes (modelled by porphyrin moiety) as the reactivity of the binuclear sites introduced into the zeolitic matrices that were recently developed in J. Heyrovský Institute of Physical Chemistry, Prague (JHI).
To understand the observed reactivity, we performed quantum-chemical calculations in the frame of Density Functional Theory (DFT) with B-P/PBE/B3-LYP functionals and the def2-TZVP basis set. Calculations were done with Turbomole program package.
In the first instance, transition metal ion (TMI) (TMI = Fe, Co, Mn, Ni) in porphyrin rings placed face-to-face at variable distances were studied. By varying the metal-to-metal distance we could study the influence of the separation of both TMI. This would affect not only the ability to split O_2/N_2O but also the further formation of highly active oxygen species, α-oxygens ([TMI $^{4+}$=O]$^{2+}$) and their interaction with hydrocarbons. Thus, the capability to activate dioxygen and N_2O by splitting was further studied for selected systems.

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P-4

The effect of iron doping on the activity and selectivity of Cu-SSZ-13 catalysts in the NH_3-SCR process

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Reducing NOx emissions from combustion engines to the limits set by European standards (Euro VI, 0.06 g km^{-1} - for gasoline engines and 0.08 g km^{-1} - for diesel engines) is a challenge for contemporary environmental catalytic chemistry. The most frequently used technology for the elimination of NOx from exhaust gases is the selective catalytic reduction of NO by ammonia (NH_3-SCR), which is characterized by high efficiency.

This study aimed to investigate the effect of doping the CuSSZ-13 zeolite with iron on the activity (widening of the operating temperature range) and selectivity (reduction of the share of side reactions) in the NH_3-SCR process. Bimetallic Cu-Fe-SSZ-13 catalysts were obtained in two stages: by introducing Cu at the step of the support zeolite synthesis (one pot synthesis), and then ion exchange carried out in solutions with various concentrations of Fe ions. Zeolites containing Cu and Fe were characterized in terms of their structure and morphology (XRD, XRF,TEM/EDX) and acid/base properties (NH_3-TPD). The activity tests were carried out in a fixed-bed reactor in a reaction mixture containing 500 ppm NH_3, 500 ppm NO, 4.5% O_2 with or without H_2O. The reaction progress of Cu-Fe zeolites was investigated by means of FT-IR spectroscopy and quadrupole mass spectrometer.

The strong influence of iron concentration on the activity of NH_3-SCR catalysts was demonstrated. Even a small addition of iron allowed to increase the range of the temperature window in which the NO conversion is 100% by approx. 40 °C. The introduction of iron significantly improved the selectivity to N_2. About half of the by-products of the reaction, *i.e.* N_2O and NO_2, are reduced.

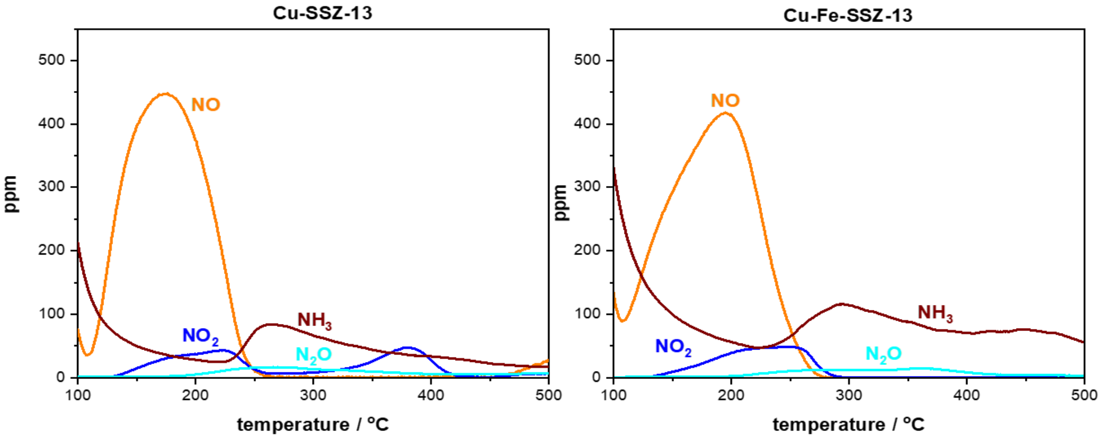

Fig. 1. Distribution of the substrates and products of the NH_3-SCR reaction in the presence of Cu-SSZ-13 and Cu-Fe-SSZ-13 catalysts.

The work was carried out within the MOST program for bilateral collaboration between Poland and China, which is financially supported by The National Centre for Research and Development, Poland, grant PNOX no. WPC1/PNOX/2019 and . from China side by the Project 2017YFE0131200.

P-5

“Self-diffusion” of ibuprofen molecules into mesopores of SBA-15

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Ibuprofen is one of the main anti-inflammatory drugs. It has been widely used in guest-host systems, where it was introduced mainly to mesoporous materials based on silica, carbons, or polymers. The main method of ibuprofen introduction into mesopores relies on making a solution of the active compound in various solvents like ethanol [1]. That method needs consequent evaporation of the solvent, which could impact the state of the final sample.

Ibuprofen introduced into mesopores experiences a specific confinement effect. The molecules of this drug have high mobility when confined into pores of 5 – 50 nm. It is particularly seen in ^{1}H MAS NMR spectra, which exhibit very narrow signals in comparison to the bulk compound. It has been showed that water vapour is essential to observe this effect [2]. Generally, it is ascribed to ibuprofen molecules located inside mesopores.

In this study, the physical mixtures of ibuprofen and SBA-15 were prepared with 9 and 25% weight of the drug. The samples were not heated or modified in any way. They were stored on a shelf in closed containers. The samples were characterized using X-ray diffractometry (XRD), magic angle spinning Nuclear Magnetic Resonance spectroscopy (MAS NMR), and N_2 sorption after 1 week or more of shelf life.

The results show that the samples after 1 week or more of the shelf life show a lower amount of crystallized ibuprofen than the samples measured right after the preparation. The mesopore volume decreases after this time which hints at the filling of the mesopores with the drug of the molecules. ^{1}H MAS NMR spectra show that there is a distinctive increase in the resolution of the spectra, which suggests that the increased number of ibuprofen molecules resides inside mesopores. Also, ^{13}C MAS NMR spectra show characteristic features for confined ibuprofen: the decreased intensity of CP spectra and the presence of the signals characteristic for confined ibuprofen (for the spectra recorded with high-power decoupling). This “self-diffusion” phenomenon is tentatively ascribed to the interaction of water vapour with ibuprofen in these samples.

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P-6

Modified silicalite-1 as acid catalysts and catalytic supports
La doped Ni/ZrO$_2$ catalyst for the upgrading of biomass pyrolysis vapors

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The constantly growing demand for energy and the need for reduction of the emission of pollutants to the environment encourage the researches to find new energy sources. The wide availability of various types of biomass and its neutrality in terms of greenhouse gas emission make it one of the most promising renewably materials for energy and fuel production. However, conversion cost of biomass conversion must be reduced to make this process economically viable. That is why the present work is focused on the development of efficient catalyst for the upgrading of biomass pyrolysis vapors to hydrogen-rich gas.

Previous research conducted at our group proved promising catalytic performance of Ni supported on ZrO$_2$ [1]. In order to increase the efficiency of H$_2$ production we decided to modify this material by La doping.

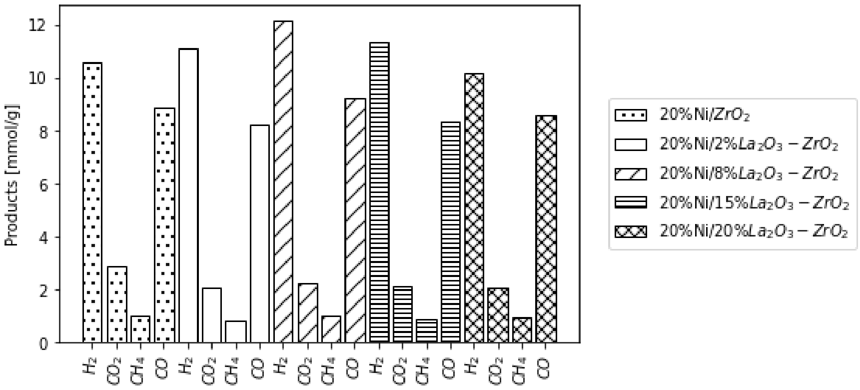

Fig. 1. Activity of La doped Ni/ZrO$_2$ catalyst in upgrading of cellulose pyrolysis vapors.

La$_2$O$_3$-ZrO$_2$ support was prepared by sol – gel method using various contents of lanthanum (2%, 8%, 15%, 20%). Nickel was deposited on the support surface by impregnation method. Catalytic activity tests were conducted under atmospheric pressure at 700°C with the use of cellulose as a model substance. The gaseous products were analyzed by gas chromatograph equipped with TCD detector. Physicochemical properties of prepared catalysts were characterized using TPR, TPD-NH$_3$, TPD-CO$_2$, XRD, BET surface analysis, ToF-SIMS and FTIR.

The obtained results showed that modification of Ni/ZrO$_2$ catalyst by La allows for the increase in the H$_2$ production of about 20% (Fig. 1). The most active material contained 8% of lanthanum. It is suggested that the presence of dopant increases the number of defects in the support structure leading to the formation of oxygen vacancies participating in biomass conversion [2,3].

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P-7

Performance of La_2O_3 promoted Co/CeO_2 catalysts for effective hydrogen production by ethanol steam reforming

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Hydrogen may be generated from ethanol by steam reforming (SRE). However, one of the main barriers of this process is the catalyst deactivation that occurs mainly due to carbon deposition on the catalyst surface, which may lead to decrease in catalytic activity and selectivity toward hydrogen. Therefore, the feasibility of SRE process requires the development of catalysts that are active and highly selective toward hydrogen, and also with high stability and low impact for coke formation. Several metallic active phase have been used for the catalytic SRE process because of their ability to break the C─C bond; mainly cobalt, nickel and noble metals. Moreover, in the case of redox supports like ceria, their high oxygen mobility promotes the mechanism of carbon removal, which in turn contributes to the high stability of the catalysts on ethanol conversion reactions [1]. On the other hand, thermal stability of ceria is poor, its surface area drops drastically at elevated temperature, leading to the decrease of its redox property and oxygen storage capacity on the surface of ceria. Therefore, it is necessary to improve the thermal properties of ceria and modify the ionic mobility by replacement of cerium with different cations of varying size and/or charge that leading to the formation of a defective fluorite structures solid solution. The doped ceria increases the surface properties and sintering temperature of the sample to higher temperatures [2, 3]. The lanthanum-doped ceria has been reported for an important role for the enhancement of the structural and catalytic properties of CeO_2-based system. The Co-0.1La/CeO_2 catalyst was obtained by simple, fast and inexpensive co-impregnation method as a potential materials being active, stable and highly selective to hydrogen and carbon dioxide in SRE reaction. Despite small addition of La_2O_3 to the catalyst of 2 wt.% corresponding to La/Co molar ratio of 0.1, catalyst exhibited much better stability, higher ethanol conversion, higher capability to C─C bond cleavage and smaller amount of by-products under SRE conditions at 420 °C than unpromoted catalyst. The addition of La_2O_3 promoter to the Co/CeO_2 catalysts did not influence on these properties of carbonaceous deposition. However, its effect on the amount of formed carbon deposits was significant. The temperature of 500 °C was required to sustain Co-0.1La/CeO_2 catalyst stable operation and selectivity to H_2 and CO_2 was equal to 94% and 88%, respectively. Besides CH_4 and CO produced in low amounts, the CH_3CHO at trace level was only detected among by-products.

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P-8

Zwiększenie aktywności katalizatora kobaltowo-ferierytowego w reakcji dopalania sadzy w wyniku domieszkowania potasem

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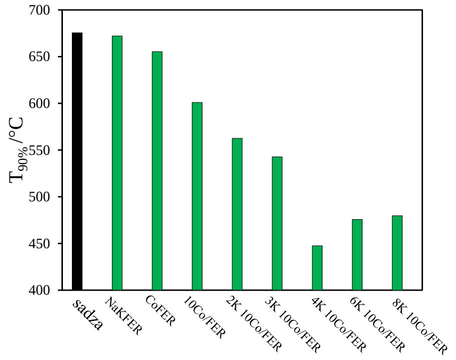
Cząstki sadzy, wykazujące właściwości mutagenne i rakotwórcze, są wysoce niebezpieczne dla organizmu człowieka. Wobec tego poszukiwane są skuteczne rozwiązania ograniczające ich emisję. Aktualnie cząstki sadzy pochodzące z niecałkowitego spalania paliw są usuwane za pomocą filtrów DPF. Niestety długotrwałe użytkowanie powoduje blokadę ich kanałów. Dlatego prowadzone są intensywne badania ukierunkowane na opracowanie skutecznego katalizatora utleniania sadzy. Najpowszechniej badane są katalizatory oparte na metalach szlachetnych, takich jak Pt, Pd, Rh. Jednakże, wobec ich wysokiej ceny oraz limitowanej dostępności, atrakcyjną alternatywę stanowią układy na bazie metali przejściowych, takich jak Co, Fe, Cu. Równocześnie, działanie katalizatorów procesu dopalania sadzy można ulepszyć poprzez dodatek promotorów alkalicznych [1]. Dodatkowo, zeolity o dobrze zdefiniowanych strukturach porowatych i rozwiniętej powierzchni zasługują na uwagę w kontekście ich zastosowania w roli nośników faz aktywnych [2].

W prezentowanej pracy zbadano serię katalizatorów kobaltowych opartych na nośniku ferrierytowym (NaKFER), domieszkowanych potasem w zakresie 0-8% wag. Katalizatory zawierały kobalt w ilości 10% wag. (10Co/FER). Zbadano także materiał referencyjny zawierający kobalt w pozycjach jonowymiennych (CoFER). Otrzymane układy scharakteryzowano metodami XRD, XRF, H_2-TPR, SEM/EDX oraz niskotemperaturowej adsorpcji N_2. Ich aktywność katalityczną w procesie dopalania sadzy (Printex U) zbadano przy zastosowaniu pomiarów termograwimetrycznych (TGA/MS) w przepływie mieszanki 5%O_2/He. Pomiary prowadzono w trybie ścisłego kontaktu sadza-katalizator. Dodatkowo zbadano stan promotora potasowego z wykorzystaniem metody desorpcji termicznej alkaliów (SR-TAD) [3].



Rys. 1. Porównanie aktywności katalizatorów w dopalaniu sadzy ($T_{90\%}$).

Zaobserwowano silny pozytywny wpływ dotacji potasem na aktywność katalizatora 10Co/FER, zależny od zawartości K (Rys. 1). Najwyższą aktywność uzyskano dla katalizatora domieszkowanego potasem w ilości 4%wag. (4K 10Co/FER). Materiał ten wykazał konwersję sadzy na poziomie 90% w temperaturze poniżej 450°C.

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P-9

Wpływ ciśnienia na utlenianie amoniaku

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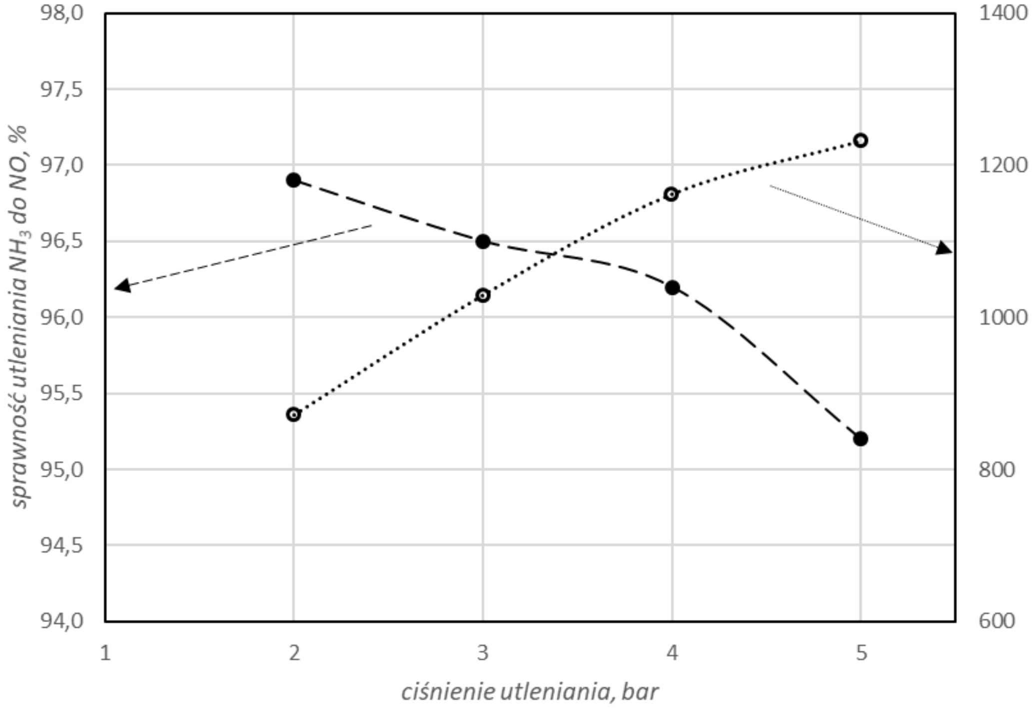
W reaktorze utleniania amoniaku w reakcji utleniania amoniaku zachodzącej na katalizatorze Pt-Rh produktami zawierającymi azot są: NO (produkt główny), N_2O i N_2 (produkty uboczne) i zgodnie z regułą przekory w reakcji:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

wzrost ciśnienia (ΔV>0) niekorzystnie wpływa na sprawność utleniania amoniaku. Z drugiej strony zastosowanie wyższego ciśnienia w procesie przemysłowym pozwala na zwiększenie wydajności jednostkowej reaktora.

Wykonane w skali pilotowej badania (Q = 5 t N/(m^{2}d), $T_{reakcji}$ = 910°C) wpływu ciśnienia w zakresie 2–5 bar pozwoliły na ilościowe określenie sprawności utleniania NH_3 do NO i selektywności reakcji (ilość powstającego N_2O) (rys. 1).



Rys. 1. Wpływ ciśninia na sprawność i selektywność utleniania.
Warunki reakcji Q= 5 t N/m^{2}d, T=910°C

Zastosowanie pod pakietem Pt-Rh warstwy katalizatora do rozkładu podtlenku azotu pozwala na obniżenie stężenia N_2O w gazach poreakcyjnych. Stopień rozkładu N_2O wzrasta wraz z ciśnieniem w reaktorze, co związane jest z zwiększeniem czasu przebywania.

Obliczone, na podstawie wyników pomiarów, wartości stałej szybkości reakcji *k* wskazują na wpływ ciśnienia na przebieg reakcji rozkładu N_2O. Otrzymane różne wartości *k= f(p)* mogą świadczyć o tym, że równanie kinetyczne reakcji rozkładu N_2O pierwszego rzędu powinno być skorygowane o poprawkę ciśnieniową.

P-10

Modyfikacja plazmą mezoporowatych materiałów węglowych w kierunku poprawy adsorpcji kationów metali przejściowych

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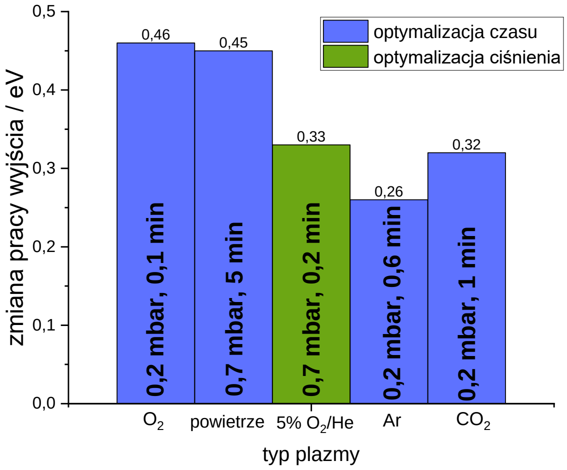
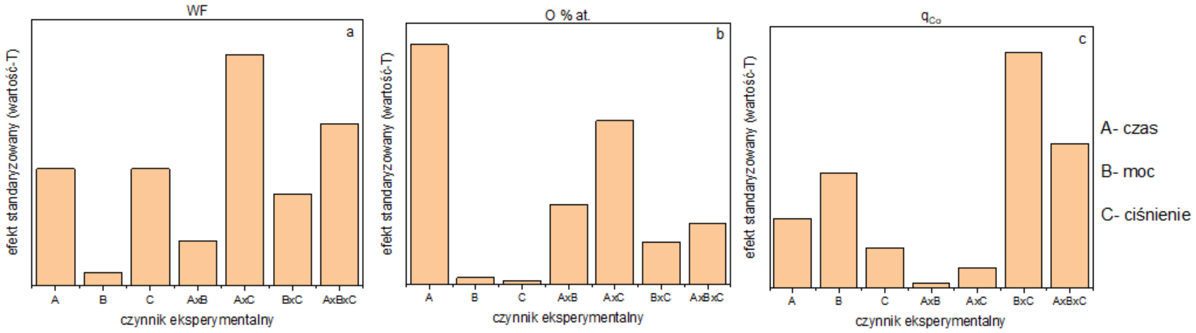
Materiały węglowe znajdują szerokie zastosowanie w procesach adsorpcyjnych i katalitycznych ze względu na dużą powierzchnie właściwą oraz wysokie przewodnictwo elektryczne. Wykonanie modyfikacji powierzchni umożliwia polepszenie ich reaktywności, a co za tym idzie poprawę własności adsorpcyjnych. Coraz częściej stosowaną metodą jest funkcjonalizacja za pomocą plazmy niskotemperaturowej, która w sposób prosty, szybki i kontrolowany pozwala na wprowadzenie polarnych grup funkcyjnych na powierzchnię badanego materiału, których typ zależy od rodzaju użytego gazu.

W przedstawionych badaniach stosując metodologię Design of Experiments (DoE) wykonano serię pomiarów mających na celu modyfikacje papieru grafenowego za pomocą plazmy. W tym celu użyto różnych gazów (O_2, powietrze, 5% O_2/He, CO_2, Ar). Metodologia ta pozwoliła na wybranie optymalnych parametrów modyfikacji dla każdej z zastosowanych plazm (czas użycia plazmy, ciśnienie i moc generatora). Zastosowanie tego rodzaju funkcjonalizacji powierzchni prowadzi do zmiany pracy wyjścia, która zależy od ilości i rodzaju grup funkcyjnych. Praca wyjścia jest parametrem opisującym właściwości elektronowe materiału, a jej pomiar można szybko wykonać przy użyciu sondy Kelvina. Największą zmianę pracy wyjścia dla papieru grafenowego zaobserwowano dla plazmy tlenowej, przy czym zastosowanie powietrza jako gazu umożliwiło uzyskania wzrostu pracy wyjścia na porównywalnym poziomie.



Wykres 1. Maksymalna zmiana pracy wyjścia dla każdego typu plazmy.

Do przeprowadzenia testów adsorpcji wykorzystano wysokopowierzchniowy węgiel mezoporowaty otrzymany z matrycy krzemionkowej (C-KIT-6) oraz najbardziej efektywną plazmę tlenową. Sprawdzono ilość i typ wprowadzonych grup funkcyjnych za pomocą spektroskopii XPS oraz właściwości strukturalne wykorzystując spektroskopię Ramana, a także przeprowadzono pomiary adsorpcji. Ponieważ materiał C-KIT-6 posiada inną morfologię niż wcześniej badany papier grafenowy ponownie wykonano optymalizację DoE dla zmiany pracy wyjścia (WF), jak również ilości wprowadzonych grup tlenowych z XPS (O % at.) i pojemności sorpcyjnej kationów kobaltu (q_{Co}).



Wykres 2. Optymalizacja parametrów modyfikacji węgla mezoporowatego C-KIT-6 za pomocą metodologii DoE przeprowadzone odpowiednio dla: a - pracy wyjścia, b - ilości wprowadzonych grup tlenowych oznaczonych z wykorzystaniem XPS, c – pojemności sorpcyjnej kobaltu.

Wykonane badania pozwalają na stwierdzenie, że ani struktura, ani morfologia badanych materiałów nie ulegają zmianie po modyfikacji, natomiast zmieniają się właściwości powierzchniowe. Metodologia DoE nie wskazuje na obecność korelacji między wynikami uzyskanymi z wykorzystaniem różnych kryteriów (WF, O %at., q_{Co}, Wykres 2), co sprawia, że w zależności od kryterium optymalizacyjnego (praca wyjścia, ilość tlenowych grup funkcyjnych, adsorpcja) uzyskuje się inne parametry plazmy wpływające na maksymalizację pożądanego efektu. Obserwowany brak korelacji między DoE dla różnych kryteriów optymalizacyjnych można tłumaczyć złożonością układu i brakiem liniowej zależności pomiędzy wykorzystanymi parametrami. Największy wpływ na wyniki adsorpcji metali na materiale węglowym miały zarówno moc generatora jak i ciśnienie w komorze plazmy, co oznacza, że kombinacja tych dwóch parametrów powinna być poddana dalszej optymalizacji celu maksymalizacji pojemności sorpcyjnej jonów metali przejściowych dla materiału C-KIT-6.

Podziękowania: Prezentowane badania stanowią część projektu OPUS o numerze 2020/37/B/ST5/01876 finansowanego przez Narodowe Centrum Nauki w Polsce.

P-11

Węgle aktywne z odpadów przemysłu spożywczego - charakterystyka otrzymanych materiałów węglowych oraz ich wykorzystanie w syntezie produktów o wysokiej wartości dodanej z α -pinenu

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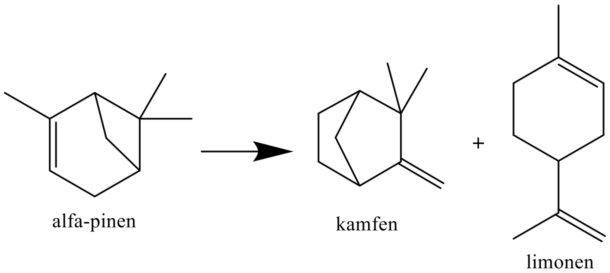
Synteza węgli aktywnych z biomasy stała się interesującym sposobem uzyskania użytecznych materiałów węglowych z surowców będących odpadami przemysłu spożywczego [1]. Biorąc pod uwagę ilość wytwarzanych bioodpadów, a także problem z ich składowaniem i bezpieczną dla środowiska utylizacją, należy dążyć do rozwoju technologii zagospodarowania tej biomasy. Zaletami węgli aktywnych pozyskiwanych z biomasy są bardzo dobre właściwości teksturalne otrzymanych materiałów i niskie koszty produkcji w porównaniu z komercyjnymi węglem aktywnym [2]. Przykładem zastosowania materiałów węglowych jest wykorzystanie ich w reakcjach katalitycznych, w tym w reakcji izomeryzacji α-pinenu. Reakcja ta pozwala na otrzymanie cennych związków organicznych (kamfen i limonen) z stosunkowo taniego surowca jakim jest α-pinen. Produkty te są wykorzystywane w wielu sektorach przemysłu takich jak np. przemysł perfumeryjny, kosmetyczny, spożywczy i farmaceutyczny [3].



Rys. 1. Główne produkty powstające w procesie izomeryzacji alfa-pinenu.

Celem pracy było otrzymanie węgli aktywnych z biomasy (skórek pomarańczy, łupin słonecznika oraz fusów kawowych) za pomocą aktywacji chemicznej z wykorzystaniem H_3PO_4 jako aktywatora chemicznego oraz karbonizacji w piecu rurowym (800°C, gaz inertny), a następnie sprawdzenie ich aktywności katalitycznej w reakcji izomeryzacji α-pinenu. Otrzymane materiały zostały scharakteryzowane z wykorzystaniem sorpcji N_2 (-196°C), SEM, XRD, FT-IR. Materiały charakteryzowały się powierzchnią właściwą w zakresie 930 - 1761 m^2/g.

Reakcję izomeryzacji α -pinenu prowadzono w szklanym reaktorze umieszczonym w łaźni olejowej z chłodnicą zwrotną. Aktywność katalityczną otrzymanych materiałów węglowych badano w najkorzystniejszych warunkach ustalonych podczas badań wstępnych. Głównymi produktami otrzymywanymi w procesie izomeryzacji α-pinenu były kamfen oraz limonen. Oba te związku znajdują szerokie zastosowanie w wielu gałęziach przemysłu.

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

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P-12

Odziaływanie tlenowych grup funkcyjnych z kationami metali przejściowych na powierzchni grafenu

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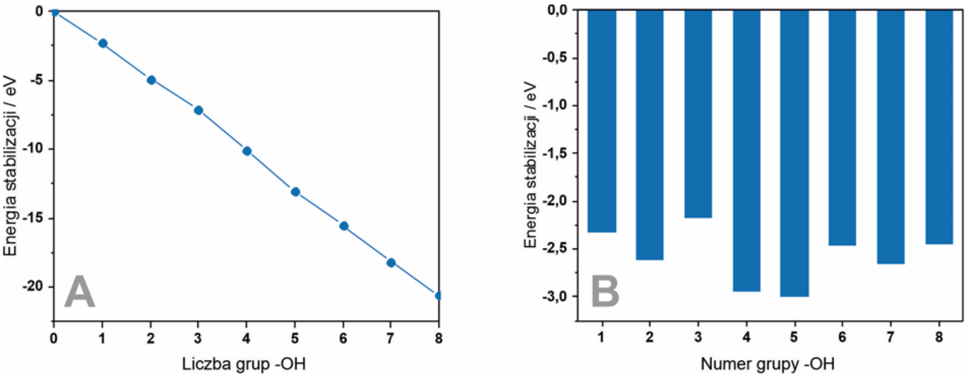
Materiały węglowe ze względu na swoje atrakcyjne właściwości m.in. rozwiniętą powierzchnię właściwą i stosunkowo wysokie przewodnictwo elektryczne znalazły zastosowanie jako katalizatory i adsorbenty. Dodatkowo, poprzez modyfikację ich powierzchni, można znacznie poprawić ich reaktywność oraz efektywność depozycji fazy aktywnej do zastosowań katalitycznych.

W ramach prezentowanych badań zaproponowano serie modeli obliczeniowych opisujących potencjalne ugrupowania stabilizowane na powierzchni grafenu. Do modelowania modyfikacji płaszczyzny wybrano grupy hydroksylowe (–OH), karboksylowe (–COOH), karbonylowe (–COH) oraz epoksydowe (-O-). Zbadano wpływ stężenia powierzchniowego tych grup na ich stabilność. Dla wszystkich modeli określono optymalną geometrię oraz obliczono energię stabilizacji. Dla najstabilniejszych konfiguracji przeprowadzono modelowanie adsorpcji kationów metali przejściowych. Wszystkie obliczenia wykonano za pomocą metody DFT.

Przeprowadzona analiza wykazała, że wraz ze wzrostem stężenia tlenowych grup funkcyjnych na powierzchni grafenu stabilność danych ugrupowań rośnie liniowo. Zależność ta wskazuje, iż kolejne grupy są stabilizowane w podobny sposób bez wyraźnych oddziaływań lateralnych, stabilizujących lub destabilizujących. Przykładowo, dla grupy hydroksylowej stabilność kolejnych grup wykreślono w funkcji ilości stabilizowanych grup, Rysunek 1A, zaś energie stabilizacji kolejnych grup –OH pokazano na Rysunku 1B.



Rysunek 1. Energia stabilizacji grup -OH na powierzchni grafenu w zależności od ich ilości, A) sumaryczna energia stabilizacji oraz B) energia stabilizacji każdej kolejnej grupy.

W celu weryfikacji obliczeń kwantowo-chemicznych próbki płatków grafenowych zmodyfikowano za pomocą niskotemperaturowej plazmy CO_2 oraz powietrza w celu wytworzenia powierzchni o różnych dominujących grupach funkcyjnych. Dla powierzchniowo utlenionych materiałów wykonano równowagową adsorpcję kationów metali przejściowych.

Podziękowania: Prezentowane badania stanowią część projektu OPUS o numerze 2020/37/B/ST5/01876 finansowanego przez Narodowe Centrum Nauki w Polsce.

P-13

Izomeryzacja α-pinenu na wermikulicie modyfikowanym kwasami

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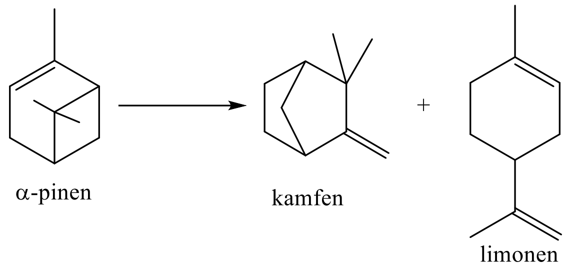
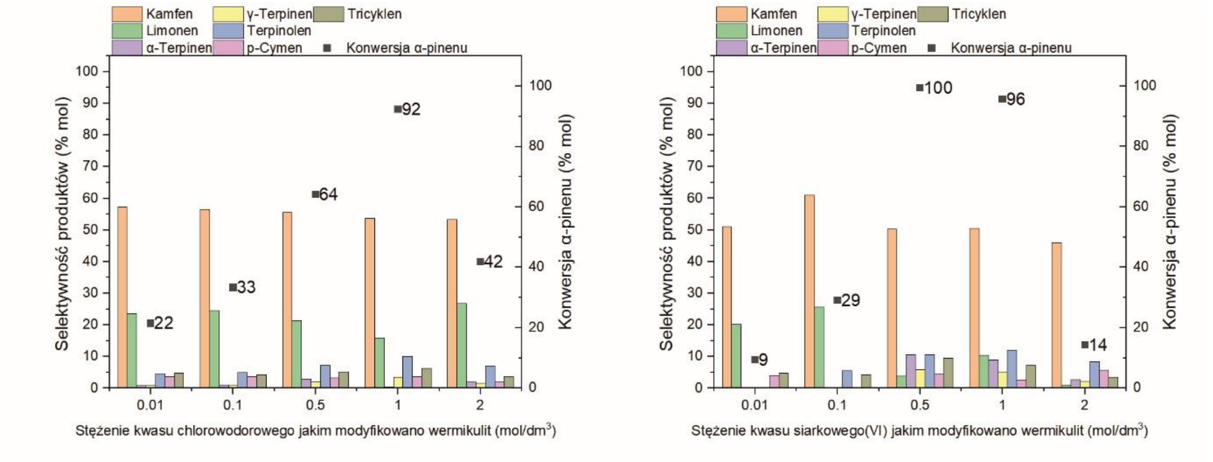
Naturalne materiały porowate dzięki takim właściwościom, jak: dobrze rozwinięta powierzchnia właściwa, dobre właściwości sorpcyjne oraz dobre właściwości jonowymienne, cieszą się dużym zainteresowaniem w wielu gałęziach przemysłu. Ich dodatkowym atutem jest ich różnorodność, wynikająca z różnic w budowie, w składzie chemicznym oraz w strukturze. Naturalne materiały porowate są łatwo dostępne w dużych ilościach. Wszystkie te zalety, a w szczególności dobre właściwości jonowymienne, wpłynęły na wybór tych materiałów do przeprowadzania różnych modyfikacji, w celu otrzymania bardziej aktywnych ich form, o pożądanych właściwościach katalitycznych, czy adsorpcyjnych w danym procesie technologicznym [1].

Modyfikacja kwasami krzemianów oraz glinokrzemianów, w tym wermikulitu, jest metodą prostą, szybką i nie wymagającą wielu etapów.–Ma ona na celu poprawienie właściwości kwasowych modyfikowanego materiału i jednocześnie ma ona wpłynąć na jego właściwości katalityczne lub adsorpcyjne. Proces ten powoduje wzrost ilości miejsc kwasowych na powierzchni modyfikowanego materiału [2]. Takie właściwości sprawiają, że wermikulit modyfikowany kwasami jest dobrym katalizatorem reakcji izomeryzacji α-pinenu. Reakcja ta prowadzi do powstania z największą selektywnością dwóch produktów: kamfenu oraz limonenu [3].



Rys. 1. Główne produkty izomeryzacji α-pinenu

Wermikulit modyfikowano kwasem siarkowym (VI) oraz chlorowodorowym o następujących stężeniach: 0,01, 0,1, 0,5, 1 oraz 2 mol/dm^3. W tym celu przygotowano naważkę wermikulitu w reaktorze szklanym i dodano roztwór odpowiedniego kwasu w następującym stosunku: 1g wermikulitu na 15 cm^3 roztworu kwasu. Reaktor umieszczono w łaźni olejowej i włączono mieszanie z intensywnością 220 rpm. Modyfikacja była prowadzona w temperaturze 80°C przez 4 h. Później zmodyfikowany wermikulit odsączono na lejku Büchnera pod zmniejszonym ciśnieniem, w celu oddzielenia roztworu od modyfikowanego materiału i przemyto go wodą destylowaną. Następnie otrzymaną próbkę wermikulitu suszono w suszarce w 100°C przez 24 h. Otrzymane próbki scharakteryzowano za pomocą następujących metod instrumentalnych: FTIR, UV-Vis, XRD oraz oznaczono kwasowość całkowitą metodą miareczkową. Badania aktywności tych próbek w procesie izomeryzacji α-pinenu prowadzono w temperaturze: 140°C, przy zawartości katalizatora (modyfikowany wermikulit) 5% wag. oraz dla czasu reakcji 2 h. Wyniki przedstawiono na wykresach poniżej.



Rys. 2. Wpływ wermikulitu modyfikowanego roztworami kwasu siarkowego (VI) oraz kwasu chlorowodorowego o stężeniach: 0,01, 0,1, 0,5, 1 oraz 2 mol/dm^3 na selektywności przemiany α-pinenu do odpowiednich produktów oraz na konwersję α-pinenu (temperatura 140°C, ilość katalizatora 5% wag., czas reakcji 2 h)

Najwyższe wartości konwersji α-pinenu uzyskano dla próbek wermikulitu modyfikowanego roztworami kwasu siarkowego (VI) o stężeniach 0,5 oraz 1 mol/dm^3. Wartości konwersji α-pinenu dla tych dwóch próbek wynosiły odpowiednio: 99,5 oraz 95,7% mol, a selektywności przemiany α-pinenu do kamfenu i limonenu (główne produkty) osiągnęły następujące wartości: kamfen 50% mol oraz limonen 5% mol. Najwyższą wartość konwersji α-pinenu uzyskano dla próbki wermikulitu modyfikowanego roztworem kwasu chlorowodorowego o stężeniu 1 mol/dm^3, a wartość konwersji α-pinenu dla tej próbki wyniosła 92,4 %mol. Selektywność przemiany α-pinenu do kamfenu i limonenu (główne produkty), wynosiły odpowiednio: kamfen 53,7% mol oraz limonen 15,8% mol. Z przeprowadzonych badań wynika, że wermikulity modyfikowane kwasami są doskonałymi katalizatorami izomeryzacji α-pinenu.

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P-14

Catalytic Reactivity of $Co_3O_4|CeO_2$ n-p Heterojunctions in $^{16}O_2/^{18}O_2$ Isotopic Exchange, CO Oxidation and N_2O Decomposition

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Spinel oxide catalysts owing to their high activity in numerous reactions of environmental relevance are recently extensively investigated. One of the way along which their activity may be enhanced is formation of catalytic junctions. An efficient way to synthesize cobalt spinel and ceria-based heterojunction exposing the most active and stable (100) facets was developed. Nanocubes of Co_3O_4 and CeO_2 were synthesized by means of hydrothermal methods and combined together by sonication and subsequent calcination. The samples were characterized by means of XRD, RS, SEM/TEM/STEM/EDX and XPS techniques. Oxygen isotopic exchange experiments were conducted to investigate surface and bulk oxygen mobility followed by CO oxidation and N_2O decomposition studies in the TPSR mode. Implementing Mathematica code allowed to solve kinetic equations to determine the corresponding kinetic parameters (activation energies and preexponential factors for the distinguished elementary steps).

Powder diffractograms as well as Raman spectra analysis did not reveal presence of any foreign phase in the synthetized samples. The TEM imaging analysis revealed cubic-shaped nanocrystals (Fig. 1 a,b) with morphology confirmed by gradient analysis of the HAADF STEM images. SEM micrographs of the heterojunctions confirm the presence of the exposed (100)-facet junctions between CeO_2 and Co_3O_4 (Fig. 1 c). EDX mapping revealed the mutual spatial arrangement of the Co and Ce moieties and indicate effective heterojunction formation (Fig. 1 d).

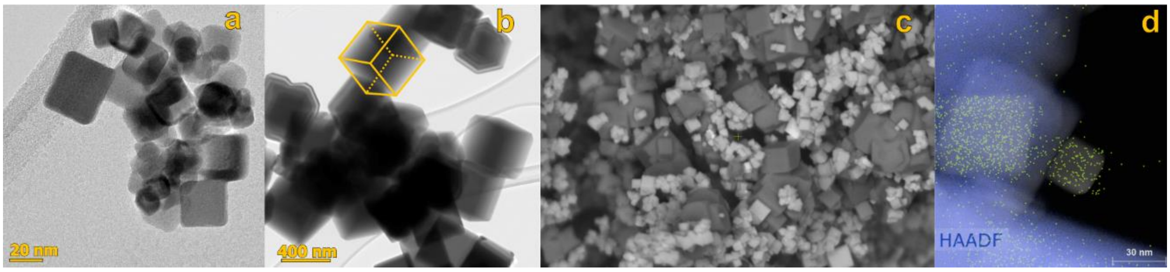

Fig. 1a, b – TEM BF images of CeO_2 and Co_3O_4 precursors, respectively, c) – HR-SEM image of the $Co_3O_4|CeO_2$ heterojunctions, d) – EDX mapping of the $Co_{10}Ce$ junctions.

XPS spectra analysis was used to determine the energy band alignment using the Kraut method. An electron transfer from Co_3O_4 into CeO_2 was found and shown to be crucial for explaining the synergistic effect of the produced n-p junction in the N_2O decomposition. Isotopic oxygen $^{18}O_2/^{16}O_2$ exchange experiments indicate occurrence of suprafacial and intrafacial oxygen exchange, following the simple and complex heteroexchange mechanism (Fig. 2b,c). N_2O decomposition test revealed a positive interface effect, with the $Co_{10}Ce$ heterojunction exhibiting the best performance, and significantly lower $T_{50\%}$ than that found for parent cobalt spinel (Fig. 2a). In contrast to N_2O decomposition, in the case of CO oxidation (Fig. 2d) the synergistic effect was not found, and the catalyst activity increased with the cobalt spinel content in a monotonous way.

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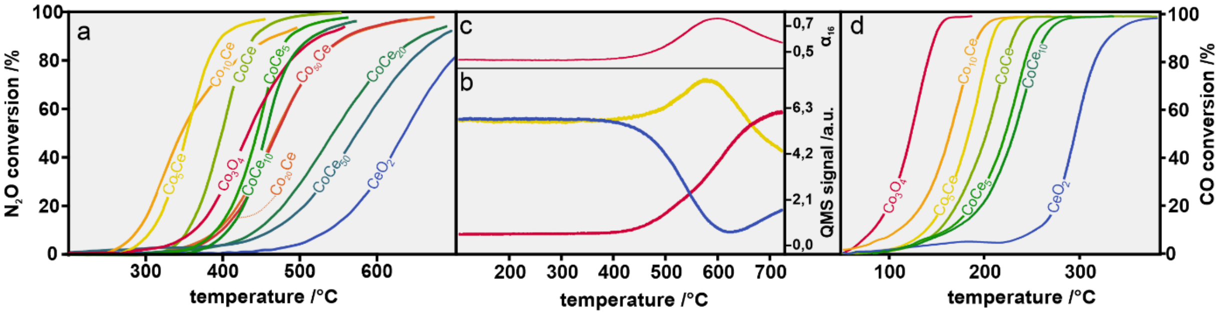

Figure 2. a) N_2O decomposition conversion curves with different heterojunctions, b) oxygen isotopic exchange reaction over CeO_2 precursor with its alfa-16 parameter dependence on temperature.

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P-15

A new organic-inorganic hybrid material: synthesis, structure determination and catalytic properties in Baeyer-Villiger oxidation

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Polyoxometalates (POMs) are a class of inorganic compounds which combine oxygen and early transition metals (e.g., Nb, V, Mo, W) at their highest oxidation states [1]. They exhibit variable structures and rich electronic and magnetic properties. There is a possibility, not often present in catalysis, to adjust the composition in a special way to allow for the introduction of those elements which are necessary to obtain desired properties [2]. They contain an utmost large number of atoms in a relatively compact, three-dimensional structure. The POM structures are not only interesting in terms of their structural diversity, but also due to the wide range of applications, e.g. in catalysis, materials science or medicine. Peroxidocompounds can be considered as a part of the POMs group. Typical for such compounds are peroxo (O-O) bonds in clusters surrounding the transition metal atom [3]. POMs have found widespread applications in catalysis [4]. In particular, they are capable of using green oxidants to catalyze numerous reactions.

The goal of our work was the synthesis of two new oxo-diperoxido-molybdenum complexes obtained with derivatives of pyridine acids and the determination of their crystal structure, physicochemical properties and catalytic properties in Baeyer-Villiger oxidation of cyclohexanone in Mukaiyama conditions.

Newly synthesized Na35dcpa and Na-isoO structures are sodium salts and organic-inorganic hybrids. The organic components, 3,5-dicarboxylicpyridine acid or N-oxide isonicotinic acid, are derivatives of pyridine acids which were incorporated in the investigated structures, respectively. The inorganic part contains a pentagonal bipyramid where the central molybdenum atom is surrounded by oxygen atoms. There are observed two peroxo groups and one apical terminal oxygen atom in each inorganic center.

The Baeyer-Villiger oxidation of cyclohexanone with molecular oxygen was performed in a thermostated glass reactor at 40^{o}C for 5h at atmospheric pressure. Both samples demonstrate relatively high catalytic activity. The activity of Na35dcpa is slightly higher than that of Na-isoO. A comparison of newly synthesized samples with their potassium counterparts reveals that K35dcpa shows the highest catalytic activity in the studied reaction. On the contrary, K-isoO is the least active among the studied catalysts. Summarizing, the catalytic activity of investigated compounds is dependent on the type of alkali metal cation and on the type of pyridine derivative as well as the amount and position of carboxylic groups.

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P-16

Selectivity tuning in HMF hydrogenation by Ni-Fe catalyst design

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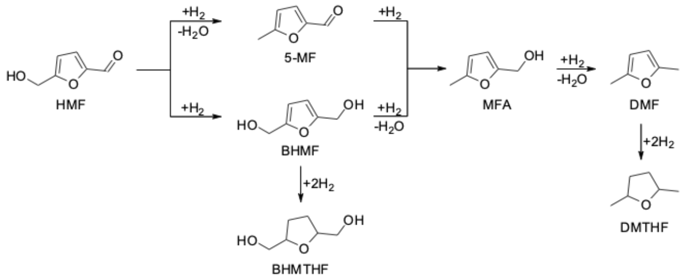
Lignocellulosic biomass constituents unlimited source of organic carbon for synthesis of alternative fuels and chemicals. Moreover, this feedstock does not compete with the food production. Biomass could be transformed into platform molecules such as 5-hydroxymethylfurfural (HMF) and subsequently hydrogenated towards plenty of industrially important chemicals like 2,5-dimethylfurane (DMF) or 2,5-bishydroxymethyltetrahydrofurane (BHMTHF).[1] Those molecules have shown significant potential to be used as biofuel, solvent, monomer for polymer and pharmaceutical production.[1] The crucial issue for this reaction is related with the selective transformation of HMF towards desired components in economically feasible way. Thus, using a proper catalyst enables to obtain desirable products with high selectivity. (Scheme 1)



Scheme 1. Reaction pathways of HMF hydrogenation

Ni-based catalysts among the non-noble metals due to their high activity are interesting and competitive alternative for HMF hydrogenation. Recently we showed that modification of this catalysts by Fe addition to Ni catalysts can increase the selectivity and stability of this catalysts. [2]. Therefore, the aim of this research was to determine the influence of support modification and catalyst preparation conditions on the selectivity and activity in HMF hydrogenation. Therefore, Ni-Fe catalysts supported on different reducible supports like zirconia and titania were tested in HMF hydrogenation. They have shown a considerable impact on the reaction selectivity. Catalysts prepared on titania support were selective towards DMF, whereas zirconia support resulted in high yield to BHMTHF. Additionally, it was proved that selectivity of the HMF hydrogenation strongly depends on both preparation method (precipitation vs impregnation) and pre-treatment conditions in the case of zirconia based catalysts. The increase of the catalyst reduction temperature for zirconia-based catalysts from 300°C to 500°C shifts a reaction pathway from furan ring hydrogenation of BHMF to hydrodeoxygenation towards 5-hydroxymethylfurfural alcohol (MFA).

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P-17

Usuwanie depozytu węglowego z katalizatorów zeolitowo-kobaltowych procesu reformingu parowego etanolu

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Reforming parowy etanolu (ang. *Ethanol Steam Reforming*, ESR) przebiega z wytworzeniem mieszaniny wodoru oraz dwutlenku węgla zgodnie z równaniem 1:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \qquad (1)$$

W praktyce powyższej reakcji towarzyszy szereg reakcji ubocznych, prowadzących do powstawania niepożądanych produktów m.in. tlenku węgla(II), metanu, acetonu, czy węgla. Rodzaj oraz ilość powstających produktów ubocznych silnie zależy od warunków w jakich prowadzony jest proces: temperatury, stosunku molowego EtOH:H_2O oraz charakteru katalizatora. Reakcje, które są odpowiedzialne za powstawanie depozytu to m.in. dehydratacja etanolu do etylenu oraz późniejsza polimeryzacja do koksu, kondensacja aldolowa acetonu, reakcja Boudouarda, odwrócony proces zgazowania węgla i rozkład węglowodorów (metanu i etylenu) [1]. Powstający depozyt węglowy, odkładając się na powierzchni katalizatora, blokuje jego centra aktywne tym samym prowadząc do jego dezaktywacji. Występuje on głównie w dwóch formach – węgla amorficznego oraz włókien (filamentów). Charakter depozytu zależy zarówno od temperatury procesu jak i od charakteru badanego katalizatora (faza aktywna, nośnik, promotory) [2]. Zawęglone materiały można regenerować poprzez usunięcie depozytu, odblokowując centra aktywne na jego powierzchni.

W przedstawionej pracy zbadano możliwość regeneracji katalizatorów zeolitowo-kobaltowych. Dla serii katalizatorów różniących się składem, wykorzystanych uprzednio w procesie ESR (>160 h, 500°C, EtOH:H_2O = 1:12), przeprowadzono badania termograwimetryczne (TG/DSC) w przepływie powietrza. Ponadto, badane katalizatory zostały scharakteryzowane pod kątem natury oraz lokalizacji zawartego w nich depozytu węglowego (TEM/EDX, XPS, RS, UV-VIS). Przebieg procesu regeneracji omówiono w odniesieniu do charakterystyki depozytu (morfologii, składu i lokalizacji) oraz właściwości powierzchniowych i strukturalnych katalizatorów (redukowalność, kwasowość i morfologia) uzyskanych na podstawie szczegółowych badań fizykochemicznych (m.in. H_2-TPR, TEM/EDX, FT-IR) świeżych katalizatorów.

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P-18

Amorphous and crystalline oxide composites active in ROS generation via decomposition of H_2O_2 for advanced oxidation processes

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Formation of reactive oxygen species (ROS) via decomposition of hydrogen peroxide is associated with a cascade of reactions which involve either redox active centres of Fenton-like catalysts or acid–base surface functional groups, which mediate electroprotic reactions [1]. Such two functions can be utilized by combining two types of oxides, redox active crystalline oxides and non-redox amorphous oxides, into one material.

This work is aimed at synthesis of the amorphous-crystalline composites by combining a series of amorphous d^0 transition-metal oxides (ZrO_2, Nb_2O_5, Y_2O_3) with selected redox-active nanocrystals (Fe_3O_4, Fe_2O_3, Co_3O_4, CuO). The resulting composites were thoroughly characterized. Elemental composition was obtained with X-ray fluorescence spectroscopy (XRF). The phase composition was established with X-ray diffraction (XRD), and subsequent transmission electron microscopic observations (TEM-EDS) combined with energy dispersive spectroscopic mapping. Raman measurements were performed to further inspect the dual nature of the composite samples. Measurements of surface zeta potential helped to establish the electrostatic interactions between amorphous and crystalline phases. Stability of the composites in presence of hydrogen peroxide was verified. The formation of possible surface ROS was monitored with Raman and EPR spectroscopy. Interaction of the composites with H_2O_2 led to its direct decomposition and O_2 release (quantified with fluorescent O_2 probe) or formation of hydroxyl radicals $^\bullet OH$ trapped with DMPO and detected with EPR.

The measurements confirmed the cooperative effect of Fenton and electroprotic mechanisms [2]. A Fenton-type mechanism of H_2O_2 decomposition was proposed, which involves formation of surface $HO_2^\bullet$ and $^\bullet OH$ radicals. The chemical reactivity of the obtained materials was tested in oxidation of o-phenylenediamine (OPD) and water-soluble methylene blue (MB) dye. The later can be treated as an example of advanced oxidation process (AOP). The calculated oxidation reaction constants showed that addition of Fenton-active phase into the amorphous composite increased the reaction rate by one or two orders of magnitude.

The mechanistic study, based on the spectroscopic identification of the products of decomposition of H_2O_2, was performed to identify and differentiate between catalase- and peroxidase-like reactivity. The pure crystalline oxides exhibited the highest activity in generation of oxygen gas, while amorphous samples the lowest. Thus, the presence of amorphous phase within the composite material slowed down the undesired (from the standpoint of application in AOP) decomposition of H_2O_2 into O_2. The general trend is that the composites can efficiently activate hydrogen peroxide, bypassing the thermodynamically stable products, therefore exhibiting preference towards peroxidase-type activity.

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P-19

Tailored Approach for Hierarchization of All-Silica Zeolites

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Elevation of mass transfer restrictions in all-silica zeolites by the adding of the secondary pores into the microporous system can bring their new utilization in both catalysis and separation fields. The impacts of zeolite type structure, crystals properties and synthesis conditions on hierarchization feasibility of all-silica ITQ-29 (LTA), silicalite-1 (MFI), silicalite-2 (MEL) and beta (*BEA) zeolites were decoupled. To explore the relationship between the zeolite characteristic, crystals properties and hierarchization feasibility the several post-treatment paths over all-silica LTA, MFI, MEL and BEA zeolites were inspected. The tailored post-synthesis methods involving detemplation, desilication and pore directing agents application were applied for materials hierarchization. The coupling of advanced FE-SEM and HR-TEM methods with detailed characterization of structural and textural properties allowed concluding on significance and co-dependency of parameters ruling the hierarchization of all- silica zeolites. The pore formation depended on (i) F- or OH- assisted synthesis method related to defect sites presence in zeolite structure and share of external surface area, (ii) the size (8-, 10- or 12-ring) and shape (sinusoidal or straight) of pores determined the preferences in pore formation. The proposed tailored approaches for hierarchization of all-silica zeolites ensure to successfully add the secondary system of pores or provide necessary conditions for it. The formation of hierarchical all-silica zeolites is pore size and shape-dependent as well as defects oriented; however, the final impact of those parameters on hierarchization is co-dependent.

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P-20

Operando UV-Vis and FT-IR studies in silver sites speciation assessment

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Silver ions incorporated to zeolite can serve as active sites in numerous catalytic reactions as the aromatization of alkanes, alkenes and methanol [1]. The reduction process of Ag^+ cations to various forms of Ag0, clusters or nanoparticles, can occur upon the thermal treatment with CO, alcohols and alkylobenzenes [2]. Further, the thermal treatment itself plays an important role in the control of Ag species nature in zeolites. An isolated Ag^+ cations are the most favoured at temperatures below 400 °C while higher temperatures facilitate their aggregation [3]. The status of Ag species in zeolites and their interaction with reactant molecules are of high imporantce [2].

The evolution of Ag species in the oxidative and reductive atmosphere was tracked in operando UV-vis studies. The temperature was increased gradually from RT to 500 °C with rate of 10 °C/min, and over 10 min stabilization every 50 °C.

It is well known fact that during oxidation at elevated temperatures the reduction of Ag^+ to Ag^0 can take place even in pure oxygen atmosphere. This is our case as the bands placed at 255 and 280 nm (Ag_m^+ and Ag_n^+ clusters, where m<n<8) as well as 367 nm (Ag_p^0, y>8) increased significantly upon the thermal treatment in synthetic air flow when the temperature was raised from RT to 500 °C. Also Ag_{NPs} can be identified at 430 nm and 550 nm on UV-vis spectrum (Fig. 1B). On the hand, the reduction under H2 atmosphere with gradual increase of temperature to 500 °C leads to the formation of new kind Ag_x^+ with lower atomicity degree (4<x<8, 300 and 320 nm) accompanied by development of Ag_{NPs} (418 nm) (Fig.1A). The acid treatment of the MOR zeolite extracted aluminum atoms from the zeolite framework, leading to a significant increase in its Si/Al molar ratio from 15 to 25 [1].

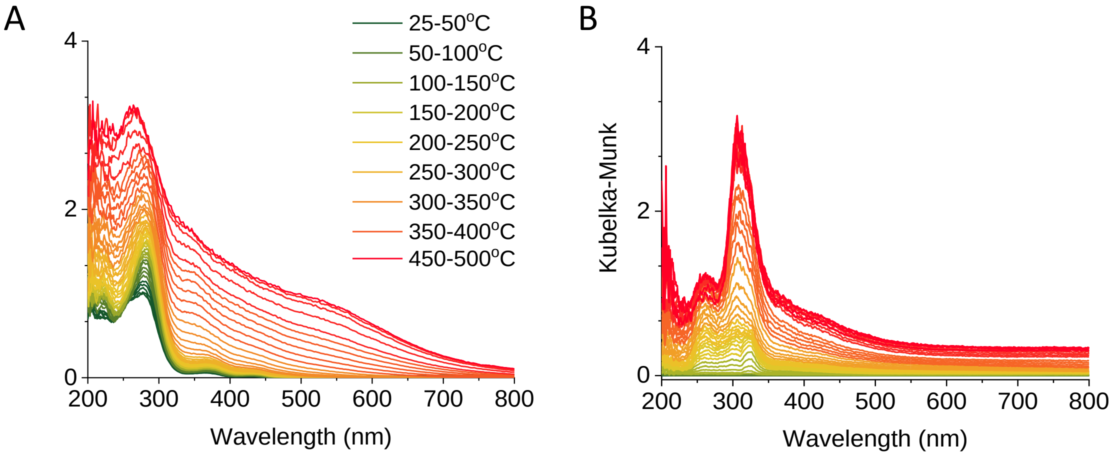

Fig.1. UV-vis spectra of Ag-ZSM-5 zeolite upon thermal treatment in reductive (A) and oxidative (B) atmosphere synthetic air and hydrogen during

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The status of silver sites in zeolites will influence the process of catalytic oligomerization of ethylene and methane activation because of the Ag^+ cation itself can serve as the reaction site. Further, the activity of protonic sites present in reduced sample can be moderated by charged silver cluster presence. This aspect of the oligomerization activity influenced by the co-presence of Ag^+ cations was studied by means of 2D COS FT-IR spectroscopy of ethylene transformation over Ag-ZSM-5 and H-ZSM-5 zeolites at 375 ^oC over 10 h.

The first period of reaction over HZSM-5 zeolite the ethylene is immediately transformed to linear hydrocarbon products with conjugated C=C bonds (1660 cm^{-1}) (Fig. 2). The positive correlation between the 1660 cm^{-1} band and 1445 cm^{-1} band (indicative for ethylene) confirms that both species in overall reaction time serve as substrates. Thus it can be found that ethylene and hydrocarbons with conjugated C=C bonds are transformed to aromatic compounds represented by 1590 cm^{-1} band. This aromatic character is confirmed by the negative correlation of 1590 cm^{-1} band with the alkyl vibration bands of the CH3/CH2 groups represented by the 1365 and 1375 cm^{-1} bands. The AgZSM-5 zeolite presents distinctly different selectivity of the process: conjugated linear species are not formed and the main products of the ethylene oligomerization process are aromatic compounds, e.g. 1,2,4-trimethylbenzene (1505 cm^{-1}) and bulky aromatics seen as 1590 and 1570 cm^{-1} bands. Homogenous nature of the oligomerization products is reflected in the maps as well-resolved high intensity correlation peaks. The participation of Ag^+ cation in ethylene transformation is also confirmed by selectivity of AgZSM-5 catalyst when compared to protonic HZSM-5 zeolite.

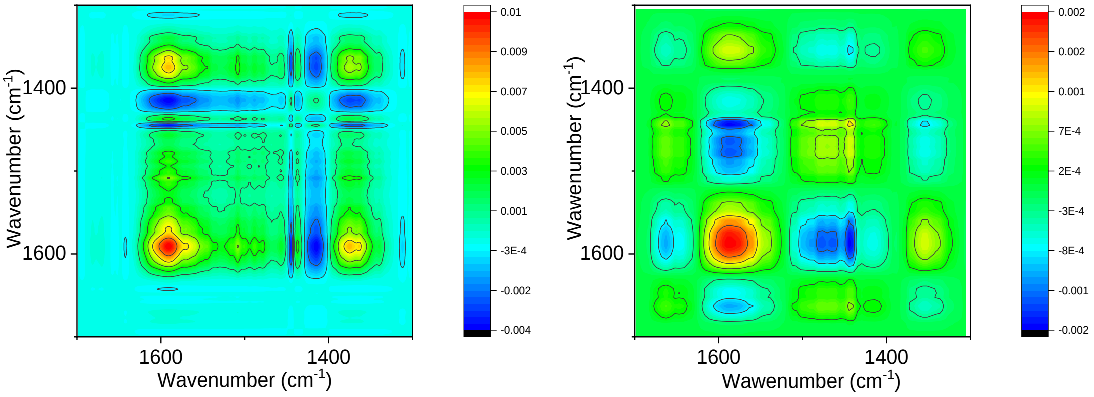

Fig. 2. 2D COS maps of FT-IR spectra registered during ethylene oligomerizaiton over AgZSM-5 (A) and HZSM-5 (B) zeolites at 375 oC for 10 h.

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P-21

Modification of anode materials used in high temperature solid oxide fuel cells

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The development of fuel cell technology plays a very important role in scientific research because such devices can convert the chemical energy of fuels into electricity with very high efficiency. Moreover, due to the lack of gaseous (e.g. NO_x, SO_x) and dust pollutants, these devices are one of the most environmentally friendly energy generators. Solid Oxide Fuel Cells (SOFC) are considered to be the most promising generators because these systems can apply various fuels such as: hydrogen, ammonia, synthesis gas, gaseous or liquid hydrocarbons (natural gas, ethanol) etc. Their advantage is also related to the fact that the SOFC operation at high temperature (600 - 1000 ^oC) enables the use of waste heat (in systems with the use of classic gas turbines), which results in greater efficiency of the devices. The high operating temperature limits the available materials for cell construction, leading to high SOFC costs. However, with the reduced operating temperature of such a cell, the overall performance drops significantly due to the increased polarization resistances of both electrodes and due to the reduced ionic conductivity of the electrolyte.

Thus, the development of electrode materials with sufficiently high efficiency and stability at the optimal cell operating temperature is crucial for the successful commercialization of SOFC technology.

This work is related to the search for methods of improving the properties of anode material in SOFC and SC SOFC (Single Chamber SOFC) devices powered by methane as a fuel. Ni-cermet based anodes are the most widely used anode materials in SOFCs due to their excellent electrochemical catalytic activity in the fuel oxidation reaction, high electrical conductivity, good stability and relatively low cost. In methane-fuelled SOFCs, internal fuel conversion is possible, which significantly simplifies the design of the device, but at the same time, causes the anode material to be exposed to contamination by carbon deposited during the conversion reaction. In addition, if such an anode is to be used in SC SOFC, it must meet additional requirements - due to the single-chamber structure of the SC SOFC, the electrodes must show a difference in their electrocatalytic properties. The anode must be electrochemically active for the oxidation process of the fuel supplying the cell, while the cathode is responsible for the reduction of oxygen, and these electrode processes must occur selectively on both electrodes in one and the same space to which the fuel-oxidant mixture is fed. The properties of the anode material largely determine the degree of conversion of methane to CO and H_2 (according to the reaction below) and thus the efficiency and effectiveness of the cell in which it can be used.

$$2CH_4 + O_2 \rightarrow 4H_2 + 2CO$$

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This work presents the methods of modifying the anode material intended for use in both SOFC and single-chamber devices. This modification concerns both, the choice of the modifying material and the surface modification technique. It is well known that both, different metals (Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt, Au) and ceramic composites can be used as elements modifying the anode structure.

In this study, the following methods of surface modification of Ni/YSZ (50-60% NiO + YSZ-Yttria Stabilized Zirconia) as anode materials were used:

1. Modification of Ni/YSZ anode using PAD (Polymer Assisted Deposition) method. Thin layers made of composite materials such as: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ and $La_{0.6}Sr_{0.4}Co_{0.2-x}Ir_xFe_{0.8}O_3$, as well as $La_{0.6}Sr_{0.4}Co_{0.2-x}Ba_xFe_{0.8}O_3$, $La_{0.6}Sr_{0.4}Co_{0.2-x}Bi_xFe_{0.8}O_3$, $La_{0.6}Sr_{0.4}Co_{0.2-x}Ca_xFe_{0.8}O_3$, $La_{0.6}Sr_{0.4}Co_{0.2-x}Mn_xFe_{0.8}O_3$.
2. Modification of Ni/YSZ anode surface using vacuum coating techniques i.e. MS method (Magnetron Sputtering). With this technique, the thickness of the coating can be tightly controlled and it is possible to obtain a uniform thickness over a large area. The coatings obtained with this technique have reproducible properties, and it is possible to coat elements with a complex morphology. A thin layer of V and Ni was applied by means of MS.
3. Modification of Ni/YSZ anode surface - deposition thin film of NiO/GDC (65wt.% NiO – 35wt.% $Ce_{0.9}Gd_{0.1}O_{2-x}$), by applying the screen printing technique.

Laboratory techniques such as: PAD, MS and screen printing are often used to obtain thin layers, which is to lead to improvement of e.g. catalytic properties of the modified surface. Since most scientific works use impregnation or change of the chemical composition of the electrode material at the stage of its synthesis, the use of thin layers as a method of improving the properties of electrodes, gives a wide field for finding new solutions to improve the catalytic properties of surfaces modified in this way.

The current research has been carried out in terms of the preparation of new anode materials using the technique of applying thin layers. These works have already brought a measurable effect, as the electrodes modified with Iridium showed better catalytic activity. The next stage of this work will be to check the catalytic properties of the modified anode materials in the methane conversion reaction, leading to the obtaining of the most desirable products, i.e. to hydrogen and CO.

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P-22

DFT studies on M_{13}/TiO_2 (M = Au, Ag, Cu) and HPA/TiO_2 catalysts

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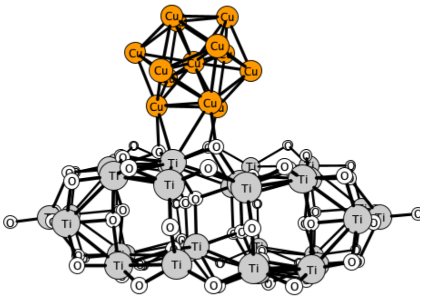
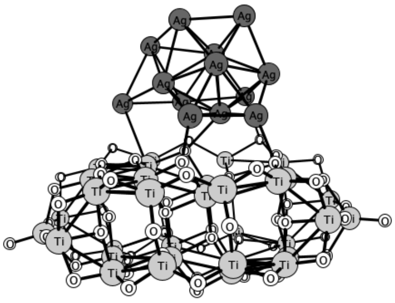
Materials composed of the active phase deposited on transition metal oxide constitute an important area of catalytic research. They are active in numerous processes, enabling transformations of various chemical species. They can be used not only in “traditional”, thermal catalytic reactions, but their application in photocatalysis emerges. Light is as ideal alternative energy source and is largely used in combination with semiconductors to drive chemical reactions. For instance, high catalytic performance of metal heteropolyacids catalysts supported on TiO_2 in methane coupling to ethane and propane at room temperature was found [1].

To understand the observed reactivity and to characterize various group of materials we performed quantum-chemical calculations in the frame of Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) with a PBE+D3 functional and the def2-TZVP basis set within a cluster approach.

We focus on both metallic clusters (Au_{13}, Cu_{13}, Ag_{13}) and heteropolyacids (HPW and HPMo Keggin anion) deposited on the (101) anatase TiO_2. For the studied systems, the geometry and electronic structure was characterized by computing selected bond lengths, Mayer bond indices, ESP charges on the exposed surface sites, and the DOS plots. We found that the shape of metal cluster strongly depends on the metal type. While copper nanoparticles are spherical, silver and gold NPs are flattened to increase metal-support interface. Heteropolyacids retail the geometry of the Kegging anion.



$Cu_{13}TiO_2$



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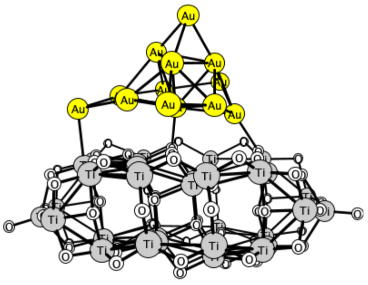

$Au_{13}TiO_2$

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P-23

Application of transition metal-modified vermiculites as catalysts in the SCR-NH_3

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In the 21st century, the dynamic development of industrialized countries is observed, which provokes contemporary society to take action to protect the environment. Currently, a number of studies are being carried out to reduce emissions of nitrogen oxides, which are considered extremely harmful to both human health and the natural environment. One of the methods is the reaction of selective catalytic reduction of nitrogen oxides with ammonia (SCR-NH_3). As the catalytic material, vermiculite modified with zrrconia, cobalt, copper, iron and nickel.

In the case of applied manganese, iron and copper ions, satisfactory values of NO conversion were obtained, ranging from 65% to 90% at temperatures of 160-180 °C. However, despite the high degree of conversion, unfortunately, the formation of harmful N_2O was also found, which in the case of the catalyst with ions of cobalt, nickel and manganese was 400 - 500 ppm at temperatures of 180-260 °C.

Vermiculites modified with copper or iron showed the best catalytic properties in the SCR-NH_3 in low temperature range (<200 °C).

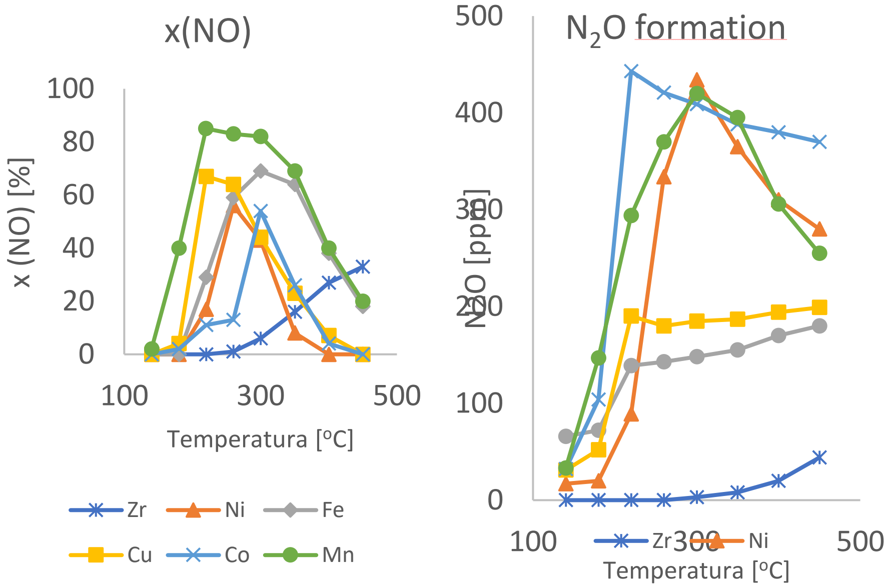

Fig. 1. SCR-NH_3 proporties: (left) NO conversion, (right) N_2O formation

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P-24

Composites of montmorillonite with TiO_2 nanoparticles prepared by inverse microemulsion method – physico-chemical and photocatalytic properties

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The aim of the work was to obtain TiO_2/clay composites of variously modified montmorillonite with titania nanoparticles prepared by inverse micellar route.

Ti pillaring solution from $TiCl_4$ precursor was used for preparation of inverse Ti-microemulsion. 1-hexanol served as an oil phase and cetyltrimethylammonium bromide as a surfactant. Montmorillonite component was prepared in two ways: a) as organomontmorillonite (HDTMA-Mt) dispersion in 1-hexanol, and b) as Na-montmorillonite (Na-mt) in water droplets dispersed in the form of inverse micelles in 1-hexanol. TiO_2 and montmorillonite suspensions were mixed in different proportions, left to interact and neutralized by addition of NH_3 (aq).The recovered precipitates were lyophilized and calcined at 450°C for 4 h. Samples containing 5, 10, 15 and 30 mmol Ti/g Mt were obtained. In selected cases the precipitates were treated hydrothermally at 180°C for 3h. The materials were characterized with XRD, N_2 adsorption/desorption at -196°C, SEM/TED/EDS, TG/DSC. Their photocatalytic properties were tested in the reaction of Rhodamine B decomposition.

Results pointed to the importance of the form of montmorillonite component. In particular, composites prepared from HDTMA-Mt, were characterized by less uniform dispersion of TiO_2 nanoparticles than those obtained from microemulsion of Na-Mt. This is illustrated in Fig. 1, which compares SEM/TED images of 15 mmol Ti/HDTMA-Mt and 15 mmol Ti/Na-Mt. The latter materials showed better performance in the photocatalytic tests. Also, hydrothermal treatment was shown to improve the photocatalytic properties of the composites.

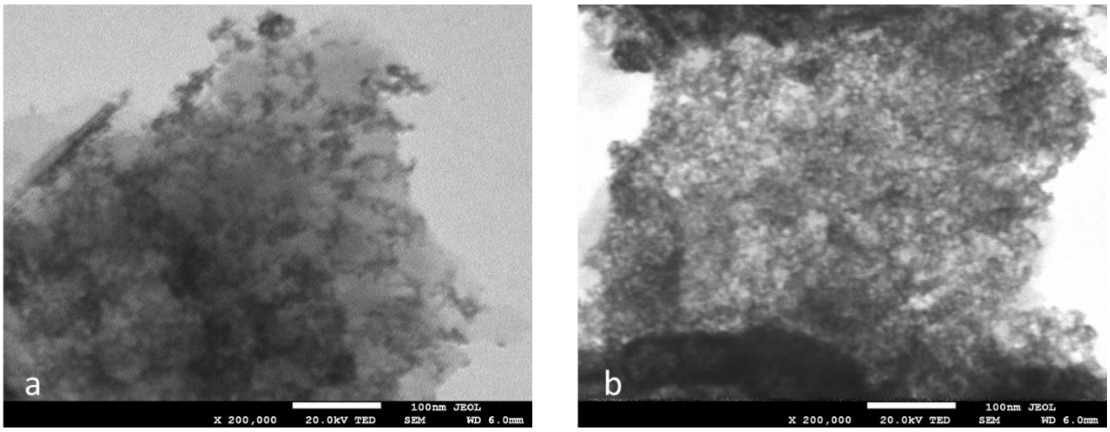

Fig. 1. SEM/TED images of a) 15 mmol Ti/HDTMA-Mt, b) 15 mmol Ti/Na-Mt.

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P-25

Polymer colloids: studies on the synthesis based on computer simulations

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A coarse-grained model was developed for studies of the synthesis of regularly branched macromolecules. Monte Carlo simulations employing the Dynamic Lattice Liquid algorithm were carried out to study large and dense systems. A core-first methodology was used in a living polymerization of stars with up to 32 arms and dendrimers consisted of 4-functional segments. The kinetics of the synthesis process for stars with different number of branches and dendrimers were compared. The size and structure of star-branched polymers and dendrimers during the synthesis was also studied. The influence of functionality of well-defined cores on the structure and on the dispersity of the system was also presented.

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P-26

Coke Nature Assessment by Spectroscopic and Chromatographic Methods

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Ethylene oligomerization has become one of the major research fields of petrochemical industry worldwide aiming at achieving high activity and selectivity to even number atom products. The heterogeneous catalysts used zeolites with proper acidity have demonstrated promising performance in practical applications. ZSM-5 is characterized by a series of channels with two directions and with the diameter of 5.5 Å, which control the shape and size of the product molecules. In addition, the protonic acid sites within the catalyst facilitate the reactions. Conversion of light olefins to transportation fuel products was gaseous olefins in the range of ethylene to pentene were converted into an olefinic gasoline blending stock by contacting the olefins with a catalyst bed made up of a ZSM-5 type zeolite[1].

In order to obtain high activity of ethylene oligomerization, the catalyst should possess acidity. However, if the acidity is too strong, there would be side reaction such as cleavage, alkylation, isomerization, or polymerization. Both Brønsted acid and Lewis acid can affect the performance of the catalyst, Lewis acid can cause the catalyst coking, while strong Brønsted acid can promote oligomerization as well as eliminate coking or reduce aromatization reaction. The carbonaceous species plug the zeolite micropores and inhibit the diffusion of reactants and products to and from active sites or even lead to poisoning of the active sites. In this respect, defining the relationship between the coke speciation and zeolitic catalysts properties which determines the carbonaceous deposit formation is important research objective. To meet this specific objective, a comprehensive approach allowing to unwrap the correlations between the coke formation process and zeolitic catalysts parameters need to be addressed. Our studies showed that the type of zeolite structure, their acidity and size of channels have huge influence for catalytic results.

The experimental studies were based on the spectroscopic properties of the preparations. The reactions were carried out in a flow-through quartz reactor, all catalytic results were recorded by a gas chromatograph with FID detection. Carbonaceous species over the catalysts with acidic property are rapidly formed during the transformation of ethylene into higher hydrocarbons (ZSM-5, CBV2314E, Zeolyst, 325 °C, 5000 ml/(g•h), 18 hours) Assessing the nature of such carbonaceous species was evaluated using operando FT-IR and UV-vis spectroscopic methods. The TPO experiments of coke removal from spent catalysts were performed from 200 to 550 °C in flow of synthetic air and followed by FT-IR and UV-vis spectroscopies. The information on the nature of the coke precursors was derived from monitoring CO_2 evolved during TPO of coke followed by FT-IR spectroscopy and mass spectrometry. The coke species formed during the oligomerization of ethylene over a series of ZSM-5 can be identified by the complex band around 1640-1550 cm^{-1}. The position of the coke bands are indicative of its nature itself. In the zeolitic catalysts the coke bands are centered at 1615 and 1575 cm^{-1} suggesting that strong acid sites facilitate condensation reactions to produce C6H7$^+$ olefinic cation (CH2=CH−CH]CH=CH]CH$^+$) or cyclic alkenyl carbenium ions C6H9+ identified by the 1575 cm^{-1} band while the ca. 1600

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cm^{-1} band presence points to the formation of polymethyl-benzenes as coke forming compounds (e.g. 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene).

The shape of the UV−vis spectra provides information that coke on spent catalyst is consisting of aromatic structures containing 1-, 2-, and 3-ring aromatic compounds can be identified by the bands appearing only at 220 and 260 nm. Both neutral and charged aromatics species formed during ethylene oligomerization over ZSM-5 zeolite the zeolitic catalysts can be identified by a band between 220-620 nm. More specifically, a complex band at 425 nm can be ascribed to 1-methylnaphthalene, in line with its relatively small bandwidth indicative of a narrow distribution of hydrocarbon species contributing to this band. The highest amounts of CO_2 are formed by the oxidation of residues in ZSM-5 zeolite at temperatures as high as 500 and 550 °C. This further confirms the aromatic character of coke species formed during ethylene oligomerization.

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P-27

Modyfikacja powierzchni grafitu przy użyciu plazmy niskotemperaturowej

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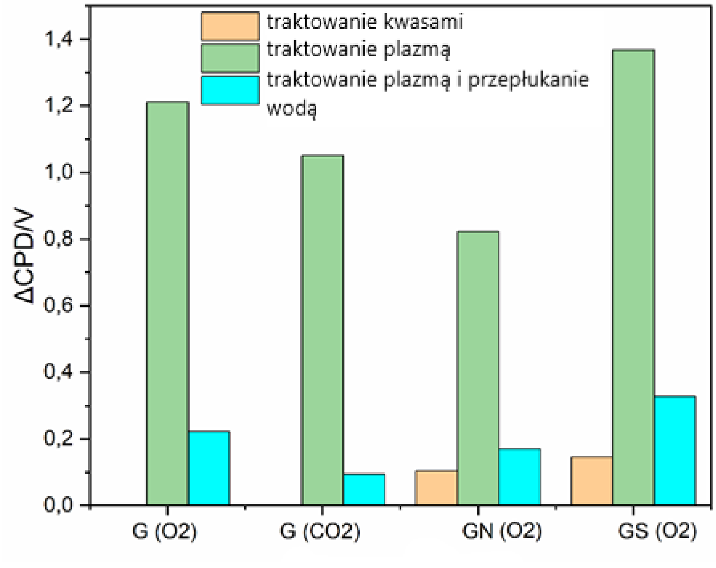
Modyfikacja materiałów węglowych za pomocą plazmy wykorzystywana jest do funkcjonalizacji powierzchni m.in. tworzenia tlenowych grup funkcyjnych. Inną powszechną metodą utleniania powierzchni jest traktowanie materiałów zawierających węgiel stężonymi roztworami kwasów. Nie istnieje jednak standardowy materiał grafitowy, gdyż każdy jest inny pod względem ziarnistości i skład zanieczyszczeń. Użycie roztworów stężonych kwasów znajduje zastosowanie w oczyszczaniu grafitu, natomiast utlenianie prowadzi się z wykorzystaniem ich mieszanin. W celu określenia zmian właściwości elektronowych powierzchni materiałów w wyniku funkcjonalizacji może wykorzystany pomiar zmian pracy wyjścia. Proces optymalizacji funkcjonalizacji jest ważny dla modyfikacji węgli, ponieważ nadmierne utlenianie powierzchni może prowadzić nawet do degradacji i zniszczenia próbki. Kolejnym ważnym aspektem jest przystosowanie zmodyfikowanych materiałów do użyteczności w środowisku wodnym. Jest to bardzo proste w przypadku utleniania kwasowego, czyli „metody na mokro”, ale znacznie bardziej trudne w przypadku utleniania plazmowego. Efekty plazmy i wynikające z nich właściwości powierzchniowe są zależne od czasu po modyfikacji – zanikają w czasie. Zazwyczaj charakterystyka materiałów węglowych po modyfikacji plazmą prowadzona jest bez kontaktu materiału z wodą. Z drugiej strony po zanurzeniu w wodzie następują duże zmiany i stabilizacja modyfikowanej powierzchni.

Celem niniejszych badań było określenie różnic między właściwościami powierzchniowymi i strukturalnymi materiałów po traktowaniu samą plazmą i plazmą oraz wodą. Jak pokazano na Rys. 1 efekt wody powoduje ogromny spadek wartości pracy wyjścia. Ponadto badania spektroskopowe wykazały znaczny spadek ilości tlenowych grup funkcyjnych na powierzchni badanych materiałów.



Rys. 1. Zmiany wartości kontaktowej różnicy potencjałów CPD (pracy wyjścia) w zależności od sposobu modyfikacji próbki. Oznaczenia próbek: N – traktowanie kwasem azotowym(V), S- traktowanie kwasem siarkowym(VI), O_2 – traktowanie plazmą tlenową, CO_2 – traktowanie plazmą CO_2.

Na podstawie uzyskanych wyników można stwierdzić, że największe zmiany pracy wyjścia (ΔCPD) pojawia się dla traktowania plazmą O_2 przy czasie 5 min, jednak po zanurzeniu w wodzie maksimum znacznie zmniejsza się i występuje dla czasu 10 min. Przy traktowaniu plazmą CO_2 największe zmiany obserwowane są dla czasu 10 min, jednak przy „efekcie wody" najbardziej optymalny czas traktowania to 5 min. Dla tych czasów tj. 10 min dla plazmy O_2 oraz 5 min dla plazmy CO_2 obserwowane są także największe spadki wartości pracy wyjścia oraz najmniejsza jej wartość po okresie 1 miesiąca w porównaniu z innymi czasami modyfikacji plazmą oraz dla próbek wcześniej modyfikowanych kwasami. Z Rys. 1 wynika także, że duże zmiany pracy wyjścia następują po zanurzeniu próbek w wodzie. Wartości pracy wyjścia w przypadku próbek traktowanych kwasami i plazmą CO_2 osiągają wartości nieznacznie większe niż przed modyfikacją plazmą.

Przeprowadzona analiza spektroskopowa (spektroskopia fotoelektronów w zakresie promieniowania X, XPS) wykazała, że ilość wprowadzonych grup tlenowych na powierzchnię grafitu wzrasta znacząco po traktowaniu plazmą. Zanurzenie próbki w wodzie po plazmie powoduje jednak zanik większości tlenu powierzchniowego, obserwowanego poprzez analizę XPS i oznacza znikomy jego przyrost. Największą zmianę pracy wyjścia dla próbek modyfikowanych plazmą i wodą zaobserwowano dla próbki oczyszczanej kwasem siarkowym(VI), a następnie traktowanej plazmą. Dla tej próbki pojawia się także największy przyrost stężenia grup tlenowych na powierzchni w wyniku działania plazmy.

Podziękowania: Prezentowane badania stanowią część projektu OPUS o numerze 2020/37/B/ST5/01876 finansowanego przez Narodowe Centrum Nauki w Polsce.

P-28

CuO-ZrO$_2$-ZnO mixed oxide catalyst doped with Mn, Ga, Ni: impact on physicochemical properties and hydrogen production via low temperature steam reforming of ethanol

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Ethanol is regarded as an attractive potential source of hydrogen generation. The major advantage of ethanol is the fact that it can be produced from biomass fermentation, which is a well-established, renewable and sustainable process. Hydrogen, which is considered to be environmentally friendly future energy carrier, can be produced from ethanol via three main reactions: steam reforming (1), partial oxidation (2) and oxidative steam reforming (3). Among mentioned methods, steam reforming is the most efficient in terms of hydrogen yield.

$$CH_3CH_2OH + 3H_2O = 6H_2 + 2CO_2 \qquad \Delta H_{298} = +174\ \mathrm{kJ/mol} \qquad (1)$$
$$CH_3CH_2OH + 1.5O_2 = 3H_2 + 2CO_2 \qquad \Delta H_{298} = -552\ \mathrm{kJ/mol} \qquad (2)$$
$$CH_3CH_2OH + 2H_2O + 0.5O_2 = 5H_2 + 2CO_2 \qquad \Delta H_{298} = -69\ \mathrm{kJ/mol} \qquad (3)$$

The CuO/ZrO$_2$/ZnO/X (where X = NiO, MnO, Ga$_2$O$_3$) catalysts were synthesized via co-precipitation method at pH = 7, using Na$_2$CO$_3$ as precipitating agent. The CuO/ZrO$_2$ weight ratio in all synthesised catalysts was fixed to 2.3. The concentration of dopants was 5 wt.%. The SRE reaction was performed at 350 ^{o}C to favour the water gas shift reaction and limit the formation of CO. The water/ethanol (S/E) ratio was equal to 10 to simulate the bioethanol. Obtained catalysts were characterised by means of XRD, H$_2$-TPR, CO$_2$-TPD, N$_2$O pulse chemisorption, µRaman spectroscopy, N$_2$ physisorption and X-ray photoelectron spectroscopy. Additionally, the spent catalysts were investigated with respect to their changes in morphology, textural properties and chemical composition.

The increase in hydrogen yield and the lowest selectivity to acetaldehyde were observed upon Cu/Zr/Zn modification with Mn and Ga. 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$_2$O. Therefore, these spent catalysts exhibited lower reduction degree (Rd) in comparison with fresh catalysts. On the other hand, the addition of Mn preserved the copper on +2 oxidation state during SRE reaction as indicated by XRD and XPS. The µRaman experiments showed that carbon deposit is formed only on the surface of Cu/Zr/Zn/Ni catalyst, which is the reason for the vast deactivation and the lower total activity of this catalyst in SRE. This was also supported by XPS, which additionally showed interaction of carbon containing by-products with the surface active sites. In the case of other synthesised catalysts, no carbon formation was stated.

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Katalityczne i fizykochemiczne właściwości układów heteropolikwas-Cu-TiO_2

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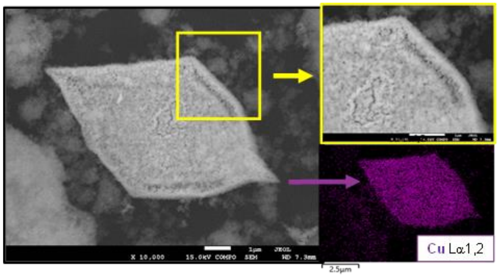
Tlenek tytanu(IV) jest materiałem powszechnie stosowanym w katalizie jako tani materiał nośnikowy dla fazy aktywnej katalitycznie. Tlenek ten charakteryzuje się wysoką stabilnością termiczną i chemiczną. Autorzy zsyntetyzowali serię potencjalnych katalizatorów HPW-Cu-TiO_2 zawierających miedź, heteropolikwas $H_3PW_{12}O_{40}$ (HPW) oraz tlenek TiO_2 jako nośnik. Zawartość miedzi i heteropolikwasu HPW w każdym katalizatorze wynosiła odpowiednio 5% i 10% wag. Po przeprowadzeniu syntezy układów HPW-Cu-TiO_2 struktura anionu HPW pozostała nienaruszona, fakt ten potwierdzono przy użyciu spektroskopii FTIR i Ramana. Status miedzi (Cu^{2+}, Cu^{+}) został ustalony przy użyciu techniki XAS. Celem naszych badań było określenie wpływu poszczególnych parametrów strukturalnych katalizatorów HPW-Cu-TiO_2, takich jak porowatość, powierzchnia właściwa, rodzaj fazy miedziowej i krystaliczność na aktywność katalizatorów miedziowych w dehydratacji n-butanolu w fazie gazowej (120-220 ^{o}C). Różnice w parametrach strukturalnych katalizatorów miedziowych wynikały z zastosowania do ich syntezy bądź metody impregnacji na mokro bądź metody impregnacji kapilarnej. Reakcja odwodnienia n-butanolu katalizowana przez zsyntetyzowane materiały doprowadziła do powstania: cis-2-butenu (cis-C4), trans-2-butenu (trans-C4), di-n-butyl eteru (DNBE) i aldehydu masłowego (BuAl). Głównym produktem konwersji n-butanolu na katalizatorach HPW@TiO2 był cis-2-buten. Metodą TPD desorpcji amoniaku określono szereg kwasowości układów HPW-Cu-TiO_2. Uzyskany szereg dobrze koreluje z szeregiem aktywności tych katalizatorów w konwersji n-butanolu.



Rys. Obrazy SEM katalizatora HPW/Cu/T805(400) z analizą EDX rozkładu miedzi.

Najwyższą konwersję alkoholu uzyskano stosując katalizator HPW/Cu/T805(400), otrzymany poprzez impregnację heteropolikwasem układu Cu-T805, który po osadzeniu miedzi wygrzano do 400 ^{o}C. Układ ten zawiera miedź w postaci CuO. Protony heteropolikwasu stanowią centra aktywne katalityczne. Protony te łatwo koordynują cząsteczki polarne takie jak: woda i alkohol. Produktem przejściowym reakcji jest powstanie sprotonowanych cząsteczek alkoholu. Obecność wody, produktu reakcji, w pobliżu centrum protonowego osłabia jego zdolność do protonowania alkoholu. Hydrofobowa powierzchnia T805 uniemożliwia dostęp wody do protonów w katalizatorze HPW/T805, a tym samym zapewnia wysoką aktywność tych katalizatorów. Z kolei wprowadzenie miedzi do układów HPW-TiO_2 zwiększa selektywność do trans-2-butenu i butanalu.

Podziękowania: Praca finansowana ze środków statutowych Instytutu Katalizy i Fizykochemii Powierzchni PAN im. Jerzego Habera.

P-30

Application of carbon-supported Fe catalysts in the continuous-flow chemoselective hydrogenation of 2-methyl-2-pentenal toward the formation of sedative drug precursor

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Implementing continuous-flow practices in the pharmaceutical industry is considered one of the most strategic fields of innovation toward greener manufacturing methods [1]. Although hydrogenation is usually carried out on noble metals, their high hydrogenation capacity affects their performance in semi - hydrogenation or the chemoselective hydrogenation of C=C or C=O double bond in the substrate, which contains two or more hydrogenate functionalities (unsaturated ketone, aldehyde or ester) [2]. Therefore, developing new catalytic systems based on transition metals as an alternative for noble metals is the primary goal of our studies.

To the best of our knowledge, the iron catalyst has not been studied in the hydrogenation of 2-methyl-2-pentenal (MPEA) under liquid-phase continuous-flow conditions. In this context, the present work analyses the influence of the metal loading on catalytic properties of carbon-supported iron catalysts in chemoselective hydrogenation of MPEA toward 2-methylpentanal (MPAA) - the sedative drug precursor [3].

Four Fe/CNR115 catalysts with 2, 6, 10 and 14 wt.% of metal have been thoroughly characterized by physicochemical methods (BET, TPR, H2-TPD, XPS and XRD) and investigated as the catalysts in the liquid phase continuous flow chemoselective hydrogenation of MPEA. We studied the effects of pressure and temperature on the activity and the selectivity toward saturated aldehyde. The liquid-phase selective hydrogenation of 2-methyl-2-pentanal to 2-methylpentanal over Norit115 carbon-supported Fe catalysts strongly depends upon the physicochemical properties of the catalytic systems and the reaction conditions. It is found that 2 and 10 wt.% Fe/CNR115 show the highest values of chemoselectivity toward the hydrogenation of the C=C bond, generating 100 % MPAA – the desired product of 2-methyl-2-pentanol chemoselective hydrogenation.

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P-31

Impact of cerium oxide on the state and hydrogenation activity of ruthenium species incorporated on mesocellular foam silica

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Metal particle size has a dominant impact on the activity of heterogeneous catalysts. Gold had been considered inactive for long period of time until Haruta [1] reported a high conversion in the low-temperature oxidation of hydrogen and CO over gold nanoparticles (<10 nm). Since that time the effect of metal particle size on catalytic performance has been widely investigated.

Herein, we are concerned with ruthenium particles loaded on the mesoporous silica support (MCF) doped with ceria. Both effects inducing interaction with Ru, that is the porous structure of the support and doping with another metal, were considered in composing effective catalyst for hydrogenation reaction.

MCF was synthesised according to procedure described in [4]. The support was impregnated with aqueous solution of cerium(III) nitrate hexahydrate to obtain 5, 10, 15 and 20 wt.% of cerium. Finally samples obtained as well as pristine MCF was impregnated with ruthenium(III) chloride solution to obtain 1 wt.% of Ru. Materials were characterized by various techniques: low temperature N_2 adsorption/desorption, XRD, XRF, ICP-OES, XPS, H_2-chemisorption. The hydrogenation of levulinic acid was performed in a pressure batch Parr reactor under 40 bar of hydrogen at at 40°C for 1 h.

The successful synthesis of MCF material was confirmed by low temperature N_2 adsorption/desorption. The modification of the support in sequence by Ce and Ru precursors did not have a negative impact on the structure of MCF material. It has been found that the presence of ceria on the silica support favours increasing dispersion of Ru species and its smaller particle size, which is beneficial for hydrogenation properties of the catalysts obtained. The size of ruthenium species in the presence of ceria is small enough to permit their location inside the pores of MCF support. Although, the dispersion continuously increases with increasing ceria amount, the 15 wt.% of Ce loading was found as an optimal in respect to the catalytic activity in the transformation of levulinic acid to γ-valerolactone, which was explained by the highest content of Ru^0 species and wider size of windows interconnecting cells of MCF than in the sample containing 20 wt.% of Ce.

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Acknowledgements: This research was funded by National Science Centre (NCN) in Poland, grant number 2019/35/N/ST5/01101 and by grant no. POWR.03.02.00-00-I026/16 co-financed by the European Union through the European Social Fund under the Operational Program Knowledge Education Development.

H_2 chemisorption and XRF measurements were carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-06024/09 - Centre of Functional Nanomaterials).

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Is there electron bifurcation in *Aromatoleum aromaticum* aldehyde oxidoreductase?

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The W-dependent aldehyde oxidoreductase from *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-metallopterin cofactor in its active site within the α subunit, which is connected via a chain of FeS clusters in the α and β subunits with a FAD in the γ subunit of the enzyme complex [1].

Although other AORs were previously reported to be active in reducing carboxylic acids to aldehydes only when coupled with strong reducing agents (such as reduced methyl viologen or Ti(III) or Eu(II) complexes) [2], AOR_{Aa} turned out to efficiently utilize electrons from H_2 oxidation for the reduction of carboxylic acids, making it a new kind of hydrogenase. Furthermore, the enzyme can be employed as a new NADH-recycling system by coupling the hydrogenase activity with the reduction of NAD^+ to NADH. The rate of H_2 dependent NAD^+ reduction equals 10% of that of the aldehyde-dependent reaction, representing the highest H_2 turnover rate observed among any Mo/W enzymes.

Carboxylic acid reduction coupled with hydrogen oxidation is a thermodynamically challenging reaction considering the redox potential difference between the reaction partners (-505 mV for benzoate/benzaldehyde;-420 mV for H^+/H_2). However, as the enzyme is able to reduce either acids or NAD^+ (redox potential -320 mV), a feasible explanation for its acid reduction activity would be the employment of electron bifurcation, as postulated during the last year conference. Electron bifurcation usually occurs for complex redox enzymes that couple the oxidation of an electron donor of intermediate redox potential (here H_2) with the simultaneous reduction of one electron acceptor of higher potential (here NAD^+) and one of lower potential (here the acid). Overall, this results in an energy-neutral overall reaction [3].

During this work, we critically examined whether electron bifurcation indeed occurs in AOR_{Aa}. The results of our kinetic experiments indicate that the observed reduction processes of acids and NAD^+ are neither synergetic nor stoichiometrically coupled, as would be expected from an electron bifurcating process. In contrast, the two alternative electron acceptors rather compete for electrons derived from H_2 [4]. Therefore, our results prove that the AOR_{Aa} hydrogenase activity does not employ a true electron bifurcation mechanism, but instead a mechanism of uncoupled reduction of acids and NAD^+.

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Acknowledgements: The work has been partly supported by the EU Project POWR.03.02.00-00-I004/16 and the National Science Center, Poland (PRELUDIUM 2017/27/N/ST4/02676).

P-33

The role of hetero metallic Cu-O-M (M = Cu, Fe, Ni) sites of SSZ-13 zeolite catalyst in the SCR process – activation of the NH$_3$ and NO$_x$ reagents

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The SCR catalytic reaction over zeolites is often discussed in terms of reduction half-cycle (RHC) with the participation of NH$_3$ and NO, and oxidation half-cycle (OHC), where NO and O$_2$ are engaged [1]. In the case of Cu loaded SSZ-13 zeolite both processes were addressed, and the performance of the Cu-SSZ-13 catalysts has been associated with the isolated Cu^{2+} and Cu^{2+}–OH^{-} centers. However, the role of the two closely spaced (juxtaposed) copper Cu^{2+}–OH cations or bridging [Cu^{2+}–O^{2-}–Cu^{2+}] entities is less explored. Possible involvement of the latter species in the SCR gains in importance for the catalyst of moderate Si/Al ratios and copper loadings. These sites are the potential active centers for the oxidation of NO to NO$_2$ which is beneficial for transformation of the standard SCR into fast SCR reaction, and also may be involved in the N–H bond activation during the RHC stage. Both these functionalities of the [Cu^{2+}–O^{2-}–Cu^{2+}] sites have been revealed by means of molecular modelling and in spectroscopic and catalytic experiments.

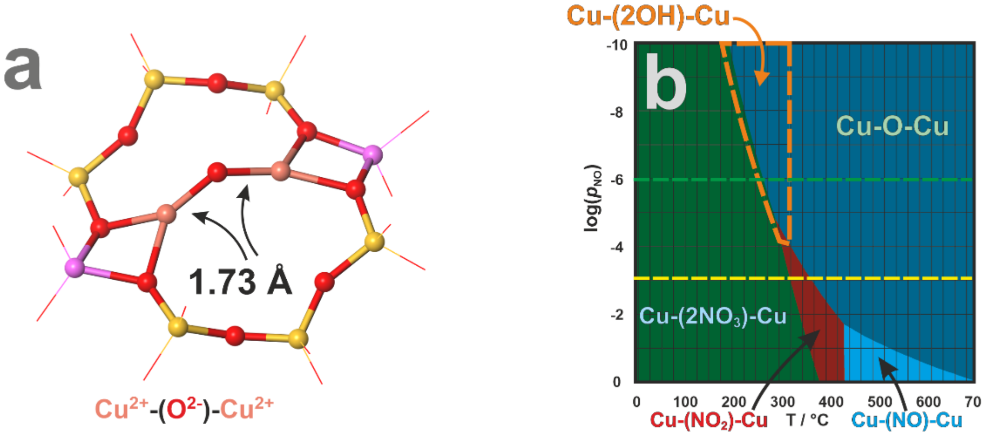

Fig. 1. Molecular picture of dual C-O-Cu center of Cu-SSZ zeolite (**a**). First principles thermodynamic diagram of dual sites coverage with NO$_x$ adspecies (**b**).

In this work we tested how the introduction of the alien cation (Fe, Ni) influence the ability of the dual [Cu^{2+}–O^{2-}–Ni^{2+}] and [Cu^{2+}–O^{2-}–Fe^{2+}] centers (**Figure 1a**) for NO$_{(x)}$ anchoring, and how it controls the efficiency of activating the N-H bond in ammonia. For these purpose we built the dimeric metal-oxo models of the active centers and tested various modes of the NH$_3$, NO and NO$_x$ attachment. We also examined NH$_3$/NO$_x$ co-adsorption with possible N-N formation. Finally we used the resulting stabilization energies to build ab initio thermodynamic diagrams (**Figure 1b**), revealing the *T*,*p* windows of optimal performance of the dual heterometal-oxo sites.

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We thank National Centre for Research and Development, Poland, for financial support of the Polish-China MOST Project PNOX (Grant No. WPC1/PNOX/2019).

P-34

Struktura i właściwości zasadowe porowatych kompozytów na bazie laponitu, jako efekt domieszkowania Fe

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Rosnące obawy związane ze zmianami klimatu i wyczerpywaniem się zasobów ropy naftowej stały się główną siłą napędową poszukiwań alternatywnych źródeł energii i produkcji chemicznej. Aby zaspokoić ten nadchodzący deficyt energii, bada się obecnie wiele różnych możliwości, aby ograniczyć naszą zależność od zasobów nieodnawialnych. W szczególności biomasa może zastąpić zasoby kopalne w produkcji zarówno paliw, jak i chemikaliów.

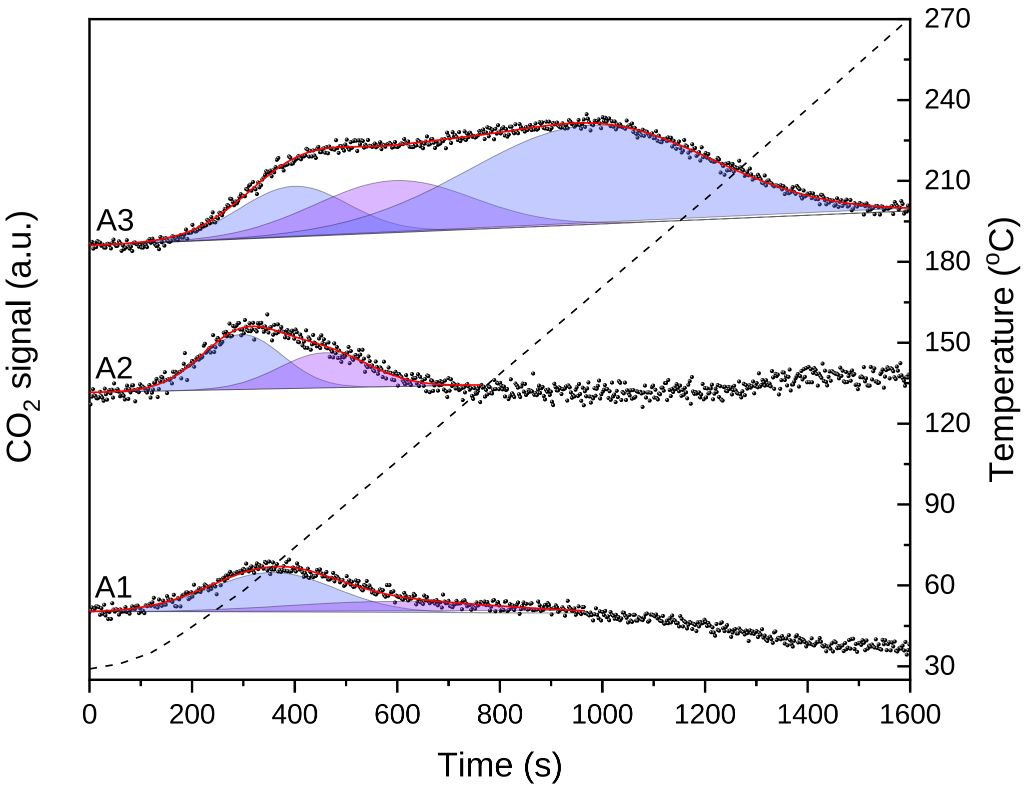
Obecne działania w kierunku zrównoważonego rozwoju oraz zapotrzebowanie zastąpienia paliw kopalnych może mieć odzwierciedlenie w przyjaznej zamianie biomasy na cenny butadien. 1,3-Butadien (BD) jest bardzo ważnym monomerem przemysły petrochemicznego do produkcji gum, kauczuków i elastomerów. Przede wszystkim ma zastosowanie do produkcji opon oraz pokrewnych produktów i części samochodowych. Dlatego reakcja bio-etanolu do butadienu może być obiecującym rozwiązaniem jednego z problemów środowiskowych [1-3]. Proponowane w projekcie wykorzystywanie materiałów pochodzenia naturalnego oraz ich kierunkowa funkcjonalizacja generująca centra zasadowe, może być interesującym *„mergingiem”* katalizowania substytutu surowców kopalnych na nanokompozytach pochodzenia mineralnego poprawiającym wydajność w/w reakcji.

Celem naszych badań było określeniu potencjału produkcji BD z bio-etanolu na hybrydowych katalizatorach mineralnych z grupy smektytów poprzez wygenerowanie na powierzchniach katalitycznych wyspecjalizowanych centrów zasadowych o różnej mocy. W prowadzonym projekcie określiliśmy wpływ metody domieszkowania mineralnego nośnika kompozytowego jonami Fe na tworzenie i dystrybucję centrów zasadowych.

Pierwszym etapem badań było otrzymanie metodą templatowania porowatych nanokompozytów pochodzenia mineralnego na osnowie Laponitu (A1) a następnie ich kierunkowa funkcjonalizacja z wykorzystaniem dwóch ścieżek dotowania kationami Fe: „Bottom-up Approache” (A2) oraz „Top-down Approache” (A3) w celu wygenerowania centrów zasadowych na powierzchni katalizatorów.

Zastosowane podejścia pozwoliły na wprowadzenie i stabilizowanie Fe w izolowanych pozycjach amorficzno-krystalicznego nośnika krzemianowego bezpośrednio podczas jego otrzymywania (A2) lub generowanie form poza sieciowego tlenku α-Fe_2O_3 metodą mechano-chemicznej aktywacji (A3). Metoda bezpośredniej funkcjonalizacji nośnika kompozytowego w niewielkim stopniu zmieniła zasadowość powierzchni (Rys.1).

P-34



Rys.1 Moc centrów zasadowych wyznaczona metodą temperaturowo-programowanej desorpcji CO_2.

Mechano-chemiczna aktywacja nośnika na osnowie Laponitu wywołała ukierunkowaną migrację jonów Mg^{II} z warstwy oktaedrycznej minerału, przyczyniła się do powstania silnie rozproszonych, nanostrukturalnych form MgO na powierzchni kompozytu oraz spowodowała wygenerowanie nowych centrów zasadowych, o dużo większej mocy niż materiał wyjściowy.

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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 badawczo-rozwojowych 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/,

S-2

Obrazowanie nanoIR - mikroskopia sił atomowych oraz spektroskopia FTIR/mikroskopia IR w skali nano (AFM-IR) oraz spektrometria TXRF/mikro-XRF jako metody oznaczania pierwiastków

Michał Kużdżał

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Nanospektroskopia w podczerwieni łączy mikroskopię sił atomowych (AFM) i spektroskopię w podczerwieni z transformacją Fouriera (FTIR). Takie połączenie pozwala na osiągnięcie rozdzielczości przestrzennej obrazowania w podczerwieni w skali nano, nawet do wartości 8 nm. Dzięki wykorzystaniu przestrajalnego lasera w zakresie podczerwieni, możliwe jest otrzymywanie widm oraz map charakteryzujących rozkład przestrzenny wybranych substancji chemicznych (np. amidy, wiązania fosforowe, fosfodiestrowe i in.). Wyjaśniając, dzięki mikroskopii AFM możliwa jest detekcja przejściowej dylatacji próbki (pęcznienie) podczas podgrzewania jej rezonansowo przy użyciu przestrajalnego lasera w zakresie podczerwieni, w wybranym zakresie spektralnym. Intensywność sygnału indukowanego fototermalnie rośnie, gdy laser jest dostrojony do częstości, dla których występują pasma absorpcyjne w badanej próbce. Szczegółowy opis metody można znaleźć m.in. w publikacji prof. Alexandre Dazziego i wsp. pt. *Theory of infrared nanospectroscopy by photothermal induced resonance* (J. Appl. Phys., vol. 107, no. 12, 2010).

W 1971 roku dwaj Japończycy, Yoneda i Horiuchi, po raz pierwszy wykorzystali geometrię całkowitego wewnętrznego odbicia w technice fluorescencji rentgenowskiej (XRF), co pozwoliło na znaczną poprawę czułości i umożliwiło badanie próbek o małych objętościach (mikrolitry). Preparatyka próbek do badań z użyciem spektrometrii fluorescencji rentgenowskiej całkowitego odbicia TXRF jest łatwa – próbkę w postaci ciekłej lub zawiesiny nanosi się na płaski nośnik (dysk) tak, aby tworzyła na nim bardzo cienką warstwę o grubości mniej niż 50 µm. Przyjmuje się, że optymalna objętość próbki to ok. 5-20 µl. Analizę ilościową wykonuje się z użyciem wzorca wewnętrznego dodawanego w znanym stężeniu do każdej próbki.

Zastosowanie spektroskopii mikro fluorescencji rentgenowskiej (mXRF) daje możliwość nie tylko analizy jakościowej w obszarze 25 mm (wzbudzenie poprzez polikapilarę), ale również mapowania składu pierwiastkowego na powierzchni próbki w zakresie nawet do 200 x 160 mm, bez specjalnego przygotowywania.

S-3

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Porometry kapilarne i porozymetry rtęciowe - aparaty kapilarno-przepływowe zaprojektowane do dokładnych pomiarów porów przelotowych w materiałach filtracyjnych. Łatwe w obsłudze i bezpieczne podczas użytkowania porozymetry rtęciowe zdolne do pomiaru rozkładu wielkości oraz objętości porów dostępnych na zewnętrznej powierzchni materiału w bardzo szerokim zakresie średnicy, nawet od 3.6nm do 1100µm.

Analizatory gęstości ciał stałych - piknometry gazowe umożliwiają uzyskanie dokładnych wyników dla dowolnego typu stosowanych celi pomiarowych. Analizatory gęstości nasypowej mogą korzystać z szeregu cylindrów o stopniowanej wielkości, co umożliwia ich dostosowanie do wymagań różnych norm i standardów. Miniaturowe mieszalniki karuzelowe gwarantują wytwarzanie reprezentatywnych próbek w dużych ilościach.

Indeks osobowy
Name index

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