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im. Jerzego Habera PAN

Polski Klub Katalizy

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Plenary lectures

PL-1

Mesoporous vanadium catalysts for selective oxidations

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Vanadium-containing oxide catalysts are efficient in alkane oxidehydrogenation (ODH) [1] and selective oxidation of a range of organic compounds (aromatics, alcohols, etc.) as well as in de-NOx. They are a paradigmatic example of the influence of nature and dispersion of VOx species on the catalytic efficiency and the selectivity of the oxidation. Though bulk vanadia catalyzes total oxidation, highly dispersed species (isolated V atoms, oligomers or monolayers) are selective to dehydrogenated or partially oxidized products [1, 2]. Thus, to increase the specific activity keeping good selectivity, efforts have been devoted to increase such dispersion either by improving the interaction with the support (for instance, with titania [2] or supported titania [3] to get it) or by using high specific surface area mesoporous supports to increase the vanadium load while keeping good dispersion.

Ordered mesoporous MCM-41provide great specific areas but siliceous surface interacts weakly with VOx species leading to V segregation with V contents >1.5 wt.%, when prepared by direct hydrothermal method. Higher V loads while keeping the dispersion of vanadium in tetrahedral isolated species can be reached with SBA-15 (3.3 wt.%) [4], or using alternative synthesis methods, like the atrane route [5], which allows obtaining MCM-41 or bimodal regular mesoporous structures up to Si/V=7 [6].

With the shift to sustainable resources of raw materials, these V-containing catalysts have been investigated for selective oxidation of biomass derived compounds, such as ethanol, giving high productivity to acetaldehyde [7]. However the hydrothermal synthesis of these mesoporous ordered materials are costly and not environment friendly (solvents, surfactants, wastes, non-mild conditions, etc.), which recalls for more sustainable supports synthesis.

Clay minerals can be an important alternative for his goal, due to their abundance in nature, low cost and quite easy structural, textural and chemical modifications. Thus, their pillaring using appropriate polycations can generate mesoporosity and high surface areas pillared clay (PILC) supports where vanadium can be dispersed, either in the pillaring polycations or by pillaring with other oxides that interact strongly with VOx species.

By using this latter strategy, Ti-PILC, prepared from a natural montmorillonite under very soft synthesis conditions, has been used as support for vanadium catalysts for the aerobic selective oxidation of ethanol to acetaldehyde. The acetaldehyde yield (74·%) and selectivity (87%) values reached are comparable with those previously reported for related mesoporous catalysts. This allows these supports to be considered as a sustainable alternative for high surface area supported vanadium catalysts.

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PL-2

Unveiling cooperability of active sites in zeolites by synergetic multispectroscopic approach

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To effectively carry out a catalytic process using heterogeneous catalysts, the ideal active centre should possess specific characteristics at the atomic level. It should be capable of participating in electron transfer and possess an open coordination sphere that allows reagents to access it and enable products to diffuse away [1, 2]. These conditions are met in zeolites, which constitute the largest group of heterogeneous industrial catalysts used in oil and hydrocarbon processing and redox catalysis. The exceptional catalytic properties of zeolite catalysts arise from the unique combination of their chemical composition and structure. The isomorphous substitution of aluminium into the SiO_4 tetrahedra generates a negative charge within the framework that is counterbalanced by two distinct types of extra-framework cationic species. The protons associated with Brønsted acid sites (SiOHAl) play a crucial role as active sites in acid-catalyzed reactions [2]. Meanwhile, bare cations and metal-oxo species function as the active sites in redox-catalyzed processes. Research has demonstrated that the proximity of these active centres within the zeolite matrix significantly influences their catalytic activity, both in acid-base and redox catalysis [3, 4]

The primary objective of this study was to achieve a comprehensive understanding at the atomic level regarding the cooperating active centres housed within zeolite matrices. These active centres are pivotal in specific acid-base and redox catalytic processes. The aim was to establish a scientific foundation for the purposeful design of catalysts that exhibit high activity and selectivity for important industrial reactions, such as propene oligomerization and aromatization [3]. To achieve this, we monitored the reaction progress and the formation of intermediates and products, on single aluminium species or aluminium pairs. This was accomplished by utilizing both fundamental and advanced ex-situ and in-situ FTIR measurements, including rapid-scan mode.

In the field of redox catalysis over zeolites, the strategic distribution of aluminium atoms within the zeolite framework has been utilized to control the creation of diverse redox active sites within metallozeolites. The investigation focused on understanding the structure, cooperation, and redox behaviour of counter iron/oxo species in zeolites with MFI, BEA, MOR, and FER topologies. These zeolites are active in crucial processes like N_2O decomposition, N_2O and O_2 splitting and subsequent methane oxidation [3, 4]. This comprehensive analysis involved a combination of techniques, including Mössbauer spectroscopy, FTIR, and XAS methods. These techniques were applied under both in-situ and ex-situ conditions, complemented by assessments of catalytic activity.

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PL-3

Application of organosilane species in material science and catalysis

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Silica is commonly used as a support for different active species in catalysis. One of the advantages of silica application is the ease of synthesis of silica of various structures, including ordered mesoporous ones. These materials, that are usually catalytically inert, can be modified in order to generate active species. Among different possible modifiers, organosilane species proved to be very effective. An important asset of organosilane species is the ease of its incorporation on the silica surface, which can be performed during the silica synthesis or by post-synthesis modification procedures. Moreover, depending on the kind of organosilane species, it can serve as a source of acidic or basic centres, that can be used e.g. in esterification [1], oxidative desulfurization [2] or Knoevenagel condensation [3,4]. Furthermore, as a result of incorporation of organosilanes species, the hydrophilic/hydrophobic character of pristine silica can be modified. In addition, the organosilane species previously incorporated on silica surface can be sacrificed in order to obtain a high dispersion or lower crystal size of another modifier, like Au or Ag. The above-mentioned aspects of application of organosilane species in material science and catalysis will be presented and discussed.

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Komunikaty ustne
Oral communications

O-1

Where is the hole? – photogenerated electron holes and their fate in photocatalysis

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Photocatalytic redox reactions comprise reduction and oxidation half-reactions driven by photogenerated electrons and holes in the conduction and valence bands, respectively. The localization and energy of these charges are usually well-defined in the case of single semiconductors used as photocatalysts; however, the situation becomes more complex for semiconductor/semiconductor, semiconductor/metal nanoparticle and semiconductor/dye systems. In this presentation, the fate of holes – or, more precisely, photogenerated oxidation centres – will be compared and discussed.

Holes photogenerated at semiconductor photocatalysts are usually consumed in oxidation half-reaction taking place at the surface. With numerous oxides, hydroxyl radicals can be generated due to one-electron oxidation of water or hydroxyl groups. The situation becomes more complicated when a photosensitizer is attached to the oxide surface. In the case of organic or inorganic dyes, their excited states often enable the electron injection into the conduction band, presenting a classical photosensitization mechanism. A positive charge, the equivalent of a hole, remains at the photosensitizer; however, its oxidation property is less apparent than that of the hole in the valence band. The problem is even more complex when a metal (Ag, Au) nanoparticle is used instead of the dye molecule. The questions arise – how does the oxidation half-reaction proceed in such systems? Where is “the hole”? How do such systems operate as photocatalysts? We tried to answer these non-trivial questions by analysing anatase and rutile TiO_2 modified with silver and gold nanostructures of different sizes. Our results show that such modification is not always advantageous. Interestingly, the surface plasmon resonance is usually not responsible for efficient photosensitization and is not in charge of the photocatalytic activity of titania in the visible light region. More likely, catalytic properties of metal nanoparticles may play a beneficial role in enhancing the overall photocatalytic activity.

Relevant problems related to the nature of reactive electron holes, including experimental verification of the hole transfer processes, can be considered in photosensitized systems based on the photoinduced hole injection [3], various photoanode architectures [4] and different types of junctions formed between two semiconductors [5]. In this presentation, the fate of holes – or, more precisely, photogenerated oxidation centres – will be compared and discussed.

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O-2

Catalytic performance of MCM-41 and MCM-48 silicas doped with copper by ADP method in the low-temperature NH_3-SCR process

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MCM-41 and MCM-48 types of mesoporous silicas modified with copper through the ammonium driven deposition precipitation (ADP) technique have showed their effectiveness as catalysts in the low-temperature process of selective catalytic reduction of nitrogen oxides by ammonia (NH_3-SCR). Parent silica materials and copper-modified samples were characterized by XRD method (porous structure of the samples), low-temperature nitrogen sorption (textural parameters), UV-Vis-DRS (form and aggregation of deposited copper species), ICP-OES (chemical composition) and H_2-TPR (reducibility of catalysts). Following their preparation, materials were then examined as catalysts in the low-temperature NH_3-SCR process.

ADP modification approach is particularly noteworthy due to challenges in uniformly applying catalytically active materials on mesoporous silica surfaces, which are known for their lack of ion-exchange ability. In ADP functionalization process $[Cu(NH_3)_4(H_2O)_2]^{2+}$ coordinated cations are electrostatically adsorbed on the negatively charged surfaces of mesoporous silicas. [1] This resulted in the copper primarily deposited in the form of highly dispersed cations, optimizing the materials' catalytic activity, especially in low-temperature NH_3-SCR applications. This research indicates that both types of modified silica achieve an NO conversion rate exceeding 90% within the temperature range of 225-325°C. However, Cu-MCM-48 exhibits slightly better performance over Cu-MCM-41. This enhanced activity can be attributed to the kind of MCM-48 channel system, which likely facilitates better dispersion and accessibility of the active sites.

Mesoporous silicas such as MCM-41 and MCM-48 offer considerable potential in catalysis, attributed to their uniformly distributed pores, large surface area and high porosity. [2] However, their lack of natural ion-exchange properties presents challenges in dispersing catalytically active components across their surfaces efficiently and uniformly. [3] This limitation not only complicates the deposition process but also makes it costly, which inhibit their widespread application in catalysis. Consequently, the use of methods like ADP for achieving uniform copper species on these mesoporous silicas highlights a significant advancement in overcoming these obstacles.

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O-3

Electric field-assisted photocatalytic reduction of carbon dioxide with water vapor

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Semiconductor photocatalysts can play a crucial role in utilizing abundant solar energy to generate environmentally friendly hydrogen, address greenhouse gases, and degrade organic pollutants [1]. The increasing concerns regarding energy and environmental issues have spurred significant interest in applications utilizing semiconductor photocatalysts. In the past fifty years, there has been rapid progress in photocatalytic technology, marked by extensive efforts focused on improving its efficiency.

The efficiency of photocatalytic reactions relies on the interplay between two competing processes: the redox reactions involving adsorbed reagents driven by photoexcited carriers (electrons and holes) and the recombination of electron-hole pairs [2]. Generally, the majority of the loss of photogenerated charges in semiconductors occurs due to multiphonon recombination at bulk defects [3]. To address this issue, various strategies have been devised to control the behavior of energy carriers and impede their recombination rate. These approaches encompass the creation of diverse semiconductor heterojunctions through the integration with a secondary substance, such as noble metals and other semiconductors [4]. This leads to the establishment of a built-in electric field that influences free electrons and holes, causing them to undergo acceleration in opposite directions due to their chargers.

Despite extensive research efforts, there is still uncertainty regarding the extent to which the electric field can amplify the efficiency of photocatalytic processes. Comparisons between current studies are challenging due to variations in process conditions, photocatalytic materials, and the unknown magnitudes of built-in electric fields. Therefore, it is crucial to conduct fundamental studies on the impact of the electric field on the progression of photocatalytic processes and establish a correlation between the strength and direction of the electric field and the physicochemical and catalytic properties of photocatalyst materials. The investigation was carried out using rutile, rutile – anatase, Pt/rutile and Pt/anatase materials. Their photocatalytic performance under the influence of electric fields was investigated in the reduction of carbon dioxide with water vapor.

In general, the electric field was shown to improve the photocatalytic activity by a factor of 1.5 – 3 times depending on the specific photocatalyst used. Among the investigated samples, the most active photocatalyst was rutile. This sample was characterized by the lowest surface area and amount of structural defects. Additionally, the study revealed that the electric field alone (without electromagnetic radiation) can activate the catalytic properties of semiconductors due to the field-enhanced thermal emission of charge carriers from traps in the bulk of material.

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O-4

Incorporation of zinc into the protic imidazolium-based ionic liquid: A novel catalytic route to esters plasticizers

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In this work, a novel acidic catalyst based on the protic ionic liquid (1-methylimidazolium triflate, [Hmim][OTf]) and zinc oxide (ZnO) was developed and evaluated for its catalytic performance. Structural analysis was conducted using various techniques including high-resolution mass spectrometry (HRMS), Fourier-transform infrared spectroscopy (FT-IR), Raman spectroscopy, nuclear magnetic resonance (NMR), and X-ray absorption spectroscopy. The results revealed an alternative structure and mechanism for the formation of the ionic liquid/ZnO adduct [Hmim][OTf] ZnO. The liquid system was synthesized with a molar ratio of [Hmim][OTf] to ZnO of 3:1 and demonstrated to be an effective acidic catalyst and solvent for the synthesis of alternative plasticizers.

Specifically, [Hmim][OTf]-ZnO catalyst (10 mol%) was utilized for the esterification of succinic acid, adipic acid, and lactic acid with two alcohols, 1-butanol and 2-ethylhexanol. Remarkably, the use of 2-ethylhexanol resulted in the complete conversion of succinic acid within 1 hour at 130 °C. The synergistic effect of the ionic liquid and ZnO was demonstrated by comparing the catalytic efficiency of the individual components when used separately. Moreover, [Hmim][OTf]-ZnO exhibited stable catalytic activity over six consecutive reaction cycles without a significant drop in efficiency.

This study underscores how structural studies can provide a basis for the rational design and development of acidic catalysts, thereby contributing to more environmentally friendly and economically feasible processes.

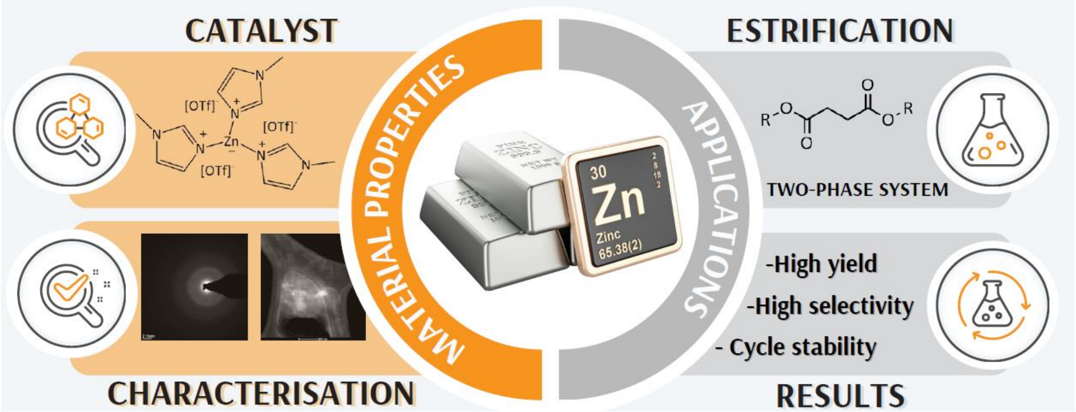

Fig. 1. Graphic illustration of the synthesis and application of incorporated of zinc into the protic imidazolium-based ionic liquid.

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O-5

Degradation of organic compounds via wet peroxidation – role of ROS formation and adsorption processes on composite and mixed oxide catalysts

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The formation of reactive oxygen species (ROS) by hydrogen peroxide activation involves many reactions occurring at the active redox centres of Fenton-like catalysts or acid-base surface functional groups mediating electroprotic reactions. By combining these two functions in one material (by obtaining a catalyst consisting of two types of oxides, redox-active transition metal oxides and the d^0 group of transition metal oxides, which are redox-inactive under ambient conditions), it is possible to obtain catalysts that can be used in advanced oxidation processes, which are a highly effective and promising method of wastewater detoxification. [1]

The present study aimed to investigate the influence of the catalyst composition (type of transition metal, presence of an admixture) and the role of the generated reactive oxygen species in the oxidation of model organic pollutants (organic dyes and antibiotics).

The obtained materials were synthesised using coprecipitation or hydrothermal methods and characterised by the X-ray diffraction (XRD) technique and Raman spectroscopy to confirm their structure. The formation of reactive oxygen species was confirmed by using EPR spectroscopy (spin trapping with DMPO and oxidation of TEMP to identify hydroxyl radicals and singlet oxygen, respectively) and Raman spectroscopy (for peroxo anions). In addition, the activity of the catalysts in organic dye degradation as a test reaction was investigated. As a model, wastewater pollutants methylene blue, rhodamine B, and ciprofloxacin were used.

The results obtained in this study showed synergy between adsorption of toxicant molecules on catalysts surface and activity in ROS formation (both hydroxyl radicals and singlet oxygen) and their ability to the degradation reactions. The highest activity in the degradation of organic dyes is demonstrated by catalysts that generate the highest amount of hydroxyl radicals due to the decomposition of H_2O_2 (e.g. CuO_x/Nb_2O_5 > V-P-Nb_2O_5 > $NbCeO_x$ > CeO_x). This is due to the fact that hydroxyl radicals are responsible for the degradation of dyes. However, in the case of ciprofloxacin degradation, we observed an unexpected role of ROS. [2] It was found that superoxo and peroxo species significantly increased the efficiency of antibiotic adsorption on the surface of Nb_2O_5 by modifying its surface charge. The highest adsorption efficiency was observed under neutral conditions, in which ciprofloxacin was a zwitterion.

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O-6

Catalytic activity of Cu, Ni and bimetallic Cu-Ni nanoparticles supported on graphitic carbon nitride

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Nanosized Ni particles dispersed finely over g-C_3N_4 are very active electrocatalysts with MOR onset at potential 0.35 V and charge transfer resistance 0.12 kΩ. The Cu incorporation in the hybrid material evoke loss of activity mostly due to Cu^+ irreversible reduction/oxidation to Cu^0 and Cu^{2+}, CuO segregation and influencing electron transfer process which results in the increasing in the redox potential. These results represent an important step towards light-enhanced electro-reactive systems and sensors in which heterojunction formation can facilitate electron-hole separation and enable more efficient energy transfer.

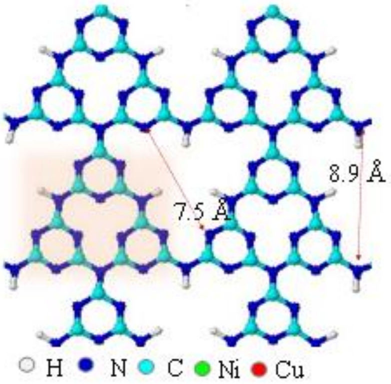

Fig. 1. Optimized structural elements of graphitic carbon nitride: heptazine (tri-s-triazine) units (marked) linked by bridging -NH- groups and N-H groups on their edges forming condensed heptazine rings.

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O-7

Metal phosphates and metal oxides doped with phosphate species as heterogeneous catalysts for the oxidation of organic compounds

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For the last few decades, metal oxides have attracted particular attention as promising heterogeneous catalysts dedicated to the oxidation of organic compounds using hydrogen peroxide and ozone as oxidants. However, very little attention has been paid to the catalysts based on metal phosphates or metal oxides doped with phosphate species, which exhibit several desirable properties.

This study is devoted to evaluating the influence of phosphate dopants on the reactivity of niobia-, ceria- and vanadia-based nanomaterials in the selective and total oxidation reactions of selected organic compounds. All catalysts used in this work were synthesized via facile hydrothermal methods and characterized by means of XRD, FT-IR, UV-vis, NH_3-TPD, XPS, TEM/EDS/EELS, N_2 physisorption, elemental analysis, and zeta potential measurements. The contribution of selected ROS to the degradation of organic compounds was estimated using ROS scavengers. The degradation pathways and products were identified using ESI-MS. The mineralization efficiency was estimated based on TOC analyses.

It was documented that samples containing phosphate species are much more efficient in the degradation of organic compounds in the presence of H_2O_2 [1] or O_3 [2] as oxidants than pristine metal oxides. For niobia-based materials, the most pronounced differences in the reactivity of the parent Nb_2O_5 and phosphate-doped samples were observed under strongly acidic conditions (pH ~ 2.4), at which the most active doped catalysts (Nb/P molar ratio = 5/1) was approximately 6 times more efficient in the removal of methylene blue (MB) than the parent Nb_2O_5 (Fig. 1). The observed enhancement in the degradation efficiency was attributed to the increased generation of singlet oxygen ($^1O_2$), which was identified as the main oxidizing agent responsible for efficient discoloration of MB. More details on the origin of the improved reactivity of phosphate-doped samples in the oxidation of organic compounds will be provided during the presentation.

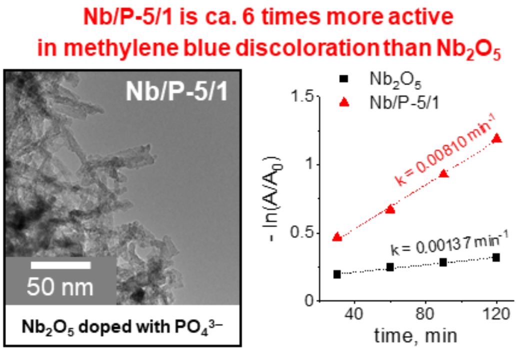

Fig. 1. HR-TEM image of the most active phosphate-doped sample and the pseudo-first order plot presenting differences in reactivity of parent Nb_2O_5 and phosphate-doped sample (*k* - estimated reaction rate constant).

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O-8

Produkcja biopaliw na drodze transestryfikacji i hydrokrakingu z użyciem katalizatorów heterogenicznych

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Produkcja czystych, przyjaznych środowisku paliw alternatywnych zgodne jest z celami zrównoważonego rozwoju oraz może przyczynić się w niedalekiej przyszłości do zastąpienia nieodnawialnych paliw kopalnianych [1,2]. Ponadto problemy środowiskowe związane z nadmierną eksploatacją paliw kopalnych, czynniki ekonomiczne i geopolityczne wpływają na kształtowanie się wysokich cen ropy naftowej, co skłania do powolnej rezygnacji z dotychczas stosowanych paliw kopalnych [3]. Potencjalnym źródłem do produkcji nietoksycznych, biodegradowalnych i odnawialnych paliw są trójglicerydy zawarte w olejach roślinnych, tłuszczach zwierzęcych czy olejach algowych [4,5]. Biodiesel produkowany z wymienionych olei cechuje się podobnymi właściwościami (gęstość, lepkość, temperatura zapłonu, temperaturą krzepnięcia i wartość opałowa) do konwencjonalnego oleju napędowego wydzielanego z ropy naftowej [6]. Dodatkowo, oleje algowe, z racji na szybkie tempo wzrostu, łatwość uprawy oraz możliwość sekwestracji CO_2 mogą stać się istotnym surowcem stosowanym do produkcji biopaliw [7,8].

W badaniach skupiono się na wykorzystaniu oleju rzepakowego i algowego odpowiednio do prowadzenia procesów transestryfikacji i hydrokrakingu z wykorzystaniem katalizatorów heterogenicznych naniesionych na komercyjne zeolity (BEA i ZSM-5; materiały z firmy Zeolyst International, Kansas City, USA – forma amonowa). Proces hydrokrakingu prowadzono z wykorzystaniem katalizatorów bimetalicznych Ni-M (M = Ce, Cu, Zr), natomiast reakcję transestryfikacji olejów katalizowano heterogenicznymi układami zawierającymi tlenki metali ziem alkalicznych (MgO, CaO, SrO) jako fazę aktywną. Poza testami aktywności katalitycznej, przeprowadzono badania właściwości fizykochemicznych spreparowanych katalizatorów technikami H_2-TPR, NH_3-TPD, CO_2-TPD, XRD, BET, FTIR oraz SEM-EDS. Uzyskane wyniki wykazały wysoką aktywność i selektywność zeolitowych katalizatorów w procesach transestryfikacji i hydrokrakingu. Wyniki aktywności katalitycznej potwierdziły promujący wpływ Ce, Cu, Zr na wartość konwersji trójglicerydów katalizatorów niklowych osiąganą w procesie hydrokrakingu. Natomiast w przypadku procesu transestryfikacji, najaktywniejszymi katalizatorami wykazującymi najwyższe wartości konwersji trójglicerydów i wydajności w kierunku tworzenia estrów metylowych wyższych kwasów tłuszczowych były katalizatory CaO, ze względu na ich najwyższą zasadowość oraz najlepsze właściwości sorpcyjne w stosunku do metanolu.

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O-9

Szkła potasowe domieszkowane metalami o właściwościach redoksowych jako katalizatory dopalania sadzy

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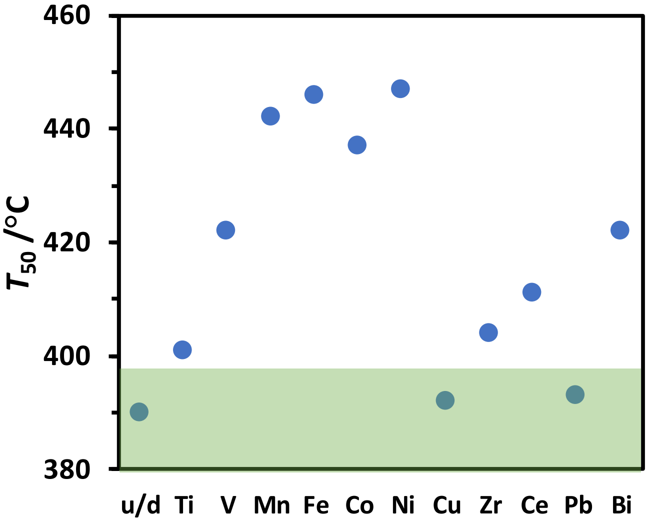
Zawieszone w powietrzu cząstki stałe, których reprezentatywny przykład może stanowić sadza wraz z osadzonymi na jej powierzchni toksykantami, mogą być odpowiedzialne za wywoływanie szeregu chorób układu oddechowego i krążenia, a nawet za rozwój zmian mutagennych, które mogą prowadzić do nowotworów. Zastosowanie metali alkalicznych można uznać za najbardziej obiecującą alternatywę dla metali szlachetnych jako składników tlenkowych układów katalitycznych do dopalania sadzy. Wśród układów opartych na alkaliach należy wyróżnić szkła, które dodatkowo funkcjonalizuje się poprzez domieszkowanie innymi metalami. Celem niniejszej pracy było wyjaśnienie, w jaki sposób domieszkowanie szkieł potasowych metalami o właściwościach redoksowych może wpływać na ich aktywność w katalitycznym spalaniu sadzy.

Szkła potasowo-krzemianowe ($25K_2O$-$59SiO_2$-$16CaO$ % mol.) zsyntetyzowano z SiO_2, K_2CO_3 i $CaCO_3$ poprzez ich topienie w temperaturze 1345°C/1 h. Szkła domieszkowane (5 % mol.) przygotowano przez następcze topienie szkła wyjściowego z odpowiednią ilością tlenku domieszki (Ti, V, Mn, Fe, Co, Ni, Cu, Zr, Ce, Pb, Bi) w temperaturze 1340°C przez 0,5h. Struktura otrzymanych preparatów została zweryfikowana metodami XRD, RS i FTIR, ich skład chemiczny metodą XRF, a właściwości powierzchniowe zbadano metodami XPS, DRIFT i UV/Vis-DR. Aktywność zsyntetyzowanych preparatów przetestowano zarówno dla dopalania sadzy w kontakcie ścisłym, jak i luźnym, w atmosferze wzbogaconej w NO i bez tego dodatku.

Przeprowadzona charakterystyka potwierdziła amorficzny charakter badanych próbek. Aktywność badanych układów w dopalaniu sadzy jakkolwiek wysoka, jedynie w przypadku szkieł domieszkowanych Cu i Pb była obiecująca w porównaniu z aktywnością wyznaczoną dla szkła niedomieszkowanego (Rys. 1). Stwierdzono korelację pomiędzy termiczną stabilnością potasu a aktywnością katalityczną. Obecność stabilnych powierzchniowych form potasu powoduje wyższą aktywność podczas całkowitego utleniania sadzy.



Rys. 1. Aktywność badanych domieszkowanych szkieł wyrażona jako temperatura 50% konwersji sadzy.

Podziękowania: Niniejsza praca została sfinansowana ze środków Priorytetowego Obszaru Badawczego *Antropocen* w ramach programu „Inicjatywa Doskonałości – Uczelnia Badawcza” w Uniwersytecie Jagiellońskim.

O-10

Zeolite nanosheets in solution – building blocks of nanoscale composites

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Zeolites are one of the most efficient catalysts having 3-dimensional (3D) aluminosilicate networks which can also form 2-dimensional (2D) structures, composed of ultrathin layers. Modification of 2D layered materials through interlayer space expansion and surface functionalization has been extensively developed [1]. The most efficient and versatile approach to exploiting the flexibility of 2D materials is through liquid exfoliation to produce solutions of monolayers [2]. Recently we have shown that exfoliation can be achieved directly in high yield by soft chemical treatment with tetrabutyl hydroxide solutions [3].

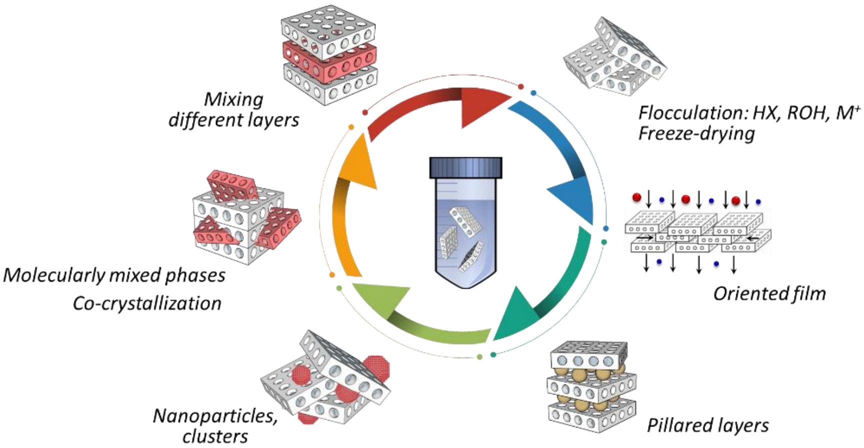

Fig. 1. Zeolite nanosheet dispersions as precursors for nanoscale composites.

Exfoliated layered zeolites can be intimately combined in solution with other compounds to form chemical combinations at will and produce novel materials that have not been possible before. They allow formation of hybrid catalyst simply by mixing zeolite layers and other active compounds. The examples are metal nanoparticles, metal oxide nanoparticles, and intimate mixtures of zeolites with different topologies (MWW/MFI) or liquid silicas.

The composites obtained with the use of the zeolite monolayers often displayed better catalytic properties than those obtained by conventional methods. Novel capabilities include top-down preparation of oriented discs and films.

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O-11

On the Design of Metal-Support Interface in Methanol Electrocatalytic Oxidation

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In this work, we present the theoretical investigation of the $SrTiO_3$ perovskite-supported Pd catalyst in the methanol electrooxidation reaction. In order to determine the metal-support interactions, we have designed a system consisting of the Pd (110) double layer supported on one of the two possible terminations of (110) perovskite surface. These terminations are characterized by different reducibility of the layer directly interacting with the Pd bilayer and result in the difference in the stability of the surface-bound intermediates. Despite the fact that the Pd surface is identical in terms of geometry, we have observed significant differences in the overpotential required for the reaction – in the case of TiO2 termination the overpotential has been determined to 0.68 V, while in the case of SrO termination – it amounts to as much as 1.35 V. We further investigate the charge transfers within the components of the system and the geometries of the intermediates to unravel the role of the electron structure on the overall efficiency of the process.

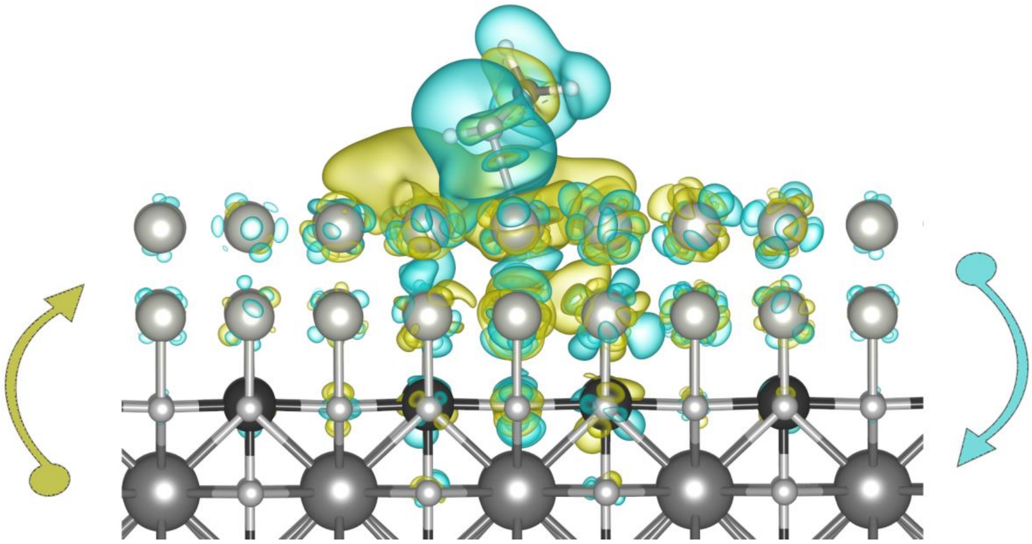

Fig. 1. Charge transferred between the catalyst surface and the reactive species.

O-12

Selective Oxidation of 4-hydroxy-3,5-dimethoxybenzyl Alcohol by Porous N-Doped Carbonaceous Materials via Sonocatalysis

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Introduction :

The selective oxidation of 4-hydroxy-3,5-dimethoxybenzyl alcohol, which serves as a lignin model compound, was studied extensively in the presence of carbon-based materials acting as catalysts. These materials have been well-known for their unique properties in sono-catalysis, making them effective in enhancing the degradation process under sonocatalytic conditions. Carbon nanotubes, graphene, activated carbon, and doped-carbon are commonly utilized in applications related to water treatment and catalysis [1,2]. Incorporation of heteroatoms such as nitrogen, phosphorus, boron, and sulfur alters their characteristics, thereby enabling the development of novel metal-free catalytic processes.In this study, we synthesized porous carbon materials, both N-doped and non-N-doped, for the selective oxidation of 4-hydroxy-3,5-dimethoxybenzyl alcohol. Experiments were conducted at varying sonication frequencies to elucidate their influence, and calorimetry was employed to precisely measure energy requirements. The interaction between pyridinic nitrogen and carbonyl groups was found to be crucial in affecting sonocatalysis, as it suppressed the radical pathway and reduced sonoactivity [4].

Experimental/methodology :

The results from silent control tests, comparing sonocatalytic tests, showed that N-doped catalysts demonstrated varying sonocatalytic activities and selectivities. N-doped carbons exhibited better conversion and selectivity to aldehydes compared to non-doped carbon (C-meso) during the silent control tests, making C-meso the best candidate for subsequent sonocatalysis. This improvement can be attributed to the presence of N-pyridinic groups, which have the ability to adsorb -OH groups from alcohols. Figure 1 compares the different species of nitrogen in N-doped catalysts, wherein pyridinic nitrogen is responsible for prohibiting the radical reaction during sonocatalysis [4].

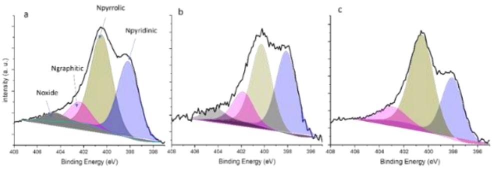

Figure 1. N1s (a) CN-meso Chit; (b) CN-meso and (c) CN-meso gluc

Results and discussion

Porous N-doped carbon materials were synthesized and evaluated as sonocatalysts for oxidizing 4-hydroxy-3,5-dimethoxybenzyl alcohol. Pyridinic N and carbonyl C=O emerged as pivotal active sites. N-pyridinic significantly influenced alcohol conversion, impacting the selectivity. This study underscores the potential of N-doped carbonaceous catalysts in heterogeneous sonocatalysis, highlighting the role of specific nitrogen species and carbon composition. The future studies will survey the effect of other heteroatoms doped with porous carbon material.

Acknowledgements :We thank National Science Center (NCN) for support within research project OPUS 20 No. 2020/39/B/ST5/00076. https://photo-catalysis.org/projects/nanoengineering-of-multicomponent-metal-free-carbonaceous-materials-for-bio-oil.

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O-13

Tailoring Ru/TiO_2 catalysts for selective transformation of biomass-derived 5-hydroxymethyl furfural to value-added chemicals

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5-Hydroxymethylfurfural (HMF) derived from lignocellulosic biomass offers a versatile platform for renewable fuels and chemical production. This work explores tailoring Ru catalysts and reaction conditions to selectively convert HMF into either ring-hydrogenated (2,5-bis hydroxymethyl tetrahydrofuran i.e., BHMTHF) or ring-opened (1,2,5-hexanetriol i.e., HToL) products, both valuable chemicals. Key factors influencing the reaction pathway were identified. Our results showed that solvent plays a crucial role, with 1,4-dioxane favoring BHMTHF and water-promoting HToL production. Lewis acidity and metal-support interaction also impact activity. Optimizing this interaction balances Lewis acidity needed for the selective formation of bishydroxymethylfuran (BHMF) as reaction intermediate in both cases. Further enhancing yields involves optimizing Ru particle size, achieved through different synthesis methods (photon-assisted *vs* traditional wet impregnation), using different precursors, and applying thermal treatments. HRTEM characterization evidenced that, the higher the Ru intensity in ToF-SIMS, the smaller the Ru nanoparticle size. Therefore, regardless of the solvent used (dioxane or water), we demonstrated the existence of a "volcano-shaped" relationship between the product yields and the Ru intensity, thereby revealing the existence of an optimal Ru nanoparticle size to reach high HMF conversion as well as high BHMTHF or HToL yields (Figure 1). Under optimized conditions, >99% BHMTHF yield was achieved in 1,4-dioxane and 75% HToL yield in water.

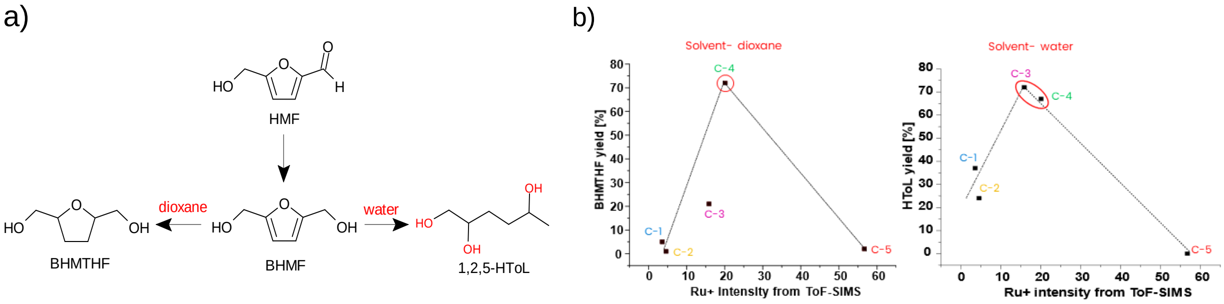

Fig. 1. a) Hydrogenation of HMF towards BHMTHF or 1,2,5-HToL b) Relationship between the Ru intensity in ToF-SIMS (as a fingerprint of the Ru nanoparticle size) and the yield to BHMTHF (in pure 1,4 dioxane) and HToL (in pure water solvent) after 12 h of reaction. C-1 to C-5 are1%Ru/TiO_2 catalysts prepared by different methods.

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O-14

Boosting Catalysts Performance in Oxygen Reduction Reaction through Transition Metal Doping of Carbon Nanotubes

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Anion Exchange Membrane Fuel Cells (AEM-FCs) are a more affordable alternative to widely used PEM-FCs however they require development of robust catalytic materials for the electrode reactions. The carbon materials are widely regarded as good Oxygen Reduction Reaction (ORR) electrocatalysts due to their relatively low cost, high availability and ease of modification [1]. The concept of modifying the carbon materials by introduction of heteroatoms (O, S, N), together with tuning their structure on purpose, is *de facto* a method for improving their catalytic properties. The ability to modify catalytic performance by heteroatom doping is, however, limited in the applicability, since it enables changing the reduction potentials only to some extent. To obtain higher catalytic efficiency, the addition of metals is needed [2].

Transition metals are widely used for this purpose because of their low price and high availability. They exhibit a high range of oxidation states, facilitating the redox catalytical activity. In this work, four types of MWCNT materials, differing in lengths and diameters, were doped with nitrogen together with iron, iron-cobalt and iron-manganese. The morphology of the resulting catalysts was characterised by X-ray diffraction, Raman spectroscopy and transmission electron microscopy (TEM), whereas elemental analysis, flame atomic absorption spectroscopy and X-ray photoelectron spectroscopy were used for the determination of the catalysts' elemental composition and chemical state of dopants. The rotating ring-disk electrode technique was applied to determine the ORR activity of the doped carbon nanotube catalysts. Finally, the best catalysts were tested in a model FC system. Transition metals were incorporated as metal and oxide nanocrystals (Fig. 1., right). The onset potential, a measure of ORR activity, of the most active catalysts reached the value of about 0.97 V *vs* RHE, just 20-30 mV below the commercial 20% Pt/C catalyst (Fig. 1., left).

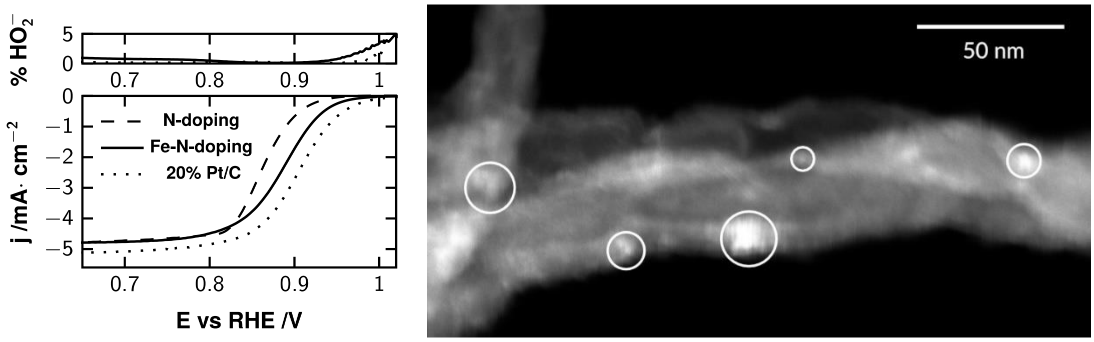

Fig. 1. LSV for ORR in 0.1 M KOH (left), TEM images of iron oxide nanoclusters (marked) on MWCNT (right).

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O-15

Catalytic activity of CuZnAl hydrotalcite derived-materials in continuous flow hydrogenation

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Given the emphasis on cost-effectiveness and environmental sustainability in manufacturing, continuous-flow techniques have become increasingly prevalent. Among these methods, continuous-flow hydrogenation has attracted significant interest for its ability to offer a secure and efficient platform for synthesising organic compounds [1]. We mention the chemoselective hydrogenation of unsaturated aldehydes to saturated aldehydes and unsaturated alcohol. For example, the hydrogenation of 2-methyl-2-pentenal (MPEA) leads to the formation of 2-methylpentanal (MPAA). This compound is an intermediate for the fabrication of drugs, among them meprobamate, classified as a sedative-hypnotic. On the other hand, the formation of 2-methyl-2-penten-1-ol (MPEO) is observed. This alcohol has potential in fragrance synthesis [2].

This work explored the catalytic performance of three CuZnAl hydrotalcite-derived materials with different metal loadings in the continuous flow chemoselective hydrogenation of MPEA. The catalysts were characterized by transmission electron microscopy (TEM), H_2 temperature-programmed reduction (H_2-TPR), and X-ray photoelectron spectroscopy (XPS).

The catalytic performance of CuZnAl materials depends on the reaction conditions, the copper chemical state, and the chemical environment present on the surface of the materials. The hydrogenation of MPEA allows the production of, primarily, MPAA (the desired product) in the presence of two other products with different ratios. Moreover, for the catalyst with the highest Cu loadings, the selectivity for MPAA decreased in favour of MPEO at high temperatures and pressures.

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O-16

Machine Learning-assisted Raman Spectroscopy to Identify Plasticizers in PVC Heritage Objects

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Works of art made of plasticized poly(vinyl chloride) (PVC) presents unique and pressing conservation challenges. Until the 1990s, the poor qualities of plastics were not widely known or considered within the art conservation community [1]. Recent research on long-term PVC degradation indicates that the identity of a plasticizer is important in studies of plasticizer loss and associated conservation challenges [2]. Non-destructive methods of analysis are frequently required in the field of heritage science: therefore, vibrational spectroscopic techniques such as infrared (IR) and Raman spectroscopy are widely employed [3].

Raman spectroscopy, as a non-destructive method, combined with machine learning (ML), was successfully applied as a quick method of plasticizer identification in PVC objects. ML algorithms such as Convolutional Neural Network (CNN), Random Forest (RF), Support Vector Machines (SVM), and Linear Discriminant Analysis (LDA) were applied for the classification and identification of the most common plasticizers used in the case of PVC such as dioctyl terephthalate (DOTP), dioctyl phthalate (DEHP), diisononyl phthalate (DINP), Bis(2-ethylhexyl) adipate (DEHA) and unplasticized PVC was used as the blank sample (**Fig. 1**). The CNN model was able to successfully classify the five plasticizers under study from their Raman spectra with a high accuracy of (98%), whereas the highest accuracy (100%) was observed with the RF algorithm. The accuracy of the model confirms the capability of one to recognize small variations in nearly identical spectra to differentiate and classify PVC plasticizers.

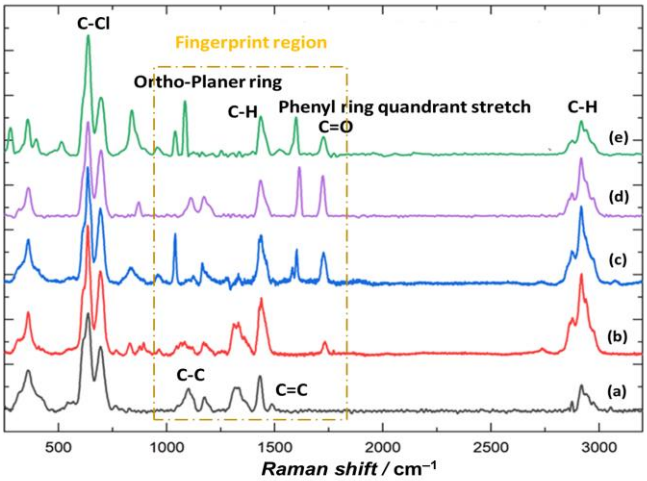

Fig. 1. The exemplary Raman spectra of PVC (a) and PVC plasticized with DEHA (b), DINP (c), DEHP (d), and DOTP (e) respectively.

The finding opens doors for the development of robust and economical tools for conservators and museum professionals for fast identification of materials in heritage collections. Therefore, conservators obtain an easily accessible way to identify and classify plasticizers in order to maintain historically significant PVC collections.

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O-17

Exploring the efficacy of copper(II) phosphate as a heterogeneous catalyst for the degradation of ciprofloxacin via photo-assisted Fenton-like process

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Pharmaceutical compounds, often inefficiently removed by conventional wastewater treatment methods, pose significant risks to both aquatic ecosystems and human health [1]. One of these pharmaceuticals is ciprofloxacin (CIP), a modern antibiotic used to treat a wide range of bacterial infections. For this reason, it is important to develop new methods for efficient elimination of this pollutant from water sources. Among these methods, Fenton-like reactions appeared as one of the most promising and environmentally benign approaches to attain this goal. In general, these processes utilize transition metal oxides (e.g. Fe_2O_3 or CuO) as heterogeneous catalysts to activate hydrogen peroxide toward formation of highly oxidizing reactive oxygen species (ROS) capable of mineralizing various organic pollutants [2]. Recent literature reports have shown that reactivity of metal oxide-based catalysts in advanced oxidation processes (AOPs) may be improved by doping these nanomaterials with phosphate ions or formation of metal phosphates [3]. This study fits in with this scientific trend and aims at exploring the potential application of copper(II) phosphate ($Cu_3(PO_4)_2$) as a novel catalyst for the degradation of CIP via Fenton-like and photo-assisted Fenton-like processes.

All catalysts used in this work were synthesized using facile precipitation or hydrothermal methods, and characterized by a wide range of research techniques, including XRD, XPS, FTIR, DR UV-vis, SEM-EDS, and nitrogen physisorption. The activity of the prepared catalysts was tested in the degradation of CIP in the presence of H_2O_2 and/or visible light ($\lambda \geq 400$nm). The efficiency of CIP degradation was followed by UV-vis spectroscopy. Pathways of antibiotic degradation were estimated based on ESI-MS analyses, while efficiency of total organic carbon (TOC) removal was determined by a TOC analyzer.

Results obtained in this study revealed that copper(II) phosphate is much more active in degradation of CIP via Fenton-like process than majority of other metal oxides and metal phosphates selected as reference materials. Only phosphate-doped Fe_2O_3 (P:Fe_2O_3) was slightly more active in CIP degradation under dark conditions than $Cu_3(PO_4)_2$. Interestingly, a different phenomenon was observed in a photo-assisted Fenton-like process in which the latter sample outperformed the former one in terms of CIP removal rate (Fig. 1). Radical scavenging tests led us to establish that the main ROS responsible for efficient degradation of CIP in the presence of copper(II) phosphate were hydroxyl radicals. Concerning the catalysts stability, it has been found that $Cu_3(PO_4)_2$ catalyst could be reused five times without any significant loss of its activity.

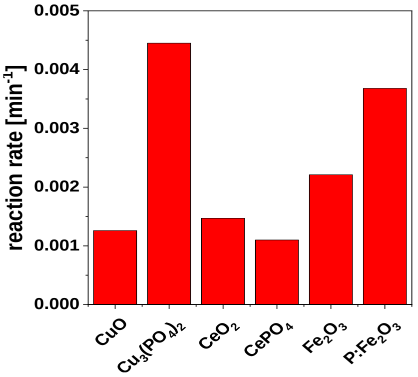

Fig. 1. Comparison of CIP degradation rates in the presence of copper(II) phosphate and other nanomaterials known for their high reactivity in photo-assisted Fenton-like processes.

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O-18

DFT and experimental investigations into mechanistic aspects of CO-PROX reaction over Co_3O_4 nanocubes - activation of reactants and evaluation of the role of surface carbonate intermediates

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Developing efficient CO-PROX catalysts is still a challenge, and depends on the comprehensive understanding of the underlying reaction mechanism that dictates the catalyst performance. There is general agreement that over TMI oxides three main types of surface reaction can take place during the CO-PROX including the desired selective oxidation of carbon monoxide, the harmful H_2 oxidation and the CO hydrogenation, with their relative rates depending critically on the changes in the redox behaviour of the cations constituting the active sites, during the progress of the CO-PROX process [1]. From a mechanistic perspective, the overall CO-PROX process encompasses both intrafacial (Mars–van Krevelen) and/or suprafacial (Langmuir–Hinshelwood/Eley-Rideal) pathways for the oxidation of the CO and H_2 reactants. The involvement of these pathways is regulated by the catalyst's structure, and the prevailing reaction conditions thus the crucial role in controlling the CO-PROX mechanism is played by the activation and stabilization of various reactive oxygen adspecies (ROS) and surface oxygen vacancies (V_O) [2].

In this work, the goal was to determine the mechanism of the CO-PROX reaction at the atomic level through molecular modelling of all conceivable reaction pathways, derived from experimental constraints. Within the developed reaction pathways, evaluation of all intermediate (O_2/O, H_2, H_2O, CO, CO_2, CO_3 adspecies) and final (gaseous CO_2, H_2O) products of postulated reactions was carried out, with a detailed resolution of their geometrical, energetic, electronic and magnetic characteristics. The atomistic thermodynamics was employed to determine the specific conditions (temperature and pressure of the reactants) favouring occurrence of the particular stages of the investigated CO-PROX process. Additionally, determining the activation barriers allowed for discussions on kinetic constraints related to each individual elementary steps of the reaction.

It was demonstrated how the cobalt-oxo $Co\text{-}O^-$, peroxo O_2^{2-}, and superoxo O_2^- adspecies control the suprafacial and intrafacial pathways of the CO-PROX mechanism. Regardless of the type of oxygen involved in the processes of CO oxidation, two distinct types of carbonate adspecies, one serving as reaction intermediates (inferred from isotopic composition) and other acting as spectators (identified through IR analysis) were identified and their surface binding configurations ($Co^{oct}\text{-}CO_3^{2-}\text{-}Co^{oct}$ and $Co^{oct}\text{-}CO_3^{2-}\text{-}Co^{oct}$, respectively) were determined. Isotopic reaction profiles of CO-PROX support the carbonate mechanism with involvement of both $\alpha\text{-}CO_3^{2-}$ and $\beta\text{-}CO_3^{2-}$ as dominant intermediates, with a minor pathway occurring through direct oxidation of CO via the MvK scheme.

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O-19

Optimization of the ethanol steam reforming conditions considering carbon formation, hydrogen production, and ethanol conversion

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As fossil fuel reserves are expected to be exhausted soon, the development of practical uses of alternative energy sources is becoming an urgent issue. Hydrogen is considered to be one of the new generation fuels for transportation and stationary applications. One of the most attractive ways of the production of hydrogen from renewable sources is steam reforming of ethanol (SRE): $C_2H_5OH+3H_2O \rightarrow 6H_2+2CO_2$, $\Delta H^0_{298K} = 173{,}2\ kJ\ mol^{-1}$. So far, many catalysts, both noble metals such as Rh, Ru, Pt, Pd, and Ir, and non-precious transition metals such as Ni, Co, and Cu as well as the combinations thereof have been extensively studied for the SRE reaction. Currently, the high-demand catalysts for hydrogen production via the SRE process seem to be low-cost, widely available Ni- and Co-based materials. To ensure a high dispersion of the metallic active phase, it is usually spread over a high surface area support material, which improves the mechanical properties of the catalyst. Mainly oxides such as Al_2O_3, CeO_2, MgO, ZnO, ZrO_2, and SiO_2 have been used as carriers for the metallic phase in the catalytic SRE reaction. Large-surface area supports, such as γ-Al_2O_3, silica mesoporous materials, and mixed oxides, e.g. $Ce_xZr_{1-x}O2$, usually allow for the formation of strongly dispersed surface precursors and retard sintering processes. A similar effect can be achieved by the introduction of certain modifiers or promoters, which change metal support interactions. Depending on the properties of catalysts and reaction conditions, additional side products of SRE are often observed in the product stream, including carbon monoxide, acetaldehyde, acetone, acetic acid, methane, ethane, ethylene and higher hydrocarbons. Moreover, the catalysts may deactivate with the time-on-stream due to the sintering and formation of carbon deposits [1-3].

In this study, reaction conditions, such as temperature, H_2O/C_2H_5 ratio, and the presence of oxygen in the feed stream, were optimized to inhibit carbon formation, achieve considerable and stable hydrogen production, and increase ethanol conversion. This result provides a reasonable suggestion for the design of an ethanol steam reforming process by experimental validation. Additionally, we aim to establish relationships between catalyst structure and performance and the direction of catalyst development was derived from lifetime tests of the catalyst.

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O-20

CO_2 and H_2O reduction at ZnS photocatalysts

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Photocatalytic conversion of CO_2 into valuable chemicals and fuels by harnessing solar energy is a sustainable and environmentally friendly approach. However, the thermodynamic stability of CO_2 necessitates high-energy inputs for its conversion, making the process energy-intensive. Hence, photocatalysts featuring highly negative conduction band edge potentials are prominent candidates for application in this field. ZnS stands out as a highly promising photocatalyst; however, it still suffers from several drawbacks, including photocorrosion. It has already been demonstrated that ZnS is capable of reducing CO_2 molecules, even in single-electron reduction processes, such as photocatalytic carboxylation. Zinc sulfide is a well-known green light emitter, and because the band gap energy of sphalerite ZnS is 3.5 eV, the emission has to occur with the participation of defect states inside the bandgap energy region. Taking into account the fact that the electron relaxation process from the conduction band to the trap states is much faster than the interfacial electron transfer, one must consider the architecture of the electronic structure as a leading factor influencing photocatalytic activity. Therefore, our work was focused on the modification methods, able to influence the electronic structure of ZnS in a controlled manner. In this work, the synthesis of sphalerite zinc sulfide was optimized in accordance with the substrates' concentration and the presence of oxygen. Furthermore, noble metal modifiers (Pt, Ag, Au, Ru) were deposited via a chemical reduction of previously suspended ions. Moreover, the influence of copper doping on the formation ofinterband electronic states was analyzed. In this presentation, the effects of these modifications will be discussed based on a thorough characterization of as-modified ZnS photocatalysts.

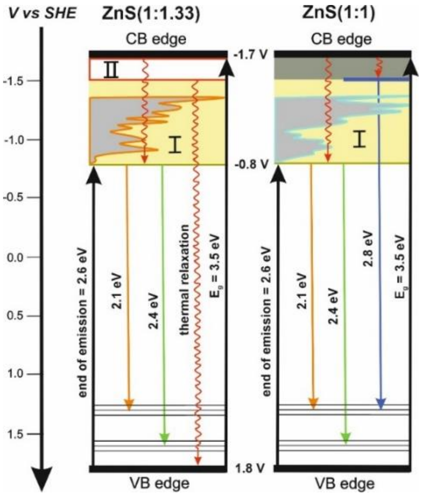

Fig. 1. Electronic structure models of Zinc Sulfide photocatalysts [1].

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O-21

Fischer-Tropsch synthesis – old way to the alternative fuel production with the new heterogeneous catalysts

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The Fischer-Tropsch synthesis is known since 1920 when these two German scientists discovered and optimized the possibility of obtaining fuel from synthesis gas [1]. During this synthesis the ultra-clean, sulfur and nitrogen-free chemicals and fuels can be produced. The source of synthesis gas can be gasification of natural gas, coal or biomass [2 – 4]. The growth in interest in FTS is a consequence of depletion of oil resources and the protection of the environment, which continuous to be destroyed, but also of global demand for fuel and global transportation and environmental policies regarding air quality and vehicle exhaust fumes emitted into the atmosphere [5]. FTS seems to be a good solution for these requirements. However, this synthesis also comes with a number of challenges that need to be solved for better industrial application. In our works [6 – 8] we reported that the zeolite BEA catalysts modified by transition metals as Co, Fe and Ni and prepared by a two-step postsynthesis method developed earlier by Dzwigaj et al. [9] makes it possible to obtain highly active catalysts for Fischer-Tropsch synthesis, resistant to metal particle sintering and exhibiting lower carbon deposition than the usual supported catalysts used in FTS. This work presents iron and cobalt catalysts of BEA zeolites for Fischer-Tropsch synthesis prepared by two different methods: classical wet impregnation and a two-step postsynthesis method which allowed the incorporation of metal ions into the framework of BEA zeolite The present work focuses on the differences in the physicochemical properties of different series of catalysts and the role of metals ions placed in the framework positions of BEA zeolite and their effect on the activity of metallic BEA zeolite catalysts.

The obtained results point that the preparation of MeBEA zeolite catalysts by two-step post-synthesis method allows to localized metal ions into BEA zeolite framework and in this way the obtaining very active, stable and selective catalysts for FTS process with high thermal resistance for sintering and carbon deposition. Moreover, these results show that the incorporation even high metal content into BEA zeolite does not destroy its original and unique structure with effect on the activity of catalysts. The difference in porosity of BEA zeolite does not influence on the activity of MeBEA zeolite catalysts in FTS but has impact on the kind of liquid products formed in this process.

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O-22

Redox properties of manganese-oxide-based catalyst ($K_2Mn_8O_{16}$) during the interactions with O_2 in the context of thermochemical redox cycles. In-situ TEM and DFT

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In this contribution, we present an analysis utilizing in-situ TEM and *ab initio* DFT techniques to examine the redox processes occurring within a manganese-oxide-based catalyst (K_2Mn8O16) during its interaction with O_2 within the framework of thermochemical redox cycles. The scientific inquiry addressed in this work is influenced by various critical factors, including scientific significance and environmental considerations. Despite extensive investigations, a comprehensive and lucid interpretation of the role played by redox changes in the catalysts involved remains elusive, primarily due to the intricate nature of thermochemical redox cycles and the multitude of factors impacting their progression.

The studies proposed herein primarily focus on two key aspects: the analysis of temperature-induced reduction of the catalysts, encompassing changes in phase, structure, morphology, and the behavior of the catalysts under oxidative (O2) conditions. The objective was to pinpoint the optimal manganese redox couple for the deep reduction and oxidation processes under investigation, along with the associated structural alterations. Special attention was devoted to examining the involvement of various oxygen species and oxygen vacancies. The proposed manganese catalytic redox material is renowned for its efficacy in catalytic redox processes, while also being cost-effective, environmentally friendly, and readily accessible. Its versatile structure and redox properties, coupled with its unique morphology - characterized by nanochannel structure and elongated nanorods - present distinct opportunities for exploring and establishing relationships between structure and catalytic behaviour at the molecular level.

The preliminary experiments facilitated an understanding of the impact of temperature on the redox behavior of the proposed manganese catalyst, including the thermal reduction (activation) of the catalysts, as well as their phase, structural, and morphological stability. The second objective, involving the analysis of the redox behavior of the proposed material during interactions with O_2, aimed to elucidate the role of catalyst redox properties, atomic structure (with a focus on various oxygen species and oxygen vacancies), and morphology within the context of thermochemical redox cycles.

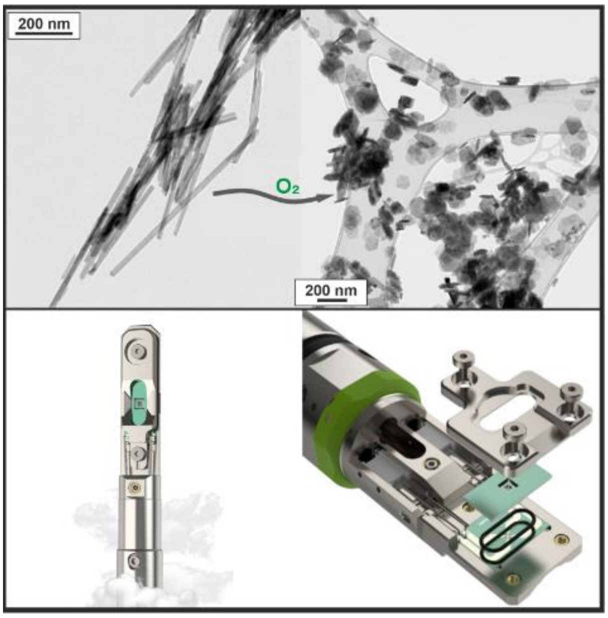

Fig. 1. Schematic presentation of soot combustion over $K_2Mn_8O_{16}$ catalyst during in-situ TEM experiment.

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O-23

Efficiency and factors affecting basic properties of smectite-derived porous composites

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The acidic environment strongly affects the mobility ability of octahedral ions of clay minerals from the smectite group. Proton attack causes gradual release of Mg^{2+}, Al^{3+} or Fe^{3+} cations from the octahedral sheet and some amortization of the tetrahedral one leading to the gradual collapse of the original structure. This phenomenon, however, can be beneficial when the mobility and migration of octahedral ions will be directed. One approach to this issue is the constitution of smectite as a structure-forming platform of crystalline-amorphous clay-derived composites with highly developed porosity.

In this work, we have focused on the determination of the efficiency and factors affecting Mg release from the octahedral sheets of $[Si_8Mg_{5.45}Li_{0.4}O_{20}(OH)_4]Na_{0.7}$ hectorite, the synthetic layered hydrous magnesium silicate introduced by templating method into porous silica-clay composites to enlarge the base properties of parent clay mineral. In this approach, we gauged the application of benign proton attack delivered by the use of mechano-chemical impregnation with a slightly acidic salt solution of $Fe(NO_3)_3x9H_2O$ salt, microwave irradiation, and hydrothermal treatment on the formation of the new base centres in the porous clay-based composites.

Our study showed that applied treatments bring about the auto-transformation of the structure of the clay-derived composite. The leached-out Mg cations were captured on the surface of the porous composite grain, confirmed by an increase of the Mg/Si ratio, and provided the source of cations to nucleate MgO moieties with weak basic properties evaluated by CO_2 sorption. The increase of the Mg/Si ratio was accompanied by the decrease of the (Mg_3OH) absorption bands intensity in hectorite and discussed regarding the formation of dispersed MgO nanostructures capable of adsorbing CO_2. CO_2-TPD study supported by DFT calculations showed that the sorption of CO_2 molecules on MgO basic centres is closely related to the coordination of oxygen sites in the MgO lattice while edge and corner O^{2-} sites facilitate the interaction with CO_2 molecules. Activation of clay-derived composite with Fe^{3+} followed by annealing resulted in the nucleation of nanocrystalline α-Fe_2O_3 of much greater basic potential and ability to capture CO_2 molecules, with the strength and quantity higher than on MgO centres and different kinetic of sorption confirmed by TG/DSC. In this work, the mechanisms leading to nucleation and formation of basic centres on the porous clay-derived composite surface are described in detail with the use of advanced XRD, SEM, FTIR, XPS, TG/DSC, CO_2-TPD methods supported by DFT calculations. This study shows that the application of solvothermal synthesis under microwave irradiation results in significant development of the surface basicity of smectite with an initially small basic character and confirms the importance of clay minerals in the uptake and retention of CO_2.

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O-24

External acidity as performance descriptor for catalytic cracking of polyolefins

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Catalytic cracking is a promising approach to chemically convert polyolefin waste into smaller hydrocarbons, which can serve as feedstock for the chemical industry. Compared to thermal pyrolysis, it can reduce the required process temperature, and further improve the selectivity to more attractive platform chemicals, e.g. aromatics.[1] In order to develop improved catalyst materials for plastic conversion, the structure-performance relationships in these systems must be understood. In conventional cracking of smaller hydrocarbons, methods like the alpha-test show that the cracking activity of e.g. ZSM-5 is directly dependent on the Brønsted acid site (BAS) content.[2] Herein we show that these conventional metrics fail to capture the activity trends in cracking of polypropylene (PP) when using Zeolite-Y catalysts. To explain differences in plastic cracking activity, characterization of 'external' acidity using bulky probe molecules and more elaborate kinetic experiments are required. As a benchmark, hexane cracking activity for different Zeolite-Y catalysts (labeled ZY_x, with x denoting SiO_2/Al_2O_3) was assessed in a fixed bed reactor at 538 °C. The obtained first order rate constants (Fig. 1a) showed an expected trend: For steamed zeolites (all but ZY_6), activity increases with increasing Brønsted acid site content which was probed by Pyridine-IR. However, the same trend does not hold if plastic cracking activity is compared. The catalysts showed similar required temperatures in cracking of polypropylene determined by thermogravimetric analysis (TGA)[3] (Fig.1b). Furthermore, ZY_{80}, which showed one of the lowest hexane cracking activities, exhibited a T_{max} 50 °C lower than ZY_{12} at low catalyst loadings. Therefore, bulk acidity is a poor descriptor for PP cracking activity. Since PP most likely does not enter micropores efficiently,[3] a more appropriate metric might be the non-micropore acidity, which was probed by IR of tri-tertbutyl pyridine adsorbed from the gas phase. The non-micropore acidity was indeed very similar for the catalysts under study, suggesting that plastic cracking occurs largely on the external surface and in mesopores of the zeolites. Therefore, when investigating structure performance relationships in plastic cracking, the use of appropriate probe molecules is vital. The results are likely applicable to other heterogeneously catalyzed processes converting large reactants, including other chemical recycling approaches.

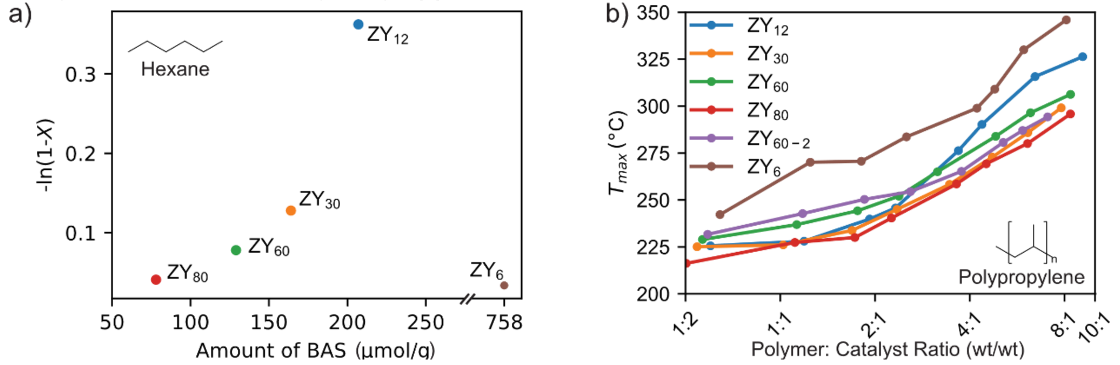

Fig. 1. a) First order rate constant for hexane cracking using ZY_x , *X* denotes conversion. b) Temperature at highest rate for PP cracking (T_{max}) at different catalyst to polymer ratios determined by TGA (5 °C/min). Lower T_{max} implies higher activity.

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O-25

Stability of ruthenium/carbon catalytic materials during operation in carbon monoxide methanation process

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The stable activity of catalysts is an important characteristic, which determines their suitability for industrial applications [1]. The purpose of this study was to investigate the stability of ruthenium systems deposited on carbon under conditions simulating long–term operation in CO methanation. Two series of Ru/carbon catalysts were prepared and studied during CO methanation in a hydrogen–rich gas stream. Two graphitized carbons substantially differing in their surface area (23 and 1457 m^2/g) were used as supports, and Ru loadings of 3 and 6 wt.% were applied. The stability of Ru/C catalysts was examined in a 240 h time on stream test. The samples were characterized by CO chemisorption, XRD, TEM, Raman spectroscopy, TG–MS studies and CO–TPD. The stability of the catalysts over 240 h in the CO + H_2 mixture depended on the support type and Ru loading. The highest CO conversion and increased activity was observed for both catalysts with Ru dispersion above 80%. The tested systems were also resistant to carbon deposition. Interestingly, a similar level of activity was obtained for 3 wt.% Ru supported on the low surface area carbon. It is presumed that the similar activity observed for systems with such different ruthenium dispersion is related to the presence of active sites of different strength and structure on the surface of both small and large Ru particles [2].

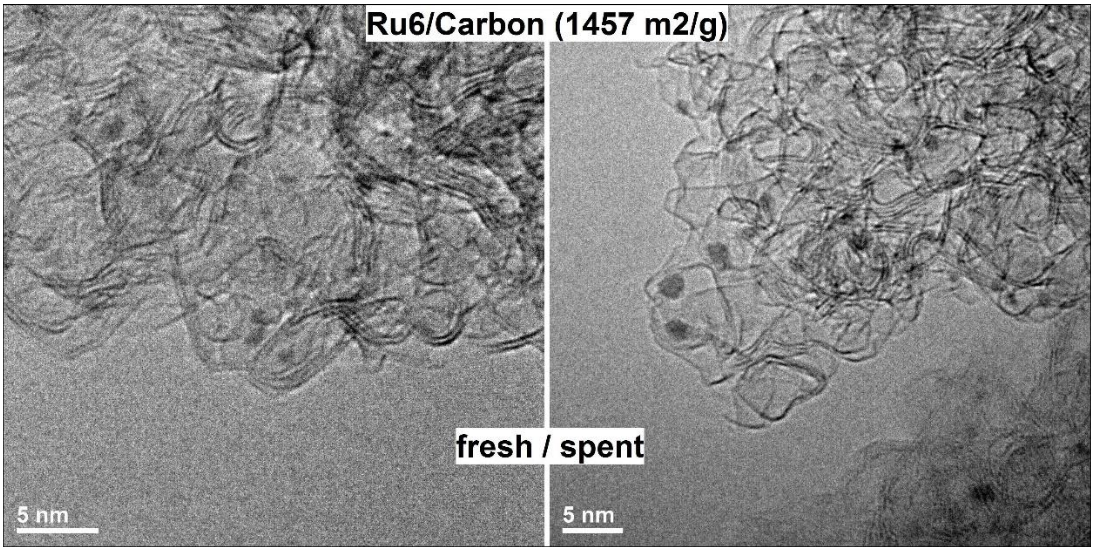

Fig. 1. TEM images of Ru6/C2 catalyst fresh and spent.

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O-26

Spicing up gold catalysts: The role of phosphate dopant in shaping the catalytic performance of Au/FeNbO$_x$ in gas-phase methanol oxidation

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Emerging from the seminal works of Haruta [1] and Hutchings [2], heterogeneous gold catalysts have attracted growing attention among researchers over the last four decades. It is well-established that the composition and properties of the support significantly influence the catalytic performance of Au-containing catalysts [3]. Among the potential dopants, phosphate ions are believed to act as both structural and electronic promoters, while also being capable of tuning the acidic-basic properties of the support. All these features can be considered as key factors shaping the catalytic performance in oxidation processes.

The main objective of this research was to evaluate the impact of doping phosphate ions on the characteristics of iron/niobium single and mixed oxides, serving as supports for gold nanoparticles (Au NPs), particularly with regards to the dispersion of the active phase, electronic and acidic-basic properties, and catalytic activity in the oxidation of methanol (MeOH). All of the metal oxide-based supports prepared for this study were synthesized using a straightforward hydrothermal method. Gold nanoparticles were deposited according to a well-established protocol involving pre-modification (grafting) of the support with a proper aminosilane [4]. The materials were characterized using a wide array of complementary techniques: XRD, DR-UV-Vis, N_2 adsorption-desorption, XPS, HR-TEM, HAADF-STEM, in situ FT-IR coupled with CO and NO adsorption, as well as test reactions (isopropanol dehydration/dehydrogenation and 2,5-hexadione dehydration/cyclization). The catalytic activity of the prepared samples was studied in gas-phase methanol oxidation using a fixed-bed flow reactor combined with gas chromatography, as well as an operando FTIR-MS system.

The study demonstrated that gold catalyst supported on P:FeNbO$_x$ (Au/P:FeNbO$_x$) was found to be much more active than those loaded on monometallic oxides and mixed oxide without phosphate modifier (Au/FeNbO$_x$). Research outcomes suggest that the increased activity of the phosphate-modified sample originated from several unique properties of this catalyst, including enhanced electron mobility between Au NPs and the support, augmented Brønsted acidity, and optimized distribution of Au nanoparticles on the catalyst surface that ensured close contact with iron phosphate, FeO$_x$ and NbO$_x$ oxide phases. Notably, additional pre-treatment with O_2 significantly increased the activity of the phosphate-modified catalyst (which was not observed in the case of Au/FeNbO$_x$). Hence, our findings indicate that phosphate doping can be perceived as a promising strategy to the development of new, much more efficient heterogeneous gold catalysts addressed to the oxidation of organic compounds.

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O-27

From waste to catalysts using biochars as supports for cobalt active phase in oxygen evolution reaction

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The increasing global demand for energy and the necessity of protecting the environment are driving researchers and industry to look for an eco-friendly alternative to fossil fuels as energy sources and carriers. [1] Hydrogen is a green, sustainable energy carrier that can be produced by the electrochemical decomposition of water. The efficiency of this process is determined by the oxygen evolution reaction (OER), which is hindered due to the complex electron transfer processes and requires the electrocatalysts to increase its efficiency. Presently employed electrocatalysts rely on noble metals, e.g., ruthenium and iridium, which are expensive and have limited resources. [2]

This research aimed to develop an electrocatalyst of the OER process based on renewable raw materials (carbonized triticale straw TS, sunflower hulls SH, pine sawdust PS, walnut shells WS, and sewage sludge SS) with a cobalt active phase. To improve the surface properties of the biochars, air plasma was applied as a simple and non-destructive method. The cobalt active phase was introduced by a deposition-precipitation method.

According to XPS analysis, plasma treatment of well-carbonized supports (TS, WS, and TS) increases the number of surface oxygen groups. On the other hand, treating supports based on sunflower husks and sewage sludge with plasma leads to a decrease in oxygen content but an increase in COO-type groups fraction while increasing the degree of carbonization (Fig. 1). Additionally, composite catalysts based on plasma-modified supports before cobalt deposition exhibit lower overpotentials.

This work presented a simple, scalable method for obtaining active catalysts for the OER process while also finding applications for materials considered as waste, thereby aligning with the principles of sustainable development.

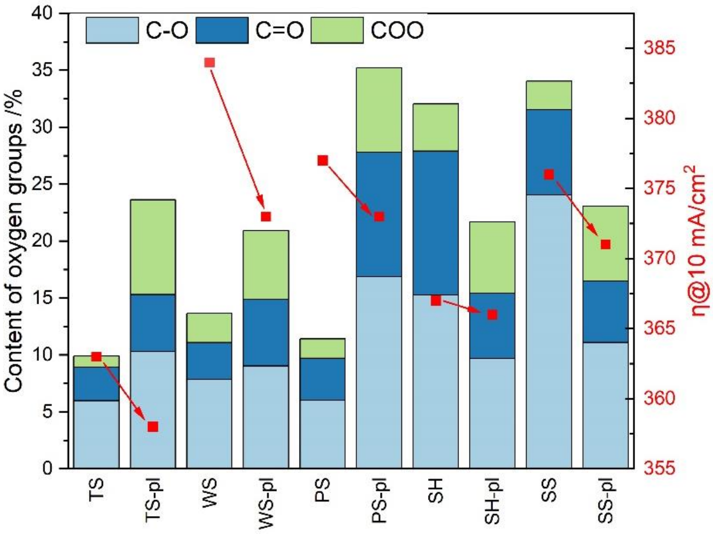

Fig. 1. XPS oxygen groups content of carriers and OER overpotential of composite catalysts

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O-28

How do phase composition and type of exposed TiO_2-anatase crystal facets influence the photocatalytic reduction of nitroaromatics?

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Titanium dioxide is one of the most widely used materials in photocatalysis and has demonstrated significant activity in organic synthesis reactions, particularly in the reduction of nitroaromatic compounds to their corresponding aminoaromatics. Amines, especially aniline derivatives, are precursors of many valuable organic molecules with a wide range of applications. It has recently been shown that the photocatalytic reduction of nitroaromatic compounds to amines can also occur with high selectivity, even in the presence of various sensitive functional groups [1, 2]. Factors that can limit this process and the impact of exposed anatase-TiO_2 facets have so far been studied to a limited extent [3]. In this research, we investigated the correlation between several intrinsic factors and the photocatalytic activity of various commercial anatase and rutile TiO_2 materials for the selective reduction of 3-nitrophenol [4]. The (photo)electrochemical analysis revealed unequivocally the differences in interfacial electron transfer, charge recombination, reduction driving force, and methanol photooxidation efficiency for titania polymorphs. Additionally, the conducted studies reveal that the photocatalytic reduction of nitroaromatic compounds strongly depends on the exposed facets, with the predominant role of the {100} facet.

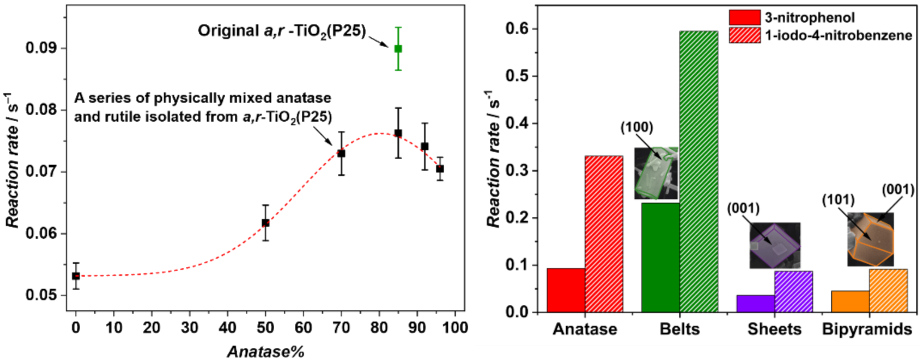

Fig. 1. Relationship between the reaction rate and the phase composition (left graph). Reaction rate at tailored anatase-TiO_2 in photocatalytic reduction of 3-NP and INB (right graph).

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Flash oral presentations

FO-1

Wpływ funkcjonalizacji powierzchni mezoporowatych katalizatorów węglowych ugrupowaniami tlenowymi i azotowymi na ich aktywność w reakcjach redoks

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Katalizatory węglowe, uznawane powszechnie za przyjazne środowisku ze względu na brak toksycznych składników, jak również możliwość łatwej regeneracji, znajdują rosnące zainteresowanie wśród badaczy skupionych na rozwijaniu procesów katalitycznych i elektrochemicznych [1,2]. Stwierdzono, iż modyfikacje materiałów węglowych ugrupowaniami azotowymi stanowią skuteczną strategię poprawiającą ich właściwości kwasowo-zasadowe oraz elektronowe. Włączenie azotu w pierścienie aromatyczne struktury grafitopodobnej skutkuje ułatwionym przenoszeniem elektronów na zaadsorbowane formy tlenu, co w konsekwencji przyczynia się do poprawy aktywności katalizatorów węglowych w reakcjach redoks z udziałem tlenu. Do najważniejszych czynników wpływających na efektywność pracy takich materiałów zalicza się strukturę chemiczną generowanych grup, ich dystrybucję, zawartość, jak również polarność. Zrozumienie mechanizmów wpływu obecności ugrupowań azotowych na zachowanie materiałów węglowych w reakcjach katalitycznych jest kluczowe dla ich zastosowania w zaawansowanych aplikacjach technologicznych.

W ramach przeprowadzonych badań otrzymano mezoporowate materiały węglowe modyfikowane ugrupowaniami azotowymi i tlenowymi przy użyciu metody odwzorowania strukturalnego twardego szablonu krzemionkowego. Jako prekursor węgla i azotu użyto mieszaniny sacharozy i mocznika o różnej zawartości azotu (N/C = 0; 0,14; 0,22; 0,30 i 0,51). Otrzymane repliki węglowe scharakteryzowano pod kątem parametrów teksturalnych (adsorpcja N_2), struktury i morfologii (SEM, XRD, spektroskopia Ramana) oraz składu powierzchniowego (XPS) i objętościowego (analiza CHNO). Materiały zostały również przetestowane w roli katalizatorów reakcjach utleniania tlenku siarki(IV) w fazie wodnej (OSA) oraz utleniającego odwodornienia etylobenzenu do styrenu (ODH). W celu szczegółowego zbadania roli ugrupowań zawierających heteroatomy, uzyskane repliki węglowe poddano dodatkowym modyfikacjom na drodze utleniania w roztworze HNO_3, redukcji gazowym NH_3 oraz sprzężenia procesu utleniania HNO_3 z następczą redukcją NH_3. Stwierdzono, że w procesie OSA materiały modyfikowane azotem charakteryzowały się wysoką wydajnością otrzymywania kwasu siarkowego(VI) wynoszącą 62-69% w porównaniu do materiału niemodyfikowanego (<10%). W przypadku w reakcji ODH obecność azotu w strukturze modyfikowanych węgli wpływała natomiast na poprawę stabilności pracy katalizatora.

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FO-2

Electroreductions at Hybrid Nanostructured Copper-Containing WO_3-Catalysts

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We demonstrate that the tungsten(VI)-oxide-intercalated nanostructured copper sites exhibit unique electrocatalytic properties toward electrochemical reductions of inert inorganic reactants, such as carbon dioxide, oxygen, nitrate(V), nitrate(III) and bromates(V). In particular, evidence has been provided that hierarchically deposited films (on glassy carbon) of copper(I) oxide decorated with tungsten(VI) oxide nanowires and, subsequently, subjected to electroreduction and voltammetric conditioning to generate hybrid Cu/WO_3 catalyst can be successfully utilized to drive reduction of carbon dioxide (saturated solution, concentration, ca. 0.033 mol dm^{-3}) in a fairly strong acid medium of 0.5 mol dm^{-3} H_2SO_4. Here formation of the partially reduced tungsten oxides (H_xWO_3 and WO_{3-y}) is accompanied by consumption of protons and sorption of hydrogen, and it tends to inhibit hydrogen evolution by shifting the proton discharge toward more negative potentials. Our observations are consistent with the view that copper is irreversibly trapped within the network of WO_3 nanowires. The dispersed metallic copper sites seem to facilitate electron transfers and charge distribution in the catalytic layers. Among important issues are the capacity of copper-containing partially reduced tungsten oxides to induce reductions of nitrates, bromates and oxygen in acid medium. On mechanistic grounds, the existence of hydrogen-rich partially-reduced tungsten oxides, H_xWO_3, which contain large population of delocalized electrons and monoatomic H, or coexisting protons and electrons, $H^+ + e^-$, is likely to induce hydrogenation of nitrogen oxo species, followed by protonation, in the vicinity of Cu to form ammonia-type products. The hybrid Cu/WO_3 system, is also characterized by improved durability, relative to pristine Cu_2O-dervided copper, as evident from electroreductions under chronoamperometric conditions. Our research aiming at optimization the material's activity and selectivity have also concentrated on application of mixed oxides, e.g. WO_3-ZrO_2. Finally, the present study demonstrates the usefulness of certain diagnostic electroanalytical approaches, such as ultramicroelectrode-based sensing, chronocoulometric probing of the diffusional-type charge propagation dynamics, or voltammetric stripping and monitoring of small organic or inorganic molecules as electroreduction products

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FO-3

Physical mixing as a simple and effective method of introducing ibuprofen into mesopores

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Ibuprofen is one of the most widely used anti-inflammatory drugs. For stable concentration of this medicament in blood, the concept of packing ibuprofen inside various drug vessels has been developed. There are many methods for introducing ibuprofen into pores [1–5]. In this research, we prove that a simple mixing of ibuprofen and SBA-15 material is a sufficient method for the introduction of ibuprofen inside pores. We also provide results from long-term studies concerning changes in the ibuprofen-SBA-15 physical mixture during its shelf-life, proving that ibuprofen molecules diffuse inside mesopores with time.

Ibuprofen molecules located inside mesopores experience high mobility. Thus, ibuprofen in confinement is easily discernible in solid-state NMR by sharp signals in ^{1}H MAS NMR spectra, and specific signals in ^{13}C MAS NMR spectra [4,5]. The number of drug molecules located in mesopores increases with the time of the mixing of SBA-15 and ibuprofen. A specific surface area of SBA-15 diminishes significantly from 551 m^2/g to ca. 340 m^2/g after mixing with ibuprofen. The long-term studies of the SBA-15 and ibuprofen mixture show that the amount of ibuprofen located inside mesopores increases with time during the 'shelf life' of the samples, therefore without any modification of the sample.

During the MAS NMR experiments, samples are being spun in a rotor with a speed of 10 kHz. NMR spectra and N_2 adsorption results show that such a high-speed rotation transports ibuprofen inside mesopores.

XRD powder patterns hint at the heterogeneity of physical mixtures of ibuprofen and SBA-15 when some crystalline ibuprofen is present in the sample. After a few months, reflexes from ibuprofen vanish in every sample examined, which proves that ibuprofen diffuses into mesopores.

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FO-4

Spinel kobaltowy dotowany bizmutem jako katalizator elektrolitycznego wydzielania tlenu w środowisku zasadowym

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Na tle kryzysu energetycznego i globalnego ocieplenia wzrasta zainteresowanie wydajnymi oraz przyjaznymi dla środowiska urządzeniami do przetwarzania i magazynowania energii odnawialnej (OZE). Wodór, jako jeden z badanych obecnie pod tym kątem surowców zyskuje coraz większe znaczenie. Uważa się, że gaz ten będzie odgrywał kluczową rolę w przyszłych mobilnych urządzeniach do konwersji energii. Elektroliza wody wykorzystana do produkcji H_2 jest jedną z najprostszych i najczystszych dróg do gromadzenia i przechowywania energii pochodzącej z OZE, jednak limitowana jest wolną reakcją wydzielania tlenu (Oxygen Evolution Reaction - OER), która uniemożliwia skuteczną i wydajną elektrolizę. Z tego powodu zbadano spinel kobaltowy dotowany bizmutem jako potencjalny katalizator wspomagający zachodzenie procesu OER [1].

Materiały zsyntezowano przy użyciu klasycznej metody strąceniowej otrzymując tlenki mieszane o wzorze sumarycznym $Bi_xCo_{3-x}O_4$, gdzie x = 0; 0,02; 0,04; 0,06; 0,08; 0,1 oraz 0,2. Obliczone masy $Bi(NO_3)_3 \times 5H_2O$ oraz $Co(NO_3)_2 \times 6H_2O$ odpowiadające wartości x rozpuszczono w HNO_3. Następnie do tak przygotowanych roztworów stopniowo dodawano rozpuszczony w wodzie $(NH_4)_2CO_3$, w celu współstrącenia wodorotlenków bizmutu i kobaltu. Otrzymane próbki suszono przez 12 godzin w temperaturze 60 °C, a następnie kalcynowano przez 4 godziny w temperaturze 500 °C, przy zastosowanym naroście temperaturowym wynoszącym 4 °C/min. Otrzymane katalizatory zbadano pod kątem reakcji deN_2O oraz OER i scharakteryzowano pod kątem właściwości elektronowych (pomiary funkcji pracy wyjścia (WF)), składu pierwiastkowego – spektroskopia fluorescencji rentgenowskiej (XRF), dyfraktometrii proszkowej (XRD) oraz spektroskopii ramanowskiej (RS), w celu zbadania składu fazowego. Badania elektrokatalityczne prowadzono przy pomocy chronoamperometrii (CA), woltamperometrii z przemiataniem liniowym (LSV), woltamperometrii cyklicznej (CV), a także elektrochemicznej spektroskopii impedancyjnej (EIS). Wartości oporu przeniesienia ładunku (R_{ct}) oraz powierzchni aktywnej (A_s) wyznaczono poprzez pomiary CV oraz EIS w roztworze równowagowym o łącznym stężeniu 5 mmol L^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$, a jako elektrolit podstawowy zastosowano 0,1 mol L^{-1} KCl.

Pomiary XRF wykazały zgodność teoretycznej i rzeczywistej zawartości Bi w próbkach. Maksima aktywności dla reakcji deN_2O i OER osiągnięto przy zawartości Bi kolejno 6,6 % i 5,5 %. W przypadku OER osiągnięto niską wartość nadpotencjału rzędu 350 mV s^{-1}. Dotacja Co_3O_4 bizmutem ułatwia proces rekombinacji tlenu w procesie deN_2O, co wynika bezpośrednio z właściwości elektronowych badanego układu. Potwierdzeniem tego jest wzrostowa korelacja między zawartością Bi w próbkach a pracą wyjścia oraz R_{ct}, a także wzrost A_s wraz ze wzrostem zawartości bizmutu w katalizatorze [2].

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FO-5

Understanding the Thermal Degradation of Poly(vinyl chloride) Plasticisers – a Case Study of Key Representatives

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When contemporary and modern art collections in galleries and museums are concerned, synthetic and semisynthetic plastics come up as a valuable part of them. From a heritage point of view, they cleared the path for artists and designers to establish new and riveting forms of expression, that have been used to depict the history of the 20th- and 21st-century civilisation [1]. The conservation of such a legacy is vitally important, but a deep understanding of ageing processes is necessary to create clear conservatory guidelines.

Poly(vinyl chloride), PVC, comprises up to 13% of contemporary art collections [2]. Hard and rigid by nature, it is usually plasticised using one or more available plasticisers. The most popular ones are based on *ortho*-phthalic acid (PAE – phthalic esters), but due to their toxicity, alternatives are emerging (NPPs – nonphthalate plasticisers). Apart from the yellowing due to the dehydrochlorination of PVC chains and the creation of conjugated double bonds, the predominant way of its ageing is plasticiser loss due to diffusion and evaporation [3]. Only a few studies took on the subject of the plasticisers' thermal degradation [4], whereas the influence of such a process on the polymer matrix has not been investigated yet.

To evaluate the thermal degradation of plasticiser and its effect on the lifetime of a PVC object, an artificial ageing test was performed. Several most popular plasticisers were chosen for this study – both representing the PAE class (DOP, DEHP, DINP, and DBP), as well as a couple of examples of NPPs (DEHT and DEHA). Plasticisers were thermally degraded as-is, as well as mixed with PVC. The fantom samples were obtained by the solvent casting method from PVC pellets, using THF as a solvent, and varying amounts of plasticiser (resulting in a 0-50 % range of concentrations). Foil samples (0.2 mm) were treated at 60 °C and 80 °C, whereas pure plasticisers were also aged at 120 °C. Artificially aged samples were comprehensively studied by spectroscopic techniques, including UV-vis-NIR, ATR-FTIR, RS, NMR, and EPR. The first results indicate the degradation of plasticisers, with the creation of monoesters, acids, and alcohols (**Fig. 1.**). Further study of the influence of these products on PVC object degradation is still ongoing and final conclusions are yet to be settled.

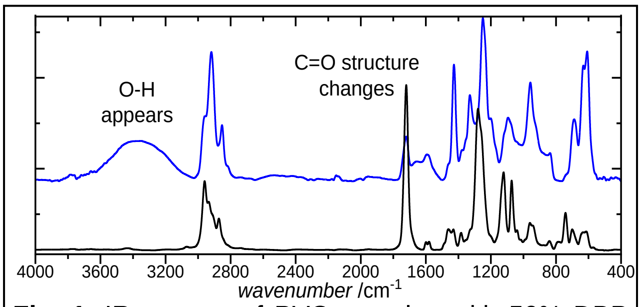

Fig. 1. IR spectra of PVC samples with 50% DBP plasticiser content – pristine (black) and after 7 weeks of ageing at 80 °C (blue) – changes labelled.

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FO-6

Synthesis and photocatalytic application of cobalt-based metal-organic frameworks

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Metal-organic frameworks (MOFs) are a novelty category of porous crystalline compounds based on metal ions or clusters (secondary building units, SBUs) in coordination with organic linkers. Presently, MOFs find extensive applications across various domains, i.e. catalysis, gas storage, drug delivery and others. This widespread adoption can be attributed to their exceptional characteristics, including remarkable crystallinity, distinct morphology, and advantageous physicochemical properties, such as high surface area, well-ordered pore structure, etc. [1,2]. In recent times, the focus on the potential use of MOFs in photocatalysis has significantly increased. This interest stems from their outstanding surface properties and structure, along with the potential for rearranging metal clusters and organic linkers. This rearrangement can bestow promising photophysical and photochemical properties to MOFs [2]. The flexibility in modifying the constituent metal clusters or bridging organic linkers enables the optimization of both the light absorption capability of MOFs and the functionality of their surface. Consequently, the crucial task of modulating these materials becomes paramount in enhancing their photocatalytic performance.

The project was aimed at synthesis of cobalt-containing MOFs based on 2-methylimidazole (2-MeIm) and 2,5-dihydroxyterephthalic acid (2,5-DHTA), resulting in Co-ZIF-8@ZIF-67 and Co-MOF-74, respectively. The compounds were prepared through a co-precipitation method. The study focused on the photocatalytic degradation of benzisothiazolinone (BIT) under UV-A irradiation. The samples obtained after the process were analysed using high-performance liquid chromatography (HPLC) and ultraviolet-visible spectroscopy (UV-Vis).

The studies revealed that Co-ZIF-8@ZIF-67 exhibited the highest activity among the investigated catalysts, while Co-MOF-74 had minimal impact on the photodegradation process, comparable with the catalyst-free reaction.

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FO-7

Synthesis of pharmaceutical precursors by catalytic selective hydrogenation in a continuous flow using metal nanoparticle-based catalysts grafted onto a polymer resin

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Traditional methods of producing vitamins and drugs still rely on using stochiometric amounts of reagents and batch reactors. However, to reduce drug prices and waste emissions, there is a need to find more sustainable solutions, including the transition from batch to flow processes and from stoichiometric to catalytic processes. Catalytic hydrogenation is considered a crucial reaction in the chemical and pharmaceutical sectors. In this study, catalytic selective hydrogenation of three substrates was conducted: 2-methyl-2-pentenal (MPEA), 2-methylbut-3-yn-2-ol (MBY), and but-2-yne-1,4-diol (BYD). The desired products of MPEA hydrogenation are 2-methylpentanal and 2-methylpentanol. The former is a flavouring agent and an intermediate in dye and resin production [1]. It is also a crucial pharmaceutical intermediate - utilized in synthesizing meprobamate, an anti-anxiety medication [2]. 2-methylpentanol (MPEO) finds application in the cosmetics and perfume industries [1]. A valuable product of MBY hydrogenation is 2-methylbut-2-en-2-ol (MBE), which is utilized in synthesizing vitamins A and E [3]. The desired product of BYD hydrogenation is but-2-ene-1,4-diol (BED), a precursor used in obtaining vitamins A and B6 [4]. This research aimed to synthesize pharmaceutical precursors by catalytic selective hydrogenation in a continuous flow using catalysts based on metal nanoparticles (Ni, Cu, and Fe) grafted onto a polymeric resin (TS-NH2). Work included catalysts synthesis, physicochemical characterization consisting of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF) and transmission electron microscopy (TEM). Reaction parameters, including temperature (10-100°C), pressure (1-60 bar), contact time, and substrate concentration relative to hydrogen, were varied to investigate their effects on product formation. Stability tests were conducted following the selection of optimal reaction conditions.

We have shown that non-noble metal nanoparticles grafted on the polymeric resin have great potential in continuous-flow selective hydrogenation processes.

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FO-8

Electroreduction of nitrogen at iron phosphide catalysts

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Industrial-scale NH_3 production mainly relies on the energy-consuming Haber–Bosch process operating at high temperature (400–500 °C) and pressure (200–250 bar) with N_2 and H_2 as feeding gases. The electrochemical N_2 reduction reaction performed under ambient condition with water as hydrogen source has been proposed as a sustainable alternative solution for ammonia production, especially when it is powered by electricity from largely distributed renewable energy sources such as solar and wind. The big challenge is to develop cost effective electrocatalysts capable of converting N_2 to NH_3 in high yield ad Faradaic efficiency, thus enabling the mass production of ammonia. The feasibility of pursuing nitrogen electroreduction reaction, or nitrogen fixation, particularly in aqueous solutions, constitutes an attractive prospect to produce ammonia under ambient, or near ambient, conditions. Development of durable, specific and reasonably efficient low-cost catalysts remains a great challenge for electrochemical science and technology. Currently, most of electrochemical approaches to N_2-fixation suffers from slow kinetics due to the difficulty of achieving the appropriate adsorption and activation of dinitrogen leading to cleavage of the strong, triple $N{\equiv}N$ bond.

A catalytic system based on iron phosphide (Fe_2P) has exhibited electrocatalytic activity toward N_2-reduction reaction in alkaline (NaOH) and semi-neutral (phosphate buffers) media. Based on voltammetric stripping-type electroanalytical measurements, Raman spectroscopic and spectrophotometric data, it can be stated that the Fe_2P catalyst facilitates conversion of N_2 to NH_3, and the process is fairly selective with respect to the competing hydrogen evolution. A series of diagnostic electrocatalytic experiments (utilizing platinum nanoparticles and HKUST-1) have been proposed and performed to control purity of nitrogen gas and to probe presence of potential contaminants such as ammonia, nitrogen oxo-species and oxygen. On the whole, the results are consistent with the view that the interfacial reduced-iron (Fe^0) centers, while existing within the network of P sites, induce activation and reduction of nitrogen, parallel to the water splitting (reduction) to hydrogen. It is apparent from Tafel plots and impedance measurements that mechanism and dynamics of nitrogen reduction depends on the applied electroreduction potential. The catalytic system exhibits certain tolerance with respect to the competitive hydrogen evolution and gives (during electrolysis at -0.4 V vs. RHE) the Faradaic efficiency, namely, the selectivity (molar) efficiency, toward production of NH_3 on the level of 60%. Under such conditions, the NH_3-yield rate has been found to be equal to 7.5 $\mu mol\ cm^{-2}\ h^{-1}$ (21 $\mu mol\ m^{-2}\ s^{-1}$). By referring to classic concepts of electrochemical kinetic analysis, the rate constant in heterogeneous units has been found to be on the moderate level of $1\text{-}2{*}10^{-4}$ $cm\ s^{-1}$ (at -0.4 V). The above mentioned iron-phosphorous active sites, which are generated on surfaces of Fe_2P particles, have also been demonstrated to exhibit strong catalytic properties during reductions of other electrochemically inert reactants, such as oxygen, nitrites and nitrates.

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FO-9

Chini clusters: quantum-chemical insights into photocatalysis

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Platinum carbonyl clusters $[Pt_3(CO)_6]_n^{2-}$ (so-called Chini clusters) consist of multiple stacking units of Pt_3 triangles stabilized by CO ligands bound in two different ways: terminal (connected to one Pt atom) and bridging (connected to two Pt atoms). Experimental studies show that used as additives on the TiO_2 surface, Chini clusters boost photocatalytic properties of TiO_2 for H_2 generation from water-methanol solutions. The aim of the study is to determine electronic and photochemical properties of Chini clusters, describe their interactions with H_2, as well as observe tendencies regarding the nuclearity number n.

We performed quantum-chemical calculations with the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods using the Gaussian 16 software. Geometries for all species were optimized using a PBE functional, while the investigation of excited states were done using a CAM-B3LYP hybrid functional.

Geometries and UV-Vis absorption spectra for Chini clusters were determined (n = 1-8). A significant red-shift of one of two main bands from 420 nm to 950 nm is observed for n = 3-8. Calculations are consistent with surface plasmon resonance effect – during excitation the electronic structure in a longitudinal direction (intertriangle) changes with an increase of n, while transverse (intratriangle) remains unaffected. Furthermore, we calculated reorganization energies for electrons and holes (λ_e and λ_h respectively) for clusters $[Pt_3(CO)_6]_4^{2-}$ and $[Pt_3(CO)_6]_8^{2-}$. Lower reorganization energies facilitate faster charge transfer processes. While former is considered to be clearly a hole transport material ($\lambda_h << \lambda_e$), latter is characterized with λ_h and λ_e of a similar order – with an increase of n, electron transfer becomes more prevalent. Thermochemical studies were performed to determine enthalpies and free energies of reactions of H_2 molecule and H atom bonding to clusters (n = 1-4 and 8). They indicate that the adsorption of these species isn't thermodynamically favourable – so the generation and release is. For bonding of H_2 to smaller clusters (n < 3) significant deformations or even decomposition of a structure are observed. H_2 binds to single Pt centre forming Pt-H bonds of ca. 1.68 Å, while the H-H bond increases from 0.74 Å to ca. 1.71 Å.

Next steps will focus on the interactions of Chini clusters with TiO_2 surfaces. Increasing photocatalytic properties of TiO_2 may be caused by electron transfers resulting in charge redistribution and the dynamics of the local charge transfer on the TiO_2 surface.

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FO-10

Electrochemical Applications of Co_3O_4-CeO_2 Nanocomposites as Catalysts and Cocatalysts

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Catalytic systems based on nanostructures of carbon-supported platinum, Pt/C (catalytic centers), and metal oxides, MO_x (cocatalytic sites), namely nanocomposites of cobalt(III,II)-oxide and cerium(IV,III)-oxide, admixed in different proportions have been investigated under electrochemical conditions toward both reductions of such inert reactants as oxygen, carbon dioxide and nitrogen as well as oxidation of water (water splitting to oxygen). Evidence has been provided that the existence of specific interactions between MO_x and noble metal (Pt) nanoparticles should improve the stability and activity of the metal catalytic sites due to modification of the Pt electronic structure and diminishing of the oxo (OH) species adsorption on Pt surface, thus promoting centers for the adsorptive activation of oxygen and the cleavage of O=O bonds. Development of catalytic systems for oxygen reduction reaction, particularly with respect to potential applications in low-temperature fuel cells, is one of the most important areas of electrocatalysis. Considerable research efforts have centered on the development of low-Pt-content catalytic systems. In other words, there is a need of better utilization of catalytic sites and significant lowering of the noble metal loadings. The activating interactions mentioned above would also facilitate dispersion of Pt catalytic centers, inhibit their detachment and further aggregation, and, consequently, prevent or decrease their degradation during the practical operation (e.g., in low-temperature fuel cells). In the present study, we have demonstrate that Co_3O_4-modified CeO_2 additive (to Pt/C) synthesized in a form of intermixed oxides with homogenously dispersed cobalt ionic sites enhance activity of Pt centers during oxygen reduction in acid medium. Conventional cyclic voltammetry and rotating ring-disk electrode voltammetry were considered as diagnostic techniques permitting to comment on the dynamic of oxygen reduction and formation of the undesirable hydrogen peroxide intermediate. The CO_2-reduction, which has also been considered here, is a much more inert process that requires breaking the double C=O bond in the stable CO_2 molecule. A common feature is the appearance of the poisoning or passivating CO-intermediate. Furthermore, when the CO_2-reduction is performed in aqueous solutions, the competitive hydrogen evolution reaction is a complicating side-reaction. The Co_3O_4-modified CeO_2 nanocomposite catalysts have been demonstrated to act as potent catalysts permitting reduction of carbon dioxide (predominantly to formate and carbon monoxide, selectively relative to hydrogen evolution). Among other inert small inorganic molecules, electroreduction of nitrogen has also been considered. Here, catalytic systems based on Co_3O_4-CeO_2 nanocomposites have exhibited electrocatalytic activity toward N_2-reduction reaction in semi-neutral medium (phosphate buffer, pH=6.1). Our voltammetric experiments indicate that the nanocomposite catalysts facilitate conversion of N_2 to NH_3, and the processes are fairly selective with respect to the competing hydrogen evolution. Finally, the Co_3O_4-CeO_2 nanocomposites have occurred to exhibit high stability and promising activity under anodic conditions, namely during electrooxidation of water (water splitting) in acid medium. In addition to promising results of experiments in 0.5 mol dm^{-3} H_2SO_4, the highest activities toward water oxidation have been observed in strongly acidic polytungstate solutions, presumably due to the formation of the highly active electrocatalytic interface formed by the oxidized CoO_x/CeO_y catalytic nanocomposites activated and stabilized by tungsten-oxo-species.

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FO-11

Operando DRIFT Studies of the Ethanol Steam Reforming over the Alkali-Promoted Cobalt Catalysts

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The steam reforming of ethanol (ESR) holds significant importance owing to its potential for hydrogen production. Catalysts play a crucial role in dictating the efficiency of this process, influencing reaction yield and selectivity. Optimal catalysts should exhibit high activity, thermal stability, and the ability to suppress undesired side reactions, thereby ensuring cost-effective and proficient hydrogen generation through ethanol steam reforming [1,2]. The present investigation aims to elucidate the impact of alkali on the activity and selectivity of the cobalt catalysts in the ESR process.

A range of alkali-doped cobalt catalysts were prepared on alpha-alumina support using a sonochemical technique for cobalt deposition and an impregnation method to introduce 1wt% of various alkali such as K, Na, Cs, or Rb. The samples underwent extensive analysis to examine their chemical and phase composition (XRF, XRD), reducibility (TPR), and morphological characteristics (TEM). Catalytic tests were carried out under the ethanol steam reforming process (500°C, 21h) using an $EtOH:H_2O$ mixture (1:4 ratio). The properties of the catalysts after the ESR process were also investigated.

The presence of alkali in the catalysts resulted in a notable enhancement in the ethanol conversion. This brought about a substantial reduction in the preference for aldehyde (about a 35% decrease), coupled with a heightened inclination towards hydrogen (an increase of 15%), carbon dioxide and methane. The impact of each alkali promoter demonstrated a similar effect. The significant contrast in the performance between catalysts without alkali additives and those doped with alkali was discussed based on operando DRIFT spectroscopy studies under ESR conditions at temperatures ranging from 200°C to 500°C, with an ethanol-to-water ratio of 1:4. Experimental data were confronted with the results of periodic DFT-GGA+U molecular modeling (performed with VASP package). The slab models were constructed, exposing the (0001) Al_2O_3 surface (with $Al_{108}O_{162}$ stoichiometry) in contact with the cobalt cluster (Co_{26}). It has been shown that alkali additives are responsible for electron transfer to the metal cluster, which strongly influences the reaction paths, increasing the adsorption energy of the aldehyde intermediate and facilitating the critical C-C bond cleavage.

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FO-12

Ceria-based catalysts for efficient soot oxidation: The role of preparation method

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In recent years, cerium oxide has gained significant attention for its potential applications across various fields, including biomedical uses, photocatalysis, as well as industrial and environmental catalysis. [1]. In the oxide, cerium exists in both +III and +IV oxidation states. Due to the ability to relatively easily shift between those two states, ceria exhibits a unique property of storing and releasing oxygen from the crystal lattice (oxygen storage capacity) depending on various conditions, such as temperature and pressure. This characteristic made cerium oxide and its modifications (for example, by doping with transition metal oxides) a promising material to implement in DPF (Diesel particle filter) as a soot oxidation catalyst. Another advantage of cerium is its low cost compared to precious metals, also commonly studied for this application [2]. It has been reported in the literature that the method of synthesis greatly influences the morphology of ceria and, thus, its catalytic activity in the reaction of soot combustion [3].

In this research, cerium oxide was prepared from $Ce(NO_3)_3{\cdot}6H_2O$ precursor using various techniques, i.e., thermal decomposition – CeO_2(TD), hydrothermal synthesis – CeO_2(HT), sonochemical synthesis – CeO_2(SC) and hard template synthesis – CeO_2(TS). The prepared oxides were doped with cobalt, also using various methods: impregnation – Co(IWI)/CeO_2(HT), Co(IWI)/CeO_2(TS), sonochemical – Co(SC)/CeO_2(HT), Co(SC)/CeO_2(TS) and hydrothermal synthesis – Co(HT)/CeO_2(HT), Co(HT)/CeO_2(TS). Selected systems were doped with potassium by the impregnation technique – KCo(SC)/CeO_2(HT) and KCo(HT)/CeO_2(HT). All the synthesised catalysts were tested in the model soot oxidation experiment (using commercial Printex U soot) in the flow of 5% oxygen in helium in tight contact mode, selected in the loose contact as well. Every tested system proved to be effective as a soot oxidation catalyst, with a temperature of 50% soot conversion not exceeding approx. 400°C in tight contact mode. The catalytic performance highly depended on the morphology of ceria, as well as on the cobalt dispersion. The highest activity was observed for the Co(SC)/CeO_2(HT) and Co(IWI)/CeO_2(TS) catalysts.

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FO-13

Badania nad wpływem podłoża $SiO_2@CeO_2$ na aktywność katalityczną faz tlenkowych Co_3O_4 i CuO w procesie całkowitego utlenienia lotnych związków organicznych

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Lotne związki organiczne (LZO) stanowią liczną grupę substancji charakteryzujących się łatwością przechodzenia w stan pary lub gazu w temperaturze pokojowej, niską temperaturą wrzenia oraz ograniczoną rozpuszczalnością w wodzie. Negatywny wpływ polutantów organicznych na organizmy żywe oraz środowisko naturalne jest powszechnie identyfikowanym problemem. W związku z tym rozwijane są różne (nie)destrukcyjne metody usuwania LZO, wśród których jedną z najbardziej skutecznych jest utlenianie katalityczne. Użycie katalizatora w reakcji dopalania LZO obniża znacząco energię aktywacji, a przez to pozwala poprowadzić proces w relatywnie niskich temperaturach [1]. Obok kosztownych i podatnych na zatrucia katalizatorów zawierających metale szlachetne, rozwijane są również układy oparte na tlenkach metali przejściowych [2]. Ich mniejszą efektywność działania można skompensować m. in. przez optymalizację rodzaju i właściwości użytego nośnika fazy aktywnej. Szczególną rolę odgrywa właściwie jego dobrana struktura i porowatość, promująca wysoką dyspersję oraz stabilność fazy aktywnej tworzonej przez naniesiony tlenek metalu przejściowego. CeO_2 jest często stosowany w roli nośnika ze względu na dużą liczbę defektów, umożliwiających łatwą wymianę tlenu sieciowego z fazą gazową, co skutkuje wysoką redukowalnością oraz zdolnością magazynowania tlenu [3].

W ramach prezentowanych badań wykonano syntezę dwóch serii katalizatorów opartych na sferycznym nośniku $SiO_2@CeO_2$ o strukturze rdzeniowo-powłokowej, na powierzchni którego osadzono fazę aktywną w postaci tlenków Co_3O_4 i CuO. Materiał $SiO_2@CeO_2$ zsyntezowano przez depozycję strąceniową tlenku ceru(IV) poprowadzoną w stałym pH w obecności zawieszonej w roztworze nieporowatej krzemionki zsyntezowanej uprzednio metodą Stöbera. Otrzymane materiały poddano kalcynacji, a następnie impregnacji na mokro wodnymi roztworami azotanów Co(II) i Cu(II) stanowiących prekursory faz tlenkowych Co_3O_4 i CuO oraz kolejnej kalcynacji. Dla prezentowanych układów wykonano szeroką charakterystykę fizykochemiczną obejmującą analizę morfologii (SEM-EDX), składu pierwiastkowego (XRF), parametrów teksturalnych (adsorpcja N_2), struktury (XRD) oraz otoczenia chemicznego (UV-Vis-DR). Kluczowym elementem badań było sprawdzenie aktywności otrzymanych materiałów w procesie katalitycznego dopalania toluenu. Zidentyfikowano właściwości charakteryzujące opisane fazy tlenkowe w relacji do obecnego w podłożu CeO_2, odpowiedzialne za wysoką aktywność w badanym procesie katalitycznym.

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Plakaty
Posters

P-1

Potencjał wykorzystania cenosfer z popiołów lotnych jako składników katalizatorów aktywnych w reakcjach redoksowych o znaczeniu środowiskowym

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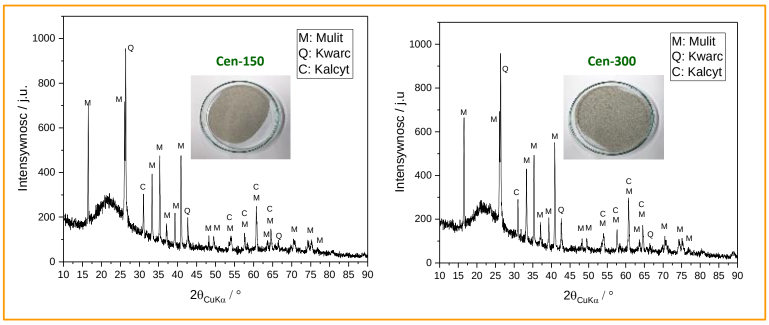
Generowane w masowej skali popioły lotne z sektora energetycznego mogą stanowić źródło cennych składników użytecznych w syntezie zaawansowanych materiałów funkcjonalnych, do których zalicza się także katalizatory. Takimi składnikami są m.in. cenosfery, łatwo wyodrębnialne z popiołów lotnych sferyczne struktury o atrakcyjnych z katalitycznego punktu widzenia właściwościach: wysokiej trwałości termicznej, dobrej wytrzymałości mechanicznej i odporności na korozję chemiczną. Pewnym problemem jest natomiast stosunkowo niska, zwykle nieprzekraczająca kilku m^2/g, powierzchnia właściwa, która obniża nieco potencjał wykorzystania cenosfer jako nośników katalitycznych. Powierzchnia powstających w temperaturach powyżej 1200°C cenosfer jest bogata w krzem, glin, żelazo i metale alkaliczne. Oddziaływanie cenosfer ze składnikami naniesionych tlenkowych faz aktywnych pozwala je efektywnie funkcjonalizować pod kątem otrzymywania katalizatorów, aktywnych w takich reakcjach redoks o istotnym znaczeniu środowiskowym, jak: uwodornienie CO_2, dopalanie sadzy, czy też selektywna redukcja tlenków azotu.

Celem niniejszych badań było wykazanie użyteczności w katalizie środowiskowej komercyjnych cenosfer funkcjonalizowanych poprzez impregnację jonami miedzi(II) i cynku. Układy zawierające 0.5-10.0 % mol. miedzi lub kombinację 0.3-6.0 % mol. miedzi i 0.2-4.0 % mol. cynku poddano wnikliwej charakterystyce metodami: XRF, XRD, RS, SEM/EDS, BET, DRIFT i UV/Vis-DR. Aktywność katalityczną wybranych próbek przetestowano w reakcji SCR NO_x, stosując amoniak jako reduktor.

Przeprowadzone testy potwierdziły istotny potencjał aplikacyjny cenosfer jako składników katalizatorów heterogenicznych. Ponadto, wykorzystanie tego typu składników, pochodzących z materiałów odpadowych, do otrzymywania wartościowych produktów finalnych, stanowi dobry przykład podejścia wpisującego się w zasady gospodarki o obiegu zamkniętym.



Rys. Komercyjne cenosfery (Cen) o średnicach 150 μm i 300 μm oraz ich skład mineralny (XRD).

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P-2

Efekt natury i stężenia fazy aktywnej na właściwości strukturalne i funkcjonalne układów MO_x/Al_2O_3 i MO_x/cenosfery (gdzie M = Cu, Cu-Zn)

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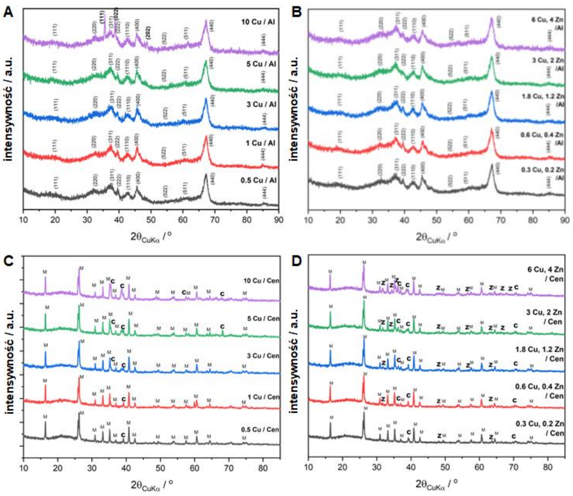
Determinująca w znacznym stopniu właściwości katalityczne architektura powierzchni układów nośnikowych istotnie zależy nie tylko od natury wybranej fazy aktywnej i nośnika, lecz także od innych czynników, do których należą: ścieżka i warunki preparatyki, temperatura i atmosfera obróbki termicznej a także stężenie naniesionej fazy aktywnej. Funkcjonalizację użytych nośników komercyjnych, tj. γ-Al_2O_3 oraz cenosfer z popiołów lotnych generowanych z sektora energetycznego, przeprowadzono metodą mokrej impregnacji. Nominalne stężenia faz naniesionych odpowiadały zawartości 0.5-10.0 % mol. miedzi lub 0.3-6.0 % mol. miedzi i 0.2-4.0 % mol. cynku i były w przypadku obu nośników analogiczne. Wszystkie próbki kalcynowano w temperaturze 400°C/4h. Zsyntezowane próbki poddano wnikliwej charakterystyce metodami: XRF, XRD, RS, SEM/EDS, BET, DRIFT i UV/Vis-DR.

Do najważniejszych wniosków płynących z przeprowadzonych badań należy potwierdzenie zdecydowanie odmiennych sposobów oddziaływania obu użytych nośników ze składnikami faz naniesionych. I tak, γ-Al_2O_3 sprzyja silniejszej dyspersji powierzchniowych form oksometalicznych CuO_x i ZnO_x, podczas gdy cenosfery wyraźnie faworyzują obecność trójwymiarowych form tlenkowych, które są stabilne nawet przy najniższych stężeniach naniesionych tlenków. Stężenie fazy naniesionej odgrywa zatem znacznie większą rolę w kształtowaniu architektury powierzchniowej w przypadku układów z γ-Al_2O_3 jako nośnikiem. Oktaedryczne tlenowe otoczenie centrów Cu(II) zostało potwierdzone we wszystkich analizowanych przypadkach. Wprowadzenie domieszek Zn(II) nie wpływa zasadniczo na specjację form oksomiedziowych, powodując jedynie dystorsję otoczenia tlenowego Cu(II).



Rys. Dyfraktogramy rentgenowskie zarejestrowane w funkcji stężenia fazy naniesionej dla próbek: 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).

Podziękowania: Badania realizowane przez P.R. zostały dofinansowane w ramach projektu POWR.03.02.00-00I004/16 oraz minigrantu Talent Management POB Anthropocene.

P-3

Synteza zeolitów 3D i 2D jako przykład waloryzacji popiołów lotnych z sektora energetycznego pod kątem otrzymywania materiałów użytecznych w katalizie

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Generowane przez sektor energetyczny w ilości ok. 600-700 mln ton rocznie, popioły lotne, będące ubocznymi produktami spalania paliw stałych, mogą być efektywnie wykorzystywane także jako prekursory zaawansowanych materiałów funkcjonalnych. Do tej grupy zaliczyć można także klasyczne trójwymiarowe (3D) i dwuwymiarowe (2D), warstwowe zeolity. Ze względu na zróżnicowany skład wyjściowych popiołów lotnych, uzyskanie pożądanych struktur z satysfakcjonującą wydajnością stanowi duże wyzwanie i musi zostać poprzedzone wnikliwą analizą takich parametrów charakteryzujących popioły, jak: stosunek zawartości pierwiastków Si/Al, obecność żelaza i pozostałości węglowych, a także skład mineralny i fazowy oraz stosunek zawartości fazy szklistej do krystalicznej. Popioły lotne charakteryzują się wysoką zawartością krzemu oraz glinu. Pierwiastki te występują w popiołach zarówno w formie glinokrzemowego szkliwa, stanowiącego materiał budulcowy kulistych ziaren zwanych cenosferami, jak i w formie krystalicznej - jako kwarc oraz mullit.

O ile synteza zeolitów o strukturach 3D z popiołów lotnych jest dobrze opanowana, o tyle otrzymywanie układów warstwowych (2D), o atrakcyjnych z katalitycznego punktu widzenia, centrach aktywnych zlokalizowanych w przypowierzchniowych warstwach zewnętrznych, dostępnych także dla cząsteczek bardziej wymagających przestrzennie, jest zdecydowanie trudniejsze. Naszym celem w ramach niniejszej pracy było sprawdzenie możliwości syntezy zeolitów z popiołów lotnych i wskazanie parametrów kontrolujących ich finalne struktury. I tak, z powodzeniem przetestowane zostały trzy różne ścieżki syntetyczne, prowadzące do uzyskania: klasycznych zeolitów typu NaX (3D) [1], prekursorów zeolitów warstwowych MCM-22 (3D → 2D) (Rys.) oraz struktur warstwowych typu bifer [2]. Otrzymanie tych ostatnich stanowi znaczący krok w stronę projektowania zaawansowanych ścieżek wykorzystania popiołów lotnych i uzyskania materiałów katalitycznych, potencjalnie aktywnych np. w reakcjach izomeryzacji węglowodorów.

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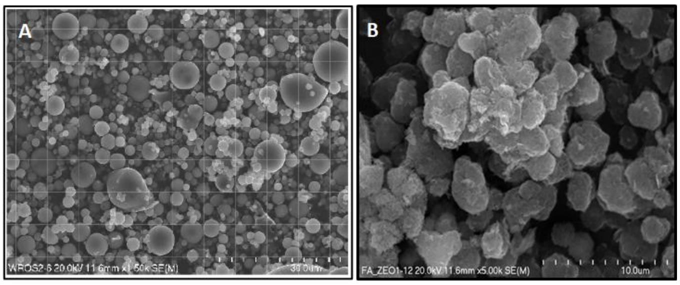

Rys. Obrazy SEM: wyjściowy popiół lotny (A), materiał posyntetyczny, zawierający MCM-22 (B).

Podziękowania: Badania realizowane przez P.R. zostały dofinansowane w ramach projektu POWR.03.02.00-00I004/16 oraz minigrantu Talent Management POB Anthropocene.

P-4

Synteza i charakterystyka katalizatorów Pt/CeO_2 na sferycznym nośniku węglowym do całkowitego utlenienia lotnych związków organicznych

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Lotne związki organiczne (LZO) uwalniane do atmosfery z licznych źródeł naturalnych i antropogenicznych wykazują działanie toksyczne względem środowiska oraz organizmów żywych, w tym również przyczyniają się do powstawania smogu fotochemicznego w obszarach zurbanizowanych. Do eliminacji LZO najczęściej stosowana jest metoda utlenienia katalitycznego, w założeniu obniżająca temperaturę reakcji do zakresu, w którym eliminowany jest efekt powstawania termicznych tlenków azotu, w przeciwieństwie do unieszkodliwiania termicznego.

W ramach pracy wytworzono serię katalizatorów opartych na sferycznym nośniku węglowym z wygenerowaną in-situ fazą tlenkową w postaci domen krystalicznych CeO_2 z naniesioną fazą aktywną w formie nanocząstek Pt. Badane materiały otrzymano metodą nanoreplikacji strukturalnej, wykorzystując jako sztywną matrycę mezoporowaty sferyczny żel krzemionkowy o średnicy ziaren 40-75 µm. Jako prekursor węgla i CeO_2 użyto wodnego roztworu sacharozy zawierającego różne ilości azotanu ceru(III). Podczas rozkładu termicznego przeprowadzonego w atmosferze gazu obojętnego w temperaturze 250 °C nastąpiło utworzenie cząstek CeO_2 rozproszonych w matrycy formującej się struktury węglowej. Następnie próbki zostały skarbonizowane w temperaturze 800 °C, a szablon krzemionkowy selektywnie usunięty roztworem NaOH. W ostatnim etapie na nośnik C-CeO_2 wprowadzono nanocząstki Pt na drodze redukcji w roztworze poliolu. Materiały charakteryzowano w trakcie oraz po syntezie przy użyciu technik SEM-EDS, adsorpcji N_2, XRD, XRF, XPS, TGA i analizy elementarnej CHN.

Na etapie przed naniesieniem Pt potwierdzono otrzymanie materiałów węglowych zawierających jednorodnie rozmieszczone domeny CeO_2, których ilość zwiększała się proporcjonalnie do zawartości azotanu ceru(III) w wyjściowym kompozycie (0-25 %mas.). Jednocześnie zaobserwowano systematyczny wzrost zawartości azotu w próbkach, co może świadczyć o wbudowywaniu się tego pierwiastka w strukturę materiału węglowego podczas rozkładu termicznego prekursora (wskutek wydzielania się tlenków NO_x). Zawartość Pt w finalnych próbkach wynosiła ok. 1,0 %mas. Otrzymane materiały charakteryzowały się jednorodną średnicą ziaren (~ 30 µm) oraz rozwiniętą powierzchnią właściwą (750-900 m^2/g).

Zsyntezowane katalizatory zostały poddane testom katalitycznym w reakcji całkowitego utlenienia toluenu, jako cząsteczki reprezentatywnej dla grupy aromatycznych LZO. Przy stężeniu toluenu w strumieniu powietrza wynoszącym 1000 ppm, w obecności najaktywniejszego katalizatora (zaw. CeO_2 = 10 %mas.), osiągnięto prawie całkowitą konwersję substratu (96,0 %) już w temperaturze 175 °C. Analogiczny katalizator na bazie komercyjnego CeO_2 jako nośnika, w tych samych warunkach reakcyjnych, wykazywał aktywność na poziomie 25,0 %.

Podziękowania: Badania wykonano przy wsparciu finansowym Priorytetowego Obszaru Badawczego Anthropocene w ramach Programu Strategicznego Inicjatywa Doskonałości w Uniwersytecie Jagiellońskim.

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P-5

The comparison of the promotional effect of Na, K, Rb and Cs on the performance of cobalt catalyst in the ethanol steam reforming

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Supported cobalt catalysts are widely studied in ethanol steam reforming (ESR) [1]. Hydrogen produced in this process is seen as an alternative energy source due to its high combustion energy and relatively low production cost [1]. A wide range of catalytic systems was investigated in ESR; among others, the cobalt phase dispersed over oxide supports. Unfortunately, they suffer from poor stability, mainly due to coke formation upon ethanol dehydration path, which leads to undesired C_2H_4 [2]. This path can be, however, significantly reduced or even eliminated by a controlled modification of the catalyst surface acidity. In the case of alumina-based systems, low acidity may be achieved by using the alpha alumina polymorph [2], while the adjustment can be achieved by alkali doping.

We synthesized a series of cobalt (10 wt%) catalysts based on porous alumina support doped with Na, K, Rb, and Cs (0-1 wt%). The samples were obtained via the incipient wetness impregnation method, characterized by a wide range of methods (e.g., XRD, in situ XPS, SEM, TEM/EDX, H_2-TPR, RS) and tested in the ethanol steam reforming process (500 °C, EtOH:H_2O 1:4, 21 h). The state of the alkali promoters was studied using a unique thermal alkali desorption method (SR-TAD).

The comparison of the catalytic results for a series of K-doped catalysts (K content equal to 0.3, 0.6, and 1 wt%) indicated a strong effect of alkali loading. The adjustment of the K-loading allowed us to get an efficient ESR catalyst (100% ethanol conversion, >90% selectivity to H_2 and CO_2, no C_2H_4 production). Moreover, the promotional effect of alkali strongly depends on the kind of promoter and changes in the series $K>Cs\cong Rb>Na$. The observed performance of the catalysts was discussed in terms of the cobalt oxidation state, active phase-support interactions, and the resistance to deactivation of the catalyst. The alkali doping strengthened the cobalt-alumina interaction, leading to a stabilization of the active phase on the catalyst surface. Consequently, the deposit formation was significantly limited, and the ethanol conversion was preserved at the level of 100%.

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P-6

Small molecules binding by (M-Por)$_2$ dimers (M = Fe, Ni, Mn, Co): DFT Studies

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Enzymes having binuclear metal sites are known in Nature, where are responsible for various chemical processes, e.g., 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. The cooperativity between two metal ions enables to perform reactions using inert molecules, which are otherwise hard to activate.

Our aim is to explore 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 do so, we performed quantum-chemical calculations in the frame of Density Functional Theory (DFT) with B-P/PBE/B3-LYP functionals with D3 dispersion correction and the def2-TZVP basis set. The calculations were done with Turbomole program package.

We proposed theoretical models in which transition metal ions (TMI = Fe, Co, Mn, Ni) in porphyrin rings were placed face-to-face at variable distances. Next, selected small molecules (O_2, N_2O, CO_2) were placed in between the two moieties. The performed calculations indicate that all investigated TMI pair can bind the O_2 and N_2O molecules placed in between. Upon dioxygen binding, the O-O distance is elongated. The effect is the stronger for the di-iron system, while the weakest for both di-nickel and di-cobalt ones. It was also shown that the dioxygen molecule can be split to form two oxo centres that can exist on both TMI sites while they are separated by ca. 4 – 6 Å. The same, activation and decomposition of nitrous oxide is also observed – the oxo group is formed on one of the metal sites, and dinitrogen molecule is released.

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P-7

Electrochemical CO_2 reduction on CuNi nanoclusters

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The persistently rising CO_2 emissions resulting from human activities pose a significant threat to climate change. Electroreduction is very interesting strategy for CO_2 recycling into value-added chemicals and liquid fuels such as formic acid, etanol, methane or carbon monoxide, which can be use to another transformations. Converting CO_2 through chemical processes is challenging due to its high stability as a molecule ($\Delta Hf° CO_2 = – 394$ kJ/mol). For this reason, the reduction of CO_2 usually require high energy input and extremely active catalysts.

Copper electrodes are optimal for the electroreduction because of their high activity and selectivity in hydrocarbon production, while also mitigating catalyst deactivation caused by strong interaction with CO. However, Cu-based systems appears to be strong attractive in the realm of investigated electrocatalysis due to the synergistic effects between their components. Bimetallic materials offer unique properties unavailable to monometallic catalysts - charge transfer in these systems can enhance reagent binding energy, improving catalytic applications

The project is focused on the 2-reduction of CO_2 to HCOOH and CO, using Cu-Ni nano clusters. Among other transition metals nickel is characterized by a high chemical stability and activity in electrochemical applications. The aim of this study is to investigate the effect of mixing Cu and Ni ratio in the clusters on the interaction with CO_2 reduction intermediates. These factors have been examined using density functional theory (DFT).

The calculation include 14 computation models, each consisting in 13 atoms recognized with the icosahedron geometry recognized as the most stable cluster [Klaja 2017]. Models differ from each other by the radio of Cu/Ni atoms. The results obtained were compared with the machine learning model by Stottko [Stottko 2023]. The conducted research enables the enhancement of knowledge regarding bimetallic systems and structural elements, facilitating the design of efficient and selective catalysts for CO_2 conversion.

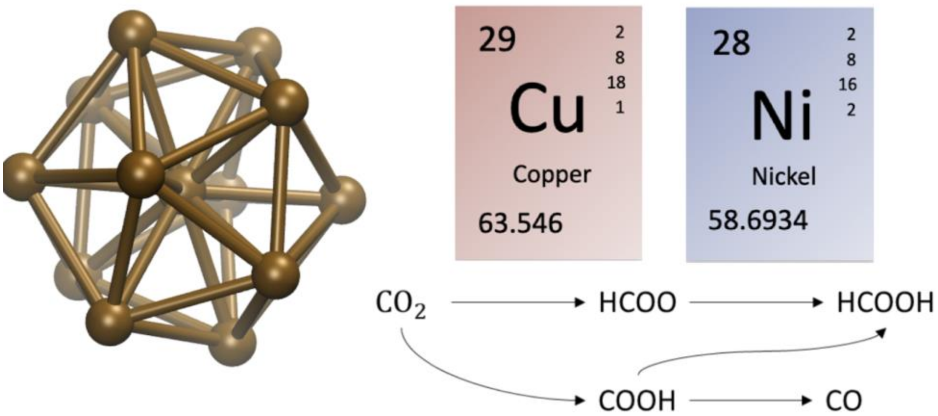

Fig. 1. Base Cu nanocluster with icosahedron geometry. Possible conversion reaction pathways CO_2.

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P-8

Silica supported nickel catalysts for CO_2 methanation reaction

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Reduction of greenhouse gas emissions and the sustainable management of natural resources belong to the most important challenges of present economy. Hydrogen produced by water electrolysis or by suitable thermochemical redox cycles to store surplus renewable energy can be converted using fossil fuel-based or biogenic CO_2 into valuable chemical compounds with a higher volumetric storage density, such as methane or higher hydrocarbons [1-7].

$$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O$$

The aim of present studies was to determine the influence of the synthesis methods and composition of silica supported nickel catalysts on their activity in the CO_2 methanation reaction and the nature of the active surface centres. Two series of silica-supported catalysts with nickel contents ranging from 2.5 to 20 wt% were prepared using different wet impregnation methods. The catalysts were studied by the application of X-ray diffraction, electron microscopy, temperature-programmed reduction and hydrogen desorption, in-situ DRIFTS adsorption/desorption of CO, CO_2 and CO_2-H_2 reaction.

It was found that an introduction of citric acid to the impregnating solution led to the development of catalysts with smaller nickel crystallites, higher active surface area and characterised with an improved catalytic performance in CO_2 methanation reaction at low temperatures. Therefore, higher activity and selectivity to methane can be achieved by the introduction of smaller quantity of Ni to silica support.

Gradual increase in the activity of catalysts with an increase in the active surface area was observed for both series of catalysts. Simultaneously, studies have shown that their activity may depend not only on the active surface area, but also on the nature of the surface centres on nickel crystallites. Thus, the catalysts with larger crystallites in the size of 8-15 nm and complex morphology may reveal beneficial catalytic properties over the catalysts with very small Ni crystallites (1-5 nm).

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P-9

MOF-74 jako adsorbenty leków z fazy ciekłej

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Postęp cywilizacyjny prowadzi do pojawiania się różnych form zanieczyszczeń, które dostają się do wód i zagrażają zdrowiu ludzi [1]. Jednym z nich są leki i ich metabolity, które przedostają się do wody między innymi z odpadami komunalnymi. Chemiczne wytrącanie, separacja na membranach, adsorpcja, wymiana jonowa, fotodegradacja czy ozonowanie to tylko niektóre z technik stosowanych w celu usunięcia tych zanieczyszczeń [2].

MOF ze względu na wysoką porowatość i wyjątkowo dużą powierzchnię właściwą mogą być wykorzystane jako adsorbenty do ekstrakcji z wody różnych zanieczyszczeń, w tym leków [3]. Mogą też służyć do zagęszczania leków, co pozwoli na redukcję objętości substancji, która musi zostać poddana oczyszczaniu.

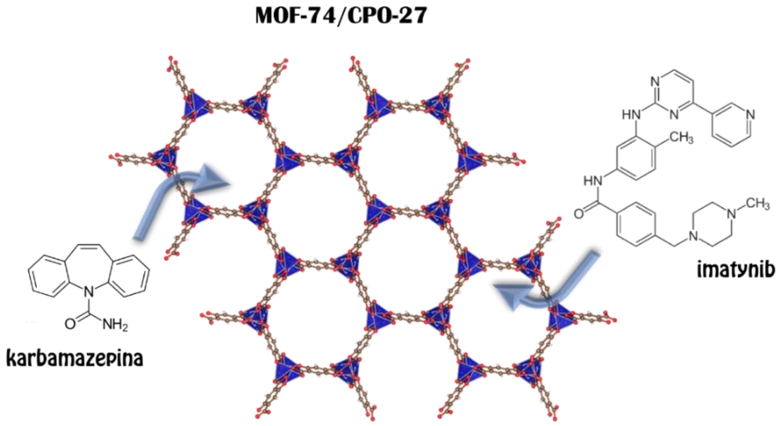

Fig. 1. Schemat sorpcji wybranych leków – karbamazepiny i imatynibu w MOF-74.

Zsyntezowano MOF-74, znany również jako CPO-27, w oparciu o kationy Zn^{2+} oraz Mg^{2+} z roztworów wodnych, w temperaturze pokojowej. Uzyskano materiały o powierzchniach właściwych odpowiednio 787 i 1051 m^2/g. W obu materiałach zaadsorbowano karmazepinę i imatynib, wybrane jako leki modelowe o dużych cząsteczkach. Zbadano stężenie leków wprowadzonych do struktury MOF, ich sposób wiązania oraz warunki degradacji materiałów MOF w środowisku o różnym pH.

W wyniku przeprowadzonych badań ustalono, że oba materiały MOF mogą być stosowane do efektywnej sorpcji farmaceutyków z wody.

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P-10

Effect of biomass type on the efficiency of catalytic pyrolysis and co-pyrolysis of lignocellulosic feedstock and waste polymer

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Hydrogen is considered one of the most promising energy carriers. It can be produced with the use of not only fossil fuels (e.g. natural gas), but also using renewable resources such as lignocellulosic biomass. Researchers are considering the development of various methods of biomass processing. This also includes high-temperature treatment [1,2]. Its efficiency depends on many factors, of which the presence of the catalyst and the nature of the feedstock are among the most important [3,4].

Taking that into account the main goal of this work is to determine the effect of biomass type on the efficiency of catalytic pyrolysis and co-pyrolysis of lignocellulosic feedstock and waste polymer to hydrogen-rich gas. The experiments were performed in two-stage flow reactor allowing for independent heating of biomass and catalyst beds. Ni supported on zirconia was used as a catalyst.

Pyrolysis was conducted with the use of cellulose (a model sample) and following types of biomass: spruce pellets, garden waste, rapeseed straw, rice husk, hay, hemp, miscanthus waste and miscanthus rhizomes. In the case of co-pyrolysis the mixtures of selected lignocellulosic materials and low-density polyethylene (LDPE) were investigated (ratio 1:1).

The obtained results showed the considerable differences in the amount of formed gaseous products. The highest hydrogen yield was observed in the case of pyrolysis of spruce pellets following by rice husks. On the other hand, the lowest H_2 content was noted for miscanthus waste. The changes in the contribution of other compounds (such as carbon monoxide, carbon oxide and methane) were not as large as in the case of hydrogen.

An analysis of the efficiency of co-pyrolysis revealed that the addition of polymer resulted in significant increase in hydrogen yield to almost 25 mmol/g of substrate. The differences among various biomass types were also evident. However, they were not as large as in the case of processing of biomass alone. The presence of LDPE resulted also in the increase in hydrogen selectivity, which increased from 40-50% in the case of pyrolysis of lignocellulosic feedstock to about 70% for the mixture of biomass and polymer.

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P-11

Synthesis, characterization, and shape analysis of manganese oxide catalysts with: nanorods ($K_2Mn_8O_{16}$), layered ($Na_2Mn_3O_7$), and euhedral (MnO_2, Mn_3O_4, Mn_2O_3, MnO) morphology in the context of thermochemical redox cycles

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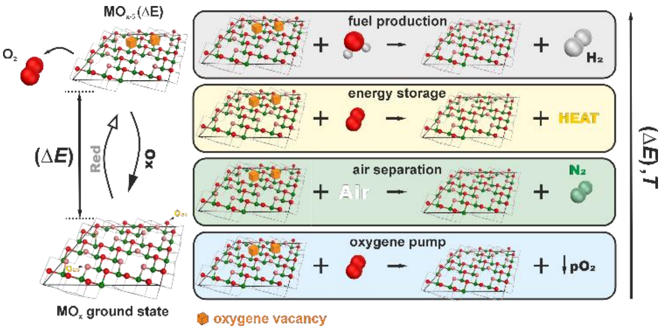

Fig. 1. Schematic presentation of two-step thermochemical redox cycles.

Within this contribution the synthesis, characterization, and shape analysis of manganese oxide catalysts with: nanorods ($K_2Mn_8O_{16}$), layered ($Na_2Mn_3O_7$), and euhedral (MnO_2, Mn_3O_4, Mn_2O_3, MnO) morphology is presented. Based on the different [MnO_6] links, MnO_2 can be divided into three categories: the chain-like tunnel structure (α-, β-, and γ-types), the sheet or layered structure (δ-MnO_2), and the 3D λ-type structure. Mn_2O_3 can adopt cubic, C-type, or spinel structure. Mn_3O_4 has a normal spinel structure, with cations hosted by the oxygen anions (O^{2-}) cubic lattice (Fd-3m), forming a stable yet flexible structure. MnO adopts a rock salt (cubic) structure, where cations and anions are coordinated octahedrally. $K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$ are derived from manganese dioxide. $K_2Mn_8O_{16}$ structure (monoclinic, I4/m) is built by edge-shared double 2×2 octahedral MnO_6 chains. Part of them is corner-shared resulting in the formation of one-dimensional tunnels, with the diameter of 0.46 nm. To compensate positive charge and stabilize the Mn_8O_{16} framework, various cations are inserted into the tunnels. As a result, manganese ions adopt a mixed valence state (coexistence of Mn^{4+}, Mn^{3+}, and Mn^{2+}). $Na_2Mn_3O_7$ structure is built up of Mn_3O_7 layers with manganese coordinated octahedrally by oxygen atoms and separated by sodium atoms located at two different sites: half of the sodium atoms occupy the prismatic sites above and below the vacant manganese sites, and the other half occupy the octahedral sites. This makes $Na_2Mn_3O_7$ different from conventional layered oxides as two different environments exist for the sodium atoms. The redox properties of the whole materials can thus be tuned simply by introducing proper ions between manganese oxide layers or by doping the octahedral framework. As a result, each catalyst system possesses the crucial features: a stable, yet versatile structure, able to accommodate (directly inside the manganese oxide framework or inside the tunnels/layers) various elements with various oxidation states tuning the coexisting Mn^{4+}, Mn^{3+}, and Mn^{2+} ions, which make them excellent catalyst materials for fundamental investigations into the thermochemical redox cycles. The increasing amount of oxidized manganese cations facilitates the surface and structural oxygen ions' mobility, thereby increasing oxidation reaction rates. The excellent redox properties of the materials are also complemented by the stable yet labile lattice structure, which promotes oxygen migrations through the bulk. Such structural and redox versatility along with well-defined morphologies provide unique opportunities for exploring the structure-catalytic behaviour relationships in thermochemical redox cycles at the molecular level.

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P-12

Synthesis and characterisation of praseodymium-modified ceria for soot oxidation

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Air pollution is one of the most serious challenges that highly developed countries face in the 21st century. There are many factors leading to its formation, but the main cause is usually the burning of fossil fuels [1]. Anthropogenic soot, which is one of the main fractions of suspended particulate matter (PM), is produced as a result of pyrolysis processes or incomplete combustion of fossil fuels. The carbon produced can take a variety of forms, from agglomerated nanoparticles to microparticles [2]. Long-term exposure to airborne dust has a negative impact on human health and contributes to the occurrence of many lifestyle diseases. This is a consequence of the absorption of PM 10 dust in the upper respiratory tract and bronchi and the penetration of PM 2.5 dust into the bloodstream [3]. Therefore, reducing emissions of pollutants into the atmosphere is crucial for the well-being of humanity. One way to do this is by developing cost-effective and efficient catalytic systems that indicate high activity in the soot oxidation process. This is considered to be a process in which complete soot oxidation takes place at a temperature lower than 400 °C [2]. Cerium oxides are promising compounds for this purpose due to their redox properties and oxygen storage ability. However, ceria is susceptible to deactivation by sintering at higher temperatures, which reduces its thermal stability. To improve thermal stability and maintain the cubic fluorite crystal structure, rare earth elements like praseodymium are introduced into its network [4].

The present study focuses on the evaluation of the catalytic activity in the soot oxidation of cerium and praseodymium mixed oxides synthesised by the one-step hard template method. The synthesis involved impregnating the porous Amberlite® XAD7HP polymer with solutions containing cerium oxide and praseodymium oxide precursors in various molar ratios followed by template removal by calcination. Physicochemical characterisation of the produced oxides was carried out using techniques such as X-ray diffraction (XRD), Raman spectroscopy (RS), temperature-programmed reduction (TPR) and X-ray fluorescence (XRF). The catalytic performance in soot oxidation was also assessed in loose and tight contact. The obtained results indicate that regardless of the molar ratio of praseodymium, the synthesised materials are characterised by similar morphology and are active in the soot oxidation process.

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P-13

Selective catalytic oxidation of diphenyl sulphide with H_2O_2 in the presence of spherical mesoporous silicas modified with iron and titanium

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Selective catalytic oxidation of aromatic organic sulphide compounds is essential for chemical and pharmaceutical industries. The oxidated products such as sulphoxides and sulphones are applied for medicine production with anti-inflammatory, anti-bacterial or anti-fungal properties [1]. Conventionally use strong oxidising agents, like nitric acid, permanganates show some limitations connected with the production of harmful side products. Thus, the application of hydrogen peroxide as an oxidant is considered as an environmentally friendly method, due to its decomposition only to water [2]. This allows operation under gentle reaction conditions, such as at atmospheric pressure and room temperature and thus considering oxidative desulphurization process (ODS) as a complementary strategy for hydrodesulphurization process (HDS). However, it is required to be conducted in the presence of catalysts or photocatalysts [3].

The synthesis of spherical silicas of MCM-41 type containing titanium, iron and both these metals simultaneously was performed by the co-condensation method. The obtained samples were characterised in terms of structure and morphology (XRD, SEM), chemical composition (ICP-OES), textural parameters (low-temperature N_2 sorption), metal form and aggregation (UV-Vis-DRS, Raman). The monometallic catalysts (Ti-, Fe-S-MCM-41) were tested in diphenyl sulphide oxidation with hydrogen peroxide and were found to be active. The main reaction product was diphenyl sulphoxide. In the case of bimetallic samples, a noteworthy increase in catalytic activity was observed that show higher substrate conversion rate and deeper oxidation to diphenyl sulphone, as a main product. These results are related to the synergistic cooperation of titanium and iron active species on silica carrier. It is postulated that such co-existence facilitate transformation of hydrogen peroxide into reactive species, like hydroxyl radicals, that play a significant role in subsequent reaction of diphenyl sulphide oxidation.

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P-14

Ce-MWW derivatives functionalised with copper – characterization and low-temperature NH_3-SCR activity

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Selective catalytic reduction of nitrogen oxides with ammonia (NH_3-SCR) is the process which is effectively used for control of NO_x emission from stationary sources [1]. However, the commercial catalyst, V_2O_5/TiO_2 system, works with high performance in the range of 300-400°C [1]. Thus, its application in the temperature range below 250°C, resulting from the requirements of modern installations, is not possible [1]. Therefore, nowadays work on the development of systems for use in low-temperature ranges is a major challenge in the field of environmental catalysis.

The presented results are devoted to obtaining active and selective catalysts for use in the low-temperature range of NO_x conversion. The synthesized catalysts are based on the modern group of layered MWW doped with cerium and ion-exchanged with Cu^{2+} cations. Materials were deeply physiochemically characterized and then tested in the role of NH_3-SCR catalysts (Fig. 1A). The activity of the obtained catalysts in the NO conversion process was higher in comparison to the commercial V_2O_5/TiO_2 system. The effective temperature operation window was shifted towards lower temperatures, 225-300°C (Fig 1A - insert). Thus, meeting the requirements of modern NH_3-SCR installations. The increased low-temperature performance of the samples may be correlated with their activity in the process of NO to NO_2 oxidation (Fig. 1B). This reaction is considered as a crucial step in the low-temperature NO conversion mechanism, fast-SCR, requiring the formation of reactive NO_2 [3].

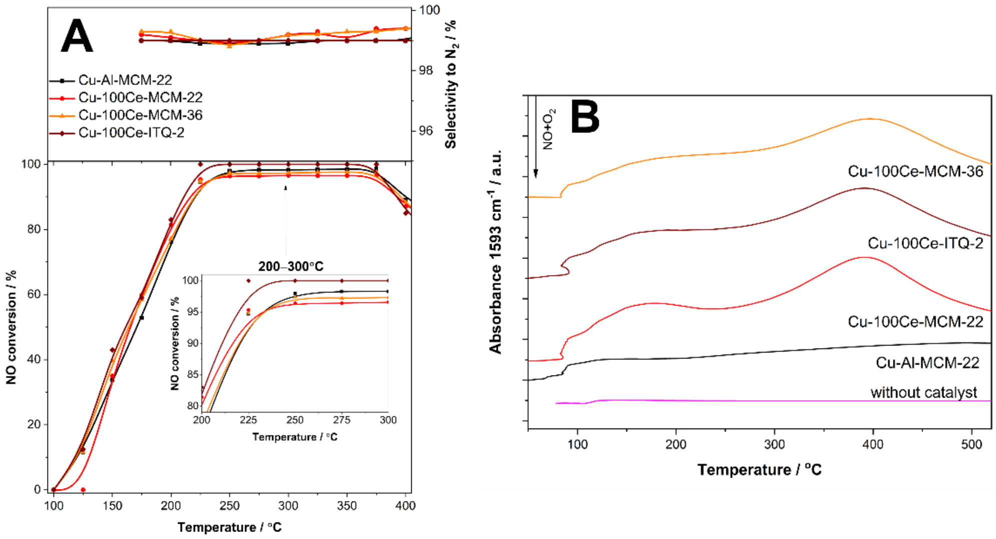

Fig. 1. Catalytic tests NH_3-SCR (A) and NO oxidation (B) over Cu-Ce-MWW derivatives.

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P-15

Enhancement of Photocatalytic Activity through Oxygen Plasma Pre-Treatment and Sonochemical Deposition of nano-TiO_2 onto Polypropylene Surface

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Photocatalysis is a dynamically developing field of research with various application possibilities, such as wastewater or air purification, self-cleaning, and antibacterial surfaces. Photocatalytic processes are induced by energy from irradiation, and after the excitation of photocatalytic material, new pathways of reactions could occur. One of the best-known and most frequently used photocatalyst is titanium dioxide due to its high activity, nontoxicity and chemical stability. [1]

To obtain a photocatalytic surface, it is necessary to anchor the titanium dioxide nanoparticles onto the material. Interactions at the surface-nanoparticle interface are extremely important for achieving a durable and active coating. Some materials, especially those that are chemically inert and hydrophobic (like polypropylene), are difficult to coat. [2] To enable good dispersion and deposition of TiO_2 at polymer surfaces, oxygen plasma can be used to generate oxygen functional groups on the surface to improve adhesion. The extent of plasma modification has been monitored by water contact angle measurements (surface wettability), IR, and XPS [3], whereas the TiO_2 particle size and dispersion were monitored by NTA, TEM, and SEM, respectively. The strategy of hybrid TiO_2/PP photocatalyst preparation is presented in Fig. 1.

Our investigations are focused on the influence of plasma treatment of polymer and subsequent sonochemical deposition of TiO_2 nanoparticles to improve the photocatalytic activity, which was measured based on the degradation of methyl orange (as a model pollutant). It has been concluded that the parameters of both oxygen plasma treatment (power, time) and sonochemical deposition (power, time, amplitude, concentration of NPs) are critical for enhancing photocatalytic activity.

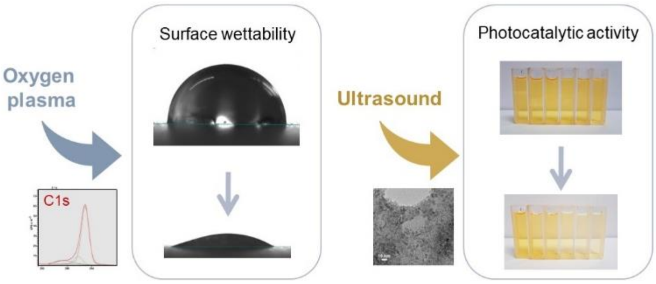

Fig. 1. The applied preparation strategy of the TiO_2/PP hybrid photocatalytic system

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P-16

Effects of Artificial Ageing on Plasticized Poly(vinyl chloride)

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Works of art made of plasticized poly(vinyl chloride) (PVC) present unique and pressing conservation challenges. Due to inherently unstable formulations, PVC can deteriorate rapidly, producing dramatic alterations unanticipated by artists and collectors [1].

The ageing leads to changes in original properties as a result of chemical and physical processes, causing changes in material structure as well as in chemical composition [2,3,4]. The latter is mostly related to plasticizer loss, whereas chemical changes primarily to the dehydrochlorination process, which leads to the formation of polyene sequences and thus yellowing of PVC objects over time [2]. Additionally, the chemical degradation of the plasticizers needs to be taken into account. Therefore, the major objective of the current research is to investigate those changes during the degradation process of the PVC plasticized with DOTP (Dioctyl Terephthalate). Accordingly, three samples of PVC containing 19, 21, and 27% of DOTP have been thermally treated at 80°C for up to 20 weeks. The samples were comprehensively characterised by ATR-FTIR, UV-Vis, Raman spectroscopy, spectrophotometry (ColorQuest), measurements of contact angles, size exclusion chromatography and dynamic mechanical analysis to recognize the effect of chemical degradation and plasticizer loss on PVC samples' performance. The appearance of the C=C double bonds in IR spectra indicates that ageing at 80°C led to dehydrochlorination and a decrease of the band originating from C=O vibration indicating plasticizer loss with ageing time (**Fig. 1**). The increased hydrophilicity is related to chloride ions trapped in the polymer, and the sample stiffening to the diffusion and evaporation of DOTP.

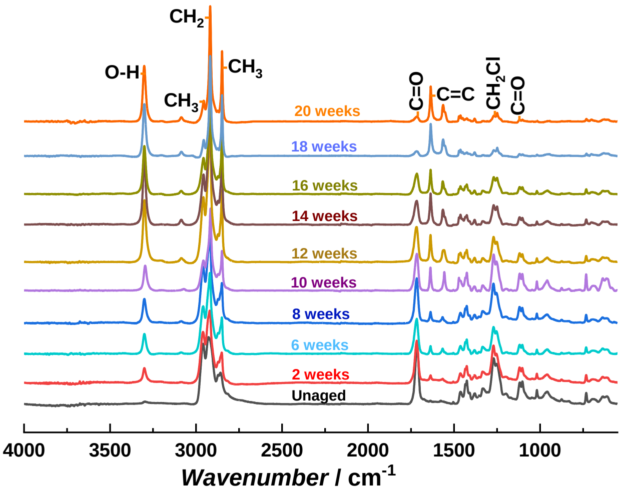

Fig. 1. **ATR-FTIR spectra of PVC plasticized with DOTP aged for indicated time at 80 °C.**

Therefore, in the conservation process of culturally significant PVC objects, it is important to address advanced stages of degradation.

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P-17

On the influence of the iron content in microstructured charcoal additives on the physicochemical properties of ANFO-based explosives

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Ammonium nitrate fuel oil (ANFO) is nowadays one of the most commonly used explosives in the mining industry and civil engineering [1]. From the chemical point of view, ANFO can be regarded as a combination of an oxygen component (ammonium nitrate(V)) with fuel oil (FO), which is characterized by a stoichiometric proportion ca 94:6. ANFO is commonly applied as a mining and civil engineering explosive due to the relatively low cost of its manufacturing process, simplicity of production and its good blasting properties. The optimization of detonation properties of the prepared ANFO-based explosives can be realized by the application of modifiers. Apart from the most commonly used additives like aluminum, which strictly influences ANFO's blasting properties, better performance could be achieved by the application of microstructured charcoal (MC) as an additive, since it was recently shown that, depending on the contents, it could have unique explosive combustion properties [2].

In the undertaken research, we studied Fe-containing MC as ANFO. The charcoal powder was liquid adsorption-treated with Fe in various ratios. Based on the results of the performed research, it may be concluded that the MC-Fe additives influenced the activation energy of the ANFO detonation. This statement was evidenced by the change in the position of the exothermic DSC peak from ca. 280 ^{o}C to 250 ◦C. The presence of Fe in the MC additive reduced the AN decomposition temperature with a simultaneous acceleration of the AN decomposition rate. From the analysis of the post-blast fumes, it may be postulated that the ANFO sample with a modifier of MC:Fe ratio of 4:1 was characterized by the least toxic chemical composition of the post-blast fumes among all studied ANFO explosives containing the MC-Fe additives. The CO content was smaller than for both pure ANFO and other counterparts containing the MC additives.

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P-18

Optymalizacja stężenia niklu oraz składu nośnika binarnego w układzie tlenkowym typu Ni/CeO_2-ZrO_2 pod kątem właściwości katalitycznych testowanych w reakcji suchego reformingu metanu

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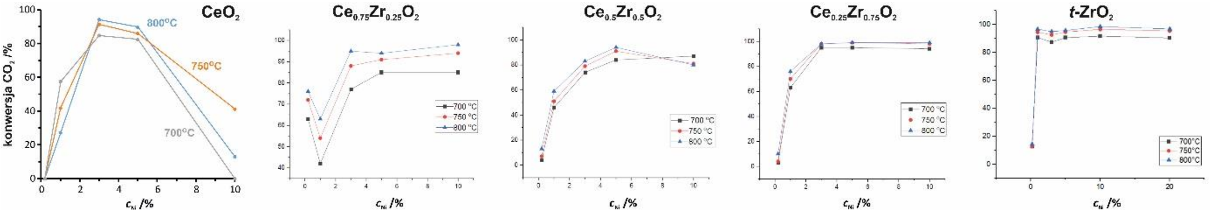
W ostatnich latach redukcja emisji gazów cieplarnianych do atmosfery stała się jednym z najważniejszych wyzwań przed jakimi stanęło nasze społeczeństwo. Jedną z możliwych opcji technologicznych zorientowanych na efektywne wykorzystanie CO_2 jest jego konwersja do gazu syntezowego. Można go otrzymać m.in. w reakcji zwanej suchym reformingiem metanu (DMR, *Dry Methane Reforming*): $CH_4 + CO_2 \rightarrow 2CO + 2H_2$. DMR jest reakcją termodynamicznie defaworyzowaną, zatem do uzyskania zadowalającej konwersji i selektywności niezbędna jest wysoka temperatura i aktywny katalizator. Przeprowadzono wiele badań w celu opracowania optymalnej formuły układu katalitycznego, takiego jak np. Ni/CeO_2-ZrO_2, aczkolwiek wpływ stężenia fazy aktywnej i składu nośnika na właściwości katalityczne nadal nie jest w pełni wyjaśniony. Celem niniejszej pracy było zbadanie i wyjaśnienie wpływu zarówno zawartości niklu, jak i składu nośnika na właściwości fizykochemiczne i aktywność katalityczną katalizatorów Ni/CeO_2-ZrO_2 aktywnych w DMR.

Nośniki CeO_2-ZrO_2 (0-100% ZrO_2) zsyntetyzowano metodą cytrynianową. Katalizatory przygotowano poprzez impregnację nośnika roztworami azotanu(V) niklu(II) (0 – 10 % wag. Ni). Próbki scharakteryzowano strukturalnie (XRD, RS), teksturalnie (SEM) oraz funkcjonalnie (XPS, DRIFT, UV/Vis-DR). Aktywność katalityczną próbek zredukowanych (5% H_2/Ar, 2h) przebadano w zakresie temperatur 550-800°C w atmosferze: 2,5% CH_4 i 2,5% CO_2 w Ar.



Rys. 1. Aktywność katalityczna w DMR wyrażona jako konwersja CO_2 na katalizatorach typu Ni/CeO_2-ZrO_2 oraz próbkach referencyjnych Ni/CeO_2 i Ni/ZrO_2.

Uzyskane wyniki wykazały, że dla wszystkich składów nośników można określić optymalne stężenia niklu, przy czym zależą one od składu nośnika (Rys. 1), co potwierdza silne oddziaływanie fazy naniesionej z nośnikiem. Badane układy typu Ni/CeO_2-ZrO_2 spełniają większość wymagań jakie stawia się katalizatorom DMR, a optymalizacja ich składu i metody syntezy jest istotna przy projektowaniu rozwiązań w skali technologicznej.

Podziękowania: Badania wykonano w ramach projektu NiCe dzięki wsparciu finansowemu Narodowego Centrum Badań i Rozwoju w ramach programu ERANet RUS Plus - S&T (nr umowy DZP/RUSPLUS S&T/270/2015).

P-19

Wpływ stężenia potasu na aktywność modelowego katalizatora Ni-K/CeO$_2$ w reakcji suchego reformingu metanu

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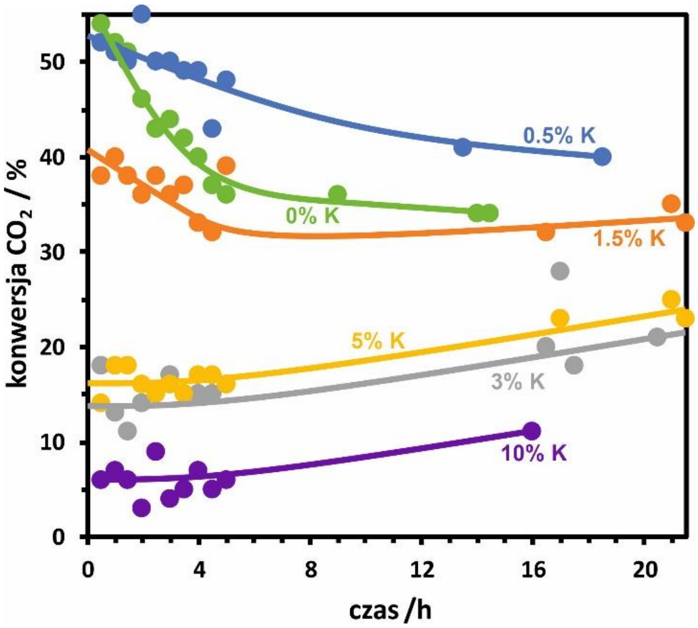
Jednym z palących globalnych problemów środowiskowych do jak najszybszego rozwiązania jest skuteczna redukcja emisji gazów cieplarnianych (GHGs), wśród których wyróżniają się dwutlenek węgla oraz metan, wnoszące wyjątkowo wysokie przyczynki do globalnego ocieplenia. Efektywna konwersja gazów cieplarnianych, zwłaszcza CO$_2$, do wartościowych produkty to najbardziej zrównoważony sposób ich waloryzacji. Dobrym przykładem efektywnego zagospodarowania GHGs jest suchy reforming metanu (DMR). Opracowanie taniego, aktywnego i stabilnego katalizatora dla tej reakcji jest jednak wymagające. Domieszkowanie alkaliami wydaje się obiecującym sposobem na poprawę odporności katalizatorów DMR na tworzenie się depozytu węglowego. Celem niniejszej pracy było określenie wpływu zawartości potasu w układzie modelowym Ni-K/CeO$_2$ na aktywność i stabilność katalizatora aktywnego w reakcji DMR.

Materiałem wyjściowym był Ni/CeO$_2$ z zawartością niklu równą 3 % wag. (naniesiony metodą suchej impregnacji). W kolejnym etapie Ni/CeO$_2$ zaimpregnowano wodnym roztworem KNO$_3$ (seria o zawartości potasu od 0 do 10 % wag.). Otrzymane próbki scharakteryzowano (m.in. metodami XRD, RS, SEM, N$_2$-BET, DRIFT, UV/Vis-DR, XPS). Badania katalityczne przeprowadzono w mieszaninie zawierającej 2,5% CO$_2$ i 2,5% CH$_4$ w Ar. Gazy poreakcyjne analizowano metodą GC/TCD. Badania stabilności przeprowadzono w formie długotrwałych testów w stałej temperaturze.

Wprowadzenie potasu nie spowodowało diametralnych zmian w strukturze i powierzchni badanego katalizatora. Jednocześnie wprowadzenie potasu spowodowało pogorszenie aktywności, a efekt ten był tym wyraźniejszy, im wyższa była zawartość potasu. Badania stabilności (Rys. 1) potwierdziły, że obecność potasu znacząco poprawia stabilność katalizatora Ni/CeO$_2$. Optymalne działanie katalizatora (biorąc pod uwagę zarówno jego aktywność, jak i stabilność) stwierdzono przy stosunkowo niskiej zawartości potasu (0,5-1,5%).



Rys. 1. Stabilność modelowego katalizatora Ni-K/CeO$_2$ (c_K = 0 – 10%) jako aktywność (mierzona konwersją CO$_2$) w funkcji czasu przebiegu reacji DMR.

Podziękowania: Badania wykonano w ramach projektu NiCe dzięki wsparciu finansowemu Narodowego Centrum Badań i Rozwoju w ramach programu ERANet RUS Plus - S&T (nr umowy DZP/RUSPLUS S&T/270/2015).

P-20

Synthesis and characterisation of polystyrene-templated ZIF-8(Zn/Ti)

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Metal–organic frameworks (MOFs) have received significant attention owing to their varied structural topologies, tunable functionalities and such applications as gas storage, gas separation or catalysis. Merging MOFs with other solid materials allows to obtain hybrid materials of improved properties. One of the possibilities is to form core–shell or hollow forms, using different templates [1]. The core−shell (CS) nanoparticles, including hollow core−shell and rattle core−shell nanostructures are obtained using e.g. hard-templating methods. The synthesis routes applied for formation of those materials are Ostwald ripening, Kirkendall effect, ion exchange, or selective etching - all leading to a wide range of CS nanoparticles [2].

ZIF-8 is one of MOFs having potential to be used in some reactions including Friedel-Crafts acylation, Knoevenagel reaction or photocatalysis. Its combination with TiO_2 (TiO_2/ZIF-8) improves Rhodamine B photodegradation [3]. ZIF-8 is composed of Zn(II) and 2-methylimidazole ligands. It shows high specific surface area, regular pores, and excellent water stability.

In this work, we obtained ZIF-8 templated on two types of polystyrene nanospheres and to improve its photocatalytic properties we have exchanged part of Zn ions to Ti ions. The influence of synthesis parameters of templated ZIF-8(Zn/Ti) (especially in terms of utilisation of polystyrene nanospheres - unmodified and modified with Zn), on its morphology, phase composition as well as crystallographic and textural properties is discussed.

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P-21

Methanol synthesis over modified MOFs

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Conversion of carbon dioxide into value-added chemicals (urea, formaldehyde, formic acid, and methanol) is one of the approaches for the reduction of CO_2 emissions. CO_2 conversion to MeOH is the most interesting - it produces a fuel or a feedstock for further production of chemicals [1]. Owing to the thermodynamic stability of carbon dioxide molecule, its activation requires an efficient catalyst. The most popular catalytic system for CO_2 hydrogenation to MeOH is $Cu/ZnO/Al_2O_3$; however, it suffers from low selectivity and short lifetime due to the recrystallisation of Cu and ZnO phases under influence of water produced as a by-product [2]. Immobilisation of Cu phase in highly porous metal-organic frameworks (MOFs) can help to overcome the drawbacks of the above-mentioned commercial catalyst [3].

In this work, we report different MOF-based catalytic materials for CO_2 hydrogenation to methanol, such as UiO-66, MOF-808, ZIF-8 and PCN-222, that were modified by the introduction of Cu phase. The physicochemical and catalytic properties of those materials are discussed.

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P-22

From dioxygen to superoxide – periodic DFT modeling and EPR study of paramagnetic Zn^{+} and Zn^{2+}-$O_2^{\bullet-}$ species in MFI zeolite

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The activation of dioxygen O_2 molecules may involve either electron or energy transfer processes. The latter implies redox transformations leading to reactive oxygen species. One such species, $O_2^{\bullet-}$ superoxide radical anion, plays an important role in catalysis, environmental chemistry, and biochemistry. One of the possible ways to generate these radicals is O_2 adsorption on low-valent transition-metal ion centers dispersed in porous materials, such as zeolites [1]. We present a theoretical and spectroscopic analysis of an excellent example of a system defined by monovalent Zn^{+} ions.

This work aims to support computationally and refine the experimental EPR studies involving the adsorption of isotopically labeled ^{17}O molecular oxygen on Zn^{+} exchanged MFI zeolite obtained by chemical vapor deposition. EPR measurements provided geometric constraints for the observed superoxide species, while periodic DFT modeling detailed its structure and electronic properties. The geometry optimization was performed at the DFT level for periodic models of MFI, containing a single Zn^{+} ion (Fig. 1) and Zn^{+}-Zn^{2+} pair, where oxygen adsorption can lead to the $O_2^{\bullet-}$ radical formation. Several possible zinc-superoxide adducts were computationally studied. Large cluster models were subsequently cut from these structures and used for calculating EPR *g* and *A* tensors.

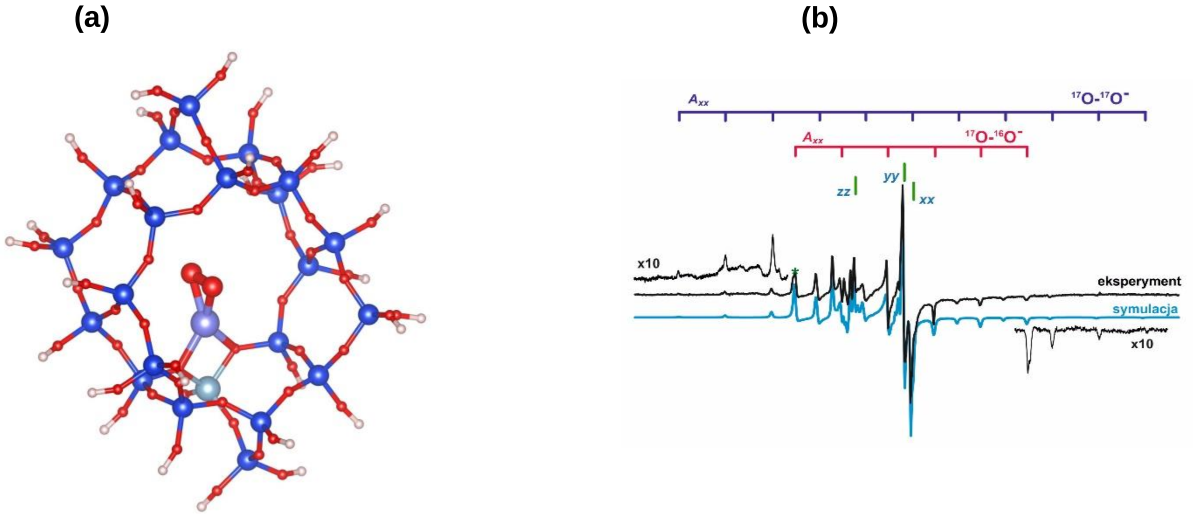

Fig. 1. (a) Cluster cut-off from the DFT-optimized periodic structure and used consequently in relativistic calculations of EPR parameters. Side-on Zn^{2+}-$O_2^{\bullet-}$ coordination with two magnetically equivalent oxygen nuclei, consistent with the analysis of respective EPR powder spectra (b), is displayed.

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P-23

The role of modification of anode materials intended for use in SOFCs in the reaction of methane reforming

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Solid Oxide Fuel Cells (SOFC) are one type of high-temperature fuel cells. These devices are constantly the subject of many scientific studies leading to obtaining the best possible parameters of their operation. SOFC fuel cells are used, among others, to generate energy intended to power vehicles. It is common knowledge that fuel cells operate with high efficiency, but commonly used materials and technologies constantly require improvement and development. SOFC cells operate at high temperatures (600 - 1000 ^{o}C), which increases the efficiency of these devices, but at the same time limits the availability of materials used for their construction, which in turn increases costs.

One of the main advantages of SOFCs is the ability to power them with various fuels, which is why many companies are interested in implementing them for transport applications. Cells of this type do not have to be powered by pure hydrogen. The fuel for these cells may be gas obtained as a result of internal fuel conversion (hydrocarbon reforming).

This research focused on testing modified anode materials for their use in the methane conversion reaction at the operating temperature of the SOFC cell. Nickel-based anodes are the most commonly used materials in SOFCs due to their excellent electrochemical catalytic activity in the fuel oxidation reaction, high electrical conductivity, good stability, and low cost. Due to these highly desirable features, Ni/YSZ anode materials were modified using the PAD method to produce thin layers 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 $La_{0.6}Sr_{0.4}Co_{0.2-x}Ba_xFe_{0.8}O_3$, $La_{0.6}Sr_{0.4}Co_{0.2-x}Bi_xFe_{0.8}O_3$, $La_{0.6}Sr_{0.4}Co_{0.2-x}Ca_xFe_{0.8}O_3$, $La_{0.6}Sr_{0.4}Co_{0.2-x}Mn_xFe_{0.8}O_3$ on Ni/YSZ base anode materials. The anode material can be considered suitable when, in addition to the fuel oxidation reaction, reforming reactions also take place on its surface.

Therefore the obtained anode materials were gauged in the reaction of CH_4 reforming leading to the production of synthesis gas according to the following equations:

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

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

These reactions determine the efficiency and fuel utilization rate of the SOFC fuel cell in which this anode material can be used.

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P-24

Gas-phase hydrogenation and decarbonylation of furfuryl aldehyde over catalysts containing Cu and Ni

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Each year, due to the concerns about energy security and climate change, there is a strong interest in developing alternative and renewable energy sources. The abundance of biomass and its carbon-neutrality make this feedstock an ideal alternative option to produce biofuels. In this context, the potential of 2-methylfuran and furan being biomass-derived energy carriers is recognized. These substances can be used both as unconventional fuels and as components that improve the knock properties of conventional ones. 2-methylfuran and furan are formed by hydrogenation and decarbonylation of furfural (FAL) that is treated as the important platform molecule in biomass conversion.

Our aim to investigate Cu and Ni catalysts, containing a low amount of the active metal phase (up to 5 wt%), supported on SiO_2, CeO_2 and ZrO_2 to learn about the mechanisms of the furfural transformations at low temperatures and the physicochemical factors which influence the reaction.

The hydrogenation and decarbonylation of furfuryl aldehyde in the gas phase at 120 – 200 ℃ were studied. Structural and morphological features of the catalysts were thoroughly investigated by several physicochemical characterization techniques (XRD, BET/BJH method, XRF, SEM/EDS, H_2-TPR and NH_3- TPD). The influence of the catalysts' parameters such as different active phase (Cu or Ni) as well as different carriers (SiO_2, CeO_2, ZrO_2) or reaction temperature was examined with respect to furfural conversion and selectivity to the most desirable reaction products: furfuryl alcohol, 2-methylfuran, and furan.

The results clearly showed that Cu-systems catalyse mainly the furfuryl aldehyde hydrogenation process, while Ni-catalysts catalyse mainly the process of its decarbonylation. The $Cu_{5.0}ZrO_2$ catalyst exhibited excellent activity which led to 85% selectivity to furfuryl alcohol at 200 ℃. Among Ni-catalysts, the highest selectivity towards the desired products shown by $Ni_{5.0}CeO_2$ (S_{FOL} = 52% at T = 120 °C; S_{furan} = 41% at T = 160 °C) and $Ni_{5.0}SiO_2$ ($S_{2\text{-}MF}$ = 26% at T = 160 °C). Among various physico-chemical properties of the materials, their reducibility influences the catalytic activity at most. The measured furfural conversion at 200 °C correlates with the total H_2 consumption calculated based on the H_2-TPR data for the nickel-based catalysts. In case of the copper-containing systems, the selectivity to all hydrogenation products also correlates with the total hydrogen consumption of the samples.

P-25

Facile engineering of (CnNn+x), with unconventional plasmonic materials with single atom for sustainable H_2 production

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Almost a quarter of the worldwide energy sector is dependent on the current catalytic process. For boosting the future economy, photocatalysis research has become the central development regime of new, clean protocols to generate energy[1]. However, single-site catalysis holds a new frontier in the realm of heterogeneous catalysis. The main goal of the present research is to reach significant enhancement in photocatalytic hydrogen evolution via solar water splitting, either by metal-free conditions or atomic engineering with single atoms. These photocatalysts may increase the production of hydrogen due to their high and efficient photocatalytic performance further with single atom engineering[2]. Such formulated energy-based materials are explored further via enhancing visible light absorption and introduction of tunable band gaps for hydrogen production as green energy storage and environmental protection[3,4,5]. Photoactive material: We will be using earth abundant material for the synthesis and non-hazardous material for synthesis. CN based material, graphene, C_3N_4, C_3N_5, C_3N_7 and N/ O/ S/ P-graphene using various earth abundant element-based precursors (C_3N_4, CnNn+x).

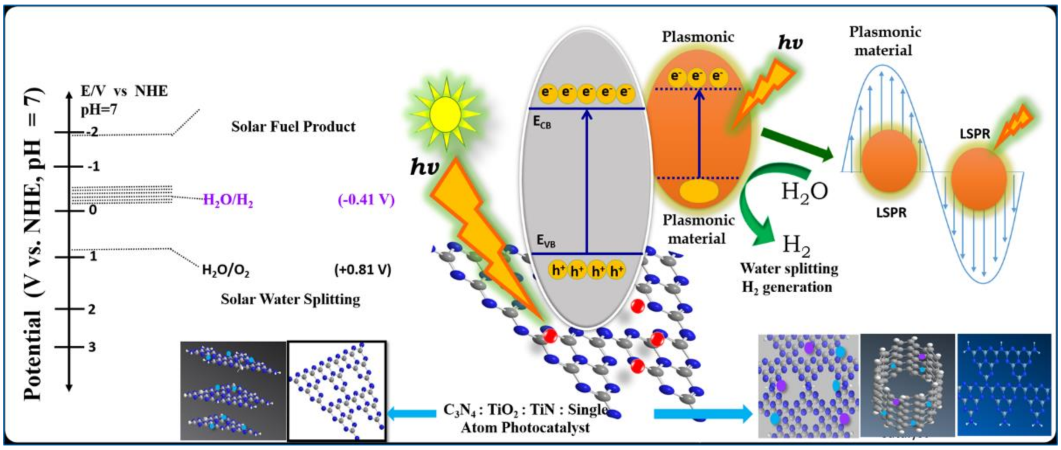

Figure 1. Schematic diagram of precise atomic engineering of plasmonic materials (TiN) with single & bimetallic atoms embedded over photoactive [earth-abundant element-based precursors (CnNn+x) for H_2 generation.

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P-26

Plasma pre-oxidation boosts cobalt dispersion on mesoporous carbon for enhanced oxygen evolution reaction

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This study investigates enhancing cobalt dispersion on ordered mesoporous carbon through low-temperature plasma pre-oxidation to boost electrocatalytic activity in the oxygen evolution reaction (OER). Using KIT-6 as a silica template and sucrose as a carbon source, ordered mesoporous carbon was synthesized via pyrolysis at 900°C. Plasma pretreatment was conducted in an oxygen plasma chamber, optimizing treatment parameters. Cobalt phase deposition was examined for plasma-modified and reference carbon support, using varying concentrations of Co^{2+} ions in ethanol. Electrochemical tests were performed using a rotating disc electrode in 0.1 M KOH solution. Plasma oxidation did not alter the carbon structure, confirmed by Raman spectroscopy. TEM imaging showed improved cobalt dispersion on plasma-treated samples. Enhanced dispersion led to a significant reduction in overpotential and improved specific activity in OER. The deposition of cobalt also increased the concentration of carboxyl-type groups, potentially enhancing catalyst performance. This study demonstrates that plasma pre-oxidation can dramatically improve cobalt dispersion on carbon support, even at high cobalt loadings, resulting in enhanced electrocatalytic performance (Figure 1).

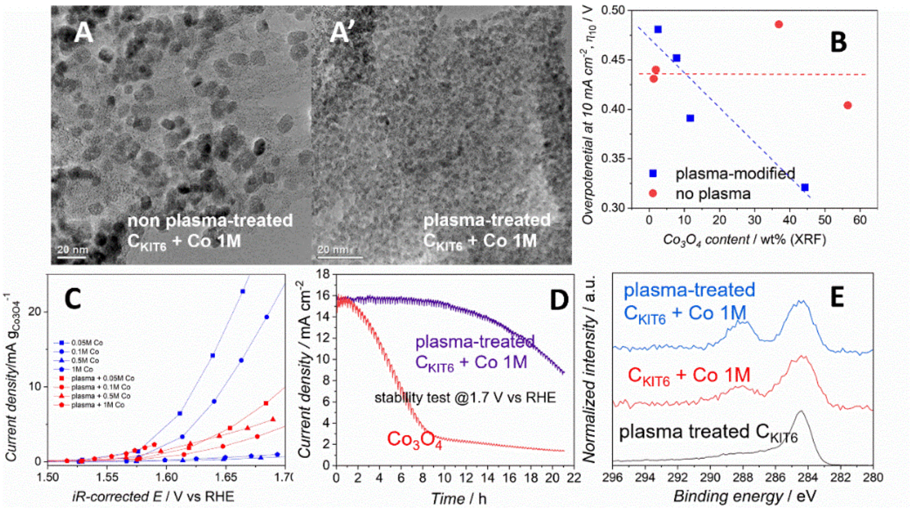

Figure 1 Morphological, electrochemical and spectroscopic characteristics of studied samples.

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P-27

Katalizatory Ni-Zr osadzone na zeolitach (BEA, ZSM-5) oraz tlenku glinu jako katalizatory do procesu hydrokrakingu oleju z alg Spirulina Plantesis

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Jedną z metod uzyskiwania alternatywnych paliw jest proces hydrokrakingu, który polega na konwersji substratów o wysokiej masie cząsteczkowej (np. trójglicerydów zawartych w olejach) do produktów o znacznie niższej masie cząsteczkowej z wykorzystaniem wodoru oraz dwufunkcyjnych katalizatorów heterogenicznych. Proces ten wymaga wysokiej temperatury reakcji (260-425°C) prowadzonej w atmosferze wodoru pod wysokim ciśnieniem (35-200 barów) [1,2]. Do produkcji biopaliw, coraz chętniej stosowana jest biomasa bądź oleje z alg, z racji, iż glony cechują się szybkim wzrostem przy niskich wymaganiach dotyczących hodowli (nawet bez wykorzystania gruntów rolnych) i możliwością uzyskania znacznie większej ilości oleju niż dla tradycyjnych roślin uprawnych [3].

Do uzyskania biopaliw z oleju algowego, zsyntezowano metodą koimpregnacji układy katalityczne Ni-Zr na zeolitach BEA, ZSM-5 i na Al_2O_3. Wszystkie katalizatory przed reakcjami kalcynowano w temperaturze 600°C przez 4 godziny w piecu muflowym, a następnie redukowano mieszaniną redukującą (5%H_2-95%Ar) w temperaturze 500°C, 600°C lub 700°C przez 2 godziny. Testy katalityczne przeprowadzono w autoklawie, pod ciśnieniem wodoru wynoszącym 75 barów, w temperaturze 320°C przez 2 godziny. Ilość katalizatora odpowiadała 1%$_{\text{wag.}}$ względem masy oleju z alg Spirulina Platensis, który został wykorzystany jako substrat. Właściwości fizykochemiczne katalizatorów zostały scharakteryzowane metodami H_2-TPR, XRD, NH_3-TPD, BET i SEM-EDS. Wyniki aktywności pokazują, że układy Ni-Zr naniesione na zeolity wykazywały wysoką konwersję oleju algowego.

W badaniach zaobserwowano wpływ temperatury redukcji układów na ich aktywność w reakcji hydrokrakingu i dla wszystkich testowanych katalizatorów stwierdzono największą aktywność (konwersję oleju) po uprzedniej redukcji w temperaturze 600°C. Jednocześnie stwierdzono, że największą aktywność wykazywał układ osadzony na zeolicie BEA, zawierający po 5% wag. Ni i Zr. Otrzymane produkty zostały zanalizowane i zidentyfikowane technikami HPLC i GC-MS. Produkty reakcji zawierają węglowodory od C_7 do C_{33} (dla katalizatorów na nośniku zeolitowym) i do C_{36} (dla układów na Al_2O_3), natomiast główny udział procentowy w produktach hydrokrakingu mają węglowodory należące do frakcji oleju napędowego (C_{14}-C_{22}). Występujące różnice w aktywności katalitycznej wynikają z różnic w powierzchni właściwej pomiędzy nośnikami oraz z różnic w kwasowości powierzchni katalizatora w zależności od temperatury redukcji.

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Wpływ rodzaju impregnacji jako metody syntezy katalizatorów Ni-Cu/BEA na aktywność katalityczną w procesie hydrokrakingu oleju rzepakowego

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Wykorzystywanie paliw konwencjonalnych jako źródło energii wiąże się ze wzrostem emisji szkodliwych zanieczyszczeń negatywnie wpływających na środowisko naturalne [1]. Dlatego też poszukiwane są alternatywne paliwa, które mogą potencjalnie zastąpić paliwa konwencjonalne [2]. Jedną z metod wytwarzania tego rodzaju paliw jest hydrokraking olejów roślinnych, który może zwiększyć aktywność i selektywność produktów ciekłych i związków węglowodorowych w porównaniu do krakingu termicznego [3] i pozwala na otrzymywanie związków o właściwościach porównywalnych do tych występujących w paliwach konwencjonalnych, lecz wykazujących się niższą lepkością, wyższą stabilnością przechowywania, wyższą wartością opałową i wyższą liczbą cetanową [4].

Celem pracy była synteza aktywnych katalizatorów na osnowie zeolitu BEA (o stosunku Si/Al = 25 z firmy Zeolyst International, Kansas City, USA – forma amonowa) zawierających nikiel i miedź do procesu hydrokrakingu olejów roślinnych. Katalizatory niklowo-miedziowe na zeolicie BEA zostały zsyntezowane metodami impregnacji następczej i koimpregnacji. Przed testami katalitycznymi, układy były kalcynowane w temperaturze 550°C przez 4 h i zredukowane w mieszaninie redukującej (5%H_2-95%Ar) w temperaturze 550°C przez 2 h. Wszystkie reakcje hydrokrakingu zostały przeprowadzone w autoklawie, w temperaturze 260°C przez 2 godziny, pod ciśnieniem wodoru 50 bar z zastosowaniem handlowego oleju rzepakowego jako substratu. W celu wyjaśnienia różnic w aktywności katalitycznej pomiędzy poszczególnymi układami, przeprowadzono badania właściwości fizykochemicznych materiałów katalitycznych za pomocą technik H_2-TPR, TPD-NH_3, XRD, BET i SEM-EDS. Otrzymane ciekłe produkty reakcji analizowano technikami HPLC i GC-MS. Badania aktywności katalitycznej wykazały istotność kolejności impregnacji powierzchni zeolitu BEA w procesie hydrokrakingu. Największą konwersję oleju rzepakowego (92,7%) odnotowano dla układu co-5%Ni-5%Cu/BEA, który został otrzymany metodą koimpregnacji, natomiast dla katalizatorów syntezowanych metodą impregnacji następczej konwersja trójglicerydów była niższa. Badania fizykochemiczne tego układu wykazały, że cechuje się on największą powierzchnią właściwą, najmniejszą kwasowością oraz najniższymi rozmiarami krystalitów. Produkty reakcji hydrokrakingu zawierają od 7 do 36 atomów węgla w cząsteczce. Największy udział procentowy (od 59,82% do 83,05%) w otrzymanych produktach mają związki zaliczane do frakcji oleju napędowego (C_{14}-C_{22}), a najczęściej pojawiały się węglowodory C_{17} i C_{18}. W produktach zidentyfikowano znacznie większą ilość n-alkanów niż alkanów rozgałęzionych, ponadto zidentyfikowano również węglowodory cykliczne i aromatyczne.

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Wpływ stosunku Si/Al w strukturze zeolitu BEA na właściwości fizykochemiczne i katalityczne układów zeolitowych z tlenkami metali ziem alkalicznych (MgO, CaO, SrO) w reakcji transestryfikacji oleju rzepakowego

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Transestryfikacja olejów roślinnych jest jedną z metod otrzymywania alternatywnego paliwa - biodiesla. Reakcja może być katalizowana przez katalizatory homogeniczne, które pozwalają osiągnąć pełną konwersję oleju w krótkim czasie prowadzenia procesu w łagodnych warunkach. Jednakże istnieje problem ich oddzielenia od produktów reakcji [1]. Problem ten znika w przypadku zastosowania w reakcji katalizatorów heterogenicznych, które można łatwo oddzielić od produktów, co daje możliwość odzysku i ponownego wykorzystywania przy zachowaniu wysokiej aktywności i selektywności [2].

Celem pracy było określenie wpływu stosunku SiO_2 do Al_2O_3 w zeolicie BEA (materiał z firmy Zeolyst International, Kansas City, USA – forma amonowa)) oraz wpływu rodzaju fazy aktywnej na właściwości katalityczne i fizykochemiczne układów katalitycznych testowanych w reakcji transestryfikacji oleju roślinnego z metanolem. Zastosowaną fazą aktywną były tlenki metali ziem alkalicznych (MgO, CaO, SrO). Katalizatory zostały otrzymane metodą mokrej impregnacji. Reakcję transestryfikacji prowadzono przez 2 h w temperaturze 180°C i 220°C przy stosunku metanol:olej = 9:1, stosując 0,5 g katalizatora. Konwersję trójglicerydów (TG) i wydajność procesu transestryfikacji prowadzonego na katalizatorach heterogenicznych do estrów metylowych wyższych kwasów tłuszczowych (FAME) określono z wykorzystaniem wysokosprawnej chromatografii cieczowej (HPLC). W ramach przeprowadzonych badań określono również właściwości fizykochemiczne układów katalitycznych przy użyciu następujących technik badawczych: CO_2-TPD, XRD, BET, FTIR oraz SEM-EDS. Uzyskane wyniki aktywności katalitycznej potwierdzają wpływ stosunku Si/Al w katalizatorach tlenków metali ziem alkalicznych naniesionych na zeolit BEA oraz rodzaju fazy aktywnej na aktywność katalityczną testowanej reakcji. Wyższą aktywność katalityczną zaobserwowano dla katalizatorów naniesionych na zeolit BEA o najwyższym stosunku krzemionki do tlenku glinu w reakcjach prowadzonych w temperaturze 220°C. Najbardziej aktywnym układem w badanej reakcji okazał się katalizator 10% CaO/BEA (Si/Al=300), który wykazał najwyższą konwersję TG wynoszącą 90,5% oraz wydajność w kierunku otrzymania estrów metylowych wyższych kwasów tłuszczowych (Y_{FAME}) wynoszącą 94,6% w reakcji prowadzonej w temperaturze 220°C. Wysoka aktywność tego układu związana jest z jego zasadowością, dużą powierzchnią właściwą, wielkością krystalitów fazy aktywnej oraz właściwościami sorpcyjnymi w stosunku do metanolu.

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Enhancing the Synthesis Process of Ti/CNT Composites by Optimizing Synthetic Conditions for Improved Material Quality

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Carbon nanotubes (CNTs) are fascinating structures that have found wide applications in various scientific fields. In particular, their potential in photocatalysis has been recognized and practically utilized. However, for effective use of CNTs in this field, it is crucial to appropriately modify their surfaces by introducing functional groups or other nanostructures. An interesting approach is incorporating metallic dopants or oxides, such as TiO_2, into the CNT structure. This combination expands the absorption range to visible light due to the presence of carbon nanotubes. The photocatalysis process is complex, but the use of CNTs helps in the efficient separation and migration of photoelectrons and holes, leading to the generation of excess holes in the valence band. Simultaneously, excited electrons move from the TiO_2 conduction band to the electron acceptor surface. Furthermore, the high specific surface area of CNTs has additional benefits, contributing to an increased number of active adsorption sites on the TiO_2/CNT nanocomposite surface. This significantly enhances the efficiency of photocatalysis, offering several benefits in areas such as renewable energy production and environmental protection by combating pollution.

In the initial stage, an ultrasonic generator chamber was prepared to produce precursor vapors necessary for CNT synthesis. The composite growth utilized ferrocene or nickelocene solutions (growth catalysts for carbon nanotubes) and titanium(IV) isopropoxide. Synthesis without these catalysts was also conducted, using a nickel foil as the growth substrate instead. The synthesis of titanium-modified carbon nanotubes took place in a quartz tube inside a long three-zone furnace, heated to 850 °C. The reaction was conducted for 30 minutes in a controlled atmosphere. Nitrogen and hydrogen were used as carrier gases to transport the generated precursor vapors of the Ti/CNT composite, maintaining a reducing atmosphere inside the quartz tube. After the material growth stage, the reactor was cooled in an argon atmosphere. The obtained powder was carefully removed from the quartz tube and subjected to purification. The first step of purification involved heating the obtained product in an argon atmosphere at 750 °C for 1 hour. Subsequently, after cooling, the Ti/CNT system was treated with a concentrated hydrochloric acid solution overnight to remove iron or nickel. The resulting catalysts underwent intensive physicochemical analyses, including X-ray diffraction (XRD), atomic absorption spectrometry (AAS), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS).

The prepared carbon composite sample underwent XRD testing to check for the presence of C-Ti bonds in the structure of the obtained material. The results confirmed the presence of reflections characteristic of the titanium carbide phase. To confirm the presence of titanium carbide, the sample underwent XPS analysis, which did not exclude the presence of surface titanium carbide on the CNT surface. Another technique used to confirm the presence of titanium in the CNT sample was SEM-EDS analysis, which revealed the presence of titanium in an amount of approximately 5% by weight and the absence of oxygen, indicating the absence of titanium in the form of oxides.

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Nanoklastery metaliczne Pd/Pt zakotwiczone na wolframowych anionach Keggina, jako katalizatory w reakcjach uwodornienia. Obliczenia DFT

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Celem pracy był opis struktury geometrycznej i elektronowej katalizatorów składających się z jonów/atomów metalu wbudowanych w strukturę heteropolikwasów, które w ostatnim czasie z powodzeniem stosowane są w katalizie i fotokatalizie [1]. Przedmiotem przedstawianych badań teoretycznych (DFT) są układy zbudowane z heteropolikwasu, który stanowi anion Keggina $PW_{12}O_{40}^{3-}$, z zakotwiczonymi nanoklasterami metalicznymi Pd/Pt_n (gdzie n=1-7). Obliczenia przeprowadzono analizując wpływ: rodzaju metalu (Pd/Pt), ładunku (Pd^{2+}/Pt^{2+} i klastery metaliczne), ilości atomów metalu (1-7) na zdolności adsorpcyjne badanych katalizatorów w reakcji z wodorem.

W ramach obliczeń wyznaczono strukturę geometryczną nanoklasterów metalicznych na anionie Keggina, scharakteryzowno strukturę elektronową każdego z układów w oparciu o analizę orbitali granicznych (HOMO/LUMO), obliczono energię adsorpcji wodoru.

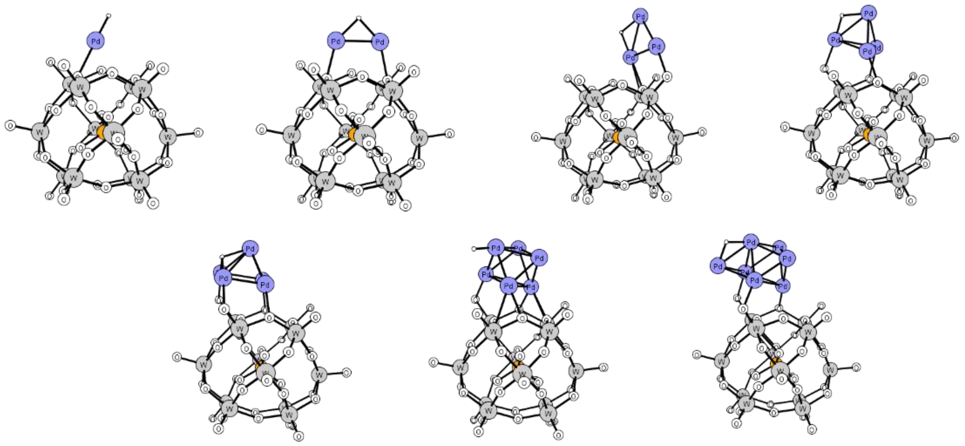

Fig. 1. Geometria klasterów Pd_n-PW gdzie n=1-7, z zaadsorbowanym wodorem.

Analiza wyników pokazuje, że liczba atomów metalu ma duży wpływ na energię adsorpcji, która jest najwyższa dla pojedynczych atomów palladu czy platyny, dla klasterów n=2-4 wartości energii maleją i zaczynają ponownie wzrastać dla nanoklasterów n=5-7.

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Niekonwencjonalna metoda badania kwasowości stałych katalizatorów GC vs. IR vs. mikrokalorymetria

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Celem badań było opracowanie nowatorskiej metody pomiaru kwasowości z wykorzystaniem katalizatorów nośnikowych typu heteropolikwas/nośnik. Opracowana niekonwencjonalna technika pomiaru kwasowości stałych katalizatorów polegała na monitorowaniu *in-situ* przebiegu reakcji odwadniania metanolu (MeOH) w fazie gazowej za pomocą spektroskopii w podczerwieni. Analiza widm IR fazy gazowej nad próbkami w trakcie trwania reakcji dehydratacji metanolu oraz wyznaczenie krzywych kalibracji, czyli korelacji pomiędzy powierzchnią pasm charakterystycznych MeOH i DME, a ich ciśnieniami cząstkowymi, pozwoliło zmierzyć konwersję metanolu, a tym samym sformułować szereg mocy kwasowej szeregu katalizatorów. Otrzymany szereg kwasowości porównano z szeregami uzyskanymi za pomocą dwóch niezależnych metod (Rys.): mikrokalorymetrycznej sorpcji amoniaku oraz dehydratacji n-butanolu analizowanej za pomocą chromatografii gazowej. Szeregi otrzymane za pomocą trzech różnych technik pomiarowych są zbieżne. Fakt ten wskazuje na skuteczność opracowanej metody badania kwasowości.

Rys. Zastosowane metody instrumentalne badania kwasowości stałych katalizatorów

Testowane katalizatory różniły się między sobą składem fazy aktywnej, nośnikiem oraz metodą syntezy. Fazę aktywną katalizatorów stanowiły komercyjnie dostępnie heteropolikwasy (HPK) typu Wells-Dawsona: $H_6P_2W_{18}O_{62}$ i $H_6P_2Mo_{18}O_{62}$. Jako nośniki heteropolikwasów zastosowano azotek boru (BN), który porównano z szeroko stosowanym nośnikiem w katalizie tlenkiem tytanu(IV) (TiO_2). Katalizatory HPK/BN i HPK/TiO_2 przygotowano za pomocą dwóch różnych metod syntezy: mokrej impregnacji i mielenia w młynku kulowym. Otrzymane materiały poddano charakterystyce fizykochemicznej stosując techniki: XRD, FT-IR, XRF, ICP-OES, SEM, BET, NH_3-TPD oraz mikrokalorymetryczną sorpcję amoniaku.

Wykazano, iż aktywność katalityczna badanych materiałów zależy od obecności mocnych centrów aktywnych w preparacie oraz od rozwinięcia pola powierzchni aktywnej implikującej dostępność centrów aktywnych dla reagenta. Potwierdzono, że na aktywność katalityczną wpływa zarówno rodzaj stosowanego nośnika jak i metoda syntezy katalizatorów.

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Synteza i charakterystyka materiałów TiO_2 dotowanych azotem do fotokatalitycznej degradacji związków fenolowych

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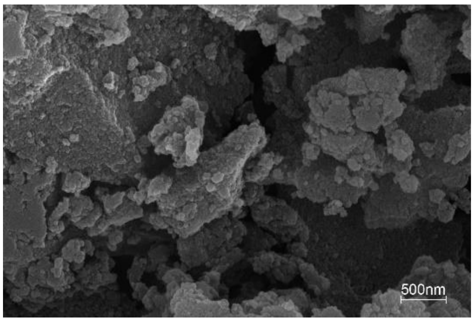
Jednym z poważniejszych problemów środowiska naturalnego jest zanieczyszczenie wód powierzchniowych spowodowane różnymi związkami organicznymi pochodzącymi ze źródeł antropogenicznych. W skali europejskiej tylko ok. 40% wód powierzchniowych pozostaje w akceptowalnym stanie ekologicznym [1]. Do szczególnie uciążliwych zanieczyszczeń organicznych występujących w wodach zaliczane są związki fenolowe i ich pochodne, szeroko stosowane m. in. w produkcji tworzyw sztucznych, żywic fenolowych, czy barwników. Obecność zanieczyszczeń fenolowych jest również identyfikowana w ściekach komunalnych oraz pochodzących z produkcji rolniczej [2]. Do usuwania związków fenolowych z wód stosowane są zwykle techniki oparte na odrębnych procesach adsorpcyjnych oraz degradacji fotokatalitycznej. Zastosowanie dwufunkcyjnego materiału, który mógłby być używany do hybrydowej adsorpcyjno-fotokatalitycznej technologii eliminacji tych zanieczyszczeń, wydaje się niezwykle atrakcyjną alternatywą w stosunku do tradycyjnych metod.

W prezentowanych badaniach skupiono się na otrzymaniu serii materiałów fotoaktywnych na bazie TiO_2 dotowanego azotem, które aktywowano termicznie zarówno w warunkach beztlenowych (zapewniających możliwość depozycji na powierzchni węgla aktywnego), jak i w powietrzu. Do syntezy zastosowano różne stosunki masowe mocznika do $TiCl_4$ (wytypowany prekursor TiO_2) w zakresie od 1:1 do 5:1. Preparatykę oparto na hydrolizie przeprowadzonej z użyciem wodnego roztworu NH_3 oraz następczej kalcynacji w temperaturach 400-900 °C. Przykładowe zdjęcie SEM materiału N-TiO_2 przedstawiono na Rys. 1.



Rys. 1. Zdjęcie SEM nanocząstek TiO_2 dotowanych azotem (mocznik:$TiCl_4$ = 5:1, kalcynacja – 500 °C)

Materiały scharakteryzowano technikami XRD (struktura), XPS (stan i skład powierzchni) oraz UV-Vis-DR (przerwa wzbroniona). Zweryfikowano ponadto ich aktywność w modelowym procesie fotodegradacji 4-nitrofenolu.

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Projektowanie nanoreaktorów rdzeniowo-powłokowych $Co_3O_4@SiO_2$ do reakcji katalitycznego dopalania toluenu

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Materiały o strukturze rdzeniowo-powłokowej cieszą się w ostatnich latach coraz większym zainteresowaniem ze względu na unikalne właściwości i szerokie zastosowanie [1,2]. O atrakcyjności tych układów kompozytowych decyduje właściwie dobrany skład poszczególnych komponentów, rozmiar formowanych cząstek oraz ich morfologia. Należy jednak podkreślić, że jedną z ich niewątpliwych zalet jest występowanie powłoki działającej jako bariera oddzielająca rdzeń od środowiska zewnętrznego, co w przypadku wykorzystania materiału w procesie katalitycznym pozwala zabezpieczyć fazę aktywną przed zachodzeniem niepożądanych przemian, jak np. spiekanie ziaren w podwyższonej temperaturze procesowej. Z tego względu materiały rdzeniowo-powłokowe, w których faza aktywna pozostaje luźno upakowana we wnętrzu sferycznej otoczki traktować można jako szczególnego rodzaju nanoreaktory.

W ramach prezentowanej pracy opracowano nanoreaktory $Co_3O_4@SiO_2$ o strukturze rdzeniowo-powłokowej, w których faza aktywna Co_3O_4 pozostawała zabezpieczona przed agregacją, a zarazem łatwo dostępna dla reagentów gazowych, wewnątrz mezoporowatej otoczki SiO_2 [3]. Do syntezy opisywanych struktur wykorzystano sferyczne szablony polimerowe wykazujące zróżnicowaną pojemność adsorpcyjną kationów metali przejściowych. Rusztowania w zastosowanej strategii syntezy warstwowej stanowiły cząstki dwóch różnych polimerów: poli(bezwodnik maleinowy-*co*-diwinylobenzen) modyfikowany dietylenotriaminą (rdzeń polimerowy o podwyższonej pojemności adsorpcyjnej) oraz polistyren (rdzeń polimerowy o obniżonej pojemności adsorpcyjnej). W przypadku użycia pierwszego z wymienionych templatów otrzymano materiały o zaprojektowanej strukturze $Co_3O_4@SiO_2$, wykazujące doskonałe właściwości katalityczne w dopalaniu toluenu. Wykorzystanie polistyrenu promowało zaś wbudowywanie kationów Co^{2+} do struktury SiO_2, co skutkowało formowaniem nieaktywnej w badanym procesie fazy krzemianowej, ale o bardzo interesujących parametrach elektrochemicznych. Rzeczywistą rolę fazy aktywnej w otrzymanych materiałach określono przy wsparciu charakterystyki fizykochemicznej wykonanej metodami XRD, adsorpcji N_2, SEM-EDS, TEM, XPS, XAS, UV–Vis-DR, FT-IR, H_2-TPR, izotermicznych analiz utleniająco-redukcyjnych oraz pomiarów elektrochemicznych.

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P-35

Kontrolowana depozycja nanocząstek MoO_x w strukturze sferycznego nośnika SiO_2 jako ścieżka syntezy aktywnych katalizatorów metatezy propenu

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Metateza jest jedną z najważniejszych, wielkoskalowych technologii odwracalnej, wzajemnej konwersji lekkich olefin. W warunkach przemysłowych proces metatezy prowadzony jest zwykle w obecności katalizatorów na bazie tlenku wolframu osadzonego na nośniku krzemionkowym w temperaturze powyżej 300 °C [1,2]. Z drugiej strony, materiały zawierające jako fazę aktywną MoO_x są obiecujące ze względu na ich wysoką aktywność i selektywność w znacznie niższych temperaturach (nawet w temperaturze pokojowej). W prezentowanej pracy podjęto próbę syntezy struktur rdzeniowo-powłokowych zbudowanych z nanocząstek MoO_x zdeponowanych wewnątrz mezoporowatej powłoki @SiO_2. Wprowadzenie cząstek fazy aktywnej do wnętrza struktury rdzeniowo-powłokowej pozwala na zapewnienie ich wysokiej dyspersji na powierzchni powłoki, jak również zabezpieczenie przed agregacją przy zachowaniu integralności strukturalnej materiału kompozytowego.

Jako templat organiczny służący do nadania sferycznego kształtu projektowanych katalizatorów posłużył polistyren (PS) o średnim rozmiarze ziaren wynoszącym 160 nm. Na sferycznym rdzeniu polimerowym osadzono mezoporowatą fazę krzemionkową. W celu otrzymania finalnych materiałów MoO_x@SiO_2 wykorzystano dwa podejścia. Pierwsza ścieżka polegała na wstępnym usunięciu z kompozytu części organicznej na drodze całkowitego utlenienia, a następnie impregnacji na mokro wodnym roztworem zawierającym prekursor fazy aktywnej w ilości zapewniającej zawartość 3, 5, 10 lub 20% mas. MoO_x w finalnym materiale. Alternatywnie impregnację poprowadzono również z użyciem kompozytu PS@SiO_2. Niezależnie od wybranej metody, materiał po modyfikacji poddano końcowej kalcynacji w celu ukształtowania struktury tlenkowej.

Otrzymane materiały scharakteryzowano pod kątem morfologii (SEM-EDS), składu pierwiastkowego (XRF), składu fazowego (XRD), otoczenia chemicznego (UV-VIS, IR) oraz porowatości (niskotemperaturowa adsorpcja N_2). W zależności od użytej ścieżki syntezy uzyskano materiały o różnych właściwościach fizykochemicznych, w tym dyspersji fazy aktywnej, co miało kluczowe znaczenie w kształtowaniu aktywności katalitycznej w procesie odwodornienia propanu stanowiącego etap aktywujący katalizator do następczej reakcji metatezy propenu. Katalizatory zawierające ok. 10% mas. MoO_x cechowały się największą aktywnością w badanym sprzężeniu reakcji, zachowując optymalny balans pomiędzy ekspozycją centrów aktywnych oraz ich stabilnością na nośniku SiO_2 w warunkach procesu.

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S-1

Najnowsze aparaty do pomiarów powierzchni właściwej, rozkładu wielkości porów oraz właściwości katalizatorów

Anton Paar Poland Sp. z o.o.
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Anton Paar w ostatnich latach pod swoją marką, kontynuuje rozwój produktów amerykańskiej firmy **Quantachrome Instruments,** założonej w 1968r i znanej jako topowa firma na świecie w dziadzienie charakteryzacji materiałów porowatych, która od 2018r należy do koncernu Anton Paar.

Analizatory adsorpcji i chemisorpcji - nowoczesne, w pełni automatyczne aparaty dokonujące precyzyjnych pomiarów adsorpcji fizycznej gazów w niskich i wysokich ciśnieniach, służące także do wyznaczania izoterm adsorpcji pary oraz pomiarów właściwości katalizatorów metodą chemisorpcji. Urządzenia zapewniają możliwość precyzyjnego ustalenia wielkości porów, obszaru powierzchni właściwej BET oraz specyficznych interakcji pomiędzy gazami i ciałami stałymi. Wszystkie te parametry są istotne dla optymalizacji produkcji, doboru adsorbentów, charakteryzacji właściwości katalizatorów, farmaceutyków, a także komponentów do produkcji baterii oraz wielu innych materiałów porowatych.

W ostatnich latach wprowadziliśmy na rynek dwa najnowocześniejsze na świecie aparaty sorpcyjne zaprojektowane całkiem od nowa z udziałem firmy Anton Paar, jednocześnie bazując na sprawdzonych rozwiązaniach Quantachrome Instruments: Nova 600/800 (BET) oraz Autosorb 6100, 6200 i 6300.

Porometry kapilarne i porozymetry rtęciowe - aparaty kapilarno-przepływowe zaprojektowane do dokładnych pomiarów porów otwartych w materiałach filtracyjnych, a także łatwe w obsłudze i bezpieczne podczas użytkowania porozymetry rtęciowe zdolne do pomiaru rozkładu wielkości oraz objętości porów dostępnych na zewnętrznej powierzchni materiału w najszerszym dostępnym zakresie średnicy od 3.6nm aż do 1100µm.

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S-2

Stabilizacja temperatury w pomiarach sorpcyjnych z wykorzystaniem gazów szlachetnych i CO_2

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Pomiary sorpcji gazów, szczególnie z wykorzystaniem azotu, nie są już nowością, a uzyskanie izoterm adsorpcji oraz desorpcji jest niejednokrotnie jednym z pierwszych pomiarów, którym poddawane są nowe materiały. Metoda oparta o równanie Brunauera, Emmetta i Tellera, towarzyszy naukowcom od połowy XX wieku i stanowi podstawę wielu badań i odkryć. W metodologię tych badań od lat wpisany jest azot, który wciąż wykorzystywany jest jako gaz pomiarowy. Coraz częściej jednak naukowcy sięgają po inne gazy, takie jak dwutlenek węgla (CO_2), metan (CH_4) czy gazy szlachetne. Okazuje się bowiem, że azot, pomimo szeregu zalet, posiada także swoje wady, które znacząco mogą wpływać na prowadzone badania.

Gazy szlachetne, takie jak krypton (Kr), argon (Ar) czy ksenon (Xe), w przeciwieństwie do adsorbatów cząsteczkowych, charakteryzują się pełną symetrią (sferycznością) i adsorbują się na powierzchni badanego ciała stałego w jednej orientacji. Przekłada się to bezpośrednio na proces tworzenia mono-warstwy gazowej, gdyż pola przekroju atomów nie zależą od ich położenia. Co więcej, atomy gazów szlachetnych nie posiadają trwałego momentu dipolowego czy kwadrupolowego, przez co nie są podatne na oddziaływanie momentów z powierzchni badanej.

Należy jednak pamiętać, iż badania prowadzone z innymi gazami niż azot, wymagają nieco innych warunków pomiarowych. W standardowym ujęciu, przy adsorpcji azotu, celkę z badaną próbką należy umieścić w kąpieli z ciekłego azotu, którego temperatura wynosi $\approx$ 77,35 K. Inaczej sytuacja wygląda w przypadku argonu czy kryptonu, które wymagają utrzymania temperatury próbki na poziomie (kolejno) 87 K i 120 K. Podobnie, w przypadku badań z wykorzystaniem CO_2, temperaturę należy utrzymywać stabilnie na poziomie 195 K. Zapewnienie odpowiedniej temperatury na poziomach tak niskich, nie jest łatwym wyzwaniem. Wymaga ono użycia takiego samego medium jak sorbowane, ale w formie ciekłej lub wykorzystania dość złożonego układu stabilizacji temperatury.

Naprzeciw tym potrzebom wyszła firma 3P Instruments, która we współpracy z wieloma niemieckimi uniwersytetami i instytutami badawczymi, opracowała urządzenie CryoTune. CryoTune jest całkowicie niezależnym urządzeniem, które wykorzystując ciekły azot, pozwala osiągnąć i stabilnie utrzymać temperaturę charakterystyczną dla gazów wykorzystywanych w badania sorpcyjnych, przez cały okres prowadzonego eksperymentu. Przyrząd ten występuje w kilku wariantach i umożliwia pomiary w temperaturach ciekłego kryptonu, argonu, ksenonu czy dwutlenku węgla. Wszystko to dzięki zintegrowanemu z dewarem modułowi pomiaru i stabilizacji temperatury, który może współpracować z aparatami sorpcyjnymi dowolnego producenta.

Rysunek 1. Aparat do pomiaru sorpcji gazów 3P Micro z urządzeniami CryoTune

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S-3

Live demonstration of 1787 Volta Potential Difference measurement

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The utterly quantum mechanical phenomenon of spontaneous charge separation between two dissimilar conductors has been confusing scientists since late 18-th century.

Two electrically neutral bodies when brought into contact will become charged if their respective Fermi levels differ. Ingenuity of A. Bennet [1] “electricity doubler” setup and insightful experimental and theoretical analysis of the phenomenon by A. Volta [2] laid down foundations of our contemporary understanding of this charging effect.

In many works today the Volta Potential Difference remains an unresolved mystery affecting variety of measurements from solid state physics to electrochemistry. This indicates that the phenomenon and its implications are far from obvious and can still drive scientific invention.

Fig. 1. Braun electroscope.

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