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im. Jerzego Habera PAN

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PL-1

New trends in the hydrogenation of CO_2 to hydrocarbons and oxygenates

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Carbon dioxide is a combustion product of hydrocarbon fuels and coal used for heat and energy generation. It is an iconic greenhouse gas and is a major contributor to current global climate change, making its capture and recycling into valuable products and fuels essential. The CO_2 chemical conversion contributes on the one hand, to lower consumption of fossil fuels (gasoline, diesel, jet fuels). On the other hand, the synthesis of fuels and chemicals from CO_2 enhances carbon- and energy-efficiency of existing technologies and contributes to elaboration [1, 2] of new sustainable "green" industrial processes. The CO_2 hydrogenation is also a major part of Power-to-X technologies, where "green" hydrogen, produced by water electrolysis with renewable electricity sources, is converted into value-added products. The key issues in the CO_2 hydrogenation reactions are the availability and sustainable production of hydrogen.

The objective of this lecture is to present a comparative analysis of catalytic CO_2 hydrogenation routes in terms of selectivity, productivity, stability, operating conditions, cost and level of technical readiness. The major emphasize is given to heterogeneous and heterogenized catalysts. Specifically, we will examine the synthesis of methanol and dimethyl ether using conventional and novel metal and oxide catalysts, the direct low-temperature synthesis of formic acid over single-atom metal catalysts, the synthesis of hydrocarbons from CO_2 using the modified Fischer-Tropsch synthesis or bifunctional oxide-zeolite catalysts.

Issues related to the thermodynamic constrains, selectivity and catalyst stability in CO_2 hydrogenation will be discussed. High yield of target products often requires optimization of process design, operating conditions and reactor design. A particular attention will be paid to the potential of transient operations to enhance the CO_2 single pass conversion, selectivity and yields of target products.

References

1. S. Navarro-Jaén, M. Virginie, J. Bonin, M. Robert, R. Wojcieszak, A.Y. Khodakov, Nature Rev. Chem. 5 (2021), 564.
2. S.A. Chernyak, M. Corda, J.-P. Dath, V. V. Ordomsky, A.Y. Khodakov, Chem. Soc. Rev. 51 (2022) 7994.

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PL-2

Pd Based Thin Film Catalyst for Acetylene Hydrogenation: Role of Second Metal

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For long-term renewable hydrogen synthesis and conversion to synthetic fuels as well as energy storage highly efficient catalysts are a prerequisite. Fundamental knowledge of catalytic mechanisms in real conditions is crucial. Within the framework of CatLab [1], a joint lab of HZB and MPG (FHI, CEC), newly specifically designed thin film catalysts have been developed. Well-defined 2D catalysts were fabricated containing a functional interface between a thin Pd film and a Si support with or without a suitable buffer interlayer. The functional interface allows to tune the electronic and catalytic properties of the catalyst. An alternative way to influence the properties of the catalyst is incorporation of a second metal. Here, to enhance catalytical performance we modified Pd thin films by introducing Au. The thin film catalysts were studied under acetylene hydrogenation reaction. While a 3 nm Pd film sputtered on a Si (100) substrate forms palladium silicide (Pd_xSi) as found by both XPS and cross-section STEM-EDS, there is no silicide formation when a SiO_2 layer is introduced between Pd and the Si substrate preventing Pd/Si interdiffusion ($Si-SiO_2-Pd$). Instead, metallic Pd (as well as Pd:C) is observed. The Si-Pd system shows negligible catalytic activity under acetylene hydrogenation, whereas inclusion of the SiO_2 interlayer ($Si-SiO_2-Pd$) results in a rather high activity. Thin PdAu films (3 nm) were co-sputtered on top of SiO_2 ($Si-SiO_2-Pd/Au$). The distribution of Pd and Au was investigated by means of TEM, XPS depth profiles and CO volumetric adsorption in connection with IR. Higher thermal stability and alloy formation was confirmed by XPS for the bimetallic system. Ab initio atomistic thermodynamics show segregation at the alloy surface as a compromise between the tendency to accumulate the more noble Au species vs. adsorbate-induced segregation of the more reactive Pd metal. Thin films of Pd and PdAu were measured under acetylene hydrogenation, whereby both films have rather high conversion rate and space-time yield. For a steady run of 18 hours (150 °C, $C_2H_2:H_2 = 1:30$), the conversion rate is as high as 84.5% (thin film Pd) and 68.7% (thin film PdAu). Selectivity remains as high as 80% ($S-C_2H_4$) and incorporation of Au promotes the selectivity, as reported in literature [2-3]. When C_2H_4 yield is normalized to the Pd in the film, the thin PdAu film show higher space-time yield. Calculated TOF indicates intrinsic activated Pd by Au. The thin film catalyst displays superior activity in comparison to reports in literature for typical Pd powder and Pd foil catalysts [4].

References

1. https://www.helmholtz-berlin.de/projects/catlab/index_de.html
2. Pei, G. X., Liu, X. Y., Wang, A., et al. New J. Chem., 38(5) (2014) 2043.
3. Zhang Y, Diao W, Williams C T, et al. Applied Catalysis A: General, 469 (2014) 419.
4. Armbrüster M, Kovnir K, Behrens M, et al. Journal of the American Chemical Society, 132(42) (2010) 14745.

Acknowledgements: CatLab project is funded by the Federal Ministry of Education and Research (BMBF)

PL-3

Catalytic Electroreduction of Environmentally and Energetically Important Inorganic Molecules: Oxygen, Carbon Dioxide and Nitrogen

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There has been growing interest in the environmentally friendly alternative energy sources and methods of formation of fuels and utility chemicals. In this respect, low-temperature electrochemical approaches comprising modern fuel cell technology, electrolytic methods, that include conventional and visible-light-induced photoelectrochemical systems, seem to be very promising. With reference to hydrogen-oxygen fuel cells special attention has been paid to development of both noble-metal-free and low-platinum-content electrocatalytic materials for the efficient oxygen reduction with the ultimate goal of lowering formation of undesirable H_2O_2 intermediate. The progress in this subject is greatly hindered by the high cost and scarcity of the state-of-the-art platinum-based materials which are regarded as the most effective cathode catalysts. An important strategy addressed here is hybridization, activation, and stabilization of carbon-supported low-content Pt-catalysts by functionalization with certain nanostructured or substoichiometric metal oxides (e.g., CeOx or H_xWO_{3-y}), both in simple or mixed forms. Among important issues are not only improvement of the catalysts' performance and ability to decompose undesirable hydrogen peroxide intermediate, but also the need to increase their stability.

Regarding the continuously rising levels of atmospheric carbon dioxide, the development of advanced technologies permitting the CO_2 utilization is highly desirable. In principle, conventional electrocatalytic and visible-light-induced photoelectrochemical approaches are well-suited for the reduction of carbon dioxide and possible generation of carbon-based fuels or chemicals. But electroreduction of CO_2l requires large over-potentials and suffers from the competitive hydrogen evolution. To overcome the problem, highly specific and selective catalysts would be required to drive effectively conversion (reduction) of carbon dioxide (and water) into fuels, syn-gas or utility chemicals. Having in mind our recent electrocatalytic results with copper-substituted polytungstates (or polyoxometallate-network-stabilized copper oxo assemblies) and regarding successful utilization of the Cu_2O films over-coated with WO_3 nanowires for both electrochemical and photoelectrochemical reduction of carbon dioxide in near-neutral media, we have pursued research along this line and proposed a hybrid catalytic system composed of copper sites immobilized in tungsten(VI) oxide nanostructures exhibiting improved high selectivity toward CO_2-reduction relative to the competitive hydrogen evolution in acid medium (0.5 mol dm^{-3} H_2SO_4).

Formation of ammonia is one of the most important chemical synthetic processes. Under industrial conditions, ammonia is primarily been synthesized from nitrogen and hydrogen via the Haber-Bosch process which requires pressurizing and heating, despite utilization of catalysts. Consequently, development of low-temperature synthetic methodology is tempting both from the practical and fundamental reasons. An ultimate goal for electrochemistry is to generate NH_3 from N_2 at temperatures lower than 100ºC, atmospheric pressure, and with use of new generation of catalysts. Currently, most of electrochemical approaches to drive N_2-fixation suffer from slow kinetics due to the difficulty of achieving the appropriate adsorption and activation of dinitrogen molecule leading to cleavage of the strong triple N≡N bond. Our recent studies, clearly demonstrate that coordinatively stabilized iron catalytic sites, e.g. iron-centered heme-type porphyrins or iron phosphide, FeP and Fe_2P phases, have been found to act as efficient catalysts for the formation of NH_3 in alkaline and semi-neutral media.

Development of durable, specific and reasonably efficient low-cost catalysts for electroreduction of O_2, CO_2 and O_2 remains a great challenge for electrochemical science and technology. Present trends and future possibilities will be addressed.

PL-4

Zeolite catalysts: design and application

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Zeolites are one of the most important heterogeneous catalysts, with a high number of large-scale industrial applications [1]. Replacement of mineral acids with acidic zeolites revolutionized the petrochemical industry in the second half of the twentieth century; the application of zeolites containing metal particles as catalysts for hydroisomerization, hydrocracking, and reforming processes has allowed the large-scale production of high-quality fuels and bulk chemicals. However, great progress achieved using zeolite catalysts for industrially relevant processes would have never been realized without accumulating a fundamental knowledge on the design of framework structure, active sites, and porosity of these materials [2,3].

This contribution addresses recent developments and trends in tailoring the structural characteristics as well as the nature and local properties of active sites in zeolite-based catalysts, with a special focus on novel extra-large pore, layered, nanocrystalline, and hierarchical (mesoporous) zeolites with enhanced pore accessibility. The latest achievements in bottom-up and top-down approaches for framework modification and isomorphous substitution in zeolites are discussed. The main preparation strategies for designing zeolite catalysts, especially those offering the control over the size of channels, location of active sites and their catalytic behaviour in emerging and industrially relevant sustainable catalytic processes are considered.

References

1. E. T. C. Vogt, B. M. Weckhuysen, Chem. Soc. Rev. 44 (2015) 7342
2. M. Shamzhy, M. Opanasenko, P. Concepcion, A. Martinez, Chem. Soc. Rev. 48 (2019) 1095
3. Y. Li, J. Yu, Nat. Rev. Mater. 6 (2021) 1156

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Komunikaty ustne
Oral communications

O-1

Wpływ funkcjonalizacji powierzchni nośnika węglowego z kobaltową fazą aktywną na aktywność elektrokatalityczną w reakcji wydzielania tlenu

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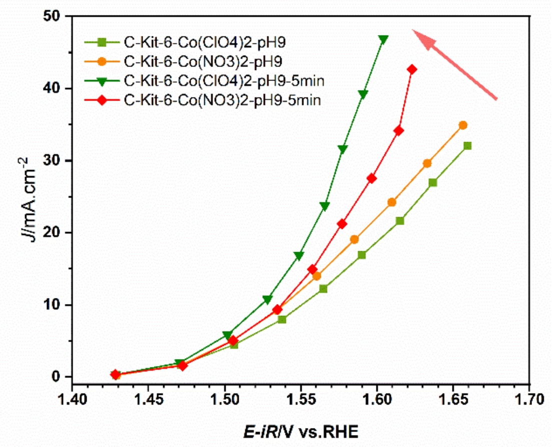
Anodowe wydzielanie tlenu jest kluczowym procesem wymagającym optymalizacji w celu poprawy efektywności produkcji wodoru w procesie elektrolizy wody. Opracowanie tanich układów katalitycznych do tej reakcji, działających w środowisku zasadowym lub obojętnym, jest konieczne do rozwoju elektrolizerów z membraną anionoprzewodzącą. Kryterium ceny spełniają materiały węglowe, które są bardzo dobrymi nośnikami faz aktywnych elektrokatalitycznie, ze względu na ich wysokie przewodnictwo elektryczne i możliwość uzyskania wysoko rozwiniętej powierzchni właściwej [1].

Modyfikacja materiałów węglowych plazmą niskotemperaturową powoduje poprawę zdolności sorpcyjnych względem jonów kobaltu, ale też umożliwia kontrolę specjacji powierzchniowych grup funkcyjnych, w szczególności tlenowych [2]. Ponadto, sposób utleniania plazmą wpływa na dyspersję kobaltowej fazy aktywnej. Zarówno rodzaj grup funkcyjnych na nośniku węglowym, jak i postać osadzonej fazy aktywnej wpływają na aktywność elektrokatalityczną [3].



Rysunek 1. Aktywność elektrokatalityczna w reakcji wydzielania tlenu katalizatorów z węgla mezoporowatego utlenionego plazmą w czasie 1 min (jasne kolory) i 5 min (ciemne kolory) z naniesioną kobaltową fazą aktywną.

Aktywność katalityczna badanych materiałów w reakcji wydzielania tlenu dodatnio koreluje ze względną zawartością grup tlenowych typu COO i ujemnie ze względną zawartością grup typu C=O znajdujących się na nośniku węglowym. Ponadto, wysoka zawartość grup typu COO korzystnie wpływa na zwiększenie dyspersji nanocząstek Co_3O_4 nanoszonych na taki materiał węglowy. Zastosowanie optymalnego utleniania plazmą niskotemperaturową wraz z doborem odpowiedniego prekursora fazy kobaltowej umożliwia uzyskanie układu katalitycznego o wysokiej aktywności w procesie anodowego wydzielania tlenu (Rysunek 1). Uzyskany materiał wykazuje nadpotencjał w badanej reakcji, wynoszący zaledwie 295 mV.

References

1. P. Stelmachowski, J. Duch, D. Sebastian, M. J. Lazaro, A. Kotarba, Materials 14 (2021) 4984
2. P. Stelmachowski, K. Kadela, G. Grzybek, M. Gołda-Cępa, K. Kruczała, A. Kotarba, Carbon 199 (2022) 141
3. A. Ejsmont, K. Kadela, G. Grzybek, T. Darvishzad, G. Słowik, M. LofeK, J. Goscianska, A. Kotarba, P. Stelmachowski,, *ACS Appl. Mater. Interfaces* 15 (2023) 5148

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O-2

Determining the correlation between chemical changes and mechanical properties of artificially aged poly(vinyl chloride)

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Works of art made of plasticized poly(vinyl chloride) (PVC) present unique and pressing conservation challenges. Until the 1990s, the poor qualities of plastics were not widely known and considered within the art conservation community. Due to the inherently unstable formulations, PVC can deteriorate rapidly, producing dramatic alterations unanticipated by artists and collectors. Yellowing or darkening of plastic works of art during exhibition and storage is one of the main issues in the case of objects made of PVC [1].

Plasticized PVC deteriorates through two processes: polymer chain degradation and plasticizer loss [2]. PVC primarily degrades through dehydrochlorination, in which the conjugated polyenes are formed, releasing hydrochloric acid [3]. This conjugated polyene structure absorbs progressively longer wavelengths of light as the process continues, explaining yellowing observed in PVC plastics over time. Therefore, the central objective of this research is to recognize the fundamental link between chemical degradation and mechanical damage and use this information to develop preventive conservation guidelines for art collections made from PVC. Various forms of unplasticized PVC samples were degraded at various temperatures and relative humidities. Analysis of the samples was done by ATR-FTIR, Raman spectroscopy, spectrophotometry, SEM, and DMA to recognize the fundamental link between chemical degradation and mechanical damage. In the Raman spectrum of PVC powder new bands related to the formation of C=C double bonds (1120 cm^{-1}, 1500 cm^{-1}), emerged after 2 months of degradation at 60 °C and are more clearly visible after 4 months (**Figure 1**). After 2 weeks of treatment at 80 °C, these bands due to the polyene chains appeared clearly, and their intensity increased with the degradation time. Furthermore, the mechanical properties of unplasticized PVC aged at 80 °C (studied by DMA) showed that the formation of conjugated double bounds is accompanied by significant polymer stiffening. Additionally, microstructure analysis using high-resolution and scanning electron microscopes revealed the presence of defects and microcracks predominantly in the crystalline areas.

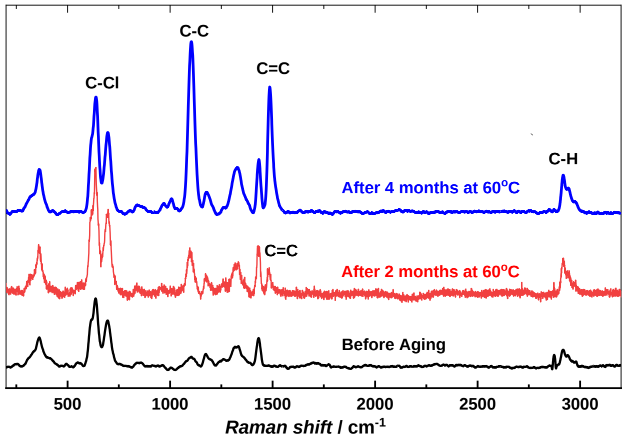

Figure 1. PVC thermally aged at 60 °C for 2 and 4 months.

References

1. N. Ledoux, G. Rayner, S. Costello, A. Chang, Studies in Conservation. (2022)
2. T. Rijavec, M. Strlič, I. K. Cigić, Acta Chim Slov. 67 (2020) 4
3. J. Bell, P. Nel, and B. Stuart, Herit Sci. 7 (2019) 1, 2019

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O-3

Synthesis and characterization of Cu/MOFs for CO_2 hydrogenation to methanol

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From the perspective of the emerging climate crisis, recent catalytic research is focused on limiting CO_2 emissions and developing new technologies to reutilise carbon dioxide into value-added chemicals. The main products, which are currently obtained from CO_2 at the industrial scale are urea, formaldehyde, formic acid, and methanol, the latter being most interesting as it could be used either as a feedstock for the further production of chemicals or as a fuel [1]. However, due to the exquisite thermodynamic stability of carbon dioxide molecules, their activation requires an efficient catalyst, usually containing copper species.

Currently, the most popular catalytic system is $Cu/ZnO/Al_2O_3$ – widely used in the industry, yet 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]. To prevent that phenomenon, the active phase might be immobilised in highly porous support like metal-organic frameworks (MOFs). Moreover, they might serve as catalytic promoters considering easily accessible metal sites, allowing easier transfer of charges, and increasing the catalytic activity of the system [3].

In this work, we report MOF-based catalytic materials for CO_2 hydrogenation to methanol. MOF structures (UiO-66, MOF-808, ZIF-8) were modified by the introduction of Cu phase employing impregnation methods or following the “bottle-around-the-ship” approach meaning crystallisation of framework around copper nanoparticles (CuNPs) synthesised beforehand. The catalytic properties of the materials were tested in the reaction of methanol synthesis conducted in a non-gradient pressure reactor. The physicochemical properties (crystalline structure, textural properties, composition, morphology) of catalysts were described before and after the catalytic tests.

References

1. J. Artz, T.E. Müller, K. Thenert, Chem. Rev. 118 (2018) 434-504
2. B. Liang, J. Ma, X. Su, C. Yang, H. Duan, H. Zhou, S. Deng, L. Li, Y. Huang, Ind. Eng. Chem. Res. 58 (2019) 9030−9037
3. H. Kobayashi, J.M. Taylor, Y. Mitsuka, N. Ogiwara, T. Toriyama, S. Matsumura, H. Kitagawa, Chem. Sci. 10 (2019) 3289-3294

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O-4

Formation of acetaldehyde from ethanol on Cu-SBA-15 and Cu-MnSBA-15 catalysts – insight into the reaction pathway

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Catalytic conversion of ethanol to valuable chemicals is a promising alternative to fossil-based processes. One of the most desired product of ethanol transformation is 1,3-butadiene. The conversion of ethanol to 1,3-butadiene is a multistep reaction. The first step, a reaction rate-limiting one, is the dehydrogenation of alcohol to form acetaldehyde. The reaction occurs typically on basic centers. The aim of the work recently published in [1] was to study the pathway of acetaldehyde formation from ethanol on copper catalysts supported on mesoporous silica SBA-15 and MnSBA-15.

SBA-15 support was modified with manganese species using manganese(II) nitrate. The source of copper was copper nitrate. The synthesis route consisted of 3 steps: i) preparation of SBA-15 and MnSBA-15 ii) functionalization of supports with 3-aminopropyltrimethoxysilane (APMS) and next iii) Cu (2.0 wt.%) anchoring. The catalysts were calcined at 773 K in air. The materials prepared were characterized by XRD, N_2 adsorption/desorption, UV-vis, XPS, EPR, pyridine adsorption combined with FTIR and test reactions: 2-propanol decomposition and 2,5-hexanedione cyclization and dehydration. Ethanol dehydrogenation (with and without oxygen) was performed in a flow system combined with FTIR measurements to get insight into the species formed on the surface of copper-containing catalysts and the gas phase composition.

Based on UV-vis and EPR studies, Cu^{2+} isolated ions and CuO have been identified in Cu-SBA-15 and Cu-MnSBA-15 fresh samples. After evacuation at 623 K $Cu^{\delta+}$ ($1<\delta<2$) isolated ions were recognized in Cu-SBA-15. The same copper species are present on the surface of catalyst before ethanol transformation in the flow system. Thanks to the absence of BrØnsted acid sites in all catalysts studied and relatively weak Lewis acidity, the dehydration of ethanol to ethene (a reaction competitive to dehydrogenation to acetaldehyde) does not occur on studied copper catalysts. Two different reaction pathways for ethanol dehydrogenation on copper containing SBA-15 are proposed depending on the reaction temperature and the presence or absence of oxygen in the reaction mixture. Without oxygen in the gas flow, the reaction occurs at higher temperature (593 K) via dissociative chemisorption of ethanol on pair of Lewis acid-base sites and ethoxy species formation. The admission of oxygen to the reaction mixture significantly increased the activity of the catalysts in ethanol dehydrogenation to acetaldehyde performed at 473 K and ethoxide intermediate is formed. Oxygen acts as an electron transmitter, enhancing the redox properties of copper active centers. The increase in basicity by the admission of manganese to the support of copper catalyst did not enhance the activity of Cu-MnSBA-15 but the synergistic interaction between copper and manganese weakens the electron transfer between copper cations and/or oxygen molecules.

References

1. I. Sobczak, J. Wisniewska, P. Decyk, M. Trejda, M. Ziolek, Int.J.Mol.Sci. (2023) 24, 2252-2276.

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O-5

Suprafacial and Intrafacial Oxygen Dynamics in Bare and Ce Doped $Na_2Mn_3O_7$ Catalysts for Soot Oxidation

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Within this contribution we present $Na_2Mn_3O_7$ layered catalysts modified with 0.1%, 1%, 10% and 50% of cerium(IV) oxide nanocrystals (Ce-$Na_2Mn_3O_7$) for soot oxidation with enhenced catalytic performance and increased resistance to water and sulfur, using low-cost raw materials and a simple preparation protocol. The samples were synthesized according to glucose-assisted thermal synthesis protocol. The speciation of cerium and the morphology of ceria nanocrystals are highly influenced by the amount of the dopant. We employed variety of advanced method, experimental (X-ray tomography, HR-TEM, STEM, operando XAS, EELS) and theoretical (DFT calculations, image simulations), to obtain in-depth characteristics of the synthesized materials (size, shape, atomic structure of the facets, electronic structure, redox properties). We also proposed the soot oxidation reaction mechanism. The reaction involves facile formation of oxygen vacancies and suprafacial/intrafacial reactive oxygen species, as well as NO_2 assisted oxidation controlled by the Mn redox state variations. Further, the result of through characterization of the catalysts was corroborated by DFT and first principle thermodynamic modeling. The high activity of the Ce-$Na_2Mn_3O_7$ catalysts, reinforced by Ce addition, shifts the soot combustion into the temperature range where the generated NO_2 is thermodynamically stable, allowing for its effective use in the whole range of the oxidation reaction. The resultant synergy between the easily available adsorbed and surface reactive oxygen species and the high yield of NO exploitation, leads to the beneficial transition of the soot combustion process from “gas-solid-solid” into the “gas-gas-solid” that is, thereby, remarkably shifted to low temperatures.

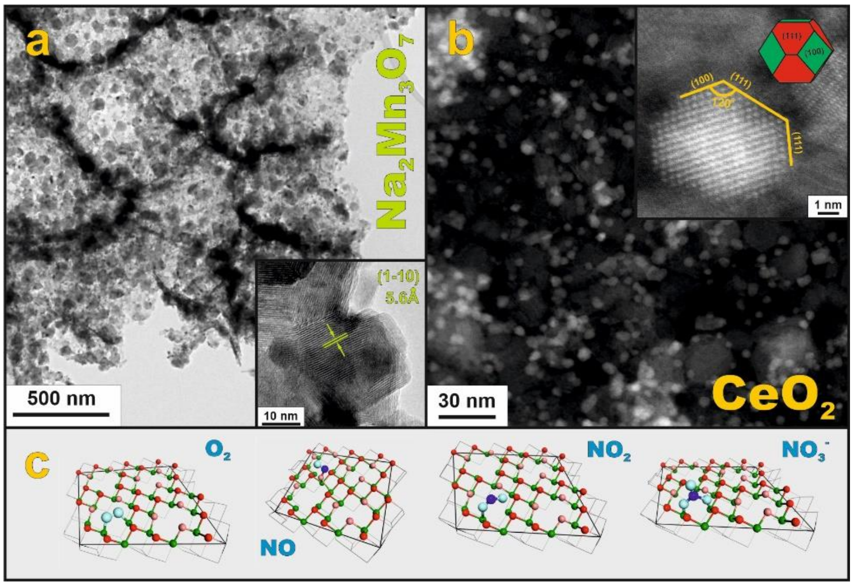

Fig. 1. a) $Na_2Mn_3O_7$ nanoplates, b) ceria nanocrystals, c) exemplary structures of O_2, NO, NO_2 and NO_3^- adsorbed on the (1-10) surface of $Na_2Mn_3O_7$ nanoplates.

Acknowledgements: The project was financed by the Polish National Centre for Research and Development PL-Ch Project MOST, WPC/4/PNOX/2018

O-6

Innowacyjny katalizator do selektywnej katalitycznej redukcji NO_x w instalacji kwasu azotowego

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Tlenki azotu (NO_x) są emitowane z instalacji kwasu azotowego ze strumieniem gazów resztkowych, w wyniku ich niecałkowitej absorpcji w kolumnie absorpcyjnej. Obecnie limity emisji NO_x z instalacji produkujących kwas azotowy określone są przez Dyrektywę Parlamentu Europejskiego (IED) i wynoszą odpowiednio 75 i 90 ppm dla nowych i istniejących instalacji [1]. Nałożone limity wymagają zastosowania efektywnych metod. Najbardziej rozpowszechnioną i skuteczną metodą jest selektywna katalityczna redukcja tlenków azotu amoniakiem (NH_3-SCR). Komercyjnie stosowane katalizatory tej technologii, najczęściej tworzone są na bazie tlenków metali przejściowych osadzonych na nośnikach (np. V_2O_5-TiO_2). Katalizatory tego typu pracują efektywnie w temperaturze do 350 ^oC, natomiast w wyższej temperaturze obserwuje się spadek aktywności i selektywności na skutek utleniania amoniaku do tlenku azotu (NO) i podtlenku azotu (N_2O).

W badaniach skupiono się na ocenie aktywności katalitycznej innowacyjnego katalizatora opartego na naturalnym zeolicie (klinoptylolicie) modyfikowanego żelazem. Materiał został wytypowany do badań z uwagi na jego powszechne występowanie, cenę, łatwość modyfikacji i obróbki, a także nietoksyczność. Łukasiewicz-INS we współpracy z AGH opracował prototyp katalizatora na bazie zeolitu [2]. Katalizator jest w postaci tabletek nośnika z naniesioną fazą aktywną, którą są jony żelaza.

Badania aktywności prowadzone przy użyciu rzeczywistych gazów resztkowych o składzie zbliżonym do składu gazów przemysłowych wykazały, że katalizator jest aktywny w typowym dla procesu „oknie temperaturowym”, zwłaszcza w wyższych jego zakresach. Badania laboratoryjne aktywności i selektywności katalizatora przeprowadzono w zakresie temperatury 250-450 ^oC. Zbadano wpływ temperatury oraz ilości żelaza na aktywność katalizatora i wytypowano najkorzystniejszy skład i warunki pracy katalizatora. Powyżej 400 ^oC uzyskano konwersję NO_x powyżej 90%, przy braku wzrostu stężenia produktu ubocznego N_2O. Katalizator o odpowiednim składzie przetestowano w instalacji pilotowej w warunkach pracy podobnych do warunków przemysłowych (GHSV= 12 000 h^{-1}, T= 370 ^oC , p= 4 bar). Wyniki badań porównawczych katalizatorów komercyjnych wykazały, że opracowany innowacyjny katalizator posiada odpowiednie właściwości katalityczne i wysoki potencjał wdrożeniowy, aby konkurować ze stosowanymi komercyjnie katalizatorami.

Literatura

[1] Zintegrowane zapobieganie zanieczyszczeniom oraz kontrola; Dokument referencyjny dla: Najlepsze dostępne techniki dla Przemysłu Wielkotonażowych Związków Nieorganicznych - Amoniaku, Kwasów i Nawozów Sztucznych, (2007)
[2] Patent Application No PL441039.

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O-7

Direct Photocatalytic Synthesis of Acetic Acid from Methane and CO at Ambient Temperature using Water as Oxidant

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Methane is one of the most abundant carbonaceous reserve feedstocks and also a notorious greenhouse gas. Its catalytic conversion towards value-added liquid oxygenates attracts considerable interest from the scientific community. The current industrial route for methane transformation to obtain acetic acid (AcOH) is an energy-intensive and indirect multistep route through methane reforming to syngas (CO and H_2), methanol synthesis and subsequent methanol carbonylation to AcOH. Direct routes of methane transformation to AcOH also have been explored in the literature [1-2], however, the indispensable use of strong oxidants such as corrosive acid or molecular oxygen inevitably leads to environmental issues, safety risks, and low selectivity due to the overoxidation of AcOH to carbon oxides.

Here, we report a new photocatalytic reaction route to synthesize AcOH from CH_4 and CO at room temperature using water as the sole external oxygen source (Fig. 1). The optimized photocatalyst consists of TiO_2 support and ammonium phosphotungstic polyoxometalate (NPW) clusters anchored with isolated Pt single atoms (Pt_1). It enables a stable synthesis of 5.7 $mmol\cdot L^{-1}$ AcOH solution in 60 hours with the selectivity over 90% and 66% to AcOH on liquid-phase and carbon basis, respectively, with the production of 99 mol of AcOH per mol of Pt. Combined isotopic and in-situ spectroscopy investigation suggests that the photo-excited electrons from TiO_2 migrate to the surface of Pt/NPW clusters, while the holes remain on TiO_2 and react directly with H_2O to produce H protons (H^+) and $\cdot$OH. More importantly, the synthesis of AcOH proceeds via a photocatalytic oxidative carbonylation of methane over the Pt_1 sites, with the methane activation facilitated by water-derived hydroxyl radicals [3].

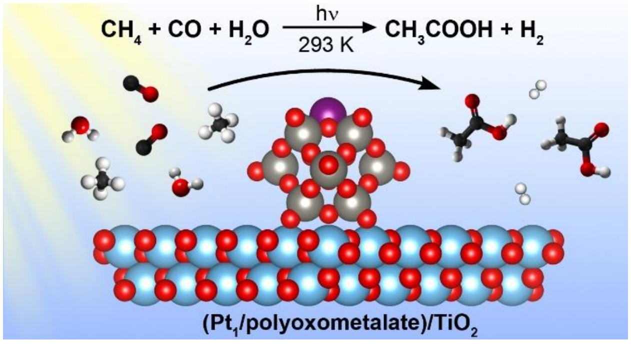

Fig. 1. Graphic illustration of the light-driven direct synthesis of acetic acid from CH_4, CO and H_2O over a ternary Pt_1/polyoxometalate/TiO_2 catalyst.

References

1. R. A. Periana, et al., Science 301 (2003) 814.
2. J. Shan, et al., Nature 551 (2017) 605.
3. C. Dong, et al., J. Am. Chem. Soc. 145 (2023) 1185.

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O-8

Phase transformation of copper and nickel catalysts during hydrogen production processes

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In recent years, a lot of efforts have been devoted to developing efficient catalysts for the hydrogen production process, namely partial oxidation and reforming of methane. Mainly, they are focused on the modification of catalyst support (to increase its basicity and prevent excess formation of coke deposit) and utilization of bimetallic active phase (to increase conversion and hydrogen selectivity) [1 - 4]. Despite the great amount of research on the modification of the catalysts, there is still not much understanding of how and when the metal species undergo oxidation-reduction transformation during hydrogen production processes. Indeed, these processes include both oxidizing (O_2, H_2O, CO_2) and reducing (H_2, CH_4, CO) agents which may either oxidize or reduce the metallic particles depending on the reaction temperature. It can be expected that at low temperatures the metal species undergo oxidation while at high temperatures they reduced back to metallic form. The extent to which these processes occur (as a function of temperature) and whether there is a co-existence of metal species with different oxidation states, however, remain unclear. Therefore, it was proposed to perform in situ investigation of the phase transformation of model catalytic systems during hydrocarbon conversion processes. Monometallic Cu and Ni supported on Al_2O_3 were chosen. Their activity and change in phase composition were studied in reactions involving soft (H_2O) and strong oxidizing (O_2) agents, i.e. steam reforming and partial oxidation of methane, respectively. The changes in oxidation states of copper and nickel particles were studied during partial oxidation and steam reforming of methane using an X-ray reactor chamber (XRD) coupled with an online mass spectrometer. Also, the susceptibility of these catalysts to oxidation and reduction by individual reaction components was investigated using TPR, TPO, and in situ XPS techniques. The obtained results showed that investigated catalysts are susceptible to complete oxidation in the oxygen atmosphere while the presence of other weaker oxidizing agents, such as water vapor and carbon dioxide resulted only in surface oxidation of metal particles. In the reaction conditions, the bulk oxidation of metal influenced significantly only the activity of the nickel catalyst. For the partial oxidation process to proceed the nickel particles had to undergo reduction during the reaction. This happened due to the solid-state interaction of metal oxide and carbon formed as a result of methane decomposition. In the case of copper catalyst, the oxidation state of metal particles did not correlate with the course of the partial oxidation reaction. Also, the oxidation of the surface of catalysts only did not alter notably the course of the reforming process.

References

1. X. Gao et al., Catalysts. 11 (2021) 1–19
2. S.M. Masoom Nataj et al., Chem. Technol. Biotechnol. 94 (2019) 1305–1314
3. Z. Bian et al., ChemPhysChem. 18 (2017) 3117–3134
4. X. Zhang et al., ChemistrySelect. 6 (2021) 3424–3434.

O-9

Ruthenium-catalyst immobilization pathways towards preparation of effective catalysts for ring-closing metathesis

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In this contribution, the designing of catalyst based on ionic liquids (ILs) dedicated for catalysis in ruthenium-based ring-closing metathesis (RCM) is presented. This reaction has opened new industrial routes to value-added molecules, especially for pharmaceuticals, agrochemicals, flavours and fragrances, and polymers. Low catalyst loadings with high-yielding processes are important requirements for economic and manufacturing-ready olefin metathesis processes. In pharmaceutical applications it is desirable to work with very low ruthenium loadings, with the content in the final active pharmaceutical ingredient less than 10 ppm. [1]

In this work, to address the challenges and seeking for the best recycling strategy, catalytic reactions were carried out heterogeneously, with ILs immobilized on the surface on carbon nanotubes (Fig. 1).

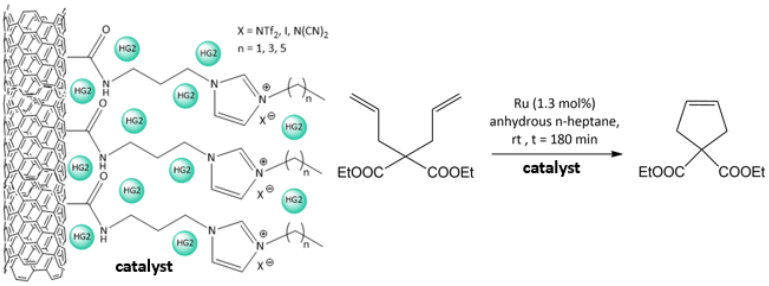

Fig. 1. Catalyst used for heterogenous ring- closing metathesis.

In this approach two strategies toward the synthesis of heterogeneous ruthenium-catalyst were explored using supported ionic liquid phase (SILP) and supported ionic liquid-like phase (SILLP) with multi-walled carbon nanotube (MWCNT) as a support. Despite lower loading of the IL, the loading of the Ru-catalyst immobilized in the SILLP material was higher. The SILLP catalyst showed enhanced stability in the RCM reaction, giving product with high yield >98.2% in 5 reaction cycles. We found that both the length of the alkyl chain at the IL as well as the anion attached influenced the immobilization and leaching of the Ru-catalyst so as the overall performance of the composite. A comparative study with Ru-complexes immobilized on pristine MWCNTs was conducted to examine the importance of the IL-phase for the construction efficient catalytic system.

In summary, ionic liquid-based strategies are presented as a generic approach to tailoring catalysts as in industrially-relevant reactions to generate both environmentally and economically sustainable processes.[2,3]

References

1. K. Grela, Olefin Metathesis: Theory and Practice, John Wiley & Sons, Inc. Hoboken, New Jersey, 2014, 608
2. K. Erfurt, I. Wandzik, K. Walczak, K. Matuszek, A. Chrobok, Green Chem. 16 (2014) 3508
3. A. Brzeczek-Szafran, K. Erfurt, A. Blacha-Grzechnik, M. Krzywiecki, S. Boncel, A. Chrobok, ACS Sustainable Chem. Eng. 7 (2019) 19880

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O-10

Oddziaływanie wybranych jonów metali szlachetnych z heteropolikwasem fosforowwolframowym i fosforomolibdenowym

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Heteropolizwiązki o strukturze anionu Keggina, ze względu na swoje unikatowe właściwości fizykochemiczne są od lat stosowane jako katalizatory zarówno w katalizie homo- jak i heterogenicznej [1]. W ostatnich latach, z dużym powodzeniem testowane są również w fotokatalizie, zwłaszcza jako kompleksy HPA-metal-nośnik tlenkowy, w których pierwszorzędową rolę odgrywają pojedyncze atomy metali, jako katalizatory jednoatomowe (SAC-Single Atom Catalyst) [2].

Przedmiotem przedstawianych badań teoretycznych (DFT) są układy zbudowane z heteropolikwasu $PW_{12}O_{40}^{3-}$/$PW_{12}O_{40}^{3-}$ z wbudowanym w strukturę kationem metalu szlachetnego (Ag^+, Au^+, Pd^{2+} i Pt^{2+}). W pierwszym etapie wyznaczono geometrię stanu podstawowego, widma UV-Vis i scharakteryzowno strukturę elektronową każdego z układów w oparciu o analizę orbitali granicznych (HOMO/LUMO) oraz całkowite (DOS) i parcjalne (PDOS) widma gęstości stanów elektronowych. Właściwości katalityczne lokowanych na anionie Keggina kationów przetestowano w reakcji z CO i C_6H_6. Wpływ nośnika na strukturę geometryczną i elektronową powstałych kompleksów zbadano poprzez ich umieszczenie na klasterze modelującym TiO_2.

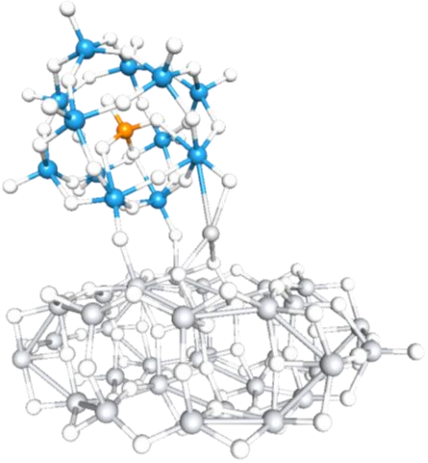

Fig. 1. Układ Ag^+-$PW_{12}O_{40}^{3-}$-TiO_2.

W wyniku obliczeń stwierdzono, że rodzaj wprowadzonego kationu i jego ładunek różnicuje energetykę i charakter orbitali granicznych, długości i rzędy wiązań w pierwszej strefie koordynacyjnej. Nośnik stwarza dodatkowe miejsca adsorpcyjne i zmienia właściwości redukcyjne układu. Kationy metalu preferują miejsca adsorpcyjne na granicy nośnik-HPA, ale wtedy redukcja układu zachodzi z udziałem atomów Ti.

References

1. L. R. Rubio, J. L. V. Vela, B. Artexte, J. M. Gutierrez-Zorilla, Polyoxometalates: Advances, Properties, and Applications, Jenny Stanford Publishing, (2022)
2. N. Zhang, et al., Silver single-atom catalyst for efficien electrochemical CO_2 reduction synthesized from thermal transformation and surface reconstruction, Angew. Chem Int. Ed., Vol 60, Is. 11, 6170-6176, (2021)

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O-11

Badania efektywności energetycznej dwufunkcyjnego układu adsorpcyjno-katalitycznego w usuwaniu lotnych związków organicznych

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Lotne związki organiczne (LZO) przyczyniają się w znacznym stopniu do wzrostu zanieczyszczenia powietrza. Jednym z przykładów ich szkodliwego działania jest udział w powstawaniu smogu fotochemicznego w obszarach zurbanizowanych. Związki te są również szkodliwe dla zdrowia ludzi, zwierząt i roślin. W ograniczeniu ich emisji do atmosfery najczęściej stosowane są oddzielnie metody niedestrukcyjne (np. adsorpcja) lub destrukcyjne (np. katalityczne utlenienie). Sprzężenie tych technik w układzie hybrydowym mogłoby jednak umożliwić bardziej efektywną pracę w cyklach adsorpcja→desorpcja→utlenienie. W ramach przeprowadzonych badań przeanalizowana została efektywność energetyczna takiego rozwiązania.

Jako układ modelowy do usuwania par toluenu zastosowano warstwy adsorbentu węglowego oraz katalizatora Pt/ZrO_2. Oba komponenty zsyntetyzowano metodą nanoreplikacji strukturalnej z wykorzystaniem sferycznego szablonu SiO_2, który pełnił również rolę separatora zabezpieczającego warstwę węglową przed utlenieniem. Faza aktywna Pt została naniesiona metodą redukcji w roztworze poliolu. Materiały zostały scharakteryzowane technikami: SEM-EDS, niskotemperaturowa adsorpcja N_2, XRD, XRF, XPS i TGA.

Największą efektywność (konwersja toluenu = 94,5%) i stabilność pracy w kolejnych cyklach odnotowano dla układu składającego się ze 150 mg katalizatora oraz 40 mg adsorbentu. Uzyskane wyniki z części eksperymentalnej uzupełniono obliczeniami teoretycznymi zapotrzebowania energetycznego, które wykazały znaczący zysk w przypadku użycia hybrydowego rozwiązania w porównaniu do klasycznego układu przepływowego pracującego w trybie ciągłego utleniania katalitycznego. Opracowano uproszczony model matematyczny, który wskazał czynniki istotne przy optymalizacji pracy podobnych dwufunkcyjnych układów warstwowych. Zaproponowane podejście wskazuje, że układy tego typu mogą być obiecującym kierunkiem poszukiwań efektywnych energetycznie układów do zastosowania w eliminacji LZO, w szczególności uwalnianych ze źródeł niskoemisyjnych.

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

O-12

Ru-pincer complexes as charge transfer mediators in CO_2 reduction

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In this work we unravel the role of the system components in the charge transfer (CT) processes occurring in the 2-electron reduction of CO_2. We focus our analysis on the pincer-complex/graphene composite system in order to explain the role of the donors of the pincer ligands on the elementary charge transfer processes. To achieve this goal, we have used the unique combination of the constrained DFT method [1] and computational hydrogen electrode [2] approach.

The results obtain this way allowed us to conclude that the catalytic performance of the system depends to a great extent on the electron donating properties of the Ru-pincer complex. We have determined, that the optimal charge transfer in the system is due to the easy, single step transfer to the activated CO_2 molecule and the energies required for such transfer are comparable to the overpotential of the reaction.

We have observed the trend in which the first coordination sphere of the Ru cation directly influences the CT energy – the more imine ligands coordinating the Ru, the lower E_{CT} is, regardless on the transfer direction. This trend fits in the HSAB theory, according to which imine ligands are considered the harder donors than carbenes. On the contrary, the overpotentials determined for the Ru-CCC, Ru-CNC, Ru-NCN and Ru-NNN pincers did not show the same trend, what implies that the interactions of the Ru site and the CO_2 reactant do not change linearly, but rather are characterized by the optimum interaction strength.

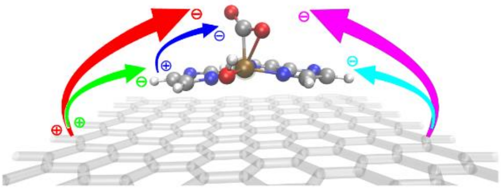

Fig. 1. Charge transfer directions investigated in this work.

References:

[1] N. Holmberg, K. Laasonen, J. Chem. Theory Comput. 2017, 13, 2, 587–601

[2] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jónsson, J. Phys. Chem. B 2004, 108, 46, 17886–17892

O-13

The application of molecular fragmentation methods for modelling of interactions between graphene and doped graphene with small molecules

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Graphene is an emerging catalytic material with possible applications in electro-, photo-, and thermal catalysis, hence the interactions of graphene and reagents are crucial to understand its catalytic activity. However, the exact quantification of these interactions is difficult due to electronic properties of graphene, and any new method is welcome, which could possibly shed more light on the complicated picture of such interactions.

In this contribution we study the applicability of the description of the interaction of graphene and doped graphene with small molecules with a new molecular fragmentation method, developed by two of us (E.M. and T.K.), for large polycyclic aromatic hydrocabons (PAHs), taking the inspiration from Systematic Molecular Fragmentation approach [1,2]. The new method, denoted by us as AROFRAG, consists in a systematic decomposition of a PAH into overlapping fragments, where the benzene molecule is the smallest unbreakable unit. Several levels of such fragmentations (denoted as models: 1st, 2nd, or 3rd) were proposed by us, with more fragments of a larger size available in the higher models.

Recently, we have shown that the AROFRAG approach provides reliable results for total and isomerization energies, if combined with the Molecules-in-Molecules (MIM) technique [3]. In this study we extend this approach to a description of interaction energies for complexes consisting of large PAH molecules, like graphene clusters, and small reactants, like water or hydrogen molecule. It turns out that the computatively-expensive part of the interaction energy, i.e. the electron correlated part, is reliably reproduced with the AROFRAG model, especially in conjunction with MIM. Therefore, the AROFRAG approach can be proposed as a cheaper alternative for more expensive methods for a description of the interaction between graphene and small reactants.

References

1. M. A. Collins, R. P. Bettens, Chemical Reviews, 115(2015), 5607–5642.
2. E. Masoumifeshani, T. Korona, Computational and Theoretical Chemistry, 1202 (2021), 113303.
3. E. Masoumifeshani, Ph.D. thesis (University of Warsaw, 2022).

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O-14

Phosphate doping as a promising approach to improve reactivity of Nb_2O_5 in catalytic activation of H_2O_2 and removal of methylene blue via adsorption and oxidative degradation

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For the last few decades, Nb_2O_5 has been attracting particular attention as a promising heterogeneous catalyst dedicated to the elimination of organic pollutants through advanced oxidation processes (AOPs) [1]. Nowadays, the interest in the application of this metal oxide for wastewater remediation is still increasing and focuses on improving of niobia reactivity by designing of novel heterostructure catalysts and/or modifying its surface properties by post-synthetic modification or metal doping [1].

This study is devoted to the evaluation of the influence of phosphate dopants on the reactivity of Nb_2O_5-based nanomaterials in the combined catalytic activation of H_2O_2 and the elimination of methylene blue (MB) from an aqueous solution via adsorption and chemical degradation. All catalysts used in this work were synthesized via facile hydrothermal method 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. Reactive oxygen species (ROS) formed *in situ* upon H_2O_2 activation were identified with Raman and EPR spectroscopies. The contribution of selected ROS to the degradation of organic compounds was estimated with the use of 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 phosphate doping strongly enhance the ability of Nb_2O_5 to activate H_2O_2, as well as to adsorb and degrade MB [2]. 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 modified catalysts (Nb/P molar ratio = 5/1) was approximately 6 times more efficient in the removal of MB than the parent Nb_2O_5. The observed enhancement of reactivity was attributed to the increased generation of singlet oxygen ($^1O_2$), which was identified as the main oxidizing agent responsible for efficient degradation of MB. More details on the origin of improved reactivity of phosphate-doped samples in activating of H_2O_2 and removing methylene blue dye will be provided during the presentation.

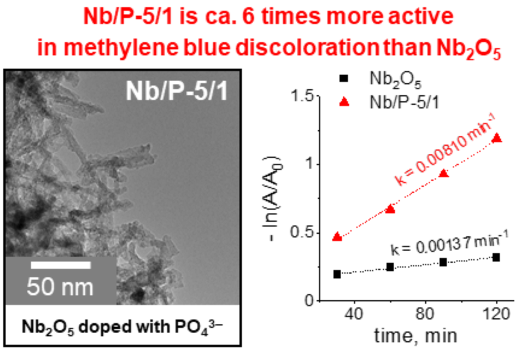

Fig. 1. HR-TEM image of the most active phosphate-doped sample and the pseudo-first order plot presenting differences in reactivity of parent Nb_2O_5 and phosphate-doped sample. “*k*” stands for the estimated reaction rate constant.

References

1. K. Su, et al., Adv. Sci., 8 (2021) 2003156
2. L. Wolski, et al., J. Hazard. Mater., 440 (2022) 129783

Acknowledgements: We thank the National Science Center, Poland (NCN), grants Sonatina2 (no. 2018/28/C/ST5/00255) and Sonata Bis7 (no. 2017/26/E/ST4/00794), for financial support of this work.

O-15

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

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Among the on-purpose technologies for propylene production the catalytic propane dehydrogenation with CO_2 (PODH-CO_2) is of particular interest to researchers. Zeolite catalysts with incorporating heteroelement ions in the framework allow to targeted control of their acid–base and redox characteristics that possible even at the synthesis step. For example, the effective catalysts for PODH were prepared by chromium [1] or vanadium [2] incorporation in siliceous SiBEA using the two-step postsynthesis procedure.

In this work, we have investigated the influence of the nature of heteroelements (Ga, Ta, Nb) incorporated into the framework of siliceous SiBEA zeolite on their acid-base characteristics and catalytic performance in the PODH-CO_2. The incorporation of the heteroelements into the framework of BEA zeolite was evidenced by the methods XRD, FTIR, ^{71}Ga MAS NMR and XPS. The prepared samples contain different amounts of acid sites – BAS and LAS, including those formed by the framework cations (Ga^{3+}, Nb^{5+}, Ta^{5+}) and extra-framework species. The content of gallium in SiBEA and present of Ta, Nb species have critical effect on acid-basic properties of the obtained catalysts. In the presence of the most active $Ga_{4.0}$SiBEA catalyst, a propylene yield of 37 % is achieved with an initial propane conversion of 57.5 % and the propene selectivity of 64 % at 873 K. For $Ga_{1.0}$SiBEA, $Ga_{2.0}Ta_{2.0}$SiBEA and $Ga_{2.0}Nb_{2.0}$SiBEA catalysts a higher propylene selectivity of 70 - 77 % was reached.

The key role of acidity, especially the presence of weak and medium strength Lewis acid sites related to the presence of well dispersed framework Ga(III) has been determined to achieve an enough high indices of the target process. These results also indicate that the incorporation of Ga(III) species into the zeolite framework with forming LAS is crucial to the catalytic performance of applied catalysts [3].

The results obtained in this work indicate that based on BEA zeolite it is possible to develop the Ga-based effective catalysts for the actual process of producing propylene by propane oxidative dehydrogenation with the involvement of CO_2.

References

1. P. Michorczyk, K. Zeńczak-Tomera, B. Michorczyk, A. Węgrzyniak, M.Basta, Y.Millot, L. Valentin, S. Dzwigaj, *J. CO_2 Util*. 36 (2020) 54 .
2. K. Chalupka, C. Thomas, Y. Millot, F. Averseng, S. Dzwigaj, J. Catal. 305 (2013) 46.
3. S.M. Orlyk,M.R. Kantserova, V.I. Chedryk,P.I. Kyriienko, D.Y.Balakin, Y. Millot, S. Dzwigaj, *J. Porous Mater*. 28 (2021) 1511.

O-16

Interaction of SCR related reactants with (Cu,Fe)-SSZ-13 and (Cu-Ni)SSZ-13 catalysts -DFT and FPT investigations

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Among many NH_3-SCR systems explored so far, Cu-SSZ-13 zeolites belongs to the group of the most active and most promising catalysts. The intricate nature of the SCR reaction, speciation and dynamics of the active sites, make copper chabazites attractive yet still challenging systems for both fundamental and applied studies. The exact nature and mechanism of this reaction is still debated, however, up to now the consensus is reached that it should be discussed in terms of reduction half-cycle (RHC) with the participation of NH_3 and NO, and oxidation half-cycle (OHC), where NO and O_2 are engaged. In our previous work considering Cu-SSZ-13 catalyst, three temperature regions of the SCR/AMO reactions, corresponding to NH_3-rich, lean, and dry conditions, were distinguished, and the main processes and intermediates of each stage were identified upon isotopic TPSR and steady state investigations, corroborated by IR/2D COS spectroscopic studies and DFT and atomistic thermodynamics modeling[1]. In the case of Cu loaded SSZ-13 zeolite its catalytic performance has been associated with the isolated (Cu^{2+} and Cu^{2+}–OH^{-} centers) and dual (closely spaced (juxtaposed) copper Cu^{2+}–OH cations or bridging [Cu^{2+}–O^{2-}–Cu^{2+}]) sites. Further optimization of the catalyst can be carried out by doping with other transition metal cations, and a review of the literature indicates that Fe and Ni are potentially promising in this context.

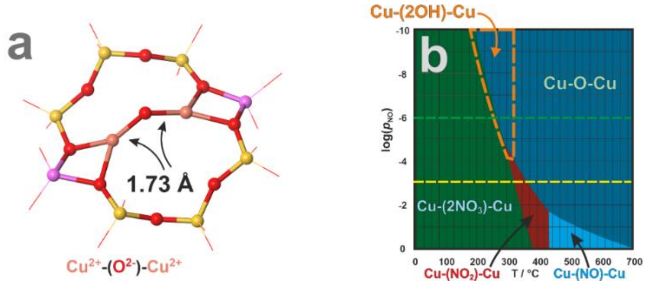

Fig. 1. Molecular picture of dual M-O-M center of M,Cu-SSZ-13 zeolite (**a**). First principles thermodynamic diagram of dual sites coverage with NO_x adspecies (**b**).

In this work we tested how the introduction of the alien cation (M = Fe, Ni) influence the ability of the monomeric (M, M-OH) and dual [M–O^{2-}–Cu] centers (**Figure 1a**) for $NO_{(x)}$ anchoring, and how it controls the efficiency of activating the N-H bond in ammonia. For these purpose we built the dimeric metal-oxo models of the active centers and tested various modes of the NH_3, NO and NO_x attachment. We also examined NH_3/NO_x co-adsorption with possible N-N formation and we used the resulting stabilization energies to build ab initio thermodynamic diagrams (**Figure 1b**), revealing the *T,p* windows of optimal performance of the dopped catalyst. Detailed analysis of the QChM results allowed for proposition of the probable sequence of steps for both NO oxidation form and ammonia N-H bond activation mechanisms over (Cu,M)-SSZ-13 zeolite.

References

1. M. Fedyna et al., Appl. Catal. B 325 (2023) 122309

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O-17

N-doped carbon materials – synthesis, characterization and evaluation as supports for heteropolyacid

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N-doped carbon materials were prepared via chemical vapour deposition (CVD) with acetonitrile (as carbon and nitrogen source) at 600 and 700 °C in the presence of metal oxides derived from layered double hydroxides (LDHs) of various compositions, i.e. Mg-Al, Mg-Cu-Al and Mg-Mn-Al. The obtained carbon materials consisted of irregular aggregates of plate-like particles. Our investigations reveal that Mn-containing species occurring in a mixture of metal oxides enhanced the quantity of carbonaceous product compared to those derived from Mg-Al LDHs. The impact of Cu-containing species was ambiguous. Both Mg-Cu-Al LDHs and Mg-Mn-Al LDHs led to higher amounts of amorphous carbon, which is an inevitable component of the carbon materials produced by CVD. Mg-Cu-Al LDHs resulted in higher contribution of graphitic carbon exposing edge plane surface, which suggests that the population of platy carbon materials could increase. On the other hand, the influence of Mg-Mn-Al LDHs was opposite. Depending on the chemical composition of LDHs and/or synthesis temperature, the resulting N-doped carbon materials had different concentrations of nitrogen, contributions of functional N-containing groups, specific surface areas and pore diameters. The carbon materials differed not only in the total pore volume and the contribution of micropores and mesopores but also in geometry of mesopores. In particular, the samples obtained at 600 °C contained slit-shaped mesopores, while those obtained at 700 °C contained bottleneck mesopores.

Among studied carbon materials, three carbon samples were selected to examine as supports for $H_3PW_{12}O_{40}$ (HPW) - heteropolyacid with Keggin-like structure. For comparison, HPW was also deposited on commercial carbon material, namely Vulcan XC-72. The catalysts were prepared by impregnation using the solution of HPW in ethanol. The nominal loading of HPW in studied catalysts was 40 wt. %. The analysis of FT-IR spectra of HPW spread on the carbon materials showed that the structure of Keggin anion after deposition remained intact. In addition, for the supported catalysts, a shift of W-O structural vibration bands was observed in comparison to unsupported HPW, which indicated the interaction of HPW with the surface groups of the support. The catalytic properties of HPW/carbon systems were evaluated in gas phase reaction, i.e. dehydration of *n*-butanol in the temperature range of 100-200 °C. The catalytic performance of HPW/carbon catalysts were compared to unsupported HPW. The conversion of *n*-butanol and the yield to the main product, *cis*-butene, for HPW/carbon samples were much higher than for pure HPW. For example, the conversion of *n*-butanol at 200 °C was 90 % and the yield to *cis*-butene was 78 % for HPW/C-MgMnAl-600, while insignificant values of conversion (13 %) and yield to *cis*-butene (11 %) were observed for unsupported HPW.

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O-18

Catalytic Systems Based on Metal-Oxide-Supported Copper Centers for Efficient Electroreduction of Carbon Dioxide in Acid Medium

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Of particular interest to the preparation of advanced catalytic materials is efficient utilization of nanosized materials with well-defined composition, structure and thickness that exhibit desirable electrocatalytic properties. There has been growing interest in the electrochemical conversion of carbon dioxide (a potent greenhouse gas and a contributor to global climate change) to useful carbon-based fuels or chemicals. Given the fact that the CO_2 molecule is very stable, its electroreduction processes are characterized by large over-potentials. It is often postulated that, during electroreduction, the rate limiting step is the protonation of the adsorbed CO product to form the CHO adsorbate. In this respect, the proton availability and its mobility at the electrochemical interface has to be addressed. On the other hand, competition between such parallel processes as hydrogen evolution and carbon dioxide reduction has also to be considered.

We explore here the ability of polynuclear inorganic metal oxo systems to stabilize and derivatize metal and carbon nanostructures. Here certain nanostructured metal oxides of zirconium, titanium, molybdenum or tungsten have been demonstrated to influence supported metal centers in ways other than simple dispersion over electrode area. Evidence is presented that the support can modify activity (presumably electronic nature) of catalytic metal nanoparticles (e.g. Cu, Ru), thus affecting their chemisorptive and catalytic properties. Metal oxide (WO_3, MoO_3, TiO_2) nanospecies can generate –OH groups at electrocatalytic interface.

A hybrid catalytic system composed of copper(I)-oxide-derived copper-nanocenters immobilized within the network tungsten oxide nanowires has exhibited electrocatalytic activity toward CO_2-reduction in acid medium (0.5 mol dm^{-3} H_2SO_4). The catalytic system facilitates conversion of CO_2 to methanol and is fairly selective with respect to the competing hydrogen evolution. The preparative procedure has involved voltammetric electroreduction of Cu_2O toward formation and immobilization of catalytic Cu sites within the hexagonal structures of WO_3 nanowires which are simultaneously partially-reduced to mixed-valence hydrogen tungsten(VI,V) oxide bronzes, H_xWO_3, coexisting with sub-stoichiometric tungsten(VI,IV) oxides, WO_{3-y}. After the initial loss of Cu through its dissolution to Cu^{2+} during positive potential scanning up to 1 V (vs. RHE), the remaining copper is not electroactive and seems to be trapped within in the network of hexagonal WO_3. Using the ultramicroelectrode-based probe, evidence has also been provided that partially-reduced non-stoichiometric tungsten oxides induce reduction of CO_2 to the CO-type reaction intermediates. The chronocoulometric data are consistent with the view that existence of copper sites dispersed in WO_3 improves electron transfers and charge propagation within the hybrid catalytic layer. The enhanced tolerance of the catalyst to the competitive hydrogen evolution during CO_2R should be explained in terms of the ability of H_xWO_3 to consume protons and absorb hydrogen as well as to shift the proton discharge at Cu toward more negative potentials. But the capacity of WO_3 to interact with catalytic copper and to adsorb CO-type reaction intermediates is expected to facilitate removal of the poisoning CO-type adsorbates from Cu sites.

O-19

Catalytic and photo-catalytic properties of heteropolyacid-TiO$_2$ materials

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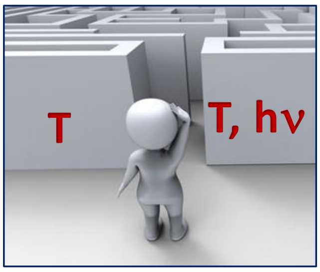
The gaseous n-butanol conversion was carried out comparatively in both the thermo-catalytic and the photo-themo-catalytic modes as innovative approach. As catalysts and also photocatalysts the solid heteropolyacid-TiO$_2$ materials were used. The application of this reaction has a twofold motivation. First this reaction is of practical relevance, being related to biomass processing, which is a potential source of n-butanol, readily acquired from sugars using Clostridium bacteria. Secondly, the alcohol dehydration over heteropolyacid-TiO$_2$ (HPA/TiO$_2$) catalysts uses their acidic protons and thus allows to establish their order of acidity. Moreover our recent research has showed that the catalytic activity of HPA/TiO$_2$ nanocomposites strongly depends on the used TiO$_2$ polymorph [1].

As an active phase $H_3PW_{12}O_{40}$ (HPW) heteropolyacid was applied. In turn the photocatalytic oxides: Fe_2O_3 and TiO$_2$ were tested as the additive and support, respectively. In the case of TiO$_2$ such as home-prepared (hp) and commercial, hydrophobic T805 and the hydrophilic P25 oxides, with different morphological forms like cubes, nanobars and tiles were applied. Two series of catalysts were synthesised: HPW/TiO$_2$ and HPW/Fe_2O_3/TiO$_2$. The authors constructed special photocatalytic chamber with UV light which was connected on-line with GC. Such way allows to monitor this gaseous reaction without or with light. The broad spectrum of techniques such as XRD, HRTEM, UV-vis, FTIR and Raman spectroscopies, XPS, BET analysis and GC were used to characterize the physicochemical (including optical) properties of these photocatalysts.

Four main factors to be of critical importance for achieving high catalytic activity of HPA/TiO$_2$ nanocomposites were identified: type of TiO$_2$ polymorphs, their surface area, hydrophobic properties, and acid strength [2]. The best performance was observed for HPW/Fe_2O_3/hp and HPW/T805 catalysts. The last one is active most likely as a result of hydrophobic nature of T805 support, that protects the proton sites from competing effect of H_2O molecules with respect to alcohol molecules. The iron addition into HPA/Fe_2O_3/TiO$_2$ nanostructures caused the increase of selectivity to di-n-butyl ether. The UV light use is mainly manifested by significant increase of cis-butene rate formation (Fig. 1).



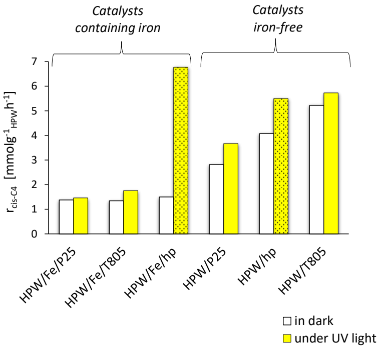


Fig. 1.Rate of cis-butene formation upon UV light and at 120 ^{o}C.

References
1. A. Micek-Ilnicka, N, Ogrodowicz., U. Filek, A. Kusior, Catal. Today 380 (2021) 84.
2. M. Synowiec, M. Radecka, A. Micek-Ilnicka, J. Catal. 417 (2023) 481.

O-20

Application of transition metals in the production of pharmaceutical intermediates using continuous flow hydrogenation

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Catalytic hydrogenation is considered one of the most important reactions in the chemical and pharmaceutical industries. It is commonly used to synthesize building blocks for vitamins, drugs, fragrances, and many other value-added products, the demand for which has been increasing over recent years [1]. One of the essential pharmaceutical intermediates obtained by the catalytic hydrogenation of unsaturated aldehyde: 2-methyl-2-pentanal is saturated aldehyde: 2-methylpentanal. This compound is used to fabricate medicine, e.g. meprobamate, which belongs to anxiolytic agents [2]. Another group of chemicals that has a crucial role in the manufacture of many agrochemicals, pharmaceuticals, dyes, and pigments is enols [3]. For example, 1,4-butene-diol produced by reducing 1,4-butyne-diol is essential for producing vitamins A and B6 [2].

This work investigated the catalytic performance of CNR115 active carbon supported Cu, Co and Fe in the continuous flow chemoselective hydrogenation of 2-methyl-2-pentenal (MPEA), and the semi-hydrogenation of 2-butyne-1,4-diol (BYD). We performed the reactions in a wide range of temperatures and pressure. The catalysts were characterized by Brunauer–Emmett–Teller (BET) surface area analysis, transmission electron microscopy (TEM), H_2 temperature-programmed reduction (H_2-TPR), temperature-programmed desorption of hydrogen (H_2-TPD) analysis, and X-ray photoelectron spectroscopy for selected samples.

Our work demonstrated that the effect of using transition metals in the continuous flow hydrogenation of MPEA leads to the formation of primarily saturated aldehyde (MPAA) (desired product). The effectiveness of the hydrogenation of BYD allows for obtaining two main products, 2-butene-1,4-diol (BED) and 1,4-butanediol (BAD), in different ratios. The results showed that the catalyst based on Co allows us to obtain desired products with the highest turnover frequency value compared to the other materials, demonstrating an attractive alternative for the pharmaceutical industry.

References:

1. L. Huanga, K. Hu, G. Ye, Z. Ye, Molecular Catalysis 506 (2021) 111535
2. M.G. Musolino, P. De Maio, A. Donato, R. Pietropaolo, Appl. Catal. A Gen., 285 (2005), pp. 50-58
3. Ramchandani, D.; López-Muñoz, F.; Alamo, C. Meprobamate–Tranquilizer or Anxiolytic, A Historical Perspective. Psychiatr. Q.2006, 77, 43–53.

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O-21

Comparison of Mechanisms of deNOx and deN$_2$O processes on Cu-Cu dimers in clinoptilolite zeolite - DFT study

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Anthropogenically produced nitrogen oxides (NOx), produced by fuel combustion or as a component of waste gases from the chemical industry, are a source of pollution that is dangerous to both humans and the environment [1]. A very important gas is N_2O [2]. This oxide is a by-product of nitric acid production and also of the NH_3-SCR process. As one of the greenhouse gases, it has a global warming potential (GWP) approximately 310 times that of carbon dioxide [3].

One of the most effective technologies for reducing oxides of nitrogen is Selective Catalytic Reduction (SCR) [4]. The reaction involves ammonia, which is the reducing agent. Currently, the most common catalyst used in industry is V_2O_5-WO_3-TiO_2.

However, due to their limitations, new types of catalysts are being searched for. Currently, Cu-promoted zeolite catalysts are commonly analysed. In order to reduce costs, save space and time, an important problem is to find a catalyst that allows the deNOx and deN$_2$O processes to be carried out simultaneously.

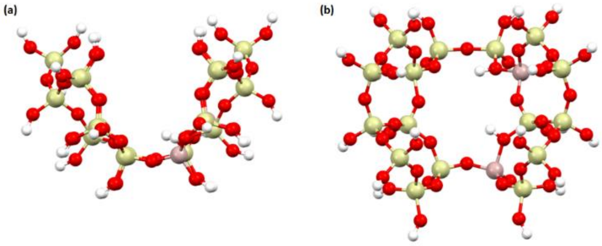

Fig. 1. Cluster model of clinoptilolite zeolite structure Al2Si16O50H30: a) view along (100) and b) view along (001).

In this study, two types of processes are presented - deNOx and deN$_2$O including two deN2O process pathways (starting with NO or N_2O). The energy barriers for each stage are presented. The molecular orbitals of the most important process steps were compared.

Calculations were performed using density functional theory (DFT) based on an ab initio method. The study compared the possibility of using clinoptilolite zeolite with copper in both deNOx and deN$_2$O processes, and the analysis of molecular orbitals provided a better understanding of the changes and energy barriers. The studies presented can be used for further analysis and comparison with experimental results.

References

1. J. Zhang, J. Liang, H. Peng, Y. Mi, P. Luo, H. Xu, M. He, P. Wu, Appl. Catal. B 292 (2021) 120163.
2. M. Inger, B. Moszowski, M. Ruszak, J. Rajewski, M. Wilk, Catalysts 10,9 (2020) 987.
3. I. Kurzydym, I. Czekaj, Molecules 27(1) (2022) 300.
4. P.J. Jodłowski, I. Czekaj, P. Stachurska, Ł. Kuterasiński, L. Chmielarz, R.J. Jędrzejczyk, P. Jeleń, M. Sitarz, S. Górecka, M. Mazur, I. Kurzydym, Catalysts 11 (2021) 824.

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O-22

Experimental studies and thermodynamic calculations on the potential application of faujasite as an ingredient of ANFO-based explosives

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Zeolites are known as crystalline and microporous aluminosilicates. Due to the presence of acid-active sites, this group of materials can be used in many catalytic industrial processes including cracking, esterification, alkylation, isomerization, the production of fine chemicals, and for environmental protection [1]. Other applications of zeolites refer to water purification and softening, the separation of gases, building materials, agriculture, etc. [1].

With reference to the current state of the art on the utilization of zeolites in industry, the use of zeolites as components in the manufacture of explosives indicates the innovative character of the presented research. The topic focused on the production and application of explosives originates from their versatile peaceful applications. One of the most commonly used explosives is ANFO (Ammonium Nitrate Fuel Oil) due to its easy and cheap procedure of production as well as its good blasting properties.

The blasting properties of prepared explosives can undergo modification by the change of their chemical composition, which allows us to optimize the selected detonation parameters, e.g. the velocity of detonation (VOD), explosion heat, and strength or toxicity of pot-blast fumes.

In the undertaken research, we studied variously modified FAU as ANFO components. The choice of zeolite of FAU-type structure implies its wide application in the chemical industry due to its unique chemical and porous structures. The FAU-type zeolite was added to the ANFO via a simple mixing procedure. Weight loading of the zeolite in the resulting ANFO-based material reached 5% wt. We studied zeolite both in protonic form (H-FAU) and the zeolite modified with copper via a wet impregnation procedure (Cu-FAU).

Experimental analysis performed by means of X-ray diffraction, FTIR spectroscopy and Atomic Force Microscopy confirmed the presence of zeolite in the prepared ANFO samples. The introduction of H-FAU and Cu-FAU to ammonium nitrate resulted in the appearance of new signals assigned to the zeolite phase as well as resulted in the apparent changes in the surface of the obtained ANFO samples. The utilization of zeolite also reduced thermal effect accompanying the ammonium nitrate decomposition.

Analysis of the results obtained from thermodynamic calculations of blasting properties led to the conclusion that the application of variously modified FAU as an additive of ANFO caused enhanced blasting properties of ANFO-based explosives, which corresponded with their changes in the status of the surface and thermal properties.

References

1. C.S. Cundy, P.A. Cox, Microporous Mesoporous Mater. 82 (2005) 1.

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Flash oral presentations

FO-1

MIL-100 doped with divalent metal ions: the influence of the type of doped metal on the activity in the propylene carbonate synthesis

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Each year carbon dioxide emissions reach 34 Gt of which a huge amount is emitted into the atmosphere [1]. The accumulation of CO_2 is considered as a major factor of the global warming. For this reason, the efforts are constantly being made to reduce the production of CO_2, as well as its efficient utilization. One of the possibilities for the reduction of CO_2 concentration in the atmosphere is its catalytic conversion to such chemicals as methanol or cyclic carbonates (e.g., propylene carbonate - PC) [2].

MIL-100 is a Metal-Organic Framework (MOF) made of the secondary building units containing Fe^{3+} ions and trimesic acid. It is known for possessing very good physicochemical properties that are important from the point of view of its application in catalysis. Those are: high specific surface area, wide pores, and good thermal and chemical resistance [3]. However, in many cases the employment of pristine MIL-100 may be limited due to the catalytic reaction mechanism involving the different active sites.

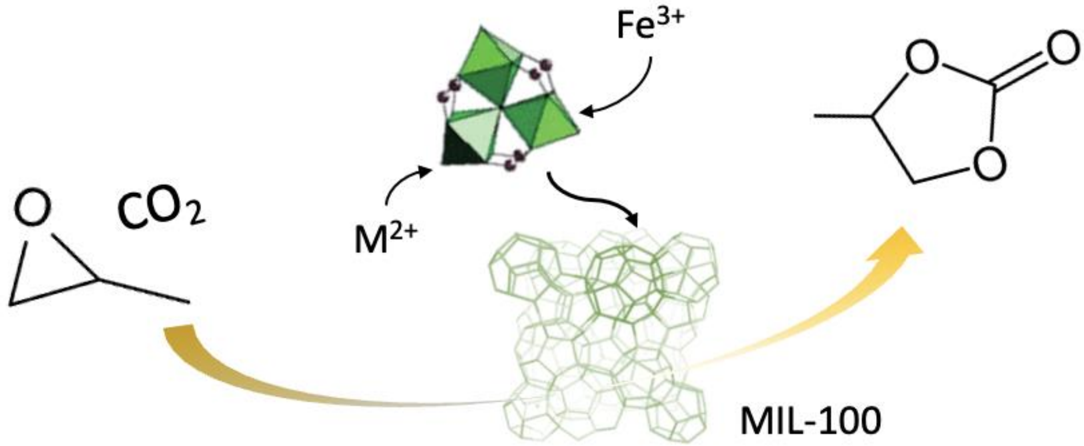

Fig. 1. MIL-100 doped with divalent metal ions.

In this work, we present the outcomes of the syntheses of MIL-100 doped with divalent metal ions that show catalytic activity in CO_2 cycloaddition to epoxides (Fig. 1). The obtained materials were subjected to physicochemical characterization (XRD, N_2 sorption, SEM(EDS), TEM, IR, ICP, and TGA) and tested in the reaction of CO_2 conversion to PC. The effect of acidic site's introduction on the catalytic performance of MIL-100 in PC synthesis was investigated.

References

1. M. Décultot, A. Ledoux, M.-C. Fournier-Salaün, L. Estel, Green Process. Synth. 8 (2019) 496–506
2. E. Alper, O.Y. Orhan, Petroleum 3 (2017) 109-126
3. G. Zhong, D. Liu, J. Zhang, Cryst. Growth Des. 18 (2018) 7730–7744

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FO-2

Efficient Oxygen Reduction in Acid Medium at Low-Pt-Content-Catalysts Admixed with Cobalt(III,II)-Oxide/Cerium(IV,III)-Oxide Nanocomposites

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The proton-exchange membrane fuel cell (PEMFC) technology is one of the most promising approaches for energy conversion in automotive applications. Despite the use of expensive noble metal electrocatalysts, the sluggish kinetics of the oxygen reduction reaction (ORR) in acid media, and formation of the undesirable hydrogen peroxide intermediate are still the main drawbacks, on top of the stability problems, when it comes to the widespread commercialization of PEMFC devices. The progress in this subject is greatly hindered by the high cost and scarcity of the state-of-the-art platinum-based materials which are regarded as the most effective cathode catalysts. Therefore, most of the current research studies have been devoted to the optimization of active centers and maximization of their utilization, which should allow the lowering of the cathode Pt loadings without loss of performance and durability.

Among important strategies is hybridization, activation, and stabilization of carbon-supported Pt catalysts by functionalization through admixing with certain nanostructured and typically substoichiometric metal oxides. Special attention is paid to application of the bi- or multi-metallic Pt-based alloys in their various forms and structures. Additionally, doping of carbon carriers with heteroatoms would produce surface functional groups and active centers capable of not only improving the catalysts' performance, but also affecting their stability. Among other important issues are such features as porosity, hydrophilicity, and degree of graphitization of carbon components, in addition to the existence of metal–support interactions, high electrochemical active surface area, electronic structure of interfacial Pt, and the feasibility of adsorptive or activating interactions with oxygen molecules.

Recent studies have demonstrated that the rational design of a catalytic system is based on nanostructures of platinum, or carbon-supported platinum (Pt/C), and metal oxide (MO_x). By combining the catalytic properties of both components, such hybrid Pt-MOx catalysts are capable of tuning of the activity and durability of Pt. Due to strong interactions of MO_x with Pt catalytic nanoparticles leading to the improved activity and durability during ORR, certain nanostructured metal oxides are considered as co-catalysts or active components of supports. 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 adsorption of oxygen and the cleavage of O=O bonds. The interactions mentioned above would also facilitate dispersion of Pt, inhibit their detachment and further aggregation, and, consequently, prevent or decrease their degradation during the fuel cell operation. In the present study, we 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.

FO-3

Effect of CaO, Al_2O_3, and MgO supports of Ni catalysts on the formation of graphite-like carbon species during the Boudouard reaction and methane cracking

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It is widely recognized that greenhouse gas emissions, such as CO_2 and CH_4, are alarmingly high and cause serves damage to the environment despite international efforts to mitigate emissions of these gases [1]. In this regard, lots of scientific efforts have been put into the investigation of the possibility of conversion of them into valuable materials, such as carbon nanotubes, graphene, fullerenes, diamonds, etc., due to their cheapness, abundance, and relative safety [1-5]. One specific process that utilizes these gases is the dry methane reforming (DRM), during which side reactions (i.e., the Boudouard reaction and methane cracking) occur to form different types of carbon deposits [6-8]. The investigation of the course of the Boudouard reaction and methane cracking was performed over Ni catalysts supported on CaO, Al_2O_3, and MgO. The catalytic samples were synthesized by the co-precipitation method. The physicochemical characteristics of the catalysts were determined using AAS, BET, NH_3- and CO_2-TPD, and TPR. Qualitative and quantitative identification of formed carbon deposits after the processes were carried out using TOC, TPO and XRD. The experimental results showed that the selected temperatures for the Boudouard reaction and methane cracking (450 and 700 °C, respectively) were found to be optimal for the successful graphite-like carbon species formation over these catalysts. It was revealed that the activity of catalytic systems during each reaction is directly related to the number of weakly interacted nickel particles with catalyst support. the highest amount of graphite-like carbon was observed on the surface of Ni/CaO and Ni/Al_2O_3 (15-20%). These catalytic systems characterized by highest concentration of strong acid-base sites and relatively good reducibility. The lowest carbon content was determined in the case of Ni/MgO (5-10%). This catalyst did not undergo complete reduction due to the formation of NiO-MgO solid solution. The mechanisms of carbon deposits formation and the catalyst support role in this process, as well as the Boudouard reaction mechanisms were suggested.

References

1. A. Erdohelyi, Catalysts. 11 (2021)
2. J. H. Park, et al., J. Chem. Eng. 241 (2022)
3. X. Xu, et al., Mater. Lett. 61 (2007) 4235-4237
4. G. M. Kim, et al., Nanoscale. 12 (2020) 7822-7833
5. G. Allaedini, et al., J. Alloys Compd. 647 (2015) 809-814
6. M. Kogler, et al., J. Phys. Chem. 120 (2016) 1795-1807
7. S. Arora, R. Prasad, RSC Adv. 6 (2016)
8. T. P. Maniecki, et al., Catal. Lett. 128 (2009) 401-404

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FO-4

Platinum nanoparticles with various surface charge deposited on silica for hydrogenation of acetophenone

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Two types of platinum nanoparticles (Pt NPs) were obtained by a chemical reduction of H_2PtCl_6 precursor by $NaBH_4$ reducing agent. Tri-sodium citrate and cysteamine hydrochloride were applied to obtain negatively Pt(-) and positively Pt(+) charged Pt NPs, respectively. The spherical silica particles (SiO_2-Ps) were prepared by Stöber process. The negatively charged SiO_2-Ps were also modified to SiO2-Ps(+) by using 3-(aminopropyl)triethoxysilane. The second series of catalysts were prepared on commercial silica Sigma Aldrich Davisil 646 (SiO_2-Dav). The catalysts were formed in electrostatically driven deposition process of Pt NPs on SiO_2. The catalyst (Table 1) formation was conducted in aqueous suspension of controlled particles mass concentration, pH and ionic strength. The catalysts were characterised by SEM, EDS, XPS, BET and XRD.

Catalyst	Details	Support surf. area (m^2/g)	Pt diameter XRD (nm)
MO-2	2%Pt(-) / SiO_2-Ps(+)	12	5
MO-3	2%Pt(+) / SiO_2-Ps(-)	15	6
MO-4	2%Pt(-) / SiO_2-Dav(-)	300	5
MO-5	2%Pt(+) / SiO_2-Dav(-)	300	6
MO-6	2%Pt in H_2PtCl_6 on SiO_2-Ps(-) reduced in-situ	15	n.d.

The tests of liquid-phase acetophenone hydrogenation were performed in Parr glass batch reactor equipped with mechanical stirring. The composition of liquid samples withdrawn from the reactor were analysed using gas chromatography with FID detector. The preliminary tests of acetophenone (ACP) hydrogenation were performed in isopropanol solvent at 30 °C and 8 bar of H_2 using MO-5 and MO-2 catalysts. After 6 h of reaction ACP conversion of 15 and 24% with the 1-phenylethanol (PE) selectivity of ca. 35 and 65% were reached for MO-5 2%Pt(+) / SiO_2-Dav(-) and MO-2 2%Pt(-) / SiO_2-Ps (+), respectively. Much better results were obtained in biphasic system of isooctane/water (1/1 v/v) even under milder pressure (1 bar H_2, Fig. 1). So far, the highest PE selectivity of 91% was reached over MO-5 2%Pt(+) / SiO_2-Dav(-) catalyst.

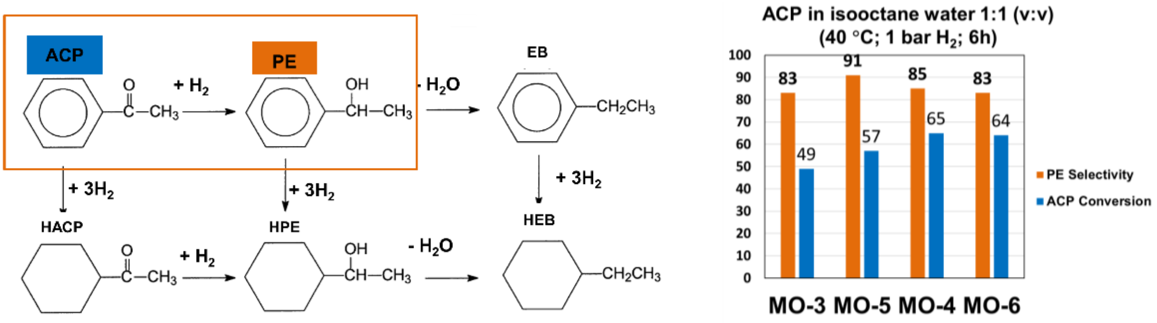

Fig. 1. The acetophenone hydrogenation in isooctane/water biphasic mixture (40 °C, 1 bar H_2, 6 h)

Acknowledgements: This research was founded by the statutory research found of ICSC PAS (Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences).

FO-5

Research of the effect of doping a copper catalyst with palladium on its catalytic properties in a chemoselective hydrogenation reaction

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An essential aspect of catalytic hydrogenation is that we can selectively hydrogenate unsaturated aldehydes, resulting in saturated aldehydes or unsaturated alcohols. They are precursors in synthesizing fragrances, flavors, or pharmaceuticals [1]. During this study, we investigated the chemoselective hydrogenation of 2-methyl-2-pentenal (MPEA). The desired hydrogenation products were 2-methylpentanal (MPAA) and 2-methylpenten-1-ol (MPEO). MPAA is a flavoring agent and an intermediate in producing dyes and resins. It is also an important pharmaceutical intermediate. The main drug for the synthesis of which MPEA is used is meprobamate, which belongs to the anti-anxiety, hypnotic drugs that cause sedation of the central nervous system [2]. On the other hand, MPEO is also a desirable hydrogenation product due to its demand in the perfume and cosmetic industries.

This study aimed to investigate the effect of doping a copper catalyst with palladium on its catalytic properties in the selective hydrogenation reaction of unsaturated aldehyde. Work included physicochemical characterization of the synthesized systems by temperature-programmed reduction (TPR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Catalytic measurements were carried out in a flow apparatus over various pressures (10-60 bar) and temperatures (25-100°C). The reaction products were analyzed using a gas chromatograph with an FID detector. The optimal pressure and temperature conditions were determined to achieve the highest selectivity to the desired product while maintaining high substrate conversion. Application of 6 wt. %Cu/C led to the formation of the product mixture (MPAA and MPEO). Adding small amounts of Pd (max. 0.06 wt.%) improved the chemoselectivity of the reaction to the formation of 100% of 2-methylpentanal at mild reaction conditions (25°C and 10 bar).

References:

1. X. Lan, T. Wang, Highly Selective Catalysts for the Hydrogenation of Unsaturated Aldehydes, ACS Catal. 10 (2020) 2764.
2. D. Ramchandani, F.López-Muñoz, C. Alamo, Psychiatric Quarterly 77 (2006) 143.

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FO-6

Spektroskopowa i chromatograficzna charakterystyka natury depozytu koksowego w zeolitach o zróżnicowanej hierarchii porów

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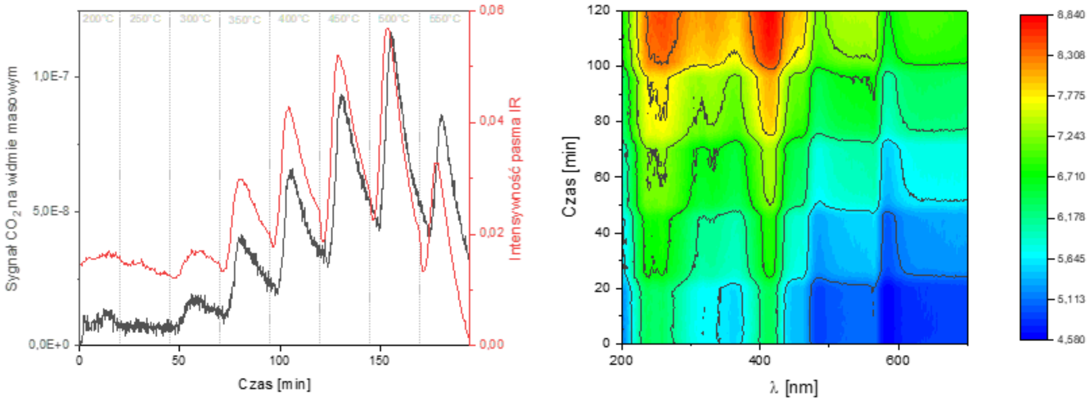
Podczas większości reakcji z udziałem węglowodorów, w których zeolity są stosowane jako katalizatory, obserwuje się spadek ich wydajności z upływem czasu. Jedną z przyczyn tego zjawiska jest dezaktywacja na skutek powstawania na powierzchni depozytu węglowego (koksu), który blokuje dostęp do centrów aktywnych dla reagentów. Katalizator, który nie pełni już swojej funkcji tak jak powinien, musi zostać wymieniony na nowy. Wiąże się to często z koniecznością zatrzymania biegnącego procesu, co generuje poważne straty finansowe. Synteza nowego katalizatora wymaga zużycia energii i odczynników, a to niekorzystnie wpływa na środowisko oraz wiąże się z kolejnymi kosztami. Powyższe powody sprawiają, że zainteresowanie tematem powstawania koksu oraz regeneracji katalizatorów wciąż rośnie. Szczególnie istotne jest opracowywanie metod regeneracji katalizatorów, co jest możliwe tylko po uprzednim poznaniu natury chemicznej depozytu węglowego.

Badaniom, oprócz komercyjnego zeolitu ZSM-5, poddano również próbki po wcześniejszej desilikacji oraz sekwencyjnej desilikacji i dealuminacji, co pozwoliło na powiązanie wpływu parametrów takich jak stężenie centrów kwasowych, powierzchnia właściwa, objętość mikro- i mezoporów z procesem koksowania i regeneracji. Koks powstały w czasie reakcji konwersji etylenu do wyższych węglowodorów wyekstrahowano za pomocą dichlorometanu i poddano analizie chromatograficznej (GC-MS) w celu identyfikacji poszczególnych związków. Proces regeneracji polegający na utlenianiu depozytu koksowego ze zużytego katalizatora (25-550 °C, 4% O_2/N_2) śledzono za pomocą spektroskopii IR i UV-vis w trybie *operando*. Pasmo pochodzące od CO_2 osiągające największą intensywność w temperaturze 500°C świadczy o przewadze związków poliaromatycznych wśród depozytu węglowego. Złożone pasmo na widmach IR znajdujące się w okolicy 1550 cm^{-1} pochodzi od związków koksu, podobnie jak pasma przy 220 nm na widmach UV-Vis.



Rys. 1. Intensywność sygnału MS oraz pasma pochodzącego od drgań CO_2 i widma UV-Vis zebrane podczas spalania koksu.

Podziękowania: Niniejsze badania zostały zrealizowane w ramach projektu Narodowego Centrum Nauki nr *2020/37/B/ST4/01215.*

FO-7

Generation of Active Iron Centers within Iron-Phosphide-Based-Catalysts for Efficient Electroreduction of Nitrogen to Ammonia

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Industrial-scale NH_3 production mainly relies on the energy-intense 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 (NRR) under ambient condition with water as hydrogen source has been proposed as a sustainable alternative solution for ammonia production, especially 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 and large current density, thus enabling the mass production of ammonia. The feasibility of performing 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≡N bond.

In the present study, we are going to concentrate on nanostructured and molecular type iron-based electrocatalytic systems for inducing NRR.Transition metal phosphides are promising non-noble earth-abundant catalysts with broad electrocatalytic properties, in particular when it comes to electroreduction of such inert reactants as carbon dioxide. Herein, we report the successful electrocatalytic reduction of nitrogen (N_2) using different phases of iron phosphide activated at 450 °C. For example, the FeP and Fe_2P phases have been found to act as efficient catalysts for the formation of NH_3 in alkaline and semineutral media. Detection of in-situ formed product has been achieved by probing the electrooxidation of NH_3 to nitrogen (N_2) using the additional working electrode modified with Pt nanoparticles. On mechanistic grounds, the iron (Fe^0) sites seem to be electrocatalytic active during the reduction of nitrogen.

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FO-8

Methane oxidation to methanol: UV-Vis-IR spectroscopy studies on the nature of iron centres in zeolites

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Nowadays, the production of methanol is mainly based on the process of reforming methane and afterwards on the Fisher-Tropsch reaction of the resulting synthesis gas. The high energy cost of such a procedure became the motivation for starting the search a catalyst that would not only reduce energy consumption but allow CH_3OH to be obtained directly from methane. The main problem of such a process is the high stability of CH_4 molecule resulting from a high C-H bond dissociation energy. Promising catalysts that can successfully overcome this barrier are iron-loaded or isomorphousy iron-substituted zeolites which offer Fe sites able to generate reactive oxygen species (α-oxygen). Not all iron centers introduced are however precursors of α-oxygen. The problem catalysis facing is to determine the nature and thus the activity of these sites, which would enable not only producing more efficient catalysts but also a better understanding of α-oxygen-mediated selective oxidation mechanism.

In our study we performed spectroscopic characterization of ion exchanged iron sites in mordenites. The main intention was to preferentially locate isolated Fe cations (0.1 and 1.0 %w.t.) in the 8-membered channels and, by manipulating the Si/Al ratio (8.4 and 14.6), to ensure high stabilization of the cation. *In situ* and *operando* IR and UV-Vis methodologies made it possible to study iron speciation, both in terms of their nuclearity and oxidation state. In the case of the $Fe_{0.1}$MOR/8.4, isolated Fe^{2+} cations located in 8-ring channels were the dominant species. As the metal content and/or Si/Al ratio increased, the predominant iron forms were either isolated Fe^{3+}-OH or bridged Fe^{3+}-O-Fe^{3+} species located in 12-ring channels.

The catalytic activity of the fine-tuned Fe centers was investigated in methane oxidation. The zeolites accommodating lower iron amount showed the highest selectivity toward methanol production as evidenced by an increase in the intensity of the bands at 235-240 nm for both the $Fe_{0.1}$MOR/8.4 and $Fe_{0.1}$MOR/14.6 in *operando* UV-Vis studies. In the case of the catalyst with lower Al content, an additional evolution of the band at 480 nm indicated the involvement of isolated Fe^{2+} cations in the production of CH_3OH. The Fe-oxo sites formed at higher amount of Fe (1.0%w.t.) were involved in the non-selective oxidation of CH_4 to CO_x. A similar situation was observed at higher temperatures for $Fe_{0.1}$MOR/8.4 and $Fe_{0.1}$MOR/14.6; an increased production of CO_x and H_2O at the expense of methanol was confirmed in operando IR-MS-GC investigations.

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FO-9

Mono- and bimetallic copper-noble metal zeolite catalysts for biodiesel production

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Nowadays, the demand for energy is met mainly by fossil fuels. However, fossil fuel resources are limited and are gradually being depleted. In addition, the use of such energy sources is not beneficial to the environment. All these facts confirm the need to replace fossil fuels with alternative fuels [1]. Biodiesel can partially or completely replace conventional diesel fuel [2]. Biodiesel has a number of beneficial physicochemical properties including high flash point, high lubricity, high biodegradability [3], better viscosity with a similar caloric power to traditional fossil fuels [4]. The main aim of this work was to determine the influence of noble metal (Pt, Ru) addition on physicochemical and catalytic properties of copper catalysts supported on BEA and ZSM-5 zeolites in the transesterification reaction of vegetable oil with methanol.

In order to achieve the intended purpose of the work monometallic copper and bimetallic copper-noble metal (Ru, Pt) systems supported on BEA and ZSM-5 zeolite were synthesized by wet impregnation method. The catalytic and physicochemical properties of the synthesized catalysts were studied using following techniques H_2-TPR, NH_3-TPD, XRD, BET and SEM-EDS. Commercial rapeseed oil and methanol were used as reactants. The catalytic tests were carried out in an autoclave (50 ml reactor capacity) equipped with a mechanical stirrer. Each catalytic activity test was carried out for 2 hours at 220°C. Prior to the reaction, the catalysts were calcined at 500°C for 4 hours and reduced at 300°C (or 400°C) for 2 hours in a mixture of 5%H_2-95%Ar at the flow rate of 50 cm^3/min. In all catalytic tests, the catalyst weight was 0.5 g. The reaction products were analyzed by HPLC (Shimadzu). During the analysis of the reaction products, a C-18 column was used and a mixture of 2-isopropanol-hexane (4/5) and methanol as the eluent. The DAD detector (wavelength: λ=205 nm) was used to determine the conversion of triglycerides (TG) and the yield of fatty acid methyl esters. The catalytic activity tests carried out for the synthesized catalysts showed that increasing the amount of copper from 5 wt. % to 10 wt. % in the reduced monometallic system improved the FAME yield from 42% (for the 5%Cu/BEA system) to about 52% (for the 10%Cu/BEA system), while for the calcined systems the FAME yield increased from 51% to 61%, respectively. Whereas, the introduction of ruthenium or platinum (1 wt. %) into monometallic copper catalyst improved triglyceride conversion from 74% for the 5%Cu/BEA monometallic system to 82% for the 5%Cu-1%Pt/BEA bimetallic system and 85% for the 5%Cu-1%Ru/BEA system. The yield of biodiesel production in the transesterification reaction realized on the calcined bimetallic systems was increased by about 8% compared to the calcined monometallic system. While, in the case of the reduced bimetallic systems the FAME yield increased by about 3% compared to the reduced monometallic copper catalyst.

References

1. A. Tangy; V.B. Kumar; I.N. Pulidindi; Y. Kinel-Tahan; Y. Yehoshua; A. Gedanken, Energy & Fuels 30 (2016), 10602-10610
2. M.S. Alvarez Serafini; G.M. Tonetto, Catalysts 9, (2019) doi:10.3390/catal9120978.
3. C.-L. Chen; C.-C. Huang; K.-C. Ho; P.-X. Hsiao; M.-S. Wu; J.-S. Chang, Bioresource Technology 194 (2015),179-186
4. K. Vasić; G. Hojnik Podrepšek.; Ž. Knez,; M. Leitgeb, Catalysts 10 (2020), doi:10.3390/catal10020237.

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FO-10

Fe-modified MWW zeolites as catalysts for selective catalytic reduction of nitrogen oxides with ammonia

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The recent research on Fe-MWW layered zeolites confirmed that the materials are promising precursors of the novel catalysts for selective catalytic reduction of nitrogen oxides with ammonia (NH_3-SCR). Additionally, it was found that their catalytic performance strongly depends on the speciation and distribution of iron within the zeolitic framework [1-4]. Therefore, it is required to find the most appropriate method to provide good dispersion of iron species, which enables to actively eliminate NO_x in relatively wide temperature window.

Therefore, the aim of the work was to prepare three representatives of zeolites belonging to MWW family (MCM-22, MCM-36, and ITQ-2) and modify them with iron according to various routes, such as introduction of Fe^{3+} into the synthesis pot (one-pot synthesis), intercalation with Fe_2O_3 pillars (in the case of MCM-36), or adsorption from the solution. All of the materials were characterized with respect to their structural, textural, acidic, and catalytic properties and the selected samples were subjected to NH_3-SCR catalytic tests before and after poisoning with sulphur dioxide.

We have observed that one-pot synthesis resulted in the highest dispersion of isolated Fe^{3+} monomeric species, which contributed to satisfactory NO reduction below 250 °C and negligible N_2O generation in the entire investigated temperature range. The most active sample, Fe-MCM-36 exhibited 50% of NO reduction only at 150 °C, however, low-temperature activity of the material drastically decreased while Fe_2O_3 was introduced in the form of pillars. In contrast, adsorption from the solution provided generation of the active sites for the low-temperature NO reduction, nonetheless, formation of oligomeric and clustered iron species promoted generation of nitrous oxide and non-desired oxidation of ammonia, especially above 350 °C. Furthermore, elimination of NO was strongly limited while the content of iron increased, due to the presence of pore-clogging and catalytically inactive aggregates of iron oxide. Last, but not least, poisoning with SO_2 affected low-temperature activity of the catalysts because of the deposition of thermally unstable ammonium sulphates.

References

1. M. Rutkowska et al. Appl. Catal. B: Envirion. 168-169, 531-539.
2. A. Szymaszek-Wawryca et al., Molecules 27 (2022) 2983.
3. J. Chen et al., Catal. Sci. Technol. 10 (19) (2020) 6583-6598.
4. J. Kornatowski et al., Microporous Mesoporous Mater. 90 (2006) 251-258.

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Plakaty
Posters

P-1

Optymalizacja właściwości katalitycznych szkieł potasowych poprzez domieszkowanie metalami przejściowymi

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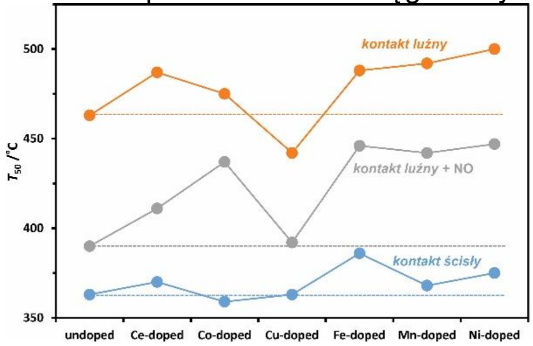
Zastosowanie filtrów cząstek stałych pozwoliło na znaczne ograniczenie emisji tych niekorzystnie wpływających na zdrowie zanieczyszczeń, głównie sadzy. Filtry takie wymagają jednak fazy aktywnej katalitycznie, która pozwoli na ich ciągłą regenerację w temperaturze gazów odlotowych, która jest niższa niż temperatura samoczynnego zapłonu węgla. Najbardziej obiecującą alternatywą do aktualnie stosowanych układów opartych na metalach szlachetnych, wydaje się być zastosowanie metali alkalicznych, ale muszą one być stabilizowane w matrycach tlenkowych. Interesujące wyniki uzyskano dla szkieł alkalicznych, brakuje natomiast badań dla tego typu układów domieszkowanych metalami redoksowymi. Celem niniejszej pracy było zbadanie wpływu domieszkowania metalami przejściowymi na właściwości katalityczne układów zawierających modyfikowane szkła potasowe aktywne w procesie dopalania sadzy.

Szkła potasowe ($25K_2O$-$59SiO_2$-$16CaO$ mol%) zsyntetyzowano z SiO_2, K_2CO_3 i $CaCO_3$ poprzez stopienie mieszaniny w temp. 1345°C podczas 1h. Szkła domieszkowane (5 % mol.) przygotowano przez przetapianie szkła z odpowiednim tlenkiem metalu w temp. 1340°C przez 0,5h. Amorficzny charakter otrzymanych próbek potwierdzono metodami XRD i RS, ich skład chemiczny metodą XRF, powierzchnię zbadano metodami XPS, DRIFT oraz UV/Vis-DR. Określono ponadto aktywność zsyntetyzowanych katalizatorów zarówno w ścisłym, jak i luźnym kontakcie z sadzą modelową w atmosferze zawierającej NO i bez niego.

Uzyskane wyniki potwierdziły wysoką aktywność domieszkowanych szkieł potasowych, szczególnie widoczną w kontakcie luźnym – różnica T_{50} dla próbek testowanych w kontakcie luźnym i ścisłym wahała się pomiędzy 80 a 120°C (Rys. poniżej). Najbardziej obiecujące wyniki uzyskano dla szkieł zawierających tlenki kobaltu oraz miedzi. Te układy wymagają dalszych badań pod względem doboru optymalnego stężenia domieszki. Sugerowany mechanizm stabilizacji obejmuje powstawanie odpowiednich form węglanowych na powierzchni szkła.



Rys. Aktywność katalityczna badanych próbek (jako temperatura 50% konwersji sadzy) w różnych warunkach prowadzenia procesu utleniania sadzy

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

P-2

Parametry popiołów lotnych z sektora energetycznego determinujące ich wykorzystanie do syntezy materiałów funkcjonalnych o znaczeniu katalitycznym

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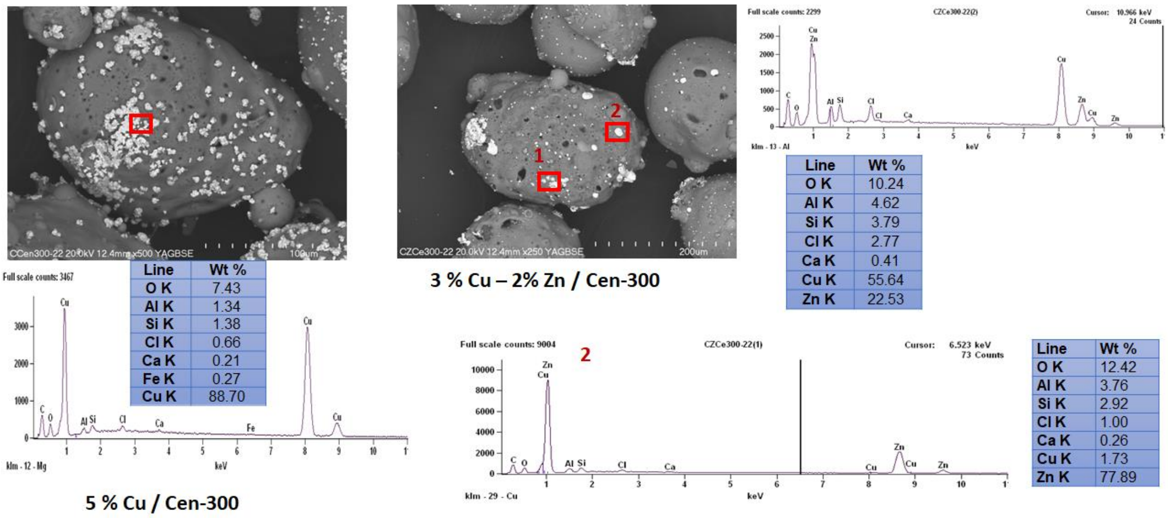
Aktualne poszukiwania efektywnych ścieżek wykorzystania popiołów lotnych, masowo generowanych przez sektor energetyki konwencjonalnej, do otrzymywania zaawansowanych materiałów funkcjonalnych, wpisują się w cele zrównoważonego rozwoju ze szczególnym uwzględnieniem gospodarki o obiegu zamkniętym. Jednocześnie, użycie popiołów lotnych jako prekursorów katalizatorów i sorbentów doskonale wpasowuje się także w obszar katalizy środowiskowej. W ramach niniejszej pracy jako materiały wyjściowe scharakteryzowano i przetestowano syntetycznie sześć rodzajów popiołów lotnych, pozyskanych jako materiały odpadowe z energetycznych kotłów pyłowych opalanych węglem. Ponadto, do syntezy układów katalitycznych użyto popiołów pochodzących ze spalania ciężkich frakcji ropy naftowej oraz komercyjnych cenosfer. Wszystkie badane próbki poddano charakterystyce z wykorzystaniem metod: XRF, XRD, RS, BET, SEM i DRIFT. Celem prezentowanych badań było przede wszystkim określenie, w oparciu o opracowany algorytm, zakresu niezbędnej optymalizacji parametrów kluczowych dla wybranych ścieżek syntetycznych, tak, aby z popiołów lotnych uzyskać nośniki katalityczne, katalizatory tlenkowe oraz układy zeolityczne. Przeprowadzone badania potwierdziły, że popioły lotne stanowią wartościowe prekursory materiałów funkcjonalnych i wskazały na kluczową dla syntezy rolę takich parametrów, jak: stosunek stężeń Si/Al, stosunek fazy szklistej do krystalicznej, zawartość pozostałości węglowych, powierzchnia właściwa oraz kształt i dystrybucja rozmiarów ziaren (Rys. poniżej).

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



Line	Wt %
O K	7.43
Al K	1.34
Si K	1.38
Cl K	0.66
Ca K	0.21
Fe K	0.27
Cu K	88.70

5 % Cu / Cen-300

Line	Wt %
O K	10.24
Al K	4.62
Si K	3.79
Cl K	2.77
Ca K	0.41
Cu K	55.64
Zn K	22.53

3 % Cu – 2% Zn / Cen-300

2

Line	Wt %
O K	12.42
Al K	3.76
Si K	2.92
Cl K	1.00
Ca K	0.26
Cu K	1.73
Zn K	77.89

Rys. Morfologia i skład powierzchni ziaren katalizatorów na bazie miedzi oraz miedzi i cynku, otrzymanych z wykorzystaniem jako nośników komercyjnych cenosfer z popiołów lotnych.

P-3

Strukturalne, teksturalne i funkcjonalne właściwości układów na bazie miedzi i cynku aktywnych w reakcji uwodornienia CO_2

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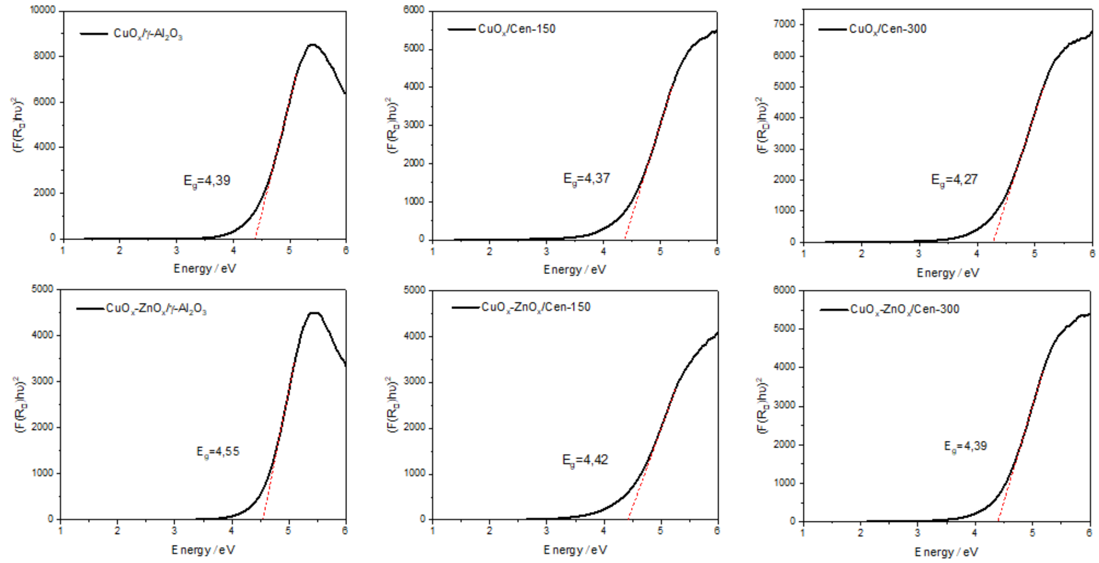
Pomimo bardzo wysokiej stabilności termodynamicznej cząsteczek CO_2, katalityczna waloryzacja tlenku węgla(IV) nie tylko jest możliwa, ale od kilku lat cieszy się rosnącym zainteresowaniem tak ze względów środowiskowych, jak i technologicznych oraz ekonomicznych. Efektywna redukcja CO_2 pozwala bowiem otrzymać z dobrą wydajnością tak istotne komercyjnie produkty, jak: gaz syntezowy, wodór czy metanol. Przedmiotem badań prezentowanych w niniejszej pracy są katalizatory nośnikowe, zawierające formy oksomiedziowe lub oksomiedziowe i oksocynkowe jako składniki fazy aktywnej w reakcji uwodornienia CO_2 do metanolu. Wskazane składniki osadzono metodą impregnacji na komercyjnych nośnikach: γ-Al_2O_3 oraz cenosferach (Cen) wyodrębnionych z popiołów lotnych.

Celem prezentowanych badań było przede wszystkim określenie wpływu stężenia poszczególnych składników fazy aktywnej na właściwości strukturalne, teksturalne i funkcjonalne, kontrolujące właściwości katalityczne finalnych układów nośnikowych. Ponadto, istotne było zrozumienie wpływu typu nośnika na specjację i stabilność faz powierzchniowych.

W toku badań przeprowadzonych metodami: XRF, XRD, RS, SEM/EDS, BET, DRIFT i UV/Vis-DR potwierdzono kluczową dla architektury powierzchniowej oraz właściwości elektronowych (Rys. poniżej) rolę nie tylko składu badanych katalizatorów, lecz także temperatury ich kalcynacji i rodzaju wykorzystanych nośników. Te same optymalizowalne zmienne preparatywne traktować należy jako determinujące aktywność i selektywność katalityczną badanych próbek w kontekście reakcji uwodornienia CO_2 do metanolu.



Rys. Zmiany szerokości energetycznej przerwy wzbronionej w zależności od składu badanego katalizatora zawierającego 5% mol. CuO lub 3% mol. CuO i 2% mol. ZnO.

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

O_2 binding by (M-porphine)$_2$ dimers (M = Fe, Ni, Mn, Co): DFT Studies

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Typically, enzymatic active sites contain single metal ions, but those bearing two metal centres in proximity (having binuclear active sites) are also known. They 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.

In the current project, we aim at the exploration of inorganic analogues of the bimetallic sites in enzymes (modelled by porphyrin moiety) as the reactivity of the binuclear sites introduced into the zeolitic matrices that were recently developed in J. Heyrovský Institute of Physical Chemistry, Prague (JHI).

To understand the observed reactivity, we performed quantum-chemical calculations in the frame of Density Functional Theory (DFT) with B-P/PBE/B3-LYP functionals with D3 dispersion correction and the def2-TZVP basis set. The calculations were done with Turbomole program package.

In the first instance, theoretical models in which transition metal ion (TMI) (TMI = Fe, Co, Mn, Ni) in porphyrin rings placed face-to-face at variable distances were designed and next the dioxygen molecule was placed in between the two moieties. The performed calculations indicate that all investigated TMI pair can bind the O_2 molecule placed in between. Upon 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, but this effect requires further study.

To sum up, by varying the metal-to-metal distance we could study the influence of the separation of both TMI. It was shown that it affects not only the ability to split O_2 but also the further formation of highly active oxygen species, α-oxygens ($[\mathrm{TMI}^{4+}{=}\mathrm{O}]^{2+}$). We also postulate that their interactions with hydrocarbons would be affected.

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P-5

Deposition of TiO_2 nanoparticles prepared by inverse microemulsion in exfoliated montmorillonite: SEM/TEM/EDX study

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The inverse micellar route was applied to produce titania nanoparticles for synthesis of TiO_2/montmorillonite (Mt) composites. Mt was prepared in two different ways: either as a cetyltrimethylammonium organoclay (CTA-Mt) to facilitate its exfoliation in the organic reaction medium (1-hexanol), or as Na-montmorillonite (Na-Mt) dispersion, prepared by a novel procedure in which clay particles were suspended in aqueous micellar cores of an inverse microemulsion in 1-hexanol.

TEM analysis showed that the TiO_2 phase was composed of uniform, rounded TiO_2 particles of 4–6 nm diameter (Fig. 1). TEM images of clay particles present in Na-Mt showed that they were thinner and smaller than those found in organoclay, pointing to the better dispersion of Mt suspension prepared by inverse microemulsion method (Fig. 1). This resulted in the TiO_2/Na-Mt composites showing better intermixing of components than the TiO_2/CTA-Mt series (Fig. 1). SEM/EDX mapping of key composite-forming elements confirmed more homogeneous blending of titania nanoparticles with clay component in TiO_2/Na-Mt composites.

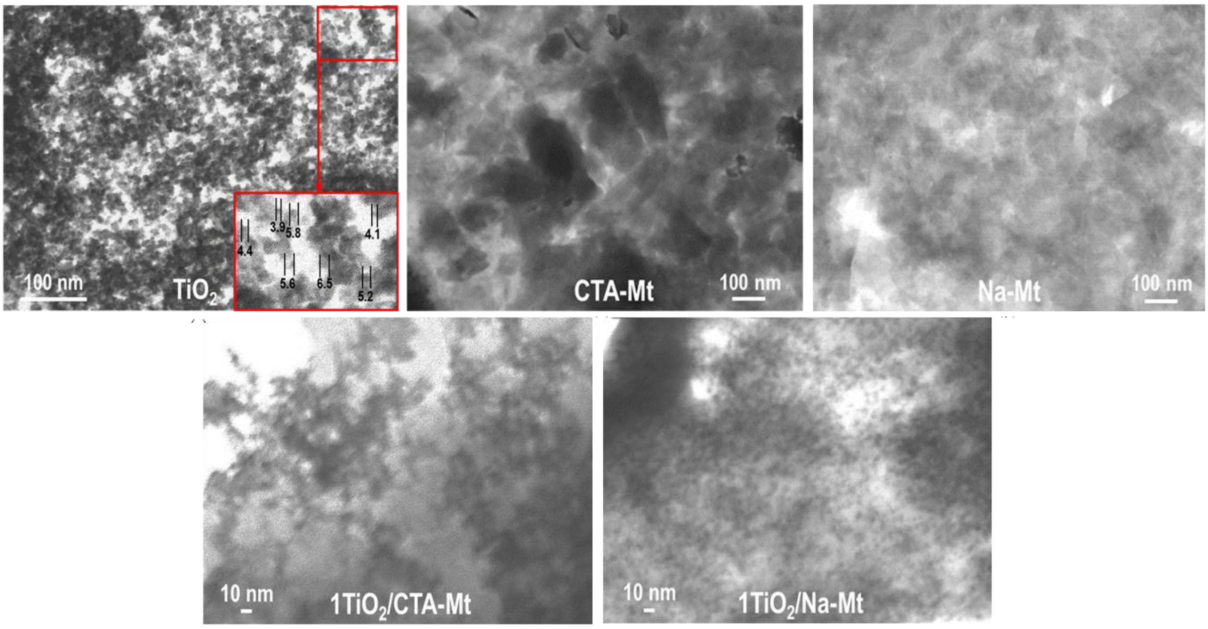

Fig. 1. TEM images of $1TiO_2$/CTA-Mt and $1TiO_2$/Na-Mt composites.

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P-6

The influence of iron and nickel doping on the activity and selectivity of Cu-SSZ-13 and Cu-SAPO-34 catalysts in the NH_3-SCR process

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The growing consumption of fossil fuels causes exceeded nitrogen oxides (NOx) emission, which can cause a series of environmental and health problems. Therefore, the problem of elimination of NOx has attracted tremendous attention in recent decades. The selective catalytic reduction of NOx by ammonia (NH_3-SCR) is widely employed to eliminate NOx, and the selection of catalyst has a major effect in the final conversion.

This study aimed to elucidate how the introduction of nickel and iron (different amounts of nickel or iron and method of synthesis) into Cu-SSZ-13 or Cu-SAPO-34 can modify its activity (widening of the operating temperature range) and selectivity (reduction of the share of side reactions) in the NH_3-SCR process. The Cu-SSZ-13 and Cu-SAPO-34 catalysts were obtained by one-pot synthesis. Two series of bimetallic Cu-Ni-SSZ-13 and Cu-Fe-SSZ-13 catalysts were synthesized by ion exchange, carried out in solutions with various concentrations of Ni or Fe ions, and impregnation with the aqueous solutions of the $Ni(NO_3)_2$ or $Fe(NO_3)_3$.

The activity tests (NH_3-SCR) were carried out in a fixed-bed reactor in a reaction mixture containing 500 ppm NH_3, 500 ppm NO, 4.5% O_2 with or without H_2O. The strong influence of nickel or iron concentration and method of synthesis of bimetallic catalysts on their activity in the NH_3-SCR process were demonstrated. Regardless of the method of nickel introduction into Cu-SSZ-13, it was found that even a small addition of Ni caused increase in the range of the temperature window in which the NO conversion is 100% and significantly reduced the share of side reactions - production of NO_2 and N_2O. In the case of the Fe-Cu-SSZ-13 catalyst series, only the introduction of iron by impregnation improved the catalytic properties. On the other hand, the introduction of iron by ion exchange caused a decrease in the selectivity to N_2 and a decrease in activity in the NH_3-SCR process, which resulted from Cu leaching from the zeolite at the ion exchange stage.

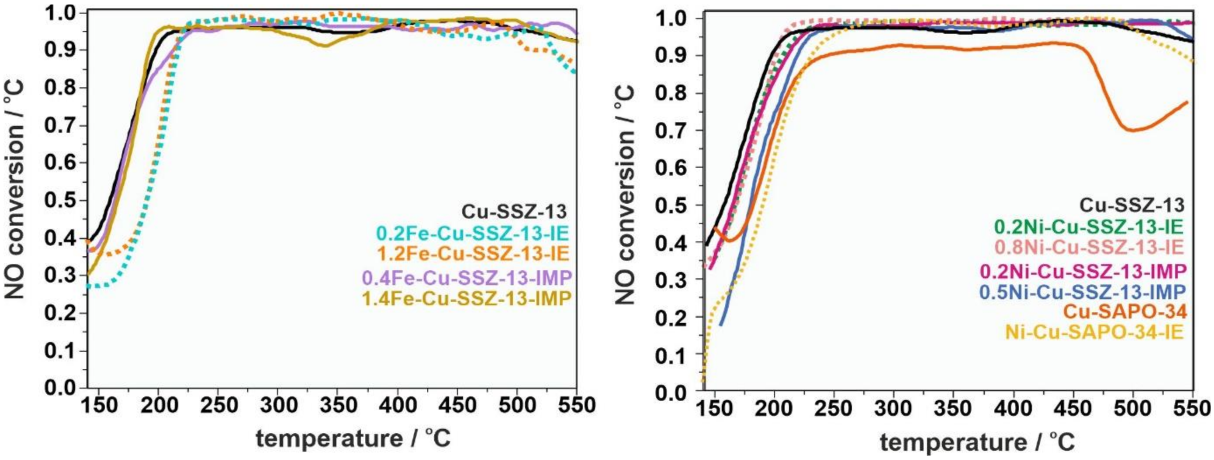

Fig. 1. NO conversion during NH_3-SCR on the Fe-Cu-SSZ-13 (left panel), Ni-Cu-SSZ-13 and Ni-Cu-SAPO-34 (right panel) catalysts obtained by impregnation and ion exchange method.

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

P-7

The state of BEA zeolite supported nickel catalysts in CO_2 hydrogenation reaction

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The increased consumption of fossil fuels and production of carbon dioxide is commonly perceived as the main reason of global warming. Waste carbon dioxide can be captured and further utilized for the production of valuable compounds and energy carriers by the application of green hydrogen, such as methane, methanol or formic acid. Despite numerous studies and examination of large number of catalytic systems, the development of cheap, active and selective catalysts at low reaction temperatures, as well as resistant for poisoning with sulphur compounds and sintering at high temperatures is still a challenge. Recently we have demonstrated that such effects can be in part achieved by the application of alumina and ceria supported nickel catalysts [1-2]. The specific microporous structure and high specific surface area of zeolites may enhance formation of the small metal nanoparticles. In addition, this effect can be enhanced by using dealumination of zeolites, which leads to the formation of vacant T-atom sites and slight surface and structural changes [3].

In the present studies the state of model catalysts based on the unmodified and dealuminated BEA zeolite supports determined under CO_2 hydrogenation reaction was investigated by the application X-ray diffraction, electron microscopy, in-situ DRIFTS and XPS spectroscopy [4]. It was demonstrated that an introduction of nickel to the unmodified BEA zeolite by the impregnation method led to the formation of nickel nanoparticles of wide size distribution and versatile morphology, which were in part located on the external surface of the zeolite crystals. In turn, the impregnation of the dealuminated BEA zeolite resulted in the formation of small regular nickel crystallites with a narrow size distribution, embedded in the microporous zeolite matrix [4]. This resulted in the increase in the activity and selectivity of the catalysts towards methane at low reaction temperatures. Moreover the catalysts showed improved sintering resistance at high temperatures. TEM studies indicated the retardation of the migration of nickel particles in that catalysts from the inner to external part of zeolite grains with the time-on-stream. DRIFTS and XPS studies of catalysts in the CO_2 methanation reaction evidenced the presence of metallic crystallites, which facilitated dissociative adsorption of CO_2, formation of differently coordinated surface carbonyl groups and their subsequent transformation to methane. Partial oxidation of nickel surface sites by the intermediate hydroxyl groups and water formed under CO_2 hydrogenation reaction was indicated. The presence of the small amounts of H_2S in the feed stream resulted in the drop of CO_2 conversion and decrease in methane selectivity with the time-on-stream, ascribed to the deposition of sulphur on nickel crystallites, retardation of deep hydrogenation of surface species formed under reaction conditions and facilitation of desorption of carbon monoxide [4].

References

1. W. Gac, W. Zawadzki, M. Rotko, M. Greluk, G. Słowik, G. Kolb, Cat. Today 357 (2020) 468.
2. W. Gac, W. Zawadzki, M. Greluk, G. Słowik, M. Rotko, M. Kuśmierz, Catalysts 12 (2022) 13.
3. S. Dzwigaj, P. Massiani, A. Davidson, M. Che, J. Mol. Catal. A 155 (2000) 169.
4. W. Gac, W. Zawadzki, G. Słowik, M. Kusmierz, S. Dzwigaj, Appl. Surf. Sci. 564 (2021) 150421.

P-8

Mechanism of the cleansing effect during the TBAOH-treatment of ultra-stable zeolite Y

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Quaternary ammonium hydroxides like tetrabutylammonium hydroxide (TBAOH) are widely used for the preparation of mesoporous zeolites [1,2]. In the case of ultra-stable zeolite Y (USY), mesopores are created only when the mixture of TBAOH and NaOH is used [3,4]. For the pure 0.2M TBAOH solution, almost no changes in porosity are observed. The motivation of this research was to elucidate changes in the properties of the material after this treatment. For comparison, the zeolite was treated with different alkali solutions that modify the mesoporosity of this material. Porosity and structural changes in the samples were characterized by ^{129}Xe NMR, solid-state ^{1}H and ^{29}Si MAS NMR, N_2 sorption, and STEM. The sample treatment with NaOH solution resulted in the formation of highly mesoporous amorphous materials with a low concentration of Brönsted acid sites (BAS). The treatment with a mixture of NaOH and TBAOH created a sample with high acidity, mesoporosity, and preserved zeolitic structure. Contrary, the treatment with 0.2M TBAOH solution created a material that possesses very similar physicochemical features to the parent material. However, ^{129}Xe NMR studies upon xenon adsorption revealed significantly different spectra for this sample. They contain two separate ^{129}Xe NMR signals and powder-like line shapes recorded at the lowest temperatures. It was ascribed to the higher loading of xenon atoms in supercages after the treatment with TBAOH solution. ^{29}Si MAS NMR spectra and STEM images show that crystals have a decreased amount of deposited amorphous material after the TBAOH treatment. Especially, the dissolution of amorphous debris from the supercages allows the increased adsorption of xenon atoms inside those cavities. This treatment method could be used for fine-tuning ultra-stable zeolite Y crystals.

References

1. J. Perez-Ramirez, C.H. Christensen, K. Egeblad, C. H. Christensen, J. C. Groen, Chem. Soc. Rev. 37 (2008) 2530
2. D. Verboekend, G. Vile, J. Perez-Ramirez, Cryst. Growth and Des. 12 (2012) 3123
3. M. Gackowski, K. Tarach, Ł. Kuterasiński, J. Podobiński, B. Sulikowski, J. Datka, Microporous Mesoporous Mater. 281 (2019) 134
4. M. Gackowski, K. Tarach, Ł. Kuterasiński, J. Podobiński, S. Jarczewski, P. Kuśtrowski, J. Datka, Microporous Mesoporous Mater. 263 (2018) 282

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P-9

Stability of Ni/La_2O_3-ZrO_2 catalyst in upgrading of lignocellulosic feedstock to hydrogen-rich gas

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The limited reserves of fossil fuels, world political situation and increasing environmental pollution encourage researchers for development of alternative methods of hydrogen production. Thermochemical conversion of lignocellulosic biomass seems to be one of the most promising among them. However, due to the low efficiency of this process the use of catalyst is necessary [1,2]. Unfortunately, the catalysts usually undergoes relatively fast deactivation due to carbon deposition [3]. Therefore, the aim of our work was to develop more stable material for the conversion of lignocellulosic feedstock to H_2-rich gas by the introduction of Ni on the surface of ZrO_2 modified by La_2O_3.

Mixed La_2O_3-ZrO_2 supports were synthesized by sol – gel method using various contents of lanthanum. Nickel was deposited on their surface by impregnation method. Catalytic activity tests were conducted under atmospheric pressure at 700°C with the use of cellulose and real biomass samples. The gaseous products were analyzed by gas chromatograph equipped with TCD detector. Physicochemical properties of prepared catalysts were characterized using TPR, TPD-NH_3, TPD-CO_2, XRD, ToF-SIMS, FTIR and TG-DTA.

Table 1. Comparison of the stability of parent and modified catalysts in cellulose decomposition.

Catalyst	**H_2 yield [mmol H_2/g]**	**H_2 selectivity [%]**
Ni/ZrO_2		
after I reaction cycle	12.4	49
after V reaction cycle	4.8	32
Ni/La_2O_3-ZrO_2		
after I reaction cycle	15.0	52
after V reaction cycle	11.0	48

The obtained results demonstrated that modified catalysts allowed for more efficient production of hydrogen than parent Ni/ZrO_2. Moreover, the presence of La led to their higher stability. The drop of hydrogen yield observed after 5th reaction cycle for modified sample was considerably lower (27%) in comparison to nickel supported on the pure zirconia (61%) (Table 1). Finally, the amount of formed H_2 was more than twice higher in the case of Ni/La_2O_3-ZrO_2 comparing to Ni/ZrO_2. It was related to the higher resistance against carbon deposition of modified catalysts, increase of their porosity, lower size of active phase crystallites and modified acidity, among others.

References

1. R. Ryczkowski, J. Goscianska, R. Panek, W. Franus, K. Przybysz, J. Grams, Int. J. Hydrogen Energy 46 (2021) 10708-10722.
2. R. Ryczkowski, K. Chałupka, W. Kwapiński, K. Przybysz, D. Fridrichová, J. Grams, Fuel 276 (2020) 118110.
3. J. Grams, A.M. Ruppert, Catalysts 11 (2021) 265.

P-10

Cobalt supported on alumina-doped manganese oxides as highly active and selective catalysts for the hydrogen production in the ethanol steam reforming process

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Energy is an indispensable element in our everyday lives. Most of the energy we used nowadays originates from fossil fuels, which are unsustainable and cause severe environmental issues. Therefore, there is a necessity to explore alternative renewable and clean energy. Unlike fossil fuels, hydrogen gas burns cleanly, without emitting any environmental pollutants. In addition, hydrogen is also abundantly available in the universe and possesses the highest energy content per unit of weight (i.e, 120.7 kJ/g), compared to any of the known fuels. Therefore, hydrogen is considered to be the energy carrier of the future and could have an important role in reducing environmental emissions. Hydrogen can be produced from biomass, a renewable and CO_2-neutral energy source with respect to the greenhouse effect. Specifically, reforming renewable biomass feedstock such as ethanol has become an increasingly important and active research area in view of hydrogen production. Stoichiometrically, the overall steam reforming reaction of ethanol (SRE) could be represented as follows: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$. However, from the reaction network, it is clear that this reaction is very complex and involves over a dozen of potential products. Therefore, it is important to reduce the production of undesirable intermediate compounds by the use of promising catalysts to drive the ethanol steam reforming reaction with fewer by-products. Typically, it involves the use of metal/oxide catalysts because both metal and oxide parts work co-operatively, with the metal component contributing to the C—C and C—H bond scissions of ethanol, and the oxide support promoting the dehydrogenation (or dehydration) reaction as well as the dissociation of water.

The chemical composition, textural properties of the support and synthesis method play important roles in the preparation of highly active steam reforming catalysts since they can improve the dispersion of metal. Thus, this work focuses on the effect of adding alumina into manganese oxides on the dispersion of the cobalt active phase and provides basic insights into the surface structure of the Co/AlXMn (where X=5, 10 and15 wt% of Al_2O_3) catalysts. The samples prepared by the wet impregnation method were characterized by XRD, XRF, low-temperature nitrogen adsorption, TEM, and H_2-TPR. Moreover, the performance of obtained cobalt-based catalysts was investigated in the ethanol steam reforming process at a temperature of 420 ºC and at a water-to-ethanol molar ratio of 12. The results showed that alumina addition as a support modifier to the Co/MnO_x catalyst improved its catalytic activity, selectivity and stability in the ethanol steam reforming process. Low alumina loading of 5 wt% was found to be the most beneficial in minimizing carbon deposition under SRE conditions. Moreover, Co/Al5Mn catalyst exhibited the highest activity for C—C cleavage.

References

1. C. Zhang, W. Zhu, S. Li, G. Wu, X. Ma, X. Wang, J. Gong, Chem. Commun. 49 (2013) 9383-9385.
2. A. Haryanto, S. Fernando, N. Murali, S. Adhikari, Energy Fuels 19 (2005) 2098-2106.
3. J.F. Da Costa-Serra, A. Chica, Int. J. Hydrogen Energy, 43 (2018) 16859-16865.
4. Z. Liu, T. Duchoň, H. Wang, E.W. Peterson, Y. Zhou, S. Luo, J. Zhou, V. Matolín, D.J. Stachiola, J.A. Rodriguez, S.S. Senanayake, J. Phys. Chem. C 119 (2015) 18248-18256.

P-11

Optymalizacja preparatyki katalizatora kobaltowego na nośniku Al_2O_3 do procesu reformingu parowego etanolu

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Stale rosnąca liczba ludności na świecie, rozwój przemysłu oraz wzrost standardów życia determinują wzrost zapotrzebowania na energię. Jednocześnie sytuacja geopolityczna, skłania coraz więcej państw do odejścia od konwencjonalnych paliw, przechodząc na odnawialne źródła energii. Na uwadze zyskuje wykorzystanie wodoru jako paliwa, który charakteryzuje się wysoką wartością opałową 33,3 kWh/kg. Interesującym procesem jest reforming parowy etanolu (ESR), dający możliwość wykorzystania biomasy do produkcji alkoholu. Katalizatory do procesu reformingu parowego etanolu bazują na metalach szlachetnych, lub zdecydowanie tańszych metalach przejściowych (Co, Ni) rozproszonych na nośnikach z tlenków nieorganicznych (m.in. Al_2O_3, ZnO, ZrO, CeO_2) [1].

W ramach prezentowanej pracy opracowano metodę preparatyki katalizatora kobaltowego na bazie Al_2O_3. W pracy zbadano tlenek glinu o różnej morfologii i składzie fazowym, porównano różne metody dyspersji fazy kobaltowej: metodą impregnacji, sonochemicznie oraz hydrotermalnie. Otrzymane materiały scharakteryzowano pod kątem właściwości fizykochemicznych (XRF, sorpcja azotu, XPS, XRD, H_2-TPR, SEM, TEM oraz spektroskopia Ramana) oraz zbadano ich aktywność w procesie ESR (T = 500°C, EtOH;H_2O = 1:4, 21 h). Przeprowadzone badania wskazują na silną zależność działania katalizatora od składu fazowego i morfologii nośnika glinowego.

[1] T. Hou, S. Zhang, Y. Chen, et al, Renewable and Sustainable Energy Reviews, (2015), 132-148, 44.

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P-12

Modified PCN-222 for methanol synthesis

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One of the most pressing problems that humanity faces in the 21st century is global warming caused by the excessive emissions of greenhouse gases, mainly CO_2. Hence, all efforts are made to reduce its production and emissions, and manage the already produced CO_2 [1]. One of the promising solutions is the catalytic conversion of CO_2 into valuable products such as methanol, which is fuel and also an important raw material in many chemical processes. However, owing to the high stability of the CO_2 molecule, it is necessary to use catalysts for its hydrogenation [2].

The recently considered candidates for the catalyst of methanol synthesis are Metal-Organic Frameworks (MOF), mainly due to their crystallinity, permanent porosity, developed specific surface area (SSA), sufficient thermal and chemical stability, as well as the possibility of versatile modification [3]. For example, the zirconium-containing PCN-222 with porphyrin linker demonstrates high SSA of up to 2200 m^2/g and very good chemical and thermal stability [4]. In addition, thanks to the presence of porphyrin linkers, the functionality of MOF may be extended, e.g., via the introduction of additional metal into the framework. All of the above features make PCN-222 an interesting material to be used as a heterogeneous catalyst.

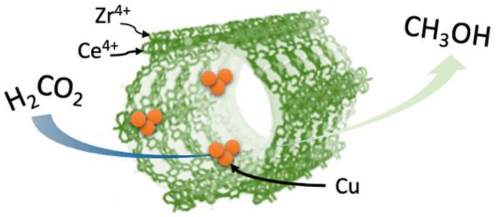

Fig. 1. PCN-222 modified with copper and cerium for methanol synthesis.

In this work we report the PCN-222 modified with copper and cerium as catalysts for CO_2 hydrogenation (Fig. 1). The synthesized materials were subjected to physicochemical characterization including XRD, N_2, and CO_2 sorption, SEM(EDS), TEM, XPS, IR, ICP, and TGA, and tested in methanol synthesis. The effect of the physicochemical properties of the obtained materials on their performance in CO_2 conversion to methanol was investigated and compared with the activity of the previously reported catalysts.

References

1. E. Alper, O.Y. Orhan, Petroleum 3 (2017) 109-126
2. M. Aresta, A. Dibenedetto, A. Angelini, Chem. Rev. 114 (2014) 1709–1742
3. M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi Acc. Chem. Res. 34 (2001) 34, 319–3304
4. D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou, Angew. Chem. Int. Ed., 51 (2012) 10307-10310

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P-13

Strategie syntezy katalizatorów z ugrupowaniami N-hydroksyftalimidowymi immobilizowanymi na nośnikach kopolimerowych i krzemionkowych do aerobowego utleniania węglowodorów alkiloaromatycznych

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Rozwój przemysłu petrochemicznego doprowadził do wzrostu znaczenia procesów utleniania jako metody otrzymywania związków zawierających tlen, które są wykorzystywane do produkcji m.in. żywności, leków, czy barwników. N-hydroksyftalimid (NHPI) został szeroko przetestowany jako obiecujący pro-ekologiczny katalizator homogeniczny w procesach aerobowego utleniania węglowodorów alkiloaromatycznych w fazie ciekłej [1,2]. Niestety, problemy związane z wydzieleniem NHPI z mieszaniny reakcyjnej znacząco utrudniają jego szerszą aplikację w przemyśle. Obiecującą alternatywą jest możliwość unieruchomienia grup NHPI na stałym nośniku. Otrzymywany w ten sposób układ heterogeniczny można łatwo izolować z fazy ciekłej na drodze filtracji i ponownie wykorzystać w procesie utleniania. W niniejszej pracy przedstawiono oryginalne podejście do otrzymywania katalizatorów z grupami NHPI immobilizowanymi na drodze ich włączenia w strukturę usieciowanego kopolimeru poli(winylodiizopropyloftalan-*co*-styren-*co*-diwinylobenzen) lub szczepienia na powierzchni mezoporowatej krzemionki (SBA-15).

Przygotowano sześć serii kopolimerów zawierających 10-90% mas. monomeru funkcyjnego (prekursor NHPI) o różnej zawartości monomeru sieciującego (1-11% mas.), co pozwoliło uzyskać zawartość 0,48-6,46 mmol $\mathrm{NHPI_{cał}/g_{kopolimer}}$. Aktywność katalityczną testowano w reakcji selektywnego utleniania *p*-metyloanizolu z dodatkiem Co(II) jako ko-katalizatora w układzie bez udziału rozpuszczalnika w aparaturze gazometrycznej. Największą konwersję (23,6%) uzyskano dla katalizatorów zawierających od 30 do 60% mas. estru diizopropylowego kwasu 4-winyloftalowego w zakresie 3-9% usieciowania, co powiązano z optymalnym stężeniem i dostępnością centrów aktywnych w strukturze pęczniejącego kopolimeru [1,3].

Immobilizację grup NHPI na nośniku SBA-15 przeprowadzono na drodze *graftingu* bezwodnika 4-chlorodimetylosililoftalowego (prekursor NHPI) na powierzchniowych grupach silanolowych w stosunku masowym 0,1-1.0% mas. i następczej aktywacji w reakcji z chlorowodorkiem hydroksyloaminy. Otrzymane katalizatory SBA-15_*x*NHPI scharakteryzowano pod kątem składu oraz struktury powierzchniowej. Potwierdzono efektywne osadzenie fazy aktywnej w ilości od 8,4 do 15,8% mas. (0,74-1,17 mmol $\mathrm{NHPI_{cał}/g_{materiału}}$). Badania katalityczne w aerobowym utlenianiu *p*-ksylenu wykonano z dodatkiem Co(II) w układzie bezrozpuszczalnikowym. Wykazano możliwość wielokrotnego stosowania katalizatorów w testowanej reakcji odnotowując konwersję 38,0% (po cyklu 1), 32,3% (po cyklu 2), 32,8% (po cyklu 3) i 30,2% (po cyklu 4), przy stabilnej zawartości grup NHPI po 1 (0,36 mmol $\mathrm{NHPI_{cał}/g_{materiału}}$) i 4 cyklu (0,35 mmol $\mathrm{NHPI_{cał}/g_{materiału}}$).

Literatura

1. P. Łątka, T. Berniak, M. Drozdek, E. Witek, P. Kuśtrowski, Catal. Commun. 115 (2018) 73.
2. P. Łątka, K. Kasperczyk, B. Orlińska, M. Drozdek, B. Skorupska, E. Witek, Catal. Lett. 146 (2016) 1991.
3. T. Berniak, P. Łątka, A. Rokicińska, K. Sidor, P. Kuśtrowski, Catalysts 11 (2021) 1474.

P-14

Optymalizacja warunków syntezy spinelu kobaltowego metodą sonochemiczna w celu uzyskania wysokoaktywnych i stabilnych elektrokatalizatorów anodowego wydzielania tlenu

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Ciągły wzrost zapotrzebowania na energię elektryczną przy jednoczesnej potrzebie zahamowania emisji gazów cieplarnianych skłania do opracowania nowoczesnych sposobów pozyskiwania energii z odnawialnych źródeł.[1] Wodór będący nośnikiem energii, można otrzymywać w procesie elektrolizy wody, podczas którego pod wpływem przyłożonego napięcia cząsteczki wody rozkładają się, na katodzie produkując wodór natomiast przy anodzie tlen. Wyzwaniem badań nad tym procesem jest stworzenie odpowiedniego elektrokatalizatora, który obniży nadpotencjał reakcji zwiększając wydajność procesu. Z dotychczasowych badań wynika, że w tym celu dobrze sprawdzają się związki metali przejściowych takich jak nikiel, żelazo czy kobalt[2]. Dobrymi katalizatorami okazały się materiały kompozytowe zawierające tlenki tych metali osadzone na nośniku węglowym dotowanym azotem, który zapewnia zwiększone przewodnictwo elektryczne układu, a więc jego wyższą aktywność[3]. Materiały kompozytowe zawierające między innymi spinel kobaltowy Co_3O_4 można otrzymywać na różne sposoby[4], jednym z nich jest szybka i wydajna metoda sonochemiczna. Metoda ta oparta jest na działaniu ultradźwiękami o wysokiej częstotliwości na roztwór zawierający kationy metalu oraz nośnik, gdzie zachodzi proces kawitacji, generujący punktowo bardzo wysokie temperatury oraz ciśnienia, dzięki którym na powierzchni nośnika osadza się faza tlenkowa[5] .

Podczas badań zoptymalizowano warunki syntezy sonochemicznej w postaci ilości użytego octanu kobaltu jako prekursora Co_3O_4, w celu uzyskania jak najlepszego katalizatora reakcji anodowego wydzielania tlenu oraz sprawdzono powtarzalność wyników dla zastosowanej metody. Do badań jako podłoża użyto dwóch rodzajów mezoporowatych materiałów węglowych: referencyjny oraz dotowany azotem. Wykonanie serii 3 syntez w takich samych warunkach oraz z tą samą ilością prekursora skutkowało otrzymaniem porównywalnej ilość osadzonego spinelu kobaltowego, co świadczy o powtarzalności syntez metodą sonochemiczną. Aktywność elektrokatalityczną wybranych układów została zbadana w układzie trójelektrodowym z wirującą elektrodą pracującą.

Bibliografia

1. C. Acar and I. Dincer, in *Comprehensive Energy Systems*, 3(2018) 1–40.
2. A. Moysiadou, S. Lee, C. S. Hsu, H. M. Chen and X. Hu, *J Am Chem Soc*, 142 (2020) 11901–11914.
3. P. Stelmachowski, J. Duch, D. Sebastián, M. J. Lázaro and A. Kotarba, *Materials*, 14(2021)
4. L. M. Al-Qirby, S. Radiman, C. W. Siong and A. M. Ali, *Ultrason Sonochem*, 38(2017) 640–651.
5. Z. Li, T. Zhuang, J. Dong, L. Wang, J. Xia, H. Wang, X. Cui and Z. Wang, *Ultrason Sonochem*, 71(2021)

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P-15

Materiały węglowe funkcjonalizowane w wyniku reakcji postplazmatycznych w plazmie niskotemperaturowej

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Materiały węglowe posiadają interesujące właściwości chemiczne dzięki czemu znajdują szerokie możliwości zastosowania m.in. w katalizie. Pomimo ich dużego potencjału nie zawsze mogą być stosowane ze względu na słabą dyspersję w rozpuszczalnikach polarnych bądź bierność chemiczną. W celu poprawienia reaktywności materiałów węglowych stosuje się głównie metody mokre umożliwiające funkcjonalizację powierzchni poprzez działanie silnymi kwasami utleniającymi. Jedną z coraz częściej stosowanych metod jest użycie plazmy niskotemperaturowej, która pozwala w sposób łatwy, kontrolowany i zgodny z zasadami zielonej chemii na wprowadzenie polarnych grup funkcyjnych na powierzchnię badanego materiału węglowego. Modyfikacja powierzchni prowadzi do zmiany pracy wyjścia - parametru zależnego od struktury elektronowej węgla. Zmiany te śledzono za pomocą metody Kelvina, która pozwala na ocenę stopnia funkcjonalizacji powierzchni.[1] Zastosowanie gazów zawierających węgiel organiczny w plazmie skutkuje syntezą filmu polimerowego na materiale węglowym.[2] Tego typu modyfikacja sprawia, że powierzchnia jest wysoce reaktywna i bogata w rodniki, co może doprowadzić do zwiększenia gęstości powierzchniowych grup funkcyjnych po utlenieniu *in situ* filmu polimerowego.

Optymalizacja funkcjonalizacji papieru grafenowego została przeprowadzona z wykorzystaniem różnych typów plazmy O_2, powietrze, 5% O_2/He, CO_2, Ar oraz C_2H_4. Wykonanie modyfikacji potwierdziło silny wpływ działania plazmy na wartość zmiany pracy wyjścia. Jednakże obserwowane zmiany nie są stabilne i zanikają w czasie. Przeprowadzono pomiary zaraz po modyfikacji jak i po stabilizacji papieru grafenowego w wodzie. Dodatkowo sprawdzono reaktywność papieru grafenowego po zanurzeniu w różnych substancjach i stwierdzono, że użycie CH_3COOH pozwala na najefektywniejsze wprowadzenie dodatkowych tlenowych grup funkcyjnych na powierzchnię badanego materiału. Ilość i typ wprowadzonych grup funkcyjnych badano za pomocą spektroskopii fotoelektronów wzbudzanych promieniowaniem X, natomiast do zbadania właściwości strukturalnych wykorzystano spektroskopię Ramana. Dodatkowo zbadano węgla po funkcjonalizacji przy pomocy termoprogramowanej desorpcji sprzężonej z spektrometrią mas wyposażoną w masowy analizator kwadrupolowy (TPD-QMS). Przeprowadzone badania wskazują, że sfunkcjonalizowany materiał po kontakcie z kwasem octowym i wodą pozwala na wprowadzenie większej ilości stabilnych grup tlenowych niż jedynie po zastosowaniu plazmy.

References

1. J. Duch, M. Gołda-Cępa, W. Piskorz, J. Rysz, A. Kotarba, *Applied Surface Science*, 2021, **539,** 148190
2. F. Khelifa, S. Ershov, Y. Habibi, R. Snyders, P. Dubois, Chem. Rev., 2016, **116**, 3975-4005

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P-16

Odziaływanie kobaltu z tlenowymi grupami funkcyjnymi na powierzchni grafenu

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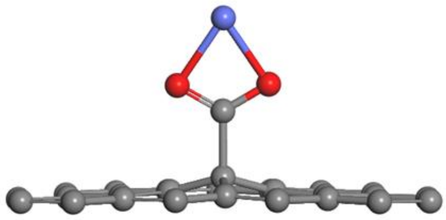
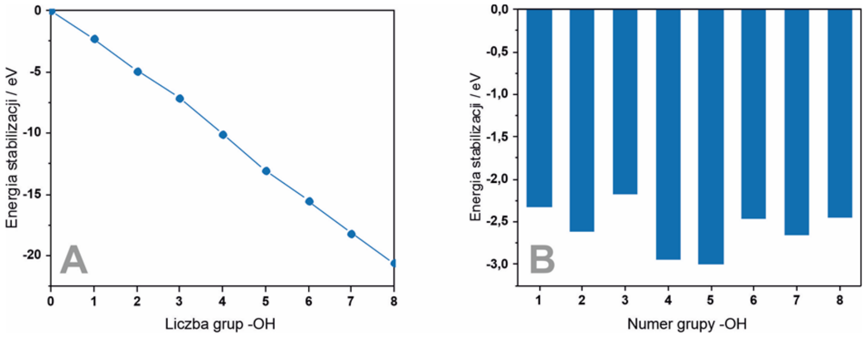
Materiały węglowe ze względu na swoje atrakcyjne właściwości fizykochemiczne m.in. rozwiniętą powierzchnię właściwą i stosunkowo wysokie przewodnictwo elektryczne znalazły zastosowanie jako katalizatory i adsorbenty. Dodatkowo, poprzez modyfikację ich powierzchni, można znacznie poprawić ich reaktywność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

W ramach prezentowanych badań zaproponowano serię układów obliczeniowych opisujących modelowe ugrupowania tlenowe na powierzchni grafenu. Do modelowania modyfikacji płaszczyzny wybrano grupy hydroksylowe (–OH), karboksylowe (–COOH), karbonylowe (–COH) oraz epoksydowe (-O-). Zbadano wpływ stężenia powierzchniowego tych grup na ich stabilność. Dla wszystkich modeli określono optymalną geometrię oraz obliczono energię stabilizacji. Dla najstabilniejszej konfiguracji - grupy karboksylowej kotwiczonej do grafenu, przeprowadzono modelowanie adsorpcji kationów kobaltu, którą badano poprzez symulację reakcji substytucji wodoru. Zaproponowano adsorpcję kobaltu metalicznego, chlorku oraz dichlorku kobaltu, azotanu(V) kobaltu oraz nadchloranu kobaltu, przykładową strukturę przedstawia Rysunek 1. Wszystkie obliczenia wykonano za pomocą metody DFT.



Rysunek 1. Fragment struktury grupy karboksylowej kotwiczonej do grafenu, na której zaadsorbowano atom Co.

Przeprowadzona analiza wykazała, że wraz ze wzrostem stężenia tlenowych grup funkcyjnych na powierzchni grafenu stabilność układu rośnie liniowo. Zależność ta wskazuje, iż kolejne grupy są stabilizowane w podobny sposób bez wyraźnych oddziaływań lateralnych, stabilizujących lub destabilizujących. Przykładowo, dla grupy hydroksylowej stabilność kolejnych grup wykreślono w funkcji ilości stabilizowanych grup, Rysunek 2A, zaś energie stabilizacji kolejnych grup –OH pokazano na Rysunku 2B. Wstępne obliczenia wykazały, że jedną z najsilniej stabilizowanych form jest kobalt metaliczny, stąd też konieczność zwrócenia szczególnej uwagi na zbadanie efektu przeciwjonu.



Rysunek 2. Energia stabilizacji grup -OH na powierzchni grafenu w zależności od ich ilości, A) sumaryczna energia stabilizacji oraz B) energia stabilizacji każdej kolejnej grupy.

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P-17

Wpływ sposobu wytwarzania nośnika cerowego na właściwości katalizatorów niklowych w procesie reformingu parowego etanolu

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Wzrost zapotrzebowania na energię elektryczną jest obecnie jednym z największych wyzwań dla współczesnego świata. Pozyskiwanie energii z konwencjonalnych źródeł, takich jak ropa naftowa, gaz ziemny czy węgiel jest coraz częściej piętnowane, ze względu na negatywny wpływ wydobycia i przetwórstwa tych substancji na środowisko. Z tego względu obserwuje się rosnące zainteresowanie alternatywnymi metodami pozyskiwania energii, zwłaszcza tymi, które bazują na wykorzystaniu wodoru, określanego mianem paliwa przyszłości. Mimo, iż jest to najbardziej rozpowszechniony pierwiastek w przyrodzie, to jego otrzymywanie wciąż sprawia wiele trudności. Jedną ze szczególnie interesujących metod jego pozyskiwania jest proces reformingu parowego etanolu (ang. steam reforming of ethanol, SRE) [1]. W większości procesów, jak również w SRE, koniecznym jest zastosowanie odpowiedniego układu katalitycznego, który umożliwi całkowitą konwersję substratów do pożądanych produktów reakcji. Za właściwości katalityczne takich układów zasadniczo odpowiada faza aktywna. Jednakże niektóre tlenki metali, wykorzystywane jako nośniki również wykazują aktywność katalityczną i tyczy się to związków, w których metal może występować na więcej niż jednym stopniu utlenienia. Doskonałym przykładem tego typu nośnika jest tlenek ceru. Jego aktywność w dużym stopniu zależy od uzyskania odpowiedniego dla danego procesu stosunku jonów Ce(III) do Ce(IV), co można osiągnąć przez odpowiednie dobranie warunków syntezy [2, 3].

Celem niniejszej pracy było określenie wpływu rodzaju rozpuszczalnika prekursora tlenku ceru tj. $Ce(NO_3)_3{\cdot}6H_2O$, na właściwości katalizatorów niklowych w procesie reformingu parowego etanolu. Nośniki w badanym układzie wytworzono tzw. metodą twardej matrycy przy użyciu porowatego polimeru [4], który nasączono roztworami prekursora tlenku ceru o różnej zawartości H_2O_2. Po usunięciu matrycy otrzymano nośniki, do których wprowadzono, niklową fazę aktywną metodą impregnacji na mokro. Aktywność i selektywność otrzymanych katalizatorów niklowych zbadano w procesie SRE w temperaturze 420 °C dla stosunku molowego etanol:woda wynoszącym 1:4. Przeprowadzone badania przy użyciu różnych technik wskazują, że zastosowanie H_2O_2 do sporządzania roztworu $Ce(NO_3)_3{\cdot}6H_2O$ prowadzi do wytworzenia nośnika o wyjątkowych właściwościach fizykochemicznych, pożądanych w reakcji SRE. Okazuje się bowiem, że nośniki wytworzone z udziałem H_2O_2 spowalniają dezaktywację katalizatora w procesie SRE.

Bibliografia:

1. M. Greluk, W. Gac, M. Rotko, G. Słowik, S. Turczyniak-Surdacka, J. Catal. 393 (2020) 4.
2. B. Jin, Z. Shang, S. Li, Y.-B. Jiang, X. Gu, X. Liang, Catal. Sci. Technol. 10 (2020) 3212-3222.
3. J.L. Contreras, J. Salmones, J.A. Colín-Juna, L. Nuño, B. Quintana, I. Córdova, B. Zeifert, C. Tapia, G.A. Fuentes, Int. J Hydrogen Energy 39 (2014) 18835-18853.
4. A. Sienkiewicz, A. Kierys, Microp. Mesop Mater 318 (2021) 111032.

P-18

Composites of ZIF-67(Co, Fe, Ni) with FLG and CNTs for OER

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Metal-organic frameworks are advanced porous materials that are characterised by high porosity, large specific surface area, and tuneable structure and composition. Thanks to the presence of metal centres with good redox properties recently they have been recognized as materials that can be used for energy storage. MOFs can be used directly as the electrode material but can also serve as a precursor to make the corresponding oxides or nanoporous carbon materials that will constitute the electrodes. Also, MOFs can be combined with other materials to form composites with electrode properties. It was found that the combination of MOF with carbon materials (C) such as graphene, graphene oxide, or CNTs can increase the electrochemical efficiency of supercapacitors [1]. The C compound improves the conductivity and ensures even distribution of MOF in the material.

The MOF/C composites are promising candidates to replace the precious metals in such electrocatalytic processes as oxygen reduction reaction (ORR), CO_2 reduction reaction, hydrogen evolution reaction (HER), oxygen evolution reaction (OER), or the reaction of water decomposition. The most common MOF components in MOF/C composites are the frameworks containing transition metals such as Fe, Co, Ni, Zn, Cu, etc. In addition, the calcination of MOF/rGO composite and the removal of metal allows obtaining a composite consisting of a high surface area nanoporous carbon and graphene [2]. The N-doped porous carbon/ graphene composite can be obtained by calcination of a composite in which a framework from the ZIF family is one of the components [3].

In this work we present the composites of mono-, bi- and tri-metallic ZIF-67(Co, Fe, Ni) with a few-layer graphene (FLG) or CNTs (and the carbonisates of those composites) as a potential electrocatalysts for OER.

References

1. A. Hosseininan, A. Amjad, R. H. Khanmiri, E. G. Kalhor , M. Babazadeh and E. Vessally, J. Mater. Sci.: Mater. Electron. 28 (2017) 18040-18048
2. K. Shen, X. D. Chen, J. Y. Chen and Y. W. Li, ACS Catal. 6 (2016) 5887-5903
3. W. Xia, C. Qu, Z. Liang, B. Zhao, S. Dai, B. Qiu, Y. Jiao, Q. Zhang, X. Huang, W. Guo, D. Dang, R. Zou, D. Xia, Q. Xu and M. Liu, Nano Lett. 17 (2017) 2788-2795

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P-19

Optymalizacja depozycji tlenku kobaltu na modelowych materiałach węglowych w celu uzyskania stabilnych kompozytów o wysokiej aktywności elektrokatalitycznej

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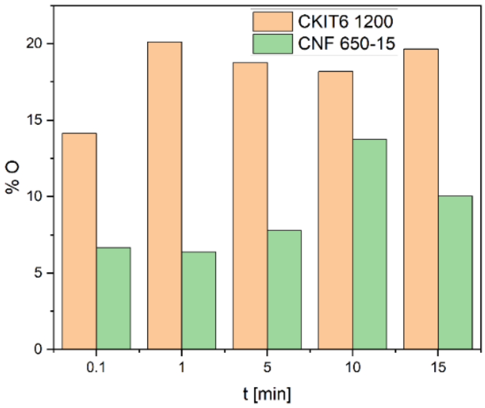
Funkcjonalizacja powierzchni materiałów węglowych wykorzystywana jest m.in. do zwiększania ich pojemności sorpcyjnej względem metali przejściowych. Użyteczną metodą jest zastosowanie plazmy niskotemperaturowej do wprowadzania powierzchniowych grup tlenowych. Aby otrzymać odpowiedni materiał konieczne jest przeprowadzenie procedury optymalizacji plazmy, aby uniknąć ubytków i degradacji materiału. Celem niniejszych badań było opracowanie materiałów opartych o materiały węglowe dotowane związkami metali przejściowych m.in. kobaltu, które znajdą zastosowanie jako katalizatory w reakcji elektrochemicznego rozkładu wody. Motywacją do podjęcia tych badań jest rosnące zapotrzebowanie na energię oraz poszukiwanie niskoemisyjnych źródeł energii.

Materiały węglowe zostały zmodyfikowane zoptymalizowaną plazmą tlenową w celu wytworzenia na ich powierzchni jak największej ilości grup funkcyjnych. Na podstawie analizy XPS (Rys. 1.) otrzymanych próbek wybrano optymalne czasy traktowania plazmą tlenową w zadanych warunkach tj. 10 min dla CNF (Carbon Nanofibers) oraz 5 min dla C_{KIT-6}-1200 (uporządkowany materiał węglowy na matrycy krzemowej KIT-6).



Rys. 1. Procentowe zawartości tlenu dla materiałów węglowych CKIT i CNF wynikające z analizy XPS materiałów traktowanych plazmą tlenową o zadanych warunkach 100 W, 0,2 mbar przy różnych czasach traktowania.

W kolejnym etapie przeprowadzono depozycję fazy aktywnej w procesie hydrotermalnym. W celu optymalizacji materiałów zastosowano roztwory jonów Co^{2+} o różnych stężeniach. Depozycję prowadzono poprzez starzenie hydrotermalne materiału węglowego wraz z prekursorem. Zoptymalizowaną procedurę dotowania kobaltem zastosowano także do materiału wyjściowego, bez wcześniejszego utleniania plazmą oraz modyfikowanego przy użyciu nadsiarczanu amonu. Otrzymane próbki badano pod względem ilości fazy aktywnej i aktywności elektrokatalitycznej w reakcji anodowego wydzielania tlenu w środowisku zasadowym.

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P-20

Molecular fragmentations and embedding techniques as tools for modelling of molecular properties - the applicability study

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The calculation of properties of large molecules is usually a greater challenge than the calculation of the energy only, what is related to the fact that many properties are defined as energy derivatives and are therefore more sensitive to subtle changes in electronic structure than the energy itself. On the other hand, accurate theories for large molecules are computationally expensive due to a high scaling of the computational resources with the molecular size. Recently, we proposed some new molecular fragmentation techniques, where double bonds are allowed to be cut (opposite to most fragmentation techniques present in the literature, for which such an operation is avoided [1]). In this contribution we present the algorithm and its accuracy for total energies and static dipole polarizabilities. We also present the application of the embedding technique [2] to obtain the electron-correlated part of energies and polarizabilities, as well as show the performance of the embedding for the calculation of the intermolecular interaction energy between a graphene cluster and a small molecule. Such a physisorbed state is as a rule the first step of the heterogeneous catalytic reaction.

References

1. M. A. Collins, R. P. Bettens, Chemical Reviews, 115(2015), 5607–5642.
2. F. R. Manby, M. Stella, J. D. Goodpaster, T. F. Miller III, J. Chem. Theory Comput. 8 (2012), 2564.

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P-21

Photocatalytic performance of metal-TiO_2 composites obtained via deposition of noble metal nanoparticles on commercial TiO_2

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This presentation shows the evaluation of photocatalytic performance of metal-TiO_2 composites obtained via deposition of metal (Pt or Ag) on commercial TiO_2 in the degradation reaction of dyes: methyl orange (MO) and rhodamine B (RB), under irradiation emitted by a UV lamp (50 W), with radiation emission in the wavelength range: 365 – 367.5 nm.

The nominal concentration of metal deposited in the form of nanoparticles (NPs) was 0.05, 0.1 and 0.5 wt. % of Pt or 0.05 and 0.1 wt. % of Ag. Metal NPs were obtained via chemical reduction of ions (Pt^{4+} or Ag^+) using $NaBH_4$. Metal NPs in the aqueous suspension were electrostatically stabilized with the addition of sodium citrate, therefore the measured zeta potential (ξ) in both cases was negative. The deposition of metal NPs on the surface of TiO_2 was carried out by adsorption. It is worth noting that TiO_2 grains in aqueous suspension (with a concentration of ~ 0.3 g dm^{-3}) formed agglomerates (with a diameter of ~ 200 nm) showing a positive ξ, therefore in the case of deposition of Pt and Ag NPs characterized by negative ξ, adsorption was additionally electrostatically assisted. Metal NPs had diameters in the range of 5 – 20 nm, among them those with a diameter of ~ 11 nm were dominating for Pt NPs or ~ 9 nm were dominating for Ag NPs.

Photocatalytic properties of the composites were examined in the reactions carried out in a suspension containing 15 mg of photocatalyst and 50 ml of dye solution (with a concentration of ~ 1 x 10^{-5} mol dm^{-3}). Before UV irradiation, degree of decolorization was checked due to adsorption of the dye on the surface of the photocatalyst during the first 2 hours of mixing the suspension in the dark. The dye concentration was spectrophotometrically monitored by recording UV–Vis spectra in the range of 350 – 650 nm for liquid samples (after separating the liquid from the photocatalyst) at each stage of the three stages of the experiment: (a) after 2 hours of mixing in the dark, (b) after exposure lasting 1 hour and (c) after exposure lasting another hour, i.e. a total of 2 hours of exposure.

Decrease in the concentration of dye in solution due to its adsorption on the surface of photocatalysts ranged from 15 to 30 %. Degree of decolorization of dye solutions in the presence of TiO_2 was: 43 or 71 % after 1 or 2 h of UV irradiation for MO, 53 or 85 % after 1 or 2 h of UV irradiation for RB. Degree of decolorization of MO solution with the addition of Pt-TiO_2 composites containing 0.05, 0.1 and 0.5 wt. % of Pt, after 1 h of UV exposure was 49, 50 and 44 %, respectively, and after 2 h of UV exposure it was 78, 82 and 72 %, respectively. Degree of decolorization of RB solution with the addition of Pt-TiO_2 composites containing 0.05, 0.1 and 0.5 wt. % of Pt, after 1 h of UV irradiation was 68, 68 and 42 %, respectively, and after 2 h of UV irradiation it was 96, 97 and 71 %, respectively. Degree of decolorization of MO solution with the addition of Ag-TiO_2 composites containing 0.05 and 0.1 wt. % of Ag, after 1 h of UV exposure was 43 and 32 %, respectively, and after 2 h of UV exposure it was 74 and 63 %, respectively. Degree of decolorization of RB solution with the addition of Ag-TiO_2 containing 0.05 and 0.1 wt. % of Ag, after 1 h of UV exposure was 57 and 56 %, respectively, and after 2 h of UV exposure it was 87 and 86 %, respectively.

Deposition of Pt onto TiO_2 increases the efficiency of the degradation process compared to pure TiO_2. The content of metal NPs on the surface of TiO_2 is important. The recommended concentration of Pt per TiO_2 is 0.1 wt. %. Spreading Ag on TiO_2 (0.1 wt. %) does not significantly increase (in the case of RB) but even decreases (in the case of MO) the efficiency of the degradation process compared to pure TiO_2.

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P-22

Specjacja centrów srebrowych w katalizatorach zeolitowych – wpływ metody preparatyki

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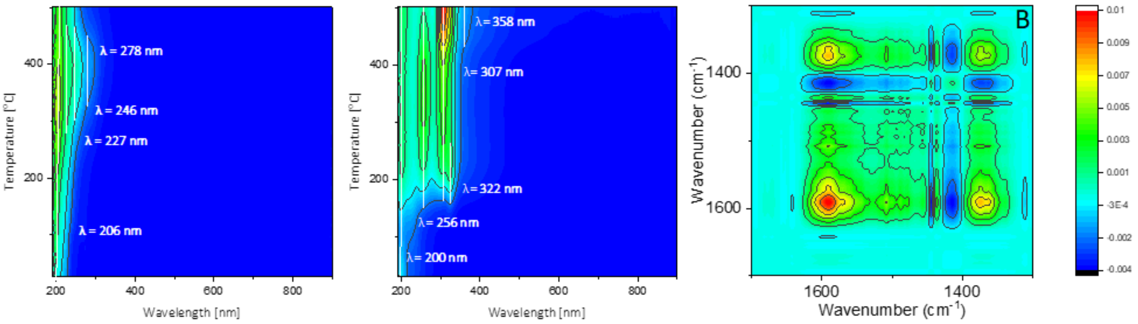
Kationy srebra wprowadzone do struktury zeolitu mogą stanowić centra aktywne w licznych reakcjach katalitycznych, jak aromatyzacja alkanów, alkenów czy metanolu [1]. Proces redukcji kationów Ag^+ do różnych form Ag^0, klastrów lub nanocząstek może mieć miejsce podczas ogrzewania w obecności CO, alkoholi i alkilobenzenów [2]. Natura centrów srebrowych w zeolitach silnie zależy od temperatury. Poniżej 400°C dominują izolowane kationy Ag^+, podczas gdy w wyższych temperaturach ulegają one agregacji.

Zmiany w naturze centrów srebrowych podczas procesów redukcji (10% H_2/He) i utleniania (10% O_2/He) badano w podwyższonej temperaturze (10°C/min, do 500°C) z zastosowaniem techniki UV-vis w trybie *operando*. Status centrów srebrowych wpływa na proces katalitycznej oligomeryzacji etylenu i aktywacji metanu, ponieważ kationy Ag^+ stanowią centrum pośredniczące w aktywacji metanu. Dodatkowo protonowe centra kwasowe są modyfikowane przez obecność centrów srebrowych o zróżnicowanej naturze. Wpływ obecności Ag^+ na oligomeryzację etylenu przeanalizowano dzięki spektroskopii 2D COS FT-IR, prowadząc reakcję w 375°C przez 10 godzin.

Podczas utleniania w podwyższonej temperaturze, redukcja Ag^+ do Ag^0 może zachodzić nawet w atmosferze czystego tlenu. W tym przypadku intensywność pasm znajdujących się w zakresie 220-250 i 280 nm (klastery Ag_m^+ i Ag_n^+, gdzie $m<n<8$) znacznie wzrasta ze wzrostem temperatury w przepływie powietrza. Z drugiej strony, wzrost temperatury w atmosferze wodoru prowadzi do utworzenia nowego rodzaju centrów srebrowych Ag_x^+ z niższym stopniem atomowości ($4<x<8$, 310 i 320 nm), czemu towarzyszy rozwój Ag_{NPs} (360 nm). Zeolit Ag-ZSM-5 podczas reakcji oligomeryzacji etylenu jest selektywny względem związków aromatycznych, m.in. 1,2,4-trimetylobenzenu (1505 cm^{-1}) i związków wielkocząsteczkowych, których drgania widoczne są jako pasma przy 1590 i 1570 cm^{-1}.



Rys. 1. Widma UV-vis zeolitu Ag-ZSM-5 podczas ogrzewania w utleniającej (po lewej) i redukującej (po środku) atmosferze. Mapa 2D COS widm FT-IR zarejestrowanych podczas oligomeryzacji etylenu z zastosowaniem Ag-ZSM-5 jako katalizatora.

Referencje

1. Tsutsumi, K.; Fuji, S.; Takahashi, H. J. Catal. 1972, 24, 8–17.
2. Aspromonte, S. G.; Mizrahi, M. D.; Schneeberger, F. A.; Ramallo Lopez, J. M.; Boix, A. V. J. Phys. Chem. C 2013, 117, 25433−25442

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P-23

Core-shell catalysts with various structure and composition for combustion of toluene

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The deepening problem of the 21st century is the increasing air pollution mainly from industrial processes and car exhaust. One of the main types of pollutants emitted into the atmosphere are harmful substances belonging to the group of volatile organic compounds (VOCs). The presence of these compounds in the environment has a negative impact on the life and health of living beings. Therefore, the main goal has become the reduction of concentration of these compounds in the atmosphere. An effective way to remove VOCs is their total oxidation to harmless products such as H_2O and CO_2. The greatest activity in this process is shown by catalysts based on noble metals and transition metal oxides. The interest in the latter ones stems from the observation that in some cases they exhibit higher catalytic activity and stability compared to noble metals. In addition, they are characterized by better availability and lower production costs. It has long been known that the catalytic activity and/or selectivity of catalysts in the oxidation reactions depend on size of particles, type of active phase and support, as well as its structural and textural properties [1,2].

In the presented work, an unusual type of materials was used, which, through its complex core-shell construction, opens up the possibility of better dispersion of an active phase and synergistic effect of a support. Typical supports of catalytically active phases, i.e. SiO_2 and TiO_2, were selected [3]. In turn, the active phase consisted of transition metal oxides - CuO and Co_3O_4. Using the bottom-up synthesis strategy based on previously prepared spherical polymer templates, i.e. diethyltriamine-functionalized poly(maleic anhydride) (MA-DETA) and polystyrene (PS), systems were constructed in which nanograins of the active phase were trapped in porous SiO_2 and TiO_2 shells. The synthesized materials were tested in terms of their phase composition (XRD), bulk and surface composition (XRF, XPS), chemical environment (UV-Vis-DR), porosity (low-temperature nitrogen adsorption), thermal stability (TG), reducibility (H_2-TPR), and morphology (SEM). Furthermore, the catalytic activity of the obtained materials was tested in the total oxidation of toluene, chosen as a model aromatic VOCs molecule. It was found that the highest activity and stability showed Co_3O_4@SiO_2 and CuO@TiO_2 systems. Their catalytic performance was discussed in comparison to commercially available materials. The advantages of using the yolk-shell structure were confirmed. Such catalyst structure, ensuring high dispersion of the active phase, allows it to be used more effectively in the tested process.

References

1. P. Kuśtrowski, A. Rokicińska, T. Kondratowicz, Adv. Inorg. Chem. 72 (2018) 385.
2. A. Rokicińska, T. Berniak, M. Drozdek, P. Kuśtrowski, Molecules 26 (2021) 3288.
3. Y. Zeng, Y. Zhan, R. Xie, K. Hu, J. Cao, D. Lei, B. Liu, M. He, H. Huang, Chemosphere 244 (2020) 125567.

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P-24

Spherical lignin-derived activated carbons for adsorption of phenol from aqueous media

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Today, contamination of surface water with organic compounds caused by human activity, together with atmospheric pollution, is one of the most serious environmental problems that needs to be resolved in the near future [1]. Among many organic pollutants, phenolic compounds deserve special attention. They are commonly used in the production of plastics, paints, dyes, and phenolic resins in the chemical industry. In addition to industry, households, agriculture, and large agglomerations also produce wastewater containing phenolic compounds [2]. Due to their toxicity, phenolic compounds can seriously negatively affect human health and the state of the environment. A quite attractive solution for removing phenolic pollutants from contaminated water is the use of adsorption techniques. Carbon materials obtained from various precursors, including biomass, can be used as effective adsorbents. Taking into account the difficulties in managing the excess amount of lignin produced, it seems reasonable to reach for this source of carbon.

In this work, kraft lignin was selected as the biomass source for the preparation of nanosized spherical activated carbon with a controlled grain diameter of 50-5000 nm. A simple way to obtain a spherical precursor from lignin involved its precipitation in a water:THF solution by changing pH. Furthermore, the spherical carbon precursor was subjected to dry chemical activation using $ZnCl_2$ or K_2CO_3 powders and carbonised at high temperature under N_2 atmosphere. The formed activated carbons were characterized in relation to their morphology (SEM). Figure 1 shows an SEM image of the carbon sample obtained from lignin activated by K_2CO_3.

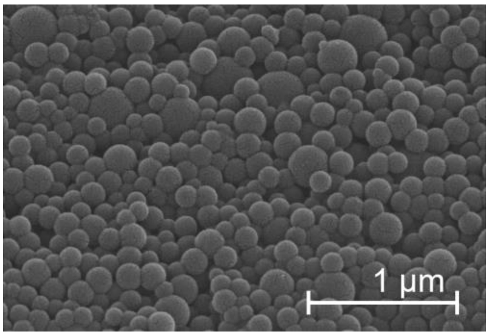

Fig. 1. SEM image of lignin-derived spherical activated carbon.

Moreover, structure (XRD), porosity (low-temperature adsorption of N_2), and surface composition (XPS) of the carbon materials were determined. The adsorption tests showed that the produced carbons exhibit an enhanced ability to adsorb phenol.

References

1. M. Choquette-Labbé, W.A. Shewa, J.A. Lalman, S.R. Shanmugam, Water 6 (2014) 1785.
2. B. Xie, J. Qin, S. Wang, Li. Xin, H. Sun, W. Chen, Int. J. Environ. Res. Public Health 17 (2020) 789.

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P-25

Immobilisation of CuNPs in MOFs structures via supercritical CO_2-assisted impregnation

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Recently, materials known as metal-organic frameworks gained great interest in academic society thanks to their unique properties and broad opportunities for application. They were successfully employed in different fields, i.e. as sorbents for gas storage and separation, catalysts, or drug carriers [1]. In this research, we concentrate on three MOF structures: UiO-66, MOF-808, and ZIF-8, and possibility of their employment as the catalysts in reactions of CO_2 conversion to methanol, cyclic carbonates, and dimethyl carbonate.

Metal-organic frameworks exhibit very promising physicochemical properties such as well-developed specific surface area, and good chemical and thermal stability. Moreover, they might be an object of a broad range of modifications done to improve their performance in catalytic processes. Modifying MOFs towards catalytical application usually involves embedding metal nanoparticles (NPs) – introducing additional active phase to the material, which is of significant importance while aiming for an increase of catalytic activity [2]. Obtaining NPs@MOF composites are mostly obtained with the employment of impregnation using different metal precursors and solvents. However, this straightforward approach has some serious drawbacks that may negatively impact the catalytic or adsorptive properties. The most significant is uneven dispersion of the introduced phase, eventually leading to the formation of the undesired large agglomerates on the outer surface of MOF. To eliminate those weaknesses a supercritical CO_2 (sc-CO_2) can be used as the solvent allowing deep penetration and even distribution of the metal nanoparticles in the MOF structure thanks to sc-CO_2's high diffusion coefficient, low viscosity, and zero surface tension [3].

In this work, we report a supercritical CO_2-assisted approach to obtain the UiO-66, MOF-808, and ZIF-8 composites with Cu nanoparticles for future application in the hydrogenation of CO_2 to methanol. Physicochemical properties such as the composition, morphology, and stability of the obtained materials were determined using X-ray diffraction, scanning and transmission electron microscopy, N_2 sorption, and thermogravimetric analysis.

References

1. K. Dymek, G. Kurowski, Ł. Kuterasiński, R. Jędrzejczyk, M. Szumera, M. Sitarz, A. Pajdak, Ł. Kurach, A. Boguszewska-Czubara, P.J. Jodłowski, ACS Appl. Mater. Interfaces 13 (2021) 45149-45160
2. P. Railey, Y. Song, T. Liu, Y. Li, Mater. Res. Bull. 96 (2017) 385-394
3. K. Matsuyama, M. Motomura, T. Kato, T. Okuyama, H. Muto, Microporous Mesoporous Mater. 225 (2016) 26-32

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P-26

Efekt NO w reakcji dopalania sadzy na katalizatorach KCo/FER

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Z uwagi na rakotwórcze oraz mutagenne właściwości sadzy, prowadzone są badania w celu skutecznego ograniczenia jej emisję w procesie katalitycznego utlenianie. Aktywne w tym procesie są katalizatory na bazie metali przejściowych tj. Co, Ni, Cu na nośnikach tlenkowych. Również, szeroko obserwowany jest pozytywny efekt dotacji alkaliami [2].

W prezentowanej pracy zoptymalizowano poziom dotacji potasem kobaltowego katalizatora na bazie ferierytu (Co/FER) w oparciu o pomiary pracy wyjścia badanych układów. Kobalt naniesiono poprzez impregnację w ilości ok 15% wag., oraz katalizatory dotowane potasem w ilości 0-8%wag. Otrzymane układy zostały poddane charakterystyce fizykochemiczne (XRF, XRD, H_2-TPR, SEM/EDX), zmierzona została zmiana pracy wyjścia pod wpływem dotacji K metodą Kelwina oraz desorpcja termiczna potasu metodą SR-TAD. Dodatkowo zbadano efekt NO obecnego w strumieniu gazów. W warunkach mieszaniny 5%O_2/He, zarówno w warunkach *tight contact* jak i *loose contact* najaktywniejszy okazał się katalizator 4K Co/FER, który jednocześnie charakteryzował się największym obniżeniem pracy wyjścia Co/FER oraz przebiegiem krzywych desorpcji, wskazującym na najlepszą dyspersją potasu. Badania katalizatorów Co/FER oraz 4K Co/FER w obecności NO (*loose contact, 3,3%*O_2*/0,33%NO/He*) wykazały odmienny efekt tego gazu, zależny od obecności K. Dla katalizatora Co/FER zauważalny jest pozytywny wpływ tlenku azotu(II), natomiast dla katalizatora 4K Co/FER z potasem na powierzchni wpływ ten jest negatywny. Obserwowany efekt wyjaśniono w oparciu o szczegółowe badania XPS oraz IR katalizatorów na różnym etapie procesu.

Referencje:

[1] CR Shaddix, et al., International Journal of Heat and Mass Transfer, 48, 2005, 3604-3614.P.
[2] Legutko, T. Jakubek, W. Kaspera, P. Stelmachowski, Z. Sojka, A. Kotarba, Topics in Catalysis 60 (2017) 162–170.

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P-27

FT-IR/PAS as a tool for solids characterization

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Since the discovery of the phenomenon of absorption of infrared radiation of a frequency corresponding to that of vibrations of particular chemical bonds, IR spectroscopy has gained much attention as a valuable tool for characterization of adsorbents and catalysts.

Fourier Transform Infrared Photoacoustic Spectroscopy (FT-IR/PAS) is one of the types of classic Infrared Spectroscopy (IR), which is based on recording the pressure changes in a measuring cell, caused by vibrations of particular bonds, triggered by periodically changed wavelengths of infrared radiation (Fig. 1). The main advantages offered by FT-IR/PAS technique are the possibility of characterization of non-homogenous or opaque materials and no need of samples dilution.

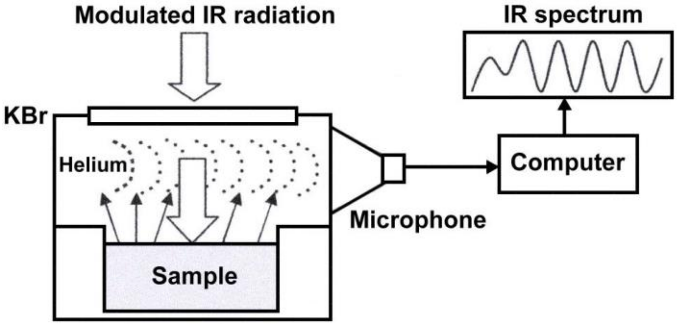

Fig. 1. Scheme of a typical photoacoustic cell [1].

Although, FT-IR/PAS analysis is not as extensively used analytical tool as IR in absorbance/transmittance mode or in DRS (Diffuse Reflectance Spectroscopy), it finds many interesting applications (investigation of soil, wood, biochar and coffee constituents, monitoring of demineralization and deproteination of dentin or identification of several inorganic pigments in cultural artefact, determination of distillation fractions of heavy gas oil). Much attention has been paid to the use of FT-IR/PAS technique for the analysis of hybrid materials, which are a group of promising multicomponent substances finding various applications, e.g. as catalysts, adsorbents, novel tools for quantitative analysis [2-6].

Recent examples of this spectroscopic technique application will be presented as well as some limits of its use.

References

1. C. Du, J. Zhou, Environ. Chem. Lett. 7 (2009) 97
2. J. Ryczkowski, Catal. Today 124 (2007) 11
3. J. Kurczewska, J. Ryczkowski, S. Pasieczna-Patkowska, G. Schroeder, Spectrosc. Lett. 49 (2016) 529
4. P. Pączkowski, M. Grochowicz, A. Chabros, B. Gawdzik, J. Ryczkowski, Polymer Testing 76 (2019) 173
5. M. Pawlaczyk, S. Pasieczna-Patkowska, J. Ryczkowski, G. Schroeder, Vib. Spectrosc. 103 (2019) 10294
6. K. Kucio, B. Charmas, M. Zięzio, S. Pasieczna-Patkowska, Physchem. Problems Mineral Proc. 58 (2022) 4

P-28

TD-DFT studies on photochemical properties of the platinium carbonyl Chini clusters

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Chini clusters of general formula $[Pt_3(CO)_6]_n^{2-}$ (where n = 1-10 usually) display attractive properties as precursors of catalysts and nanostructures like nanoparticles and nanowires. They can be used as coatings for photocatalytic TiO_2 particles or fluorescent quantum dot, because they display characteristic UV−visible absorption spectra with two bands in the visible and a remarkable dependence on the nuclearity number n. The objective of the present research is to study geometry and electronic properties of the Chini clusters $[Pt_3(CO)_6]_n^{2-}$, where n = 1-7, as well as to model their photochemical properties.

To do so, we performed quantum-chemical calculations in the frame of Density Functional Theory (DFT) with B3LYP and CAM-B3LYP functionals. The 6-31G(d,p) basis sets for C and O while LANL2DZ pseudopotentials for Pt were used. The calculations were done with Gaussian 16 program package.

The geometries of the systems were determined (see Figure 1): Pt-Pt distance within one unit is equal to 2.75 Å while the separation between Pt_3 triangle units is ca. 3.15 Å, in a reasonable agreement with the XRD data. The theoretical spectra show that the cluster have three intensive absorption spectra at ca. 300, 400, and 600 nm. Their intensity as well as the exact position varies depending on the nuclearity n. The analysis of the clusters' orbitals allowed to determine the character of the excitations.

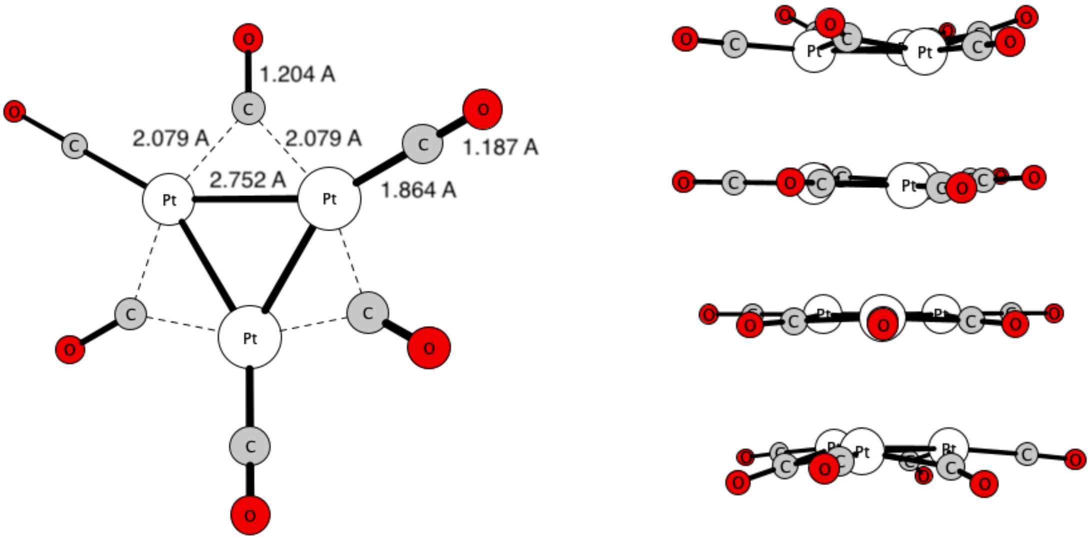

Fig. 1. Geometry of the basic unit of the Chini complex with the typical bond lengths (left) and the structure of the four $[Pt_3(CO)_6]^{2-}$ units (right).

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P-29

Controlled radical copolymerization of monovinyl and divinyl monomers: A computer simulation study

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A simple model for the copolymerization process was developed [1]. The formation of branched (stars, hyperbranched polymers, and dendrimers) and cross-linked macromolecular systems was studied. Coarse-grained chains were embedded in the vertices of a face-centered cubic lattice with excluded volume interactions implying good solvent conditions. A living copolymerization of monovinyl and divinyl monomers was carried out in bulk, in a slit, and for chains grafted in a slit. Monomer, cross-linker and initiator were initially randomly distributed in the system but in the case of grafted chains initiator molecules were randomly anchored to one confining walls of the slit. The simulations of the copolymerization processes were performed using the Dynamic Lattice Liquid algorithm, a version of the Monte Carlo method based on the concept of cooperative motion of objects in dense systems [2]. The kinetics of the polymerization process was determined and it was shown that all the studied architectures exhibit low dispersity although it is higher for hyperbranched macromolecules. [1, 3]. The influence of the initial initiator to cross-linker ratio, slit width and grafting on copolymerization and gelation was studied. It was also found that the influence of a confining slit was rather small, while the grafting of chains influenced the location of the gel point significantly especially for wider slits [4].

References

1. P. Polanowski, K. Hałagan, A. Sikorski, Polymers 14 (2022) 2522.
2. Pakula, T. Simulation on the Completely Occupied Lattices, In: Simulation Methods for Polymers, M. Kotelyanskii, D. N. Theodorou, Eds., Marcel Dekker, New York, NY, USA, 2004.
3. P. Polanowski, K. Hałagan, A. Sikorski, Comput. Methods Sci. Technol. 28 (2022), 109.
4. P. Polanowski, A. Sikorski, Int. J. Mol. Sci. 24 (2023), 2701.

P-30

The influence of the active phase composition, reaction temperature and oxidation state on the Cu-Fe catalysts activity, selectivity and stability in the steam reforming of methanol

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Hydrogen is considered the fuel of the future. It is a clean energy source that does not emit CO_2, CO, SO_2, NO_x, particulate matter or hydrocarbons, unlike fossil fuels. More and more stringent environmental regulations mean that there is a growing interest in the use of hydrogen as a fuel for fuel cells, where it is converted into useful electricity, which could then be used in stationary applications or in electric vehicles. Among the many methods proposed for the production of hydrogen, the most common and energy efficient catalytic process is steam reforming of methanol (SRM) $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$. During the conversion of methanol with steam, under the most favourable process conditions, as much as three moles of hydrogen can be obtained from one mole of methanol. The production of hydrogen as a result of the conversion of methanol with water is a process that requires a properly selected catalytic system. There are a number of possible pathways in the methanol steam reforming process which may lead to the generation of undesirable products depending on the reaction conditions, the methanol/water ratio, the temperature and in particular the catalytic properties of the catalyst used. In order to obtain a complete and selective conversion of methanol steam reforming, it becomes important to develop a specific and efficient catalyst system. Therefore, the best catalyst for SRM should be stable, active and selective to the most desirable products (H_2 and CO_2) under the process conditions. The most commonly used catalysts in the steam reforming of methanol are mainly copper-based systems, as well as metals of 8-10 groups of the periodic table. Copper catalysts show high activity and selectivity to hydrogen in low-temperature SRM, and are also a cheaper alternative to noble metals. Nevertheless, copper-based catalysts have pyrophoric properties and are deactivated by thermal sintering. One way to improve the stability of these systems and reduce their costs is to add a second or more metals, usually from 8-10 groups of the periodic table, which show better stability, good selectivity to hydrogen, but lower methanol conversion compared to the copper catalyst. Fe is demonstrated to be an effective species to improve the stability of Cu particles on the surface in the SRM. The presence of Fe species can improve the dispersion of copper by inhibiting the copper-sintering and this way improve activity of catalyst. The aim of this work is determination of the relationship between active phase composition, process temperature, oxidation state and the conversion of reactants, selectivity, stability of Cu-Fe/CeO_2 catalysts in the SRM.

Catalysts with different Cu and Fe content with CeO_2 support were prepared by the impregnation method. The catalytic tests showed that the phase composition and oxidation state of the active phase metals of catalysts differed depending on the form in which the catalysts were characterized, as well as on their reduction temperature. Isothermal catalytic tests (at 260°C) of Cu-Fe/CeO_2 catalysts showed that the addition of iron to the monometallic copper catalyst improved its stability in the SRM. A decrease in the selectivity of SRM to carbon monoxide was also observed. Furthermore, the addition of iron to the monometallic copper catalyst increased the selectivity of the process towards the WGS (water gas shift) reaction: $CO + H_2O \rightarrow CO_2 + H_2$. All of the tested systems showed 100% selectivity to H_2 and CO_2 in the SRM.

P-31

Operando FTIR methodology in chemical recycling of plastics

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Plastic films are polymers made from crude oil, not recyclable biologically. Apart from landfilling, incineration and mechanical recycling are standard solutions, however accompanied by loss of plastic quality and emission of toxic compounds. Depolymerization back to the original monomers is ideally the best approach to chemical recycling and is already taking place for some polyamides and polyesters. It is not yet the case for polyolefins, although they contribute significantly to plastic waste. Recycling by thermal and catalytic cracking is a promising approach with low environmental impact, high feasibility, and profitability. Pyrolysis process was the largest technology segment of the global recycled plastic and plastic waste to oil market, still producing a broad range of hydrocarbons requiring further processing to meet the requirements of transportation fuels or higher value (petro)chemicals. Catalysis has a role to play in solving such an important environmental challenge. Catalytic chemical recycling, for instance, could bring a combination of higher activity and better selectivity control (narrower product distribution requiring less downstream processing) while working under milder operating conditions (e.g., temperature).

The main objective of this research was to develop further technology of plastics waste conversion to valuable products which can serve as feedstock to an oil refinery, additives to fuel or semi-products for chemical industry. Inspection into interaction of polymer chain and catalytically active surface sites is a precondition for defining the catalysts properties - the catalyst’s activity relationship and, at the final step, designing the zeolite catalysts with targeted performance and maintenance.

A series of medium pore zeolites of various topologies and pore hierarchy (microporous vs. hierarchical) were studied in the catalytic cracking of polypropylene and polyethylene in the framework of their chemical recycling. Two important zeolites features impact their catalytic performances and allow them to be designed as efficient catalysts: their porosity and acidity. The latter also play a key role in catalyst deactivation and regeneration. Comprehensive thermogravimetric ,UV-vis and IR *operando* spectroscopic analysis of the cracking, coking and catalyst regeneration processes, indicated the rules for the active catalyst design.

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P-32

Hydrocracking of rapeseed oil on bimetallic Ni-Ce/ZSM-5 zeolite catalysts – the method for biofuel production

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Hydrocracking of vegetable oils is considered as a promising method for obtaining a range of biofuels (e.g., green diesel) that can have similar characteristics to conventional diesel [1,2]. This provides the possibility of direct application of the fuel thus produced into existing infrastructure without modification [1]. Hydrocracking process converts triglycerides from vegetable oils into hydrocarbon-containing biofuels including n-paraffins, isoparaffins, cycloparaffins, aromatics and olefins [2,3]. This method of biofuel production requires higher temperatures to break the bonds of triglycerides from vegetable oils in comparison with the transesterification reaction, however, the products created by the process feature a higher cetane number and higher oxidative stability [4].

The purpose of this study was to examine the catalytic and physicochemical properties of nickel catalysts with ceria addition supported on HZSM-5 zeolite in the hydrocracking process of commercial rapeseed oil. The physicochemical properties of the obtained catalytic systems were investigated using following techniques: H_2-TPR, TPD-NH_3, XRD, BET. The catalytic activity tests were performed in an autoclave (reactor capacity of 50 mL) with a mechanical stirrer. All experiments were carried out for 2 hours at 300°C and 325°C at 75 bar H_2. Before the catalytic tests, systems were calcined at 600°C for 4 h and reduced at 500°C for 1 h in a 5% H_2-95%Ar mixture at the flow rate of 50 cm^3/min. The amount of catalyst used was about 1% by weight of oil in each catalytic activity test. The reaction products obtained in the process were analysed using an HPLC chromatograph with a DAD detector to determine triglyceride conversion (TG). Selectivity of the products was determined by gas chromatography coupled to mass spectrometry (GC-MS). The obtained activity results indicate that cerium has a beneficial effect on catalytic activity of nickel catalysts. The introduction of cerium on the HZSM-5 zeolite improved triglyceride conversion compared to the unmodified zeolite, while bimetallic Ni-Ce systems have significantly better conversion than monometallic catalysts. The highest oil conversion (95.6%) was obtained over 5%Ni-15%Ce/HZSM-5 system containing the smallest amount of nickel by weight, but the highest amount of cerium during the process performed at 300°C. Hydrocracking products were hydrocarbons containing from 7 to 33 carbon atoms in the molecule (C_7-C_{33}).

References

1. B. Al Alwan.; S.O. Salley; K.Y.S. Ng, Applied Catalysis A: General 485, (2014), 58-66
2. X. Yang; J. Liu; K. Fan; L. Rong, Scientific Reports 7, (2017), 41654
3. A.N. Aini; M. Al-Muttaqii; A. Roesyadi; F. Kurniawansyah, Key Engineering Materials 884, (2021), 149-156
4. C. Liu; J. Liu; G. Zhou; W. Tian; L. Rong, Journal of the Taiwan Institute of Chemical Engineers 44, (2013), 221-227

P-33

The efficiency of hydrotalcite-derived materials in selective hydrogenation processes

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Current pharmaceutical production routes still generally use stoichiometric amounts of soluble reagents. However, the increasing pressures on resources and the environment drive a search for more sustainable alternatives, including the transition from batch to continuous and from stoichiometric to catalytic processes [1,]. Our work follows this trend.

The main goal of our study was the continuous flow synthesis of vitamins A, E and B6 and medicines precursors with CuZnAl hydrotalcite-derived materials as catalysts. Three catalysts with different Cu loading were investigated in the semi-hydrogenation of two unsaturated alcohols: 2-methyl-3-butyn-2-ol and 2-butyne-1,4-diol and chemoselective hydrogenation of 2-methyl-2-pentanal, at the wide range of temperatures and pressures. Hydrotalcite-derived materials showed high activity and stability in hydrogenation. Product distribution strongly depended on the metal loading.

The thorough characterization of catalysts by various physicochemical methods allowed to creation of a relationship between the structure and reactivity of hydrotalcite-derived materials. 100% of the selectivity toward desired products, 2-metyl-3-buten-2-ol, 2-butene-1,4-diol and 2-methylpentanal were obtained at mild reaction conditions.

References:

1. F.J. A. G. Coumans, Sh. Mitchell, J. Schütz, J. Medlock, and J. Pérez-Ramírez, ACS Omega 3, 11 (2018) 15293–15301
2. A.J. Fernández-Ropero, B. Zawadzki, K. Matus, W. Patkowski, M. Krawczyk, D. Lisovytskiy, W. Raróg-Pilecka, A. Śrębowata, Catalysts 12 (2022) 19

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P-34

Effect of the support composition on catalytic and physicochemical properties of cobalt-based catalysts in the steam reforming of ethanol

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The amount of research focusing on environment-friendly and sustainable energy sources has increased substantially in the last decades due to growing concerns about environmental problems and the diminishing availability of fossil fuels. Hydrogen appears to be one of the most promising energy vectors as it is considered to be environmentally benign. The amount of energy produced during hydrogen combustion is higher than that evolved by any other fuel on a mass basis, with a low heating value that is 2.4, 2.8 and 4 times higher than that of methane, gasoline or coal, respectively. There are four basic methods for hydrogen production: water electrolysis, a gasification reaction using coal and coke as the feedstock, a partial oxidation reaction using heavy or residual oil as the feedstock, and steam reforming using different kinds of hydrocarbons as the feedstock. Among the oxygenated hydrocarbons, ethanol is regarded as an important candidate for hydrogen-producing in the steam reforming process because is not hazardous and can be produced economically and sustainably in large amounts from biomass such as agriculture wastes or forestry. Different catalytic systems have been investigated for the steam reforming of ethanol (SRE), including both precious metals and non-noble metals. Among the different metals studied, cobalt-based catalysts were found to have high C—C bond activity in the SRE process. Moreover, also the support is essential in the synthesis of efficient catalysts of SRE reaction since it helps in the distribution of metal in the catalyst and enhances its activity via metal-support interactions.

Considering the above points, the purpose of the present work was to study the performance of the Co/CeO_2, Co/MnO_x and CeXMn (where $X(\%mol)=nCe/(nCe+nMn)\cdot 100\%$) catalysts under an SRE reaction and to determine the role of the support composition on the stability and resistance to carbon deposit formation. The catalysts were prepared by the impregnation method and characterized using several techniques in order to study their textural, structural, and redox properties before being tested in an SRE reaction. The BET surface area of cobalt-based catalysts was found to be the highest for the Co/CeO_2 sample and decreased with increasing MnO_x amount. Moreover, the reduction temperature of CoO_x gradually shifted to a higher value with the increase in the MnO_x amount, indicating that the presence of MnO_x made the reduction process of CoO_x phase more difficult The best performance in the SRE process among the tested catalysts showed the Co/CeO_2, exhibiting the highest ethanol conversion, selectivity to the two most desirable products and the lowest selectivity to by-products in comparison with catalysts containing MnO_x.

References

1. K. Wang, B. Dou, B. Jiang, Y. Song, C. Zhang, Q. Zhang, H. Chen, Y. Xu, Int. J. Hydrogen Energy 41 (2016) 12899-12909.
2. H.F. Abbas, W.M.A. Wan Daud, Int. J. Hydrogen Energy 35 (2010) 1160-1190.
3. H. Idriss, Platinum Metals Rev. 48 (2004) 105-115.

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P-35

Microwave-activated hybrid composites based on clay minerals for CO_2 capture - SEM/EDS and spectroscopic studies

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As many indications point out, an increase in greenhouse gas emissions into the atmosphere cause the global warming and climate change. The main reason for their formation is the excessive use of fossil fuels, rapid industrialization and urbanization. Among the gases that have been identified as a major cause of these changes is carbon dioxide, which level in the atmosphere is rising at an alarming rate. Therefore there is a continuous need for the development of novel materials that can be used for CO_2 capture. Clay mineral-derived composites can be considered strong candidates for CO_2 removal due to their easy accessibility, susceptibility to modification, high structural stability even up to 700°C and the safety of the environment in which we live.

The inspiration for this work was our previous studies which showed that clay minerals are sensitive to an acidic environment, which contributes to the release and some mobility of the octahedral sheet ions from the structure. In this work we focused on the detailed study of the structural transformation of layered hydrous magnesium silicate, Laponite with the structural formula $[Si_8Mg_{5.45}Li_{0.4}O_{20}(OH)_4]Na_{0.7}$ in the formed porous crystalline-amorphous composite during benign proton attack applied upon impregnation with a slightly acidic salt solution. A series of porous clay-based composites were treated with iron nitrate solution under mechano-chemical doping and activated by microwave radiation, and comparatively investigated towards the formation of basic centres active in CO_2 sorption. The modification had a significant impact on the surface composition of the sorbents and brought about the formation of safe Mg and Fe oxides. In this work, the mechanisms (Fig.1) leading to nucleation and formation of basic centres on the PCH surface are described in detail with the use of XRD, SEM/BSE/EDS, FTIR, XPS, TG/DSC, CO_2-TPD methods. The difference in surface basicity and contribution of surface species in the efficient sorption of CO_2 molecules as well as the mechanism of CO_2 sorption on these centres are discussed.

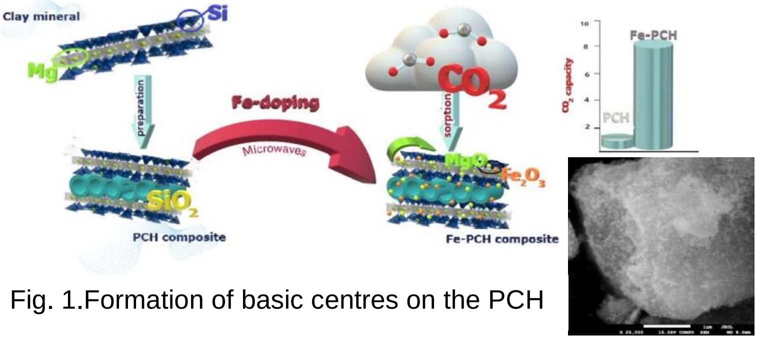

Fig. 1.Formation of basic centres on the PCH

References

1. M. Zimowska, M. Śliwa, H. Pálková, J. Gurgul, R. P. Socha, Applied Surface Science 619 (2023) 156768

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P-36

Structure evolution of perovskite-type $YF_{e0.5}Co_{0.5}O_3$ triggered by the calcination temperature

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Perovskites with a general formula ABO_3 (A – Y or rare earth element, B – 3d transition metal) have been intensively studied in recent years due to their interesting magnetic, magneto-optical, electrical, and many other properties [1]. Among them, the most promising are the well-known simple perovskites $YFeO_3$ and $YCoO_3$. $YFeO_3$ crystallizes in a distorted perovskite structure with Y^{3+} in A-sites and Fe^{3+} in B-sites surrounded by six oxygens. The crystal structure of $YFeO_3$ heavily depends on the method of synthesis and sintering. At present, three structural yttrium orthoferrite modifications are reported: orthorhombic o-$YFeO_3$ (*Pbnm*), hexagonal h_2-$YFeO_3$ (*P63/mmc*), and amorphized hexagonal <h_1>-$YFeO_3$ (*P63cm*). The polymorphism of yttrium orthoferrite is explained based on the ionic radii ratio. In the case of $YCoO_3$ distorted perovskite, the crystal structure with orthorhombic symmetry (space group *Pbnm*) has been determined from the powder neutron diffraction data by Mehta et al. [2]. The synthesis and crystal structure determination of $YCo_{1-x}Fe_xO_3$ (x = 0, 0.33, 0.5, 0.67, and 1) was reported by Dimitrovska-Lazova et al. [3]. Much better quality and crystallinity of isomorphous samples were obtained by using citric acid as a fuel in a solution combustion method. The crystal structure of all perovskites was determined to be orthorhombic with *Pnma* space group, however, some deviations from the ideal perovskite structure were found. With increasing iron content, the deformation of octahedra as well as the increase of octahedra tilting angles have been reported, which leads to better stabilization of the perovskite structure.

Here we present the synthesis of $YCo_{0.5}Fe_{0.5}O_3$ at several temperatures and analyze in detail, its crystal structure and morphology (Fig. 1). Some preliminary ^{57}Fe Mössbauer spectroscopy results are also presented.

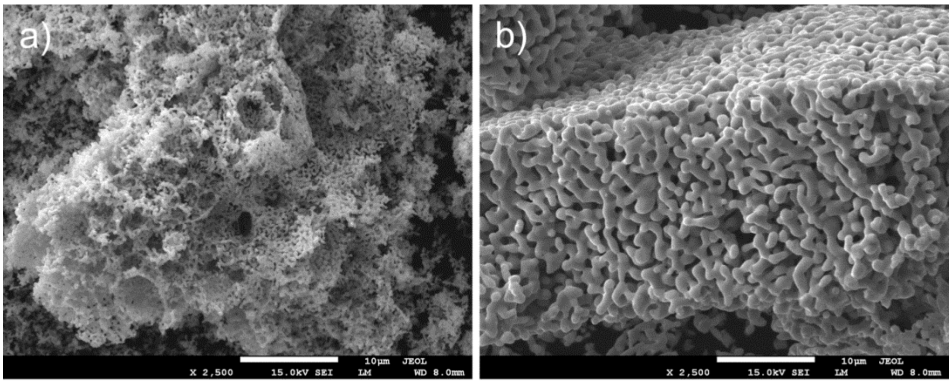

Fig. 1. The morphology of YFeCo-1:0.5:0.5-cit sample calcined at 950 °C (a) and at 1100 °C (b).

References

1. A. Benali, M. Bejar, E. Dhahri, M. Sajieddine, M. P. F. Graca, M. A. Valente, Mater. Chem. Phys. 149-150 (2015) 467-472.
2. A. Mehta, R. Berliner, R. Smith, J. Solid State Chem. 130 (1997) 192-198.
3. S. Dimitrovska-Lazova, S. Aleksovska, P. Tzvetkov, J. Chem. Sci. 127 (2015) 1173-1181

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S-1

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Skorzystaj z zalet wszechstronnej platformy XRDynamic 500 obejmującej szerką gamę zastosowań z optymalnymirozwiązaniami dla dyfrakcji proszkowej, XRD poza warunkami otoczenia, analizy PDF, SAXS i wielu innych.

Najwyższa jakość pomiarów dyfrakcyjnych - Nowoczesny i zautomatyzowany dyfraktometr proszkowy XRDynamic 500 zapewnia najwyższą dostępną jakość pomiarów w swojej klasie za sprawą implementacji nowatorskich koncepcji. Wysoka rozdzielczość zagwarantowana jest dzięki szerokiemu promieniowi goniometru oraz zapewnieniu próżni na ścieżce optycznej wiązki rentgenowskiej. Doskonały stosunek sygnału do szumu wynika z powstrzymania rozpraszania wiązki przez powietrze, pozwalając na otrzymywanie doskonałej jakości dyfraktogramów nawet dla najbardziej złożonych próbek proszkowych.

Przystawki do badań poza warunkami otoczenia - XRDynamic 500 jest wszechstronną platformą idealnie współpracująca z przystawkami do badań dyfrakcyjnych poza warunkami otoczenia. Przeprowadzanie badań strukturalnych próbek w warunkach zmiennej temperatury, atmosfery, wilgotności czy napięcia nigdy nie było prostsze. Zmiana konfiguracji urządzenia oraz projektowanie eksperymentów non-ambient jest niezwykle wygodne. Przystawki sa automatycznie rozpoznawane i w pełni sterowalne z poziomu oprogramowania sterującego dyfrakometrem.

Analiza danych - XRDanalysis jest nowoczesnym pakietem oprogramowania do przeprowadzania analizy danych dyfrakcji proszkowej w oparciu o najdokładniejsze modele matematyczne. Program umożliwia bezproblemową i szybką identyfikację/kwantyfikacje faz, analizę mikrostruktury, obróbkę danych z eksperymentów w warunkach otoczenia jak i poza nimi. Przejrzysty interfejs wspiera nowych użytkowników XRD jednocześnie nie nakładając ograniczeń dla użytkowników zaawansowanych.

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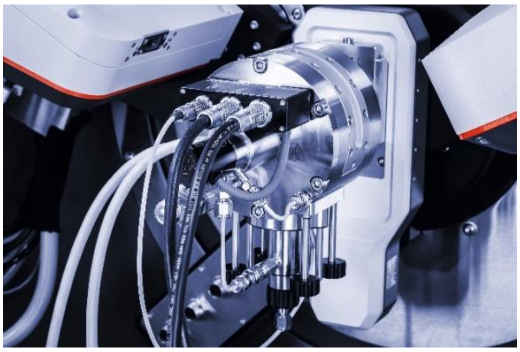

S-2

Aparatura do pomiarów powierzchni właściwej, rozkładu wielkości porów oraz właściwości katalizatorów metodami adsorpcji gazowej i chemisorpcji

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Linia produktów amerykańskiej firmy **Quantachrome Instruments,** założonej w 1968r i znanej jako topowa marka na świecie w dzidzienie aparatury badawczej do charakteryzacji materiałów porowatych., obecnie należąca 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, charakeryzacji własności katalizatorów, farmaceutyków, a także komponentów do produkcji baterii oraz wielu innych materiałów porowatych.

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 do 1100µm.

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