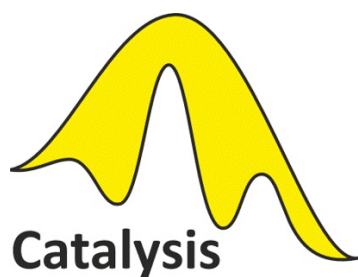


17th Pannonian International Symposium on Catalysis

7. – 11. 9. 2026, Hotel Kamzík, Malá Morávka, Czech Republic



Book of abstracts

Preface

This Book of Abstracts contains contributions presented at the 17th Pannonian International Symposium on Catalysis (PISC 2026), held from September 7–11, 2026, at Hotel Kamzík in the Jeseníky Mountains, Czech Republic.

Organized by the Catalysis Division of the Czech Chemical Society, PISC 2026 continues the long-standing tradition of biennial meetings held in the Pannonian region, bringing together the catalysis communities of Austria, Czechia, Hungary, Poland, Romania and Slovakia. Over the years, the PISC series has established itself as an important forum for scientific exchange and collaboration in catalysis, connecting established researchers with early-career scientists and providing opportunities to discuss both fundamental and applied aspects of the field.

The contributions collected in this volume reflect the broad scope and interdisciplinary character of contemporary catalysis research. They cover a wide range of topics, including fundamental aspects of catalytic reactions and mechanisms, catalyst preparation and characterization, advanced catalytic materials, reaction engineering, photo- and electrocatalysis, environmental catalysis, and the development of sustainable catalytic processes. The presented work demonstrates the diversity of approaches currently shaping the field and highlights the important role of catalysis in addressing current and emerging challenges in clean energy, environment protection, and sustainable chemical production.

We believe that this collection of abstracts provides a valuable overview of the scientific programme of PISC 2026 and will serve as a record of the ideas, results, and discussions presented at the symposium. At the same time, we hope that it will contribute to further scientific exchange and collaboration within the catalysis community.

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David Kubička, Lucie Obalová

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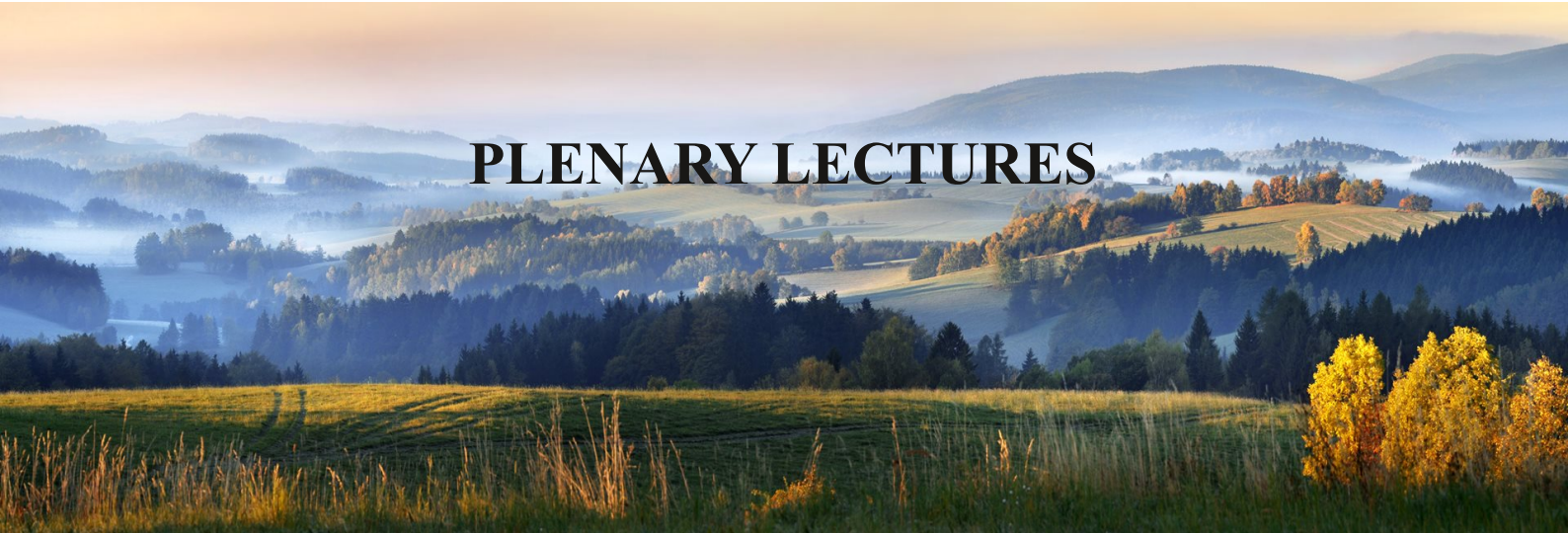
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PLENARY LECTURES

Perspectives for Academic–Industrial Research in Development and Scale-up: Show Case — Selective Oxidation Catalysts

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Heterogeneous catalysts, Academic-Industrial Collaboration, Catalyst Development, Catalyst Scale Up, Reproducibility and Repeatability

The presentation addresses the fundamental challenges and gaps that define successful collaboration between academic research and industrial catalyst development, using the selective catalytic oxidation of o-xylene to phthalic anhydride (PA) over supported vanadia (V/TiO_2) catalysts as a detailed case study.

The industrial reality of heterogeneous catalysis is framed through three inescapable "Fundamental Laws": (1) Money — economic viability must be maintained; (2) ESHA — Environment, Safety, and Health considerations are non-negotiable constraints; and (3) Quality — the ability to repeatedly and reproducibly manufacture a catalyst with identical properties constitutes the core industrial imperative. Beyond these fundamental laws, industrial catalyst R&D is governed by eleven mandatory tasks, ranging from mass balance closure for all steps of catalyst synthesis, the determination of the reaction kinetics and energetics of all preparation steps, and the waste stream quantification, to preparation equipment selection and finally statistically verified quality control.

The chosen showcase — the PA catalyst — is a shell-type supported vanadia catalyst, with the VO_x/TiO_2 active mass (plus promoters) coated on inert steatite ring carriers, which sounds easy and straightforward, but it is not, as will be shown. The industrial PA process employs axially layered catalyst beds of 3 to 7 layers (depending on manufacturer), where each layer is deliberately engineered with a distinct activity/selectivity profile to manage the strongly exothermic reaction, control hotspot formation, and ensure both high conversion and product quality. This level of reactor-catalyst co-design rarely features in academic research but is central to industrial reality. Furthermore, kinetic analysis using the Weisz–Prater criterion confirms serious pore diffusion limitations, making the catalyst shell thickness a decisive and tightly controlled design parameter — a level of engineering rigour that academic catalyst studies frequently overlook as they mostly focus on powder catalysts only.

Bridging laboratory findings to industrial reality requires a catalyst synthesis as well as performance testing infrastructure that is itself of near-industrial scale. On the synthesis side of the PA catalyst, the industrial coating process employs a toroidal, moving-bed coater — specialised medium to large-scale equipment with no academic equivalent — to deposit a precisely controlled active shell (50 μm) of VO_x/TiO_2 onto steatite carriers. The presentation poses the critical questions directly: Do we really know what happens here? Can we really control the processes? Do we repeatedly and reproducibly make the same catalyst? These are not rhetorical — they remain genuinely open. Reproducing this synthesis at laboratory scale, with bench-scale equipment and chemicals frequently used at lab scale but unavailable in tonne quantities, does not answer them. On the performance testing side, pilot units of industrial tube dimensions, molten-salt cooled, with test campaigns typically lasting three to six months are required to generate data that is actually predictive of industrial behaviour. Both constraints — synthesis and testing

infrastructure — are largely absent from academic research programmes, and this absence defines the most critical practical boundary between the two worlds.

The active VO_x surface species are not pre-formed during catalyst production but emerge *in situ* in the reactor during calcination, reactor start-up, and the break-in period, raising fundamental questions about the atomic processes that occur at the catalyst surface, and their reproducibility in relation to reactor and process control. Only *operando* spectroscopic investigations under realistic process conditions and recorded along the roughly 4 m long catalyst bed could provide the needed information on the atomic surface chemistry and thus generate true knowledge.

The overarching message to the academic community is therefore clear: understanding catalyst surface complexity, mastering *in situ* and *operando* spectroscopic characterization during all steps of catalyst production and operation, rigorously addressing reproducibility issues, and engaging with the full engineering complexity of the real reactor system are the most impactful areas where academic contributions can meet pressing industrial needs.

Pyrolysis Oil as a Circular Feedstock: Thermocatalytic and Photocatalytic Routes and Reaction Engineering Challenges

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Keywords: aromatization reactions; partial oxidation, photocatalytic oxidation; styrene; cresols

Pyrolysis involves the thermal treatment of organic materials, typically specific waste fractions such as lignocellulosic or polymeric wastes, under non-oxidising conditions, producing mainly a liquid product known as pyrolysis oil. Although pyrolysis technologies have been known for decades, their relevance has increased significantly in recent years due to two main drivers. First, they offer an attractive route for the management of municipal, agricultural, and plastic wastes, whose landfilling or incineration is becoming increasingly restricted because of environmental concerns [1]. Second, pyrolysis oils have emerged as promising alternative carbon feedstocks for the production of fuels and chemicals, contributing both to industrial decarbonisation and to the circular economy by replacing fossil-derived raw materials. Depending on the feedstock, pyrolysis oils exhibit very different compositions and properties. Two major categories can be distinguished: biomass-derived pyrolysis oils (BPOs) and plastic-derived pyrolysis oils (PPOs). BPOs are rich in oxygenated and phenolic compounds, which reduce oil stability and its quality as a direct fuel, whereas PPOs generally contain lower oxygen contents and higher aromatics concentrations, but also significant amounts of olefins and organochlorinated compounds. In addition, both types of oils typically contain moisture, salts, and other heteroatomic species that complicate downstream processing and upgrading [2,3].

Although these oils are currently processed in oil refineries to increase the circular character of the manufactured chemicals and fuels, the development of more specific approaches would be useful for increasing the economic value of these oils, with the subsequent increase in the attractiveness of the pyrolysis for waste management. Two general approaches can be considered for fulfilling this scope: the direct use of these oils as feedstocks for obtaining high-performance oils (aromatic oils for pitch manufacture, dielectric oils, hydrogen chemical storage, etc.) or the selective extraction of chemicals from the oils (styrene, phenols, cresols, etc.), which can be used as raw materials for manufacturing chemicals. The oxidative transformation of o-cresol into salicylic acid (which can be performed using both thermochemical and photochemical approaches) or the manufacture of naphthalene from styrene (recovered from polymer pyrolysis oil) will be considered key examples in this lecture.

Both approaches present major challenges. For the use of the whole pyrolysis oil as a raw material, the main issues are due to the complex nature of the pyrolysis oils. Even considering only those oils coming from polymeric wastes (relatively rich in aromatic compounds and poorer in oxygenated organics than biomass-derived oils), the oxygen content is not negligible, and the chlorine content could be important. This point is a source of complexity since chlorine is a poison for many catalysts, and the removal of organochlorinated compounds by physical methods such as adsorption is not easy when working with complex matrices. At this point, only hydrochlorination reactions could be useful for removing chlorine (using, for example, hydrotreatment catalysts); however, being able to remove these impurities without hydrogenating aromatic structures is a key issue.

Concerning oil upgrading itself, the most usual approach is increasing the concentration of

aromatics in pyrolysis oils by aromatisation reactions using acidic zeolitic catalysts. These processes, usually performed on acid zeolites (such as ZSM-5 or BETA zeolites), involve a complex set of reactions: Diels–Alder condensations, alkylations and dealkylations, deoxygenations, etc., with these reactions also involving the formation of coke deposits. Due to this fact, catalyst deactivation effects are important in these processes, and the proposed chemical reactors should cope with these effects. Thus, although most published studies on these reactions are performed in fixed-bed reactors, moving fluidised-bed reactors (such as those used in Fluid Catalytic Cracking) seem more appropriate for upscaling these processes.

The other approach (upgrading of separated compounds/fractions of the pyrolysis oil) has the separation itself as the first issue. These separations involve the use of distillation (for example, for separating aromatic olefins from plastic-derived pyrolysis oils) or extraction (separation of phenols and cresols from biomass pyrolysis oils using aqueous solutions of different acidities). The application of these technologies to a complex matrix can lead to important technical and environmental issues that threaten the viability of the technologies.

Among the upgrading technologies for the recovered chemicals, the conversion of o-cresol to salicylic acid is an example of interest, given the high added value of this chemical. Two routes can be considered to carry out this reaction, which is still scarcely studied: a catalytic route using heterogeneous catalysts and oxygen or hydrogen peroxide as oxidants, and a photocatalytic route. Our research group has carried out an extensive search for heterogeneous catalysts for this reaction, including supported and unsupported transition metal oxides, and noble metals supported on conventional supports. The oxidation of the methyl group is especially challenging, with strong competition from deep oxidation and polymerisation reactions. Transition metals (mainly Co) in basic media have proven to be the optimal approach for performing this reaction, whereas the solvent also plays a key role, protic organic solvents providing the best results, while the use of water or solventless conditions increases polymerisation. Active phase leaching is also important, but it can be controlled with rigorous pH control.

Concerning the photochemical approach, the complexity of the reaction means that the most common photocatalysts proposed for this kind of reaction (TiO₂, carbon nitrides, or sulphonated anthraquinone) were not active at all. By contrast, photocatalysts operating according to the ligand-to-metal charge transfer (LMCT) principle are active for this reaction, especially homogeneous Cu or Fe salts. However, this reaction only proceeds at room temperature in organic solvents, and the deactivation of catalysts by the formation of ions with intermediate oxidation states is still an open question to be solved. As in the case of the thermocatalytic conversion, the separation of the catalysts and reaction products is challenging.

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Acknowledgements

This work has been funded by MCIN/AEI/ 10.13039/501100011033 (PID2023-147180OB-I00). A. Girase, G. Lomidze, S. Cañete, I. Krivtsov and L. Faba are acknowledged for their contribution to this contribution.

Optical spectroscopy as a “Swiss army knife” in understanding catalysts

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Introduction

The study of heterogeneous catalysis is crucial for advancing industrial processes in energy, chemicals, and environmental applications. Spectroscopic techniques have emerged as powerful tools to investigate the complex phenomena occurring at the catalyst surface during reaction processes. These methods provide detailed insights into the structural and electronic properties of catalyst materials, as well as their dynamic behavior under reaction conditions. Techniques such as infrared (IR), Raman, ultraviolet-visible (UV-Vis) and X-ray Absorption (XAS) spectroscopies, just to mention some of them, enable the observation of key intermediates, reaction mechanisms, and changes in the active sites of catalysts. However, though some spectroscopic tools (e.g. IR or UV-vis) are nowadays broadly available, their fundamentals are often not fully handled by the final user, sometime leading to gross errors in their application and reporting of results. Moreover, operando spectroscopies, which allow measurements under actual catalytic reaction conditions, have greatly enhanced our understanding of catalyst behavior in real-time. However, to be properly applied, they need devoted advanced experimental tools to measure and to analyze the results. The combination of these spectroscopic and molecular modelling approaches has been instrumental in unraveling the molecular-level interactions between catalysts and reactants, identifying reaction pathways, and guiding the design of more efficient, selective, and durable catalytic systems. The present contribution aims to illustrate potentialities and limits of spectroscopies, in characterizing zeolites and Metal organic Frameworks, selecting a few case studies.

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KEYNOTE LECTURES

Support-Driven and Alkali-Promoted Cobalt Catalysts for Ethanol Steam Reforming

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Keywords: Cobalt catalyst, Alkali promotion, Supported catalyst, Ethanol steam reforming, Hydrogen production

Hydrogen production via ethanol steam reforming (ESR) represents a promising pathway toward sustainable energy systems, combining the utilization of renewable bioethanol with the generation of low-carbon hydrogen [1]. Over the past years, my research has focused on the rational design of cobalt-based catalysts for ESR, with particular emphasis on understanding and controlling the key physicochemical factors governing catalytic activity, selectivity, and long-term stability. In this keynote, I will present a comprehensive overview of these contributions, encompassing systematic studies of cobalt catalysts supported on classic oxides and zeolitic materials, as well as detailed investigations into the role of alkali promotion.

A major part of this work has been devoted to cobalt catalysts supported on alumina. Our investigations demonstrated that catalytic performance is not dictated solely by surface acidity, but rather results from a subtle interplay among support phase composition, textural properties, and metal–support interactions. By comparing cobalt systems supported on alumina and employing advanced cobalt deposition methods, clear correlations between cobalt dispersion, reducibility, cobalt phase composition, and ESR activity were established [2,3]. Key outcomes of these studies include the identification of alkali metal promoters as highly effective modifiers of the catalyst surface properties, enabling switching between ethanol dehydration and dehydrogenation pathways, while significantly enhancing catalyst stability by strengthening the cobalt–alumina interaction.

In parallel, extensive research on zeolite-supported cobalt catalysts was conducted, motivated by the unique structural features of zeolites that favor high metal dispersion and active site accessibility. Although zeolites have traditionally been regarded as unsuitable supports for ESR due to their intrinsic acidity, our studies demonstrated that this limitation can be overcome through targeted compositional engineering. In particular, systematic variation of the Si/Al ratio in ZSM-5 supports allowed precise control of acidity and revealed the exceptional potential of high-silica and pure-silica zeolites [4,5]. Cobalt catalysts supported on nanocrystalline pure-silica ZSM-5 exhibited complete ethanol conversion, hydrogen selectivity exceeding 90%, elimination of undesired ethene formation, and outstanding stability under demanding reaction conditions.

Throughout this work, special emphasis has been placed on establishing surface–structure–performance relationships using a broad range of advanced characterization techniques, including pre- and post-reaction analyses as well as operando and *in-situ* spectroscopic studies. These approaches provided mechanistic insights into catalyst activation and deactivation processes and clarified the role of alkali promoters at the molecular level. Collectively, the results presented in this lecture challenge the conventional perception of both oxide- and zeolite-based ESR catalysts and demonstrate that cobalt systems, when properly engineered, can achieve performance comparable to that of noble metal catalysts.

Finally, the keynote lecture illustrates how integrating insights gained from oxide- and zeolite-supported systems enables the development of a rational mechanistic framework based on surface–structure–performance relationships. On this basis, general and transferable design principles are established for the development of highly efficient and robust cobalt-based catalysts.

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Acknowledgement: This study was financially supported by the National Science Center, Poland, project number 2024/55/B/ST5/02291

Metal-support interactions in Ni-based Catalysts for Dry Methane Reforming: Insights from Model and Powder Systems

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Keywords: metal-support interactions, dry methane reforming, Ni-catalyst, interfacial phenomena

Introduction. Dry methane reforming (DMR) is an attractive catalytic route for the simultaneous utilization of CO₂ and CH₄ to produce syngas,¹ a key intermediate for the synthesis of fuels and chemicals. Despite its environmental and industrial relevance, the reaction remains highly demanding due to severe catalyst deactivation caused by sintering, carbon deposition, and structural instability under harsh operating conditions. Nickel-based catalysts are widely investigated as cost-effective alternatives to noble metals;² however, their performance strongly depends on the nature of the support and the resulting metal–support interactions.

Methodology. Model systems enable controlled investigation of metal–support interfaces under well-defined conditions, providing fundamental insight into interfacial phenomena, while powder catalysts offer structural complexity and practical relevance. Together, these complementary approaches reveal the dynamic behaviour of both Ni species and the support during DMR, including interfacial redox processes and phase transformations. Integrating findings from both platforms provides a more comprehensive understanding of the structure–stability–reactivity relationships governing Ni-based catalysts and offers guidance for the rational design of more robust and efficient DMR materials.

Results. Model Ni/ZrO₂ catalysts provide direct insight into the evolution of the metal–support interface under DMR conditions. Using XPEEM spectromicroscopy, we monitored the local oxidation state of Ni and demonstrated that zirconia strongly influences the reducibility and stabilization of Ni species, while the presence of Ni simultaneously promotes structural modifications of the support. Comparison with powder catalysts shows that these interfacial phenomena are not limited to idealized systems but also occur in practical catalysts. In particular, *in situ* Raman spectroscopy reveals a Ni-induced transformation of zirconia from the monoclinic to the tetragonal phase under reaction conditions,³ confirming the mechanistic insights obtained from the model studies. The excellent agreement between

both platforms highlights the dynamic and reciprocal nature of the metal–support interaction, linking interfacial restructuring with enhanced resistance to sintering and improved catalyst stability.

Conclusions. Metal–support interactions play a pivotal role in determining catalyst reducibility, metal dispersion, resistance to sintering, and the balance between methane activation and carbon removal. Depending on the support, the strength and nature of these interactions can dramatically alter the redox behaviour, phase stability, and carbon tolerance of Ni-based catalysts. Combining model and powder systems provides complementary mechanistic and practical insights, establishing a powerful strategy for understanding catalyst behaviour under reaction conditions and for the rational design of next-generation DMR catalysts.

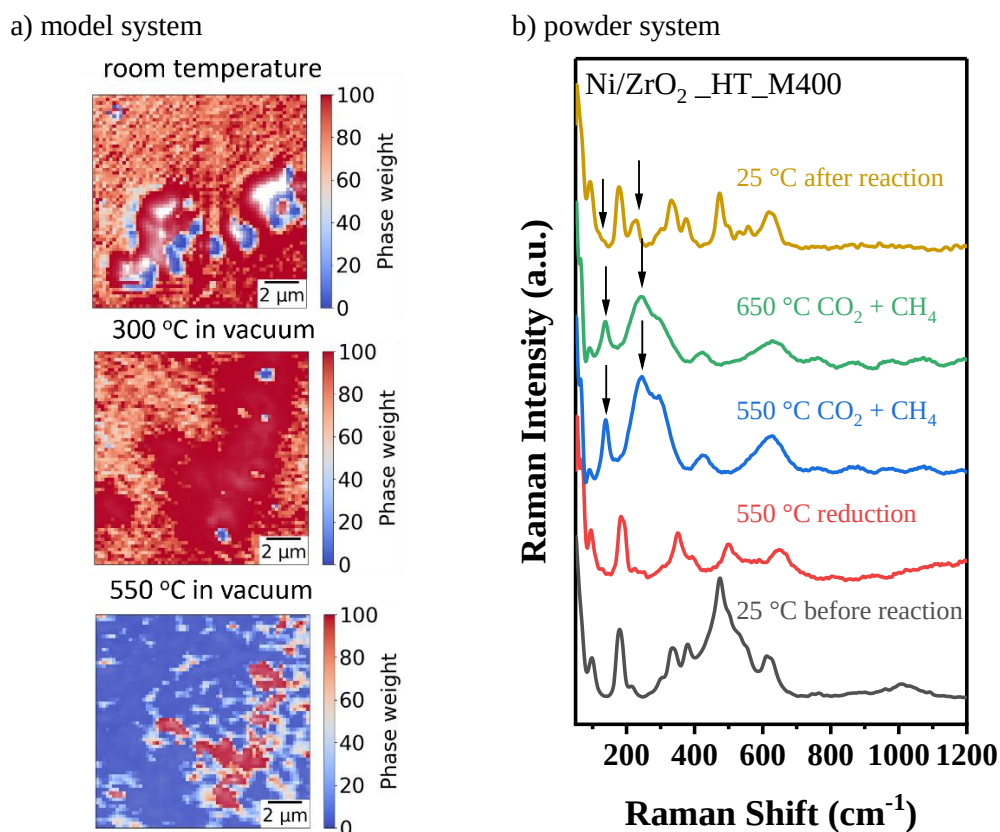


Fig. 1: Evidence of bidirectional metal–support interactions leading to Ni-induced zirconia phase transformation from monoclinic to tetragonal structure, established through (a) nanoscale chemical mapping of the Ni/ZrO₂ model catalyst and (b) *in situ* Raman spectroscopy of powder catalysts under reaction-relevant DMR conditions.

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Opportunities and Challenges in CO₂ valorization by MOF-derived catalysts

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Keywords: MOF-derived materials, ordered porosity, CO₂ hydrogenation

Metal-organic frameworks (MOFs), a class of highly versatile materials obtained by interconnecting diverse organic linkers with various metal centers, are in the spotlight of the scientific community due to their outstanding properties, such as well-defined crystalline structures, exceptionally high surface areas, and tunable porosity. Additionally, their enhanced gas sorption and storage capacity, as well as the possibility of providing catalytic functionalities either at the metal nodes or by confining other species in the pores (i.e., metal nanoparticles), made MOFs especially attractive for various catalytic applications. However, their usually low thermal or solvent stability limits their use on a larger scale in heterogeneous catalysis. In this context, MOF-derived materials have emerged as a viable alternative for obtaining stable catalytic materials, while largely retaining the high surface area and porosity of the parent MOF. These MOF-derived materials are generally obtained by thermal treatment and consist of porous metal oxides, carbons, or metal(metal-oxide)@carbons, with composition depending on the conditions used during the treatment (oxidizing, reducing, or inert atmosphere) [1].

Herein, the catalytic performance of MOF-derived materials for CO₂ hydrogenation to either methane (CO₂-to-CH₄) or methanol (CO₂-to-MeOH) will be discussed. In both cases, an inexpensive and easy-to-synthesize Al-based MOF, MIL-53(Al) [2], was used as a starting material to synthesize the MOF-derived materials: (a) alumina-based Ni catalysts for CO₂-to-CH₄, and (b) porous carbon [3] to promote CuO-ZnO-Al₂O₃ catalyst for CO₂-to-MeOH. Different synthesis approaches were considered in either case, and the obtained samples were characterized from a structural, morphological, and functional point of view using XRD, BET, TPR, SEM/TEM/EDX, H₂/CO₂-TPD, and DRIFTS. The influence of the synthetic approach on catalytic performance in the CO₂-to-CH₄ and CO₂-to-MeOH will be discussed in relation to the structural and textural characteristics of the MOF-derived catalysts, as well as their interaction with H₂ and CO₂, the reactants of the considered CO₂ valorization processes.

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Development of Innovative Process Routes for Sustainable Aviation Fuels

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The development of Sustainable Aviation Fuels (SAF) requires the integration of catalyst development, reaction engineering, process modelling, and scale-up strategies. This keynote lecture provides an overview of relevant SAF production pathways and subsequently focuses on two process routes currently investigated: a Fischer-Tropsch-based pathway with experimental investigation of the reverse water-gas shift (RWGS) reaction and a multistep Alcohol-to-Jet (AtJ) pathway.

Within the Fischer-Tropsch-based route, the experimental work focuses on the RWGS reaction for the production of CO-rich syngas from CO₂ and H₂. Perovskite- and nickel-based catalyst systems were investigated and compared for their application in low-temperature RWGS. Following catalyst development at laboratory scale, selected catalyst formulations were pelletized and transferred to an experimental reactor with an internal diameter of approximately 15 mm and a catalyst bed length of approximately 20 cm. This approach enables the transition from catalyst development toward application under technically relevant reactor conditions. While Fischer-Tropsch synthesis itself is not experimentally investigated within the current setup, experimental RWGS results can be integrated into process simulations to investigate the overall process route from CO₂ and H₂ via syngas toward Fischer-Tropsch products.

Based on this experimental and modelling framework, current research aims to further develop the experimental infrastructure toward data-driven process investigation and optimization. Machine-learning-based methods are intended to support the analysis of catalyst deactivation, identify operating parameters with the strongest influence on reactor performance, and derive suitable operating strategies under changing process conditions.

A second experimental platform addresses an Alcohol-to-Jet process based on a multistep reaction route comprising methanol-to-dimethyl ether conversion, DME-to-olefins conversion, oligomerization, and subsequent hydrogenation. The current experimental configuration employs commercially available catalysts for the investigation and integration of the individual reaction steps. Future research will additionally address catalyst development to improve process efficiency, selectivity, and product yield.

The combination of catalyst development, experimental reaction engineering, process simulation, and data-driven methods provides a framework for bridging laboratory-scale research and prospective industrial implementation. Digital representations of the experimental processes are intended to support the evaluation of operating strategies and future scale-up scenarios, thereby contributing to the systematic development of integrated SAF production routes.

Selective heterogeneous catalysts and their applications in petrochemical processes

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Keywords: zeolites, heterogeneous catalysts, linear alkylbenzenes, methane dehydroaromatization, biodiesel

The petrochemical industry plays a significant role in the economic growth of modern society. It is estimated that approximately 90% of industrial chemical processes are catalyzed. Of these, the greatest attention is paid to heterogeneous catalysis. Compared to homogeneous catalysts, heterogeneous catalysts offer undeniable advantages, such as the possibility of regeneration and reuse. From an environmental perspective, this is a significant benefit. This is particularly true in the petrochemical industry, where there is currently an effort to fully or partially replace older processes with ones that are more environmentally friendly while also providing products with high selectivity.

One of the processes under investigation is the preparation of linear alkylaromatics via alkylation. Linear alkylbenzenes (LAB), which are formed by the alkylation of aromatic hydrocarbons with linear 1-alkenes, are important intermediates in the production of various types of surfactants and synthetic oils. Currently, global LAB production stands at approximately 4.25 million tons per year (data from 2023) and is trending upward. The main problem with this industrial process is the use of environmentally harmful homogeneous catalysts (HF, AlCl_3 ...) and low selectivity for the desired products. This process results in a variety of alkylated aromatics. 2-phenyl isomers, which are the most biodegradable, as well as linear alkylated aromatics are the most valued. Current research is focused on replacing these catalysts with solid, heterogeneous, more environmentally friendly ones that exhibit high selectivity for the desired products. One possible alternative is solid acid catalysts, mainly zeolites. Commonly tested structure types include zeolite Y, mordenite, and beta [1-3]. Zeolites can be used in their parent form or modified through various post-synthesis treatments. Currently, research is focusing considerable attention on hierarchically structured zeolites.

In alkylation, the main feedstock consists of aromatic hydrocarbons, which are currently obtained primarily from crude oil. One possible alternative for producing aromatics appears to be the dehydroaromatization of methane. This process produces a mixture of BTX aromatics, hydrogen, and C_2 and C_3 hydrocarbons as byproducts. Among other things, the aromatics prepared in this way can serve as a high-octane component of automotive gasoline. From a catalytic perspective, Mo/ZSM-5 catalyst appears to be the most promising one for this process [4-6]. This may be due to the structure of ZSM-5 zeolite, the active sites located within the zeolite's pores or channels, and the shape and size of the pores. The nature of the products formed during the reaction is primarily determined by the properties of the zeolite used as a support for the active metal. Zeolite ZSM-5, particularly due to 3-D structure and pore diameter, which is close to the dynamic diameter of the benzene molecule, promotes the formation of aromatic hydrocarbons such as benzene, toluene, and xylenes. The disadvantages of the process include high temperatures, typically around 700 °C, low methane conversion, and catalyst stability issues due to coke formation. Therefore, research is intensively focused on finding a

catalytic system that provides favorable methane conversion, selectivity toward aromatic hydrocarbons, stability throughout the reaction, and the possibility of catalyst regeneration.

Utilization of heterogeneous catalysts can improve the environmental impact of various productions, which currently utilize homogeneous catalysis. Another such process is transesterification of oleaginous feedstocks into biodiesel. Apart from relying on homogeneous catalysts, the production of biodiesel currently processes mostly edible feedstocks. In industry, vegetable oils are primarily used for biodiesel production over animal fats due to their physicochemical properties. A drawback remains the use of edible oils (rapeseed, sunflower, palm...). A solution to this problem may be the use of non-food vegetable oils (*Camelina sativa*, *Jatropha curcas*, *Pongamia pinnata*, etc.) or waste oils (coffee oil from SCG or waste cooking oils) [7-9]. Mixing different types of oils could also help reduce dependence on edible oils. Another current drawback of biodiesel production is the use of homogeneous catalysts. Replacing them with heterogeneous catalysts significantly reduces the water consumption in the process, which is required to wash out the homogeneous catalyst. The advantages of heterogeneous transesterification also include the possibility of catalyst regeneration and reuse, a cleaner byproduct (glycerol), and greater resistance of the catalysts to free fatty acids (FFA). When using a heterogeneous catalyst, separating biodiesel from the reaction mixture is simpler, and the catalyst can be reused in the reaction after regeneration. The resulting waste glycerol is purer compared to homogeneous transesterification and therefore does not require such thorough purification for further industrial use. However, the disadvantages remain: longer reaction time, higher reaction temperature, and the need for a larger amount of catalyst to achieve a high FAME content in the biodiesel (96.5 wt. % according to EN 14 214). Our research therefore focused on the use of camelina oil or waste coffee oil as a feedstock for transesterification, with hydrotalcites in the form of mixed oxides used as heterogeneous catalysts.

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Acknowledgement: This work was supported by the Slovak Research and Development Agency under the Contract no. VV-MVP-24-0331.

Beyond the Catalyst: How CO₂ Electrolyzer Cells Really Operate

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Keywords: CO production, Gas diffusion electrodes, CCU, electrolyzer engineering, carbon dioxide

Introduction

Electrolysis technologies have received increased attention in recent years. This is rooted both in the rapidly increasing amount of available renewable energy, and in the aim to develop sustainable industrial technologies. The intermittently available renewable energy can be stored in the form of chemical bonds by electrochemically producing high-energy-density products. As for industrial sustainability, the waste production can be reduced by electrochemically performing redox reactions, the process safety can be increased, and the environmental footprint of the process can be decreased – depending on the source of electricity. Electrochemical CO₂ reduction has attracted considerable attention as a route to close the anthropogenic carbon cycle while directly utilizing renewable electricity. Efficient catalysts, electrode- and cell architectures are available for selective operation for simple products at high current densities. Limited operational stability, however, still hampers large-scale deployment.

Methodology

All the electrochemical measurements shown during my presentation were performed in a custom-designed zero-gap electrolyzer cell, and using test frameworks that were developed in our laboratory. In the zero-gap electrolyzer cell the catalyst-coated electrode supports are directly pressed to an anion exchange membrane (AEM), while these are in direct contact with the electrolyzer cell body on their back. This arrangement minimizes the electrical resistance of the cell. However, direct contact between the elements also imposes tight interdependencies, implying that the least efficient component of the cell will inherently limit the total performance. Our studies aim to deconvolute these effects, identify the bottlenecks of cell operation and offer routes for designing more efficient components.

Results & discussion

In my presentation I will give detailed insight into the operation of zero-gap CO₂ electrolyzers through our recent results, but also highlighting important results from other research groups. In particular, I will talk about three distinct topics:

- The importance of the ion balance in the electrolyzer cell
Cations are co-catalysts in the electrochemical reduction of CO₂ (CO₂RR). Therefore, their presence at the cathode is a pre-requisite for high-performance operation. However, overly high amounts of cations at the cathode cause performance fading, often denoted as “flooding”. This delicate balance decides how the cell operates. We present that the key for long-term stable performance at high current densities can be maintained by ensuring the right ion concentration in the cathode. This can be achieved by either controlling the composition of the electrolyte solution recirculated at the anode, or by directly injecting solutions in the cathode compartment of the cell.^{1,2}

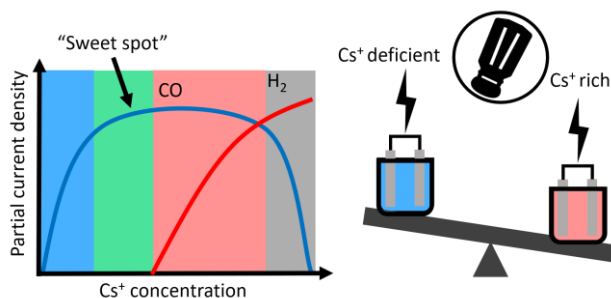


Fig. 1: Ion balance in the cathode is decisive for the operation of CO₂ electrolyzers.

- The effect of operational conditions (including the used test framework)
Using commercially available components (gas diffusion layers, catalysts, membranes etc.), the cell performance and stability still vary in a wide range, dictated by the experimental conditions. On top of that, the effects of these are also convoluted, making cell operation optimization challenging (not to mention cell aging...). We present a high-throughput methodology, assisted by artificial neural network based data analysis for the complex evaluation of cell performance.³
- The effect of cathode structure
The structure of the cathode is decisive for all performance metrics of CO₂ electrolysis. The catalyst support, the particle size of the catalyst, the used binder and the catalyst layer deposition method all affect how the electrolyzer cell works. Even the non-ideal compression of the electrode can limit the performance notably.⁴

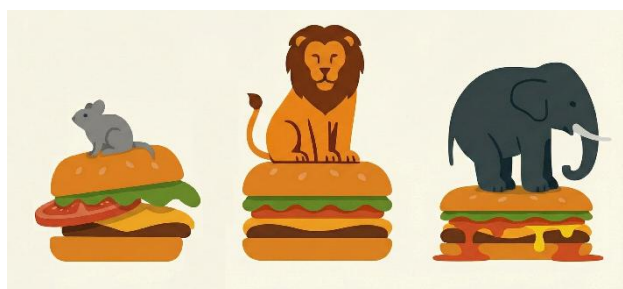


Fig. 2: Optimal cathode gas diffusion electrode compression is key for high-performance CO₂RR.⁴

Conclusions

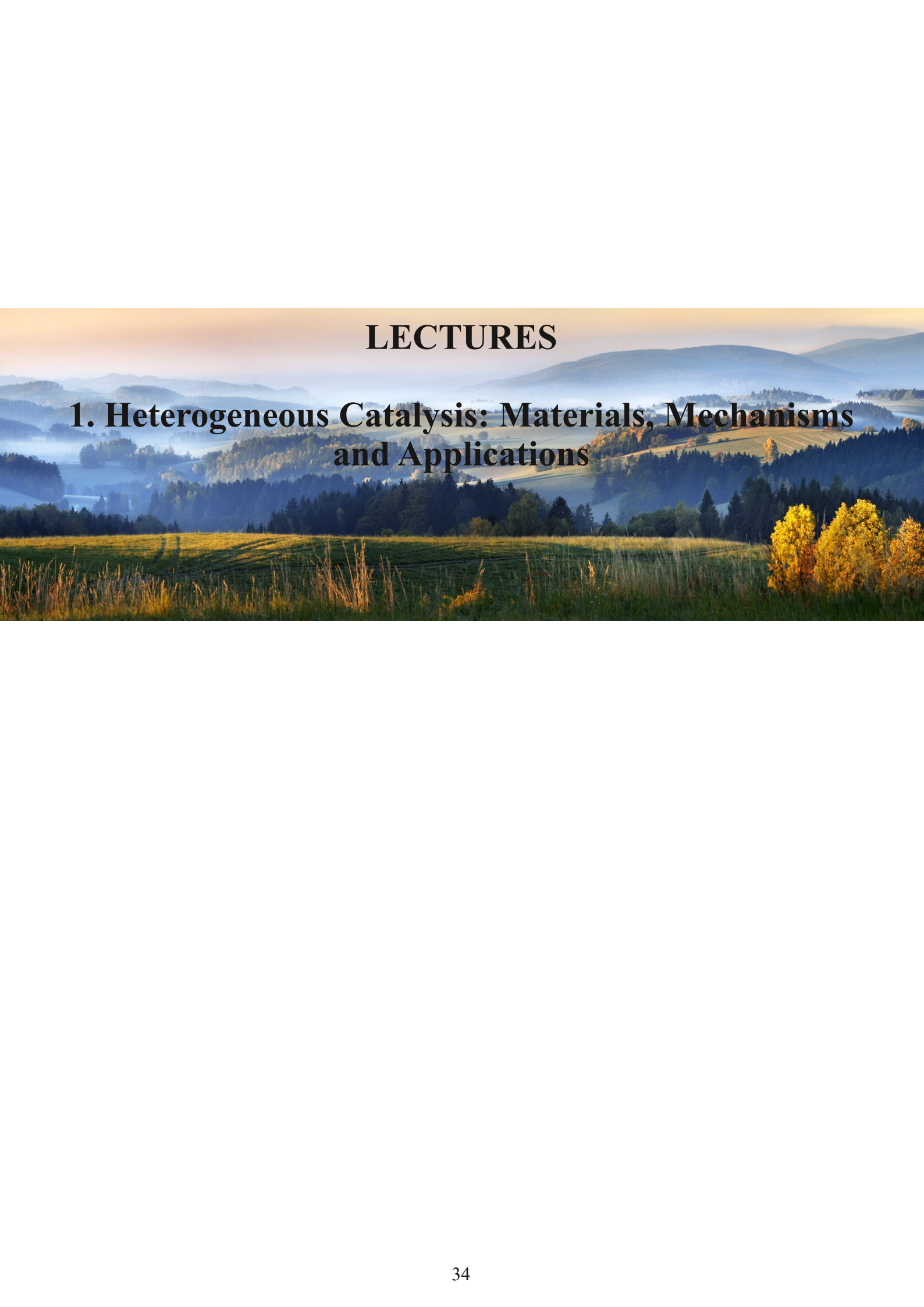
Beyond the applied components, the operation of zero-gap electrolyzer cells depend heavily on how the cell is assembled and operated. Here we demonstrate multiple case studies highlighting this complexity, and the intertwined nature of these effects.

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Acknowledgement

This research was supported by the Lendület Program of the Hungarian Academy of Sciences (MTA). Project no. 2025-1.2.1-HU-RIZONT-2025-00021 has been implemented with the support provided by the Ministry of Culture and Innovation of Hungary from the National Research, Development and Innovation Fund, financed under the 2025-1.2.1-HU-RIZONT funding scheme.



LECTURES

1. Heterogeneous Catalysis: Materials, Mechanisms and Applications

Physisorption, chemisorption, catalytic reactors and other characterization tools for heterogeneous

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Keywords: Characterization, performance testing, chemisorption

Heterogeneous catalyst development requires a combination of complementary characterization and performance testing methods to understand both intrinsic surface properties and real catalytic behavior. This presentation introduces key approaches for catalyst assessment, with emphasis on dynamic chemisorption techniques such as TPR, TPO, TPD, TPSR, pulse chemisorption, dynamic BET, SSITKA, and high-pressure chemisorption. These methods provide information on active-site density, acid/base site strength, metal dispersion, adsorption behavior, reducibility, oxidation behavior, and surface reaction pathways. The presentation also discusses microreactor systems for evaluating catalyst performance under realistic operating conditions.

A complete catalyst evaluation strategy links chemisorption data with reactor performance testing: chemisorption helps determine what the catalyst is, while reactor experiments show what the catalyst does under practical conditions. The presentation further places these methods within a broader catalyst-characterization workflow that may include gas adsorption for BET surface area and pore-size analysis, vapor and high-pressure sorption, breakthrough curve analysis, SEM imaging, and elemental composition by XRF and crystalline phases, phase transformations and crystallite size by XRD techniques.

From Intermediate Accumulation to Rapid Turnover: Functionalization-Dependent CO₂ Hydrogenation Pathways on Ru and Re Clusters on MXene

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Keywords: Ruthenium, Rhenium, MXene, CO₂ hydrogenation

Introduction

The hydrogenation of CO₂ remains one of the most intensively studied catalytic routes for carbon utilization, particularly for the production of synthetic fuels and carbon-neutral chemical feedstocks. Despite extensive mechanistic investigations, the relationship between surface functionalization, intermediate coverage, and catalytic turnover remains poorly understood, especially for rhenium catalysts. ¹ In this work, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) combined with steady-state isotopic transient kinetic analysis (SSITKA) was employed to investigate the influence of surface functionalization on the CO₂ hydrogenation mechanism over Ru- and Re-based catalysts supported on modified MXene materials.

Methodology

First, Ti₃C₂T_x MXenes were synthesized using HF or NH₄HF₂ etchants, enabling a comparison between nitrogen-free and nitrogen-containing surface terminations followed by Ru or Re precursors addition to NH₄HF₂-etched MXene. Then, arginine was introduced prior to HF-etched MXenes addition during the deposition of Ru or Re precursors, providing a controlled means to influence metal dispersion through organic chelation. SSITKA analysis was performed by monitoring the transient evolution of integrated DRIFTS bands following isotopic switching, allowing estimation of characteristic surface response times of surface intermediates.

Results and discussion

Transmission electron microscopy analysis confirmed the formation of highly dispersed Ru and Re clusters with average sizes of approximately 1 nm on the MXene surface. Arginine functionalization stabilized predominantly metallic Ru species, whereas NH₄HF₂-treated Ru exhibited a higher fraction of oxidized Ru species. The NH₄HF₂-treated Re catalyst remained largely metallic, while arginine functionalization promoted a broad mixed-valence distribution including Re²⁺, Re⁴⁺, Re⁶⁺, and Re⁷⁺ species. Functionalization additionally modified the fluorine termination chemistry and altered the relative contribution of carbide-related Ti–C surface species, indicating significant restructuring of the MXene interfacial environment.

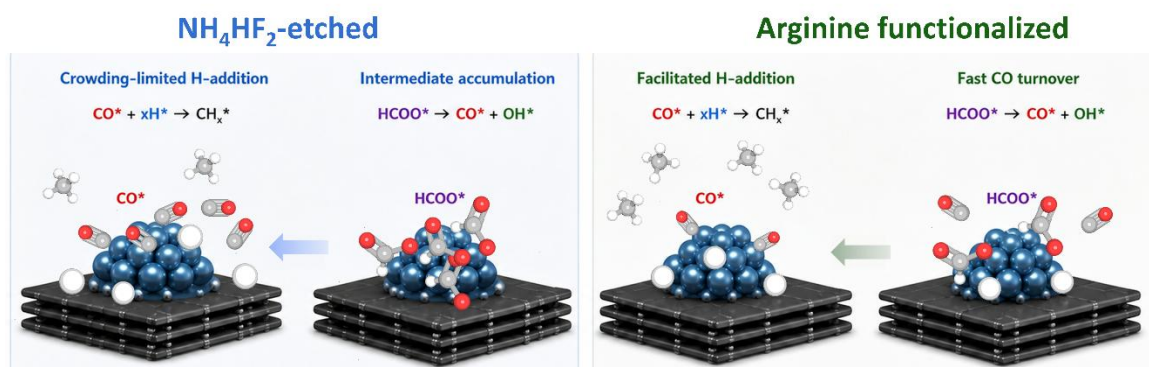


Figure 1 Kinetic action during CO₂ hydrogenation.

The NH₄HF₂-treated Ru catalyst exhibited an exponential transient response in the carbon-containing spectral region with characteristic residence times consistent with accumulation and turnover of surface carbonaceous intermediates. The arginine-functionalized Ru catalyst displayed a predominantly linear transient response, indicating rapid steady-state turnover without measurable accumulation of an intermediate pool. Such behavior suggests that functionalization suppresses stabilization of long-lived carbon-containing species while maintaining catalytic turnover. The NH₄HF₂-treated Re catalyst displayed significantly longer characteristic transient times, while the arginine-functionalized sample exhibited an initial exponential regime followed by linear behavior, suggesting transition from limited intermediate accumulation toward turnover-controlled surface dynamics. The coexistence of highly oxidized Re species together with weak carbon-related DRIFTS signals is consistent with RWGS-dominated reaction pathways involving oxygen-mediated surface processes rather than methanation-type chemistry. The observed transition from exponential to linear transient behavior demonstrates that surface functionalization can fundamentally alter the kinetic state even for the same active metal.

Conclusions

Operando SSITKA–DRIFTS combined with XPS revealed that surface functionalization strongly influences the transient surface chemistry of Ru- and Re-based CO₂ hydrogenation catalysts. Arginine functionalization suppresses accumulation of carbonaceous intermediates in Ru systems while promoting highly oxidized mixed-valence Re surfaces associated with oxygen-mediated RWGS-type pathways. The results demonstrate that functionalization can shift catalysts between fundamentally different kinetic states by modifying intermediate residence time, surface coverage, and surface redox properties.

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Acknowledgement

This research was funded by the Austrian Science Fund (FWF) [10.55776/ESP8745324] (ESPRIT Eco-Friendly MXene-Supported Precious Metal Catalysts).

Copper Catalysts Supported on 2D Materials for Selective Oxidation of Benzyl Alcohol

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Keywords: heterogeneous catalysis, copper catalysts, 2D materials, benzyl alcohol oxidation, *in situ* DRIFTS

Introduction

Selective oxidation of primary alcohols to the corresponding aldehydes represents a key transformation in organic synthesis, as carbonyl compounds serve as important intermediates in fine chemical production. However, achieving high selectivity is often challenging due to the tendency of aldehydes to undergo further oxidation to carboxylic acids. [1]

Traditional oxidation methods frequently rely on stoichiometric and environmentally burdensome oxidants (e.g. Cr(VI), Mn(VII), heptavalent iodine and DMSO-coupled reagents), which motivates the development of more sustainable catalytic systems utilizing clean oxidants such as O₂ or H₂O₂. While homogeneous catalytic systems often provide high activity and selectivity, their practical application is limited by difficult separation of the catalyst from the reaction mixture. Therefore, increasing attention is devoted to heterogeneous catalysts, which allow easier separation and recyclability. However, their performance strongly depends on the availability of active sites, transport phenomena and catalyst stability. [1–3]

Copper-based catalysts represent an attractive alternative to noble metal systems due to their low cost and versatile redox properties, enabling both radical and non-radical oxidation pathways. In particular, the activation of peroxides may proceed via Fenton-like mechanism involving reactive oxidation intermediates, with the nature of the dominant oxidizing species depending on the reaction conditions. [4,5]

Methodology

Copper-based catalysts supported on selected 2D materials were prepared by wet impregnation followed by chemical reduction. The materials were characterized using X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS).

Catalytic activity was evaluated in the oxidation of benzyl alcohol using hydrogen peroxide and *tert*-butyl hydroperoxide as oxidants at 50 and 80 °C.

To gain deeper insight into the reaction mechanism and the nature of the active sites, *in situ* DRIFTS experiments were performed using a high-temperature reaction cell, where CO adsorption was used to probe surface sites and monitor the evolution of surface intermediates under reaction conditions.

Results and Discussion

The catalytic performance of the prepared materials was evaluated in the oxidation of benzyl alcohol. The use of *tert*-butyl hydroperoxide resulted in higher benzyl alcohol conversion and benzaldehyde yields compared to hydrogen peroxide, with the maximum yield reaching approximately 24 % (4 h, 80 °C). At higher reaction temperature, an increase in conversion was accompanied by further oxidation to benzoic acid (Fig. 1).

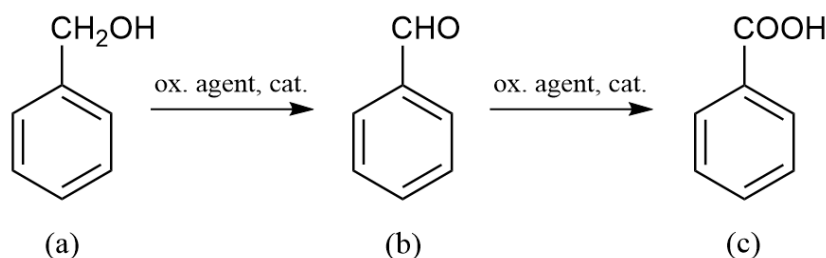


Fig 1: Reaction scheme of the oxidation of benzyl alcohol (a) to benzaldehyde (b) and benzoic acid (c) [1]

The nature of the support influenced catalyst stability, with graphene oxide-based catalysts exhibiting lower copper leaching compared to the other tested supports (germanane and silicane) and better preservation of their layered structure after reaction. Reusability tests gave benzaldehyde yields of 30 % in the first cycle and 23 % in the third cycle (24 h, 50 °C), which may be associated with copper leaching or aggregation into larger particles.

Characterization confirmed the presence of copper nanoparticles dispersed on the support, although partial aggregation, possibly related to the preparation method, was observed. Structural changes of the support were also detected, particularly partial reduction of graphene oxide.

The *in situ* DRIFTS experiments provided further insight into adsorption processes and the nature of the active sites.

Conclusions

Copper catalysts supported on 2D materials represent an attractive approach for the selective oxidation of benzyl alcohol, combining the advantages of non-noble metals with tunable support properties. The results highlight the importance of oxidant selection and catalyst stability, particularly in relation to copper leaching and structural changes of the support. *In situ* DRIFTS experiments contributed to a deeper mechanistic understanding of active sites and reaction pathways.

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Acknowledgement

This project was supported by the Czech Science Foundation (GACR No. 23-08083M).

Development of ZSM-5 Catalyst with Enhanced Mesoporosity for MTG Process

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Keywords: MTG, ZSM-5 zeolite, gasoline production

Gasoline production from renewable sources is a widely discussed and investigated approach that aims to achieve independence from fossil fuels [1]. Processing green methanol to synthetic gasoline is an interesting technology which will likely depend on the development of energy prices in the future. The core of MTG process is a selective and stable catalyst, usually based on ZSM-5 zeolites [2]. The crystalline structure of ZSM-5 is highly shape-selective for the gasoline range of hydrocarbons and prevents creation of larger molecules. However, its strong acid sites and diffusion limitations in the micropores cause fast coking and deactivation [3].

The objective of this research was to develop a post-synthesis modification of ZSM-5 zeolite to create a hierarchical micro-mesoporous structure resulting in a catalyst with improved lifespan. A post-synthesis modification procedure consisting of desilication and dealumination was developed on lab-scale by optimizing conditions like temperature, time, and concentration of the leaching solutions. The micro-mesoporous structure was characterized by BET and mercury porosimetry. The catalytic testing was carried out in a fixed-bed continuous flow reactor at constant temperature and methanol flow. The effect of time on stream on conversion was investigated to determine the catalytic activity and deactivation rate of the prepared samples. Shaping of the catalytically active powder into mechanically stable particles is an essential step to scale up the catalyst into a commercially competitive product. The influence of permanent binders on the catalyst performance, such as activity, selectivity, and longevity, was studied.

The targeted enhancement of micro-mesoporosity was achieved by an optimized modification method, and the volume of mesopores increased up to 10-times. The feasibility of the catalyst preparation was successfully validated on the pilot scale. The developed catalyst was tested at industrial conditions and exhibited required activity and selectivity showing potential for industrial catalyst qualification.

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Acknowledgement

The project MTG-CZ is co-financed by the Technology Agency of the Czech Republic within the FW-TREND Program, Project no.: FW10010328.

Controlling ZSM-5 Porosity and Morphology for Methanol Dehydration to Dimethyl Ether

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Keywords: ZSM-5; dimethyl ether; methanol dehydration; mesoporosity; catalyst stability

Dimethyl ether (DME) is regarded as a clean alternative fuel and an important chemical intermediate, commonly obtained via methanol dehydration over solid acid catalysts. Zeolites, owing to their Brønsted acidity and high thermal stability, are particularly suitable for this reaction. Nevertheless, the exclusively microporous character of conventional zeolites, combined with excessive acid strength, may restrict the diffusion of reactants and products and accelerate catalyst deactivation through coke deposition. Therefore, the development of ZSM-5 catalysts with improved molecular transport and accessible acid sites remains an important route towards more efficient DME synthesis [1].

In this work, different strategies were applied to tune the porosity, morphology, and surface properties of ZSM-5 for methanol dehydration to DME. Mesoporous ZSM-5 was prepared by alkaline desilication using NaOH under varied treatment times [2]. A second approach was based on a controlled synthesis procedure designed to limit crystal growth and generate interparticle mesoporosity [3]. In the third strategy, spherical ZSM-5 particles were synthesised and subsequently modified by desilication [4]. Representative electron microscopy images of the obtained materials are shown in Fig. 1.

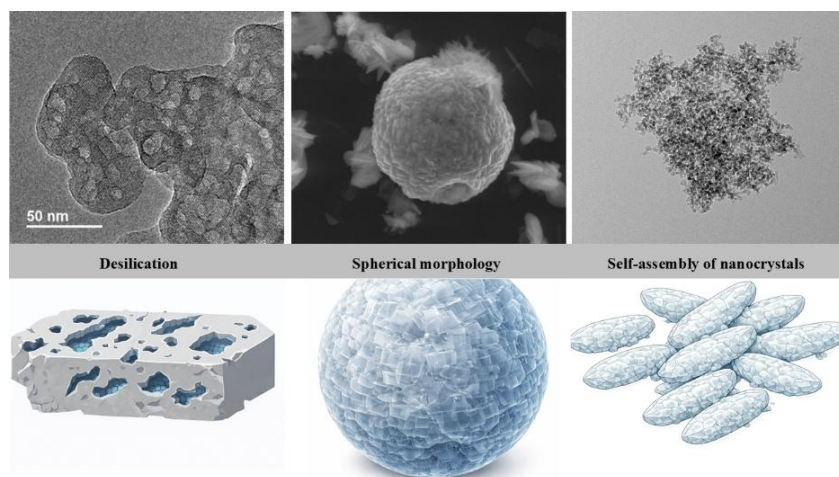


Fig. 1: Representative microscopy images and schematic representation of selected ZSM-5 modification strategies: desilication, spherical morphology formation, and self-assembly of nanocrystals.

The introduced modifications affected the textural properties, acidity, and morphology of ZSM-5, leading to enhanced catalytic performance in DME synthesis. The improvement was especially evident in long-term stability tests carried out for 50 h of continuous operation at 250 °C, where the modified catalysts displayed increased resistance to deactivation associated with coke formation.

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Copper-based catalysts bridging Fenton-like and electroprotic pathways for ROS Generation in H₂O₂-driven AOPs

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Keywords: Fenton-like reaction, electroprotic mechanism, UV-Vis, EPR, advanced oxidation processes

Advanced oxidation processes (AOPs) based on hydrogen peroxide are a versatile platform for eliminating persistent organic contaminants from industrial effluents, including dyes, pesticides, and pharmaceuticals. Their effectiveness is derived from their capacity to the in-situ generation of reactive oxygen species (ROS), primarily hydroxyl radicals ($\bullet\text{OH}$) and singlet oxygen ($^1\text{O}_2$). These ROS possess the ability to initiate deep oxidative transformation and, in favorable cases, mineralization of highly resistant molecules. Classical homogeneous Fenton chemistry ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) is widely regarded as benchmark. However, its application is limited by the narrow operational pH windows, the formation of iron sludge, and the limited control over the identity and selectivity of ROS. The aforementioned drawbacks are motivation to the development of heterogeneous Fenton-like catalysts, which offer separability, enhanced robustness, and opportunities to engineer reaction pathways. Furthermore, ROS generation can proceed through non-classical routes, including the electroprotic mechanism, where coupled electron–proton transfer is mediated by acid–base surface functionality rather than direct redox exchange with the catalyst surface. A catalyst that integrates redox-driven and electroprotic ROS generation within a unified material framework offers a compelling strategy to enhance activity while enabling practical "handles" to steer ROS distribution and oxidative selectivity. In this study, we propose a materials-design strategy for the development of copper-based composite oxide catalysts. This strategy involves the integration of two key components: (i) a crystalline, redox-active phase comprising Cu species, and (ii) a highly reducible oxide support capable of contributing acid–base functionality and electroprotic behaviour, as exemplified by Nb_2O_5 . The fundamental hypothesis is that by integrating the Cu(II)/Cu(I) cycle, which is thermodynamically advantageous for Fenton-like in comparison to traditional iron-based cycles, with an electroprotic support, we can achieve three primary objectives: (a) enhance the efficiency of H_2O_2 activation, (b) optimise the utilisation of a limited amount of redox-active phase, and (c) enable the modulation of ROS selectivity through the selection of promoters and the regulation of surface speciation. Furthermore, in comparison with Fe(III) , copper complexes are ordinarily less stable, which has the potential to reduce the risk of long-lived site blocking and facilitate sustained turnover under operational conditions.

A series of catalysts was synthesised using solvothermal and precipitation routes, spanning single oxides (CuO_x , Nb_2O_5), mixed Cu–Ce and Cu–Fe oxides, and selected copper hydroxo-nitrate materials. A comprehensive characterisation of the materials was undertaken to establish a correlation between their structural and surface chemical properties and their performance in terms of ROS generation. The identification of crystalline phases and the assessment of the degree of crystallinity were achieved by means of powder X-ray diffraction (XRD). Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) provided information on morphology and local elemental distribution. X-ray photoelectron

spectroscopy (XPS) was used to resolve surface elemental speciation and oxidation states, with particular attention paid to the coexistence of Cu^{2+} and Cu^+ as a prerequisite for rapid redox cycling. The measurement of the band gap and the subsequent examination of the application of these catalysts in photocatalysis was conducted utilising a solid-state UV-Vis spectrophotometer.

The capacity and selectivity of ROS generation from H_2O_2 decomposition were investigated by electron paramagnetic resonance (EPR) spectroscopy employing established molecular probes. The detection of hydroxyl radicals was accomplished through the utilisation of spin trapping with 5,5-dimethyl-1-pyrroline N-oxide (DMPO), while the monitoring of singlet oxygen formation was facilitated by employing 2,2,6,6-tetramethyl-4-piperidone (TEMP/TEMPO-type probe chemistry, contingent upon the specific experimental implementation). This dual-probe EPR strategy enabled a mechanistically informative comparison across catalyst families: whether the system predominantly channels oxidizing power into $\bullet\text{OH}$ -type pathways typical of Fenton-like redox turnover, or into $^1\text{O}_2$ -type pathways that may arise or be amplified through promoter effects and surface-mediated activation routes. The formation of superoxide intermediates on catalytic surfaces was determined by means of solid-state EPR.

The catalytic performance was evaluated in an AOP-relevant model reaction: the oxidative degradation of the azo dyes Direct Blue 15 (DB15) and methylene blue (MB) using H_2O_2 as the oxidant precursor. Reaction progress was monitored in different conditions by UV-Vis spectrophotometry, providing degradation/discoloration kinetics suitable for ranking catalysts and correlating activity with ROS signatures. Across the studied series, materials containing two redox-active metals consistently exhibited the highest degradation rates, outperforming single-metal Cu-based analogues. This enhancement is consistent with the concept of synergistic redox coupling and/or enhanced oxygen vacancy chemistry and surface oxygen mobility, as introduced by the second metal. This can accelerate H_2O_2 activation and sustain the Cu(II)/Cu(I) turnover, which is essential for radical formation.

Surface speciation was identified as a significant activity descriptor. XPS evidence for coexisting copper oxidation states ($\text{Cu}^{2+} / \text{Cu}^+$) has been shown to correlate with increased catalytic rates, thus supporting a mechanism in which facile Cu(II)/Cu(I) cycling promotes efficient formation of highly reactive intermediates, including $\bullet\text{OH}$. It is important to note that promoter selection altered not only the overall activity but also the ROS distribution. Ce incorporation resulted in a shift of the oxidative regime towards a relatively larger contribution of singlet oxygen compared with Cu-only materials, as evidenced by EPR probe responses. This observation suggests an actionable design principle: namely, that by selecting an appropriate promoter (for example, Ce vs Fe) and regulating surface composition and oxidation states, it is possible to adjust the equilibrium between radical-dominated oxidation and $^1\text{O}_2$ -influenced pathways. Such tunability is valuable for complex wastewater matrices, where maximising mineralisation is not always the sole objective; selective transformation toward less harmful products and minimisation of undesirable by-products can be equally important.

Ongoing work focuses on mechanistic quantification and kinetic deconvolution of ROS scavengers, with the aim of attributing observed pollutant conversion rates to specific oxidant identities. Furthermore, the work aims to evaluate how ROS speciation evolves with catalyst composition and surface state. Such studies are expected to refine structure-activity-selectivity relationships and provide a stronger basis for catalyst optimization under realistic water treatment constraints.

Acknowledgement: This work was financially supported by the National Science Center, Poland (NCN), grant OPUS27 2024/53/B/ST4/03929.

Metallosilicate microspheres by microwave-assisted sol-gel and their activity in ethanol conversion

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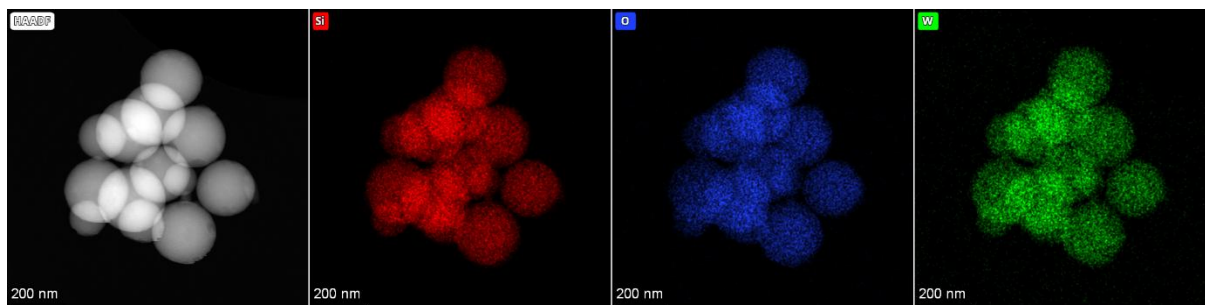
Keywords: Tungsten; Rhenium; Silica; Ethanol; Catalyst.

Alcohol dehydration and dehydrogenation are key transformations for upgrading biomass- and renewable-derived alcohols into value-added alkenes and carbonyl compounds, providing sustainable routes to olefins, aldehydes, and downstream chemicals at mild to moderate temperatures. Ethylene, in particular, is one of the world's most important chemical commodities, serving as a fundamental building block for polyethylene, vinyl chloride, ethylene oxide, ethylbenzene, and poly(ethylene terephthalate). At present, ethylene production relies predominantly on the steam cracking of petroleum-based feedstocks, and the rapidly growing global demand for alkenes continues to drive fossil fuel consumption.

Tungsten- and rhenium-based heterogeneous catalysts offer efficient pathways for alcohol conversion, exploiting the intrinsic bifunctional acid–redox character of W- and Re-containing active sites.[1–3] Tungsten oxide (WO_x) species dispersed on silica supports exhibit strong and tunable Brønsted and Lewis acidity, allowing high ethylene selectivity through unimolecular ethanol dehydration while suppressing side reactions. Despite notable advances using mesoporous supports and tailored synthesis strategies, achieving homogeneous metal dispersion, controlled acidity, and long-term stability through rapid and scalable preparation methods remains a major challenge.

Here, we report novel microspherical W–SiO₂ and Re–SiO₂ heterogeneous catalysts synthesized via an innovative microwave-assisted condensation approach.[4] This method integrates microwave preparation of a metal (W, or Re) naphthalene dicarboxylate-based hybrid precursor with a single-step condensation using (3-aminopropyl)triethoxysilane, eliminating the need for pre-formed silica supports required in conventional impregnation routes. After calcination, amorphous, porous microspheres are obtained containing highly dispersed tungsten (2, 6, and 12 wt.%) or rhenium (2 wt.%) species, with no detectable crystalline WO₃ even at the highest W loading (Fig. 1). In ethanol dehydration at 420 °C, the W–SiO₂ microspheres exhibit higher activity and ethylene selectivity than a conventional 12 wt.% WO₃/SiO₂ catalyst. The 2W–SiO₂ catalyst achieves the highest ethylene productivity per mole of tungsten (520 mmol mmolW⁻¹ h⁻¹), retaining 230 mmol mmolW⁻¹ h⁻¹ after 1000 min on stream, indicating good long-term stability. On a mass-specific basis, the 12W–SiO₂ catalyst reaches 133 mmol g⁻¹ h⁻¹, outperforming previously reported tungsten–silica systems. Interestingly, the Re–SiO₂ microspherical catalysts exhibit high activity in ethanol dehydrogenation, achieving 55% conversion with >90% selectivity toward acetaldehyde.

Fig. 1: STEM-EDS elemental maps of 12W-SiO₂ microspheres.



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Acknowledgement (optional)

The work was supported by the MEYS CR within the DKRVO (RP/CPS/2024-28/007) project. The authors acknowledge CF CryoEM and CF NMR of CIISB, Instruct-CZ Centre, supported by MEYS CR (LM2023042) and European Regional Development Fund-Project „UP CIISB” (No. CZ.02.01.01/00/23_015/0008175). CzechNanoLab project LM2023051, funded by MEYS CR, is gratefully acknowledged for the financial support of the XPS measurements at CEITEC Nano Research Infrastructure. The work was financially supported by the Grant Agency of Masaryk University (GAMU) under the grant numbers MUNI/A/1298/2022.

Plasma- and Sonochemical-Assisted Nanoparticle Deposition: A General Toolbox for Robust Supported Catalysts

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Keywords: plasma functionalization; ultrasound-assisted deposition; supported catalysts; metal nanoparticles; oxide nanoparticles; interfacial engineering

Supported catalysts require high nanoparticle dispersion, strong adhesion to prevent catalyst deactivation, and tailored interfacial chemistry/electronics to steer activity and selectivity. We present a general, binder-free fabrication concept that couples low-temperature plasma activation of supports with ultrasound/sonochemical-assisted nanoparticle deposition, offering a versatile route for the fabrication of functional surfaces and robust supported catalysts.

In the first step, oxygen plasma is used to activate inert supports by creating oxygen-containing surface groups (e.g., -OH, C=O, -COOH) and enhancing wettability/compatibility with colloids, enabling controlled nanoparticle immobilization. This approach was shown to be effective for polymer substrates, where oxygen plasma treatment facilitated subsequent anchoring of photocatalytically active oxide nanoparticles and markedly improved coating formation. In the second step, nanoparticles are deposited from aqueous suspensions using electrostatic control (pH/ ζ -potential) and/or ultrasound-assisted deposition. Electrostatic deposition can give uniform initial coverage, but stability under operation may remain limited. The application of ultrasound increased loading and delivered stable performance over consecutive cycles, indicating significantly improved anchoring of photocatalytically active nanoparticles under cavitation-driven dispersion and impact.

Beyond oxide active phases (e.g., TiO₂, ZnO, Co₃O₄, Fe₂O₃), the platform naturally extends to metal nanoparticles (e.g. Au, Ag, Ni, Cu) on carbon supports, where electronic metal–support interactions can tune interfacial charge transfer. Notably, Ag nanoparticle decoration on graphene was shown to decrease the work function and promote electron transfer to O₂, enhancing ROS formation, providing a typical example of stimulating surface reactivity.

Overall, plasma activation combined with sono-assisted deposition emerges as a broadly applicable toolbox for the fabrication of durable, highly dispersed supported catalysts relevant to multifunctional active surfaces as well as photocatalytic processes.

Acknowledgement: This study was funded by the Ministry of Education and Science, Implementation Doctorate within “Funkcjonalne powłoki nanokompozytowe” project (DWD/6/257/2022).

Anton Paar - Autosorb 6300, physisorption and chemisorption analyzer

Jiří Špringer

^a Anton Paar Czech Republic s.r.o.

Keywords: Autosorb, physisorption, chemisorption, pulse titration

Instrument Autosorb 6300 - physisorption and chemisorption analyzer with integrated TCD, titration loop, mass flow controller (MFC), and dedicated vapor source input. Designed for measurements of active metal area, reduction/oxidation temperatures, specific surface area, and pore size distributions from 0.35 to 500 nm.



Fig. 1:

Insights into the Structure and Catalytic Activity of Highly Dispersed Cu Catalysts on ZrO₂/SiO₂ for Ester Hydrogenolysis

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Keywords: ester hydrogenolysis, methyl butyrate, ZrO₂/SiO₂

Heterogeneous Cu-based catalysts are widely used in hydrogenolysis and biomass hydrodeoxygenation reactions, due to the reduced Cu⁰ and Cu⁺ active sites. However, these active sites are prone to sintering under reaction conditions. To prevent sintering of the active sites in unsupported catalysts and enhance the structural and textural properties, the supported copper catalysts (e.g., Cu/SiO₂, Cu/Al₂O₃, Cu/ZrO₂, Cu/CeO₂) are commonly used [1, 2]. ZrO₂-promoted copper-based catalyst is preferred under aqueous conditions over other traditional supports, such as γ -Al₂O₃ or SiO₂, which are less stable. At the same time, the relatively low specific surface area and poor mechanical strength of ZrO₂ bring certain challenges, such as agglomeration, which restrict its potential applications to some extent [3, 4]. To address this limitation, the deposition of ZrO₂ onto high-surface area SiO₂ can effectively reduce the agglomeration and enhance Cu dispersion. Moreover, the role of Lewis acidic Zr (IV) site can easily combine with silica to form a metal oxide complex, which might be beneficial for the hydrogenolysis of ester to produce alcohol. Therefore, we report an efficient approach involving surface modification of silica by zirconia with an attempt to develop a highly efficient and stable Cu-based catalyst.

The catalysts were synthesized by the deposition precipitation (DP) method, where 1, 3, 5, and 7 wt% of ZrO₂ were deposited on SiO₂, and then 8 wt% of Cu was deposited following the DP method. Pyridine FTIR data of ZrO₂/SiO₂ supports showed that increasing ZrO₂ contents increase the Lewis acidity and generates Brønsted acidity. XRD and H₂-TPR data exhibited that ZrO₂ loading improved the Cu particle dispersion and the reducibility of the catalysts. To study the correlation of catalyst properties and catalytic behavior, methyl butyrate hydrogenolysis was used as a model reaction where butanol was the targeted product and butyl butyrate was the by-product from the transesterification reaction. Increasing ZrO₂ content increases conversion relative to the Cu/SiO₂ catalyst. The mechanism of methyl butyrate hydrogenolysis and the formation of other by-products, i.e., butanoic acid, butyl butyrate, and butane-1-methoxy, were analyzed with respect to the catalyst structural characteristics and acid properties.

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Acknowledgement: Financial support from the Czech Science Foundation (project No. GA25-17746S) is greatly acknowledged.

Design and development of supported Fe–Co bimetallic catalysts for ammonia synthesis

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Keywords: cobalt; iron; supported catalyst; ammonia synthesis

The Haber-Bosch process produces millions of tons of ammonia annually, essential for manufacturing fertilizers to support the growing global population. Since 2010, global ammonia production has been approximately 130–150 million tons per year, accounting for 2% of global energy consumption [1]. The continuous demand for ammonia has driven intensive research into developing new catalysts with a favorable activity-to-cost ratio, aiming for higher activity than commercial iron-based catalysts. Iron is not the only metal of interest in ammonia synthesis. Studies show that other transition metals, such as cobalt, ruthenium, nickel, and molybdenum, can be used. Their activity can be further tuned by careful selection of support and promoters, or by combining the active metals to create bimetallic systems. In this study, we investigated the effect of single (Co, Fe) and bimetallic (Fe–Co) catalysts supported on different supports, such as neodymium oxide and barium cerate (BC), on their properties and performance in ammonia synthesis.

The supports were synthesized by precipitation, as described previously [3,4]. The preparation of Fe, Co single and bimetallic Fe–Co (Fe:Co mass ratios of 95:5, 80:20, 50:50, 20:80) catalysts involved impregnating the support with the respective nitrate metal salt(s). The nominal metal(s) content was fixed at 10 wt%. The catalytic activity was evaluated in ammonia synthesis at 470 °C and 6.3 MPa. Detailed characterization of the catalysts was carried out using XRD, XPS, STEM-EDS, and temperature-programmed desorption (e.g., N₂-TPD and H₂-TPD).

Catalyst testing revealed differences in activity depending on the support choice. For the catalysts supported on barium cerate, the activity ranged from 0.3 g_{NH₃} g^{−1} h^{−1} to 2.6 g_{NH₃} g^{−1} h^{−1}, with the lowest value observed for Fe/Nd₂O₃ and the highest for Co/Nd₂O₃. Combining Fe and Co resulted in an improved reaction rate (1.2 g_{NH₃} g^{−1} h^{−1}) compared to the Fe/BC catalyst; however, it was still about 2 times lower than that of the Co/BC catalyst. For catalysts supported on neodymium oxide, in turn, the activity was almost no dependent on the cobalt addition. The activity of all catalysts varied from 1.0 g_{NH₃} g^{−1} h^{−1} to 1.2 g_{NH₃} g^{−1} h^{−1}, with the lowest value observed for Fe/Nd₂O₃ and the highest value observed for Co/Nd₂O₃. These results demonstrate that the catalytic behavior is primarily dependent on the nature of the support. While Nd₂O₃ limits the performance regardless of composition, barium cerate promotes the formation of highly active sites and enables a composition-dependent activity trend. The Fe–Co system exhibits a synergistic effect only on the barium cerate support, where cobalt enhances the effectiveness of active sites, whereas on Nd₂O₃ this effect is suppressed. This is likely due to differences in metal–support interactions and the ability of the support to stabilize electronically and structurally active phases.

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Acknowledgement: This research has received funding from the European Union, within HORIZON Europe Research and Innovation Actions, HORIZON-CL4-2023-TWIN-TRANSITION-01-42 NEO-CYCLE project, no. 101138058. Views and opinions expressed are, however, those of the authors only and do not necessarily reflect those of the European Union. The European Union cannot be held responsible for them.



Funded by
the European Union

Boosting Methanol Steam Reforming Activity: Flame Forged Cu-Fe-Oxides

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Keywords: MSR, Catalysis, FSP, Spinel, Perovskites

Introduction

Methanol steam reforming (MSR) is a key catalytic process for decentralised hydrogen production, where Cu-based catalysts remain the industrial benchmark due to their high activity at moderate temperatures [1]. However, insufficient stability and undesired CO formation still limit their applicability [2]. Mixed Cu–Fe oxides have emerged as promising alternatives, as iron can modify copper dispersion, redox properties, and metal–support interactions. In particular, structural motifs such as spinels and perovskites offer tunable cation environments that directly affect catalytic performance. In this contribution, we compare Cu–Fe oxide catalysts prepared by flame spray pyrolysis (FSP) with conventionally synthesised materials, focusing on the influence of synthesis route and crystal structure (spinel vs perovskites) on MSR activity and selectivity.

Methodology

Cu–Fe oxide catalysts with the respective elemental composition CuFe_2O_4 (spinel-type oxide, abbreviation CF) and $\text{Nd}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.9}\text{Cu}_{0.1}\text{O}_3$ (perovskite-type oxide, abbreviation NCF-Cu10) were synthesised via FSP and benchmarked against materials prepared by a modified Pechini method. Phase composition and crystallinity were characterised by XRD, while morphology and particle size were analysed using SEM imaging. Temperature-programmed reduction (TPR) was employed to assess the individual redox behaviour. Elemental composition was verified by MP-AES. Catalytic MSR performance was evaluated in continuous-flow fixed-bed reactors under relevant reforming conditions, with a focus on specific activity and CO/CO_2 selectivity.

Results

Catalytic testing of the Pechini-derived Cu–Fe oxide catalysts reveals clear structure–performance relationships in MSR. Among the investigated materials, CF exhibits a significantly higher specific activity than NCF-Cu10 under identical reaction conditions. In addition to the enhanced activity, CF exhibits markedly improved CO_2 selectivity, indicating a more favourable reaction pathway with suppressed CO formation.

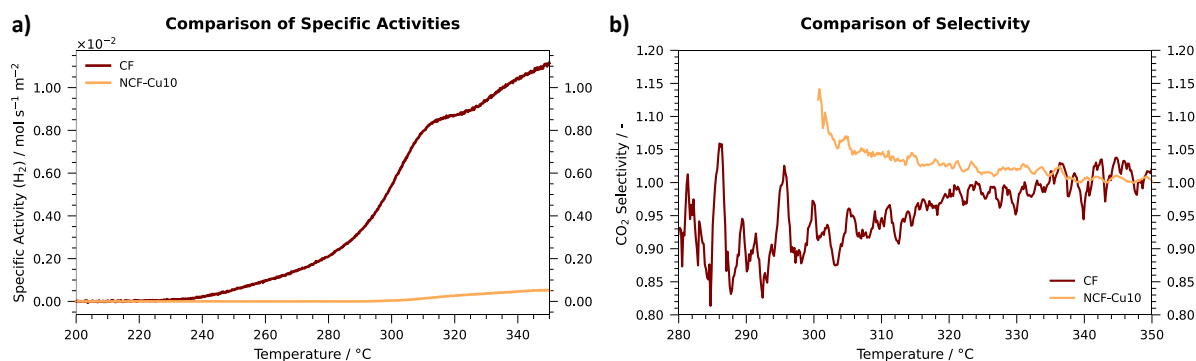


Fig. 1: a) Comparison of specific H_2 formation rates (specific activity) under MSR conditions over CF and NCF-Cu10. b) Corresponding CO_2 selectivity profiles. For clarity, the temperature axis was truncated because low product formation at lower temperatures reduces the signal-to-noise ratio.

These findings indicate that the spinel-type CF provides a more effective catalytic environment compared to NCF-Cu10. Structural and morphological analyses support distinct differences between the catalysts with different elemental compositions.

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Acknowledgement

This research was funded in part by the Austrian Science Fund (FWF) [10.55776/COE5] (Cluster of Excellence MECS) and by the Austrian Agency for Education and Internationalisation (ASEA-UNINET).

From waste to value: FCC catalysts in plastic recycling

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Keywords: zeolites, plastics, FCC catalyst, *operando*

Plastics provide substantial convenience in daily life, with applications in food packaging, textiles, electronic components, and mechanical parts. Global plastic production is expected to triple over the next 40 years; however, limited recyclability presents a significant environmental challenge. At present, only around 10% of plastic waste is recycled [1], highlighting the need to consider plastic waste as a valuable resource. Fluid catalytic cracking (FCC) catalysts provide a well-established and flexible platform for converting low-value heavy oil fractions into gasoline-range hydrocarbons and light olefins, primarily utilizing high-silica FAU and MFI zeolites. Given that the chemical composition of plastics closely resembles that of crude oil fractions, it is reasonable to leverage the extensive experience of FCC technology for their conversion.

In this study, both fresh and equilibrium (modified by Cyclic Propylene Steaming) commercial FCC catalysts, supplied by W.R. Grace & Co., were employed for the catalytic cracking of polypropylene (PP) and low-density polyethylene (LDPE). The catalysts were calcined either at 550 °C – representative of standard crude oil cracking conditions, or at 800 °C – simulating regeneration conditions (yielding Cat-F800 and Cat-Eq800) prior to characterization. Structural, textural, and acidic properties were characterized using conventional techniques, including X-ray diffraction (XRD), low-temperature nitrogen sorption, and *in situ* Fourier-transform infrared (FTIR) spectroscopy with CO, pyridine (Py), and di-tert-butylpyridine (dTBP) as probe molecules. The results were compared to zeolite USY-31 (CBV760) and pseudo-boehmite alumina extrudate. Comprehensive thermogravimetric (TGA-GC&MS) and spectroscopic (*operando* FTIR-GC&MS) investigations of the cracking process, including catalyst coking and regeneration, provided detailed insights that help establish guidelines for the rational design of application-specific catalysts. The MCR-ALS algorithm was employed to extract concentration profiles and pure spectra of spectroscopically active components during PP isothermal cracking and coke oxidation for each catalyst.

Dealumination during the steaming of Cat-F to produce Cat-Eq modifies the original microporosity of the zeolitic analogs. Consequently, the S_{micro} and V_{micro} values for both Cat-Eq catalysts decrease by approximately 30% relative to their Cat-F counterparts. The ^{27}Al MAS NMR spectra (Fig. 1A) for Cat-F and Cat-Eq reveal significant changes in aluminum coordination. The uncalcined Cat-F exhibits an intense and relatively broad Al(VI) signal at 0 ppm, which reflects a considerable proportion of octahedrally coordinated, hydrated aluminum species originating from both the binder and the zeolite phase. The concentration of Brønsted acid sites (BAS) in Cat-Eq is reduced by approximately 3.5-fold compared to Cat-F due to dealumination. Following a more severe thermal treatment at 800 °C, the BAS content decreases even further; however, the remaining acid sites show a significant increase in acid strength.

All catalysts significantly lower the PP decomposition temperature compared to its thermal degradation (Fig. 1B). In addition, a linear correlation is observed between $T_{50\%}$ and the strength of Brønsted acid sites across all catalysts. Importantly, the reduction in micropore volume and the number of intrinsic Brønsted acid sites in Cat-Eq and Cat-Eq800 does not lead to any significant loss in catalytic performance. For LDPE, in contrast to PP, no straightforward correlation is found between the cracking temperature and the strength of Brønsted acid sites. Instead, the temperature at which 50% conversion is achieved is linked to the density of Brønsted acid sites (BAS/S_{BET}). These results suggest that the influence of polymer structure, carbocation stability, and intracrystalline diffusion are crucial. PP undergoes cracking more easily due to the presence of tertiary carbons, which generate relatively stable carbocations and thus lower the activation energy required for β -scission. In contrast, LDPE consists predominantly of secondary carbons, leading to less stable carbocation intermediates and greater resistance to cracking.

Operando FTIR&GC-MS studies were carried out isothermally to investigate the chemical recycling of PP (275 °C) and LDPE (230 °C) over the catalysts. This setup enables real-time monitoring of surface reactions while simultaneously analyzing the products released, providing direct correlation between catalyst surface processes and product composition. The two most active catalysts, Cat-F800 and Cat-Eq800, exhibit identical conversion levels, which permits a direct comparison of their product selectivity and cracking behavior.

A detailed analysis of the physicochemical properties of laboratory-made and commercial FCC catalysts (fresh and equilibrated) coupled with their performances in the cracking of pure polymers under laboratory conditions (conversion, selectivity, coking and coke removal) indicates that laboratory prepared catalysts can help rationalize the performances of existing commercial catalysts, either “fresh” or “equilibrated” (*i.e.* simulating many cycles of reaction/coking/coke removal) and contribute to their optimal design.

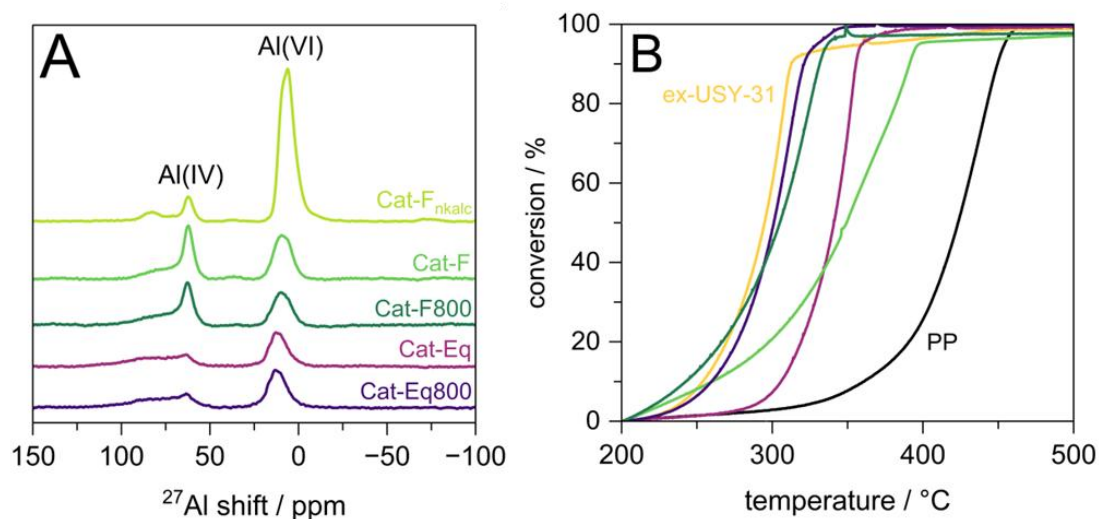


Fig. 1: (A) ^{27}Al MAS NMR spectra of commercial FCC catalysts and (B) PP catalytic cracking conversion as a function of temperature

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Acknowledgement

This research was funded by the National Science Centre, Poland [Grant No. 2021/43/B/ST4/00307].

Challenges of scaling up the manufacturing of heterogeneous catalysts to industrial scale

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Keywords: Scale-up, Supported metal oxide catalysts, Industrial manufacturing

In this presentation, the scale-up towards industrial manufacturing of supported metal oxide catalysts will be discussed. Key challenges and all aspects that need to be addressed when scaling up from a laboratory recipe to an industrial scale process will be presented for various production processes like precipitation and impregnation, as well as for the post-processing technologies like washing, drying, calcination, and shaping. The importance of a robust process, quality control and standardized analytical methods to ensure consistent material properties and application performance is emphasized.

LDH-derived CuZnAl mixed oxides as catalysts for catalytic transfer hydrogenation of furfural: The effect of co-precipitation conditions

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Keywords: CuZnAl mixed oxides; Cu surface area; catalytic transfer hydrogenation; furfural hydrogenation.

Furfural (FF) has considerable potential as a feedstock for the sustainable production of bio-based chemicals. Its annual production is about 300,000 tons, and 65% is used to obtain furfuryl alcohol (FA). FA is an important intermediate between pentoses and bio-based furan derivatives. It is generally produced by direct FF hydrogenation with molecular hydrogen. However, pure H₂ is difficult to transport and store. Additionally, it is produced from fossil reserves. A promising environmentally and economically beneficial approach for FF hydrogenation is catalytic transfer hydrogenation (CTH) using alcohols as H₂ donors. But a lot of work is necessary to develop highly active, selective, and stable catalysts for this process. As evidenced from previous literature, Cu-containing catalysts are promising catalysts for the FA production. Many studies are focused on the comparison of physico-chemical properties and performance of the Cu catalysts prepared by different synthesis methods or by varying Cu content. However, the influence of synthesis variables on the physico-chemical properties and catalytic performance of Cu catalysts has not yet been fully disclosed.

In this study, we investigated the influence of synthesis conditions on the physico-chemical properties of CuZnAl layered double hydroxides (LDHs) and derived mixed oxides (MOs) with the fixed chemical composition (atomic ratio (Cu+Zn)/Al=3, Cu/(Cu+Zn)=0.7), as well as the activity and selectivity of the CuZnAl MOs in FF hydrogenation. The CuZnAl LDH precursors were prepared by a routine co-precipitation method, but using varying synthesis conditions (pH, temperature, and coprecipitation duration). CuZnAl MOs were obtained by the calcination of the LDH precursors at T=350 °C. The properties of all prepared samples were examined by AAS, XRD, SEM, H₂-TPR, NH₃-TPD, N₂ physisorption, and N₂O chemisorption. The performance of CuZnAl MOs was evaluated in CTH of FF at mild reaction conditions and N₂ atmosphere (FF+isopropanol reaction mixture, T=135 °C and p_{N2}=5 bar, t=0-4 hours) using a Parr stirred autoclave and isopropanol as an H₂ donor. During the experiments, reaction samples were periodically withdrawn from the autoclave and analysed by GC. The stability of prepared catalysts was evaluated in the long-run experiments at t=130 °C and p_{N2}=5 bar using a flow unit with a fixed

catalyst bed and FF+isopropanol reaction mixture. According to AAS, the chemical composition of all prepared solids was close to target values, proving the efficiency of the synthesis method. However, incomplete precipitation of Zn was observed at pH below 6, resulting in increased Cu content in the samples. SEM evidenced the layered morphology of both as-prepared and calcined materials. Additionally, this method proved that synthesis conditions affected the size and morphology of LDH platelets. XRD showed that, regardless of coprecipitation variables, the CuZnAl precursors were phase-pure LDHs. Co-precipitation temperature substantially influenced the size of coherent domains (crystallite size) of the LDH phase, which varied from 7 nm ($T=20\text{ }^{\circ}\text{C}$) to 21 nm ($T=60\text{ }^{\circ}\text{C}$). Crystallite size also increased with increasing pH for the LDH samples from below 8 nm ($\text{pH}\leq 6.5$) to above 14 nm ($\text{pH}=9-10$). While the XRD patterns of all MOs showed the absence of reflections from copper, zinc, and aluminium oxides, with only one broad peak at about $2\theta\text{ }(^{\circ}) = 35$, indicating that either the samples were amorphous or the oxide particles were very small. According to N_2O chemisorption data, Cu surface area in the samples was also dependent on the synthesis conditions: the growth of both coprecipitation temperature and pH values resulted in a decrease in Cu surface area. According to H_2 -TPR, the reduction temperature of CuO for all MOs was about $250\text{ }^{\circ}\text{C}$, i.e., higher than the typical value for the reduction of bulk CuO. This proved that Cu atoms were embedded into the MO structure. Reduction profile became more complicated with the increase of both precipitation pH and temperature, as well as the shortening of the co-precipitation duration. This proved the impact of synthesis conditions on the generation of Cu species, which differ in their properties. All the MOs were tested in the CTH of FF. Three series of catalytic experiments were carried out, investigating the impact of each of the variables: pH, temperature, and duration. The activity of MOs increased linearly with decreasing coprecipitation pH values in the range of 6-10, and FF conversion reached 100% after 3 h of the reaction over MO prepared at pH 6. The impact of coprecipitation duration was more complicated: FF conversion increased with the growth of synthesis time from 30 min to 90 min, but further increase in the coprecipitation duration resulted in a decline in FF conversion. This proved the existence of the optimal co-precipitation time. At last, FF conversion decreased with increasing coprecipitation temperature from 20 to $60\text{ }^{\circ}\text{C}$. Taking into account the results of physico-chemical characterization, it was concluded that the improvement in the performance of CuZnAl catalysts correlated with the decrease in the crystallite size of the materials and the growth of Cu surface area. In all cases, FA selectivity was above 95% (with 5-MF as the main by-product), thus evidencing the high efficiency of the CuZnAl MOs in the CTH of FF to FA. Additionally, experiments in a flow unit demonstrated the stable performance of Cu containing catalyst during 70 hours of TOS. The obtained results showed that, even at a similar chemical composition of the reaction mixture, coprecipitation variables significantly affect the properties and performance of the prepared CuZnAl catalysts. The optimization of these parameters allows preparing CuZnAl catalysts that ensure 100% FF conversion with over 95% FA selectivity.

Acknowledgement: The authors thank GAČR for financial support (project No. 25-16024S)

Molecular modeling of a catalytic oxide heterojunction of the $\text{Co}_3\text{O}_4|\text{CeO}_2$ type – insight into redox properties based on interactions with an oxygen molecule

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Keywords: DFT molecular modeling, cobalt spinel, ceria, ab initio thermodynamics, catalytic heterojunctions

Cobalt oxide–ceria heterostructures ($\text{Co}_3\text{O}_4|\text{CeO}_2$) have attracted considerable attention because of their wide-ranging applications in sensing, photocatalysis, catalysis, and, more recently, electrocatalysis. These hybrid systems display pronounced synergistic effects, resulting in photo-, electro-, and thermocatalytic performances that surpass those of the individual components. Their catalytic properties have been extensively studied in reactions such as CO, CH_4 , and C_3H_6 oxidation, CO-PROX, and N_2O decomposition. In all these processes, oxygen activation and surface mobility are key factors, participating in multiple elementary steps of the reaction mechanisms, often described by interfacial Mars–van Krevelen (MvK) and suprafacial Langmuir–Hinshelwood (LH) pathways. It is widely accepted that the presence of CeO_2 , along with catalyst morphology, significantly influences the activity of the spinel phase by affecting oxygen activation and the formation of oxygen vacancies. In the synthesis of catalytic heterojunctions, co-precipitation is commonly used but suffers from several limitations, including limited control over particle size and morphology, compositional heterogeneity, and the potential formation of unwanted phases. A more controlled strategy involves preparing Co_3O_4 and CeO_2 separately with well-defined structures and subsequently assembling them into heterojunctions via methods such as sonication or electrodeposition. This approach enables more precise tuning of the interface structure.

Density functional theory (DFT) plays a crucial role in modeling $\text{Co}_3\text{O}_4|\text{CeO}_2$ heterojunctions, as it provides atomistic insight into the interface and its impact on electronic properties. DFT allows for quantitative evaluation of charge transfer between ceria and the spinel phase, changes in oxidation states ($\text{Ce}^{3+}/\text{Ce}^{4+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$), and the stabilization of oxygen vacancies and surface oxygen species, which are central to O_2 activation mechanisms [2]. Additionally, it facilitates the calculation of adsorption energies, identification of active interfacial sites, and exploration of reaction pathways leading to superoxide or peroxide species. These insights help establish a direct link between the local electronic structure and catalytic performance, supporting experimental observations and enabling the rational design of improved CeO_2 –cobalt spinel catalysts.

A major challenge in such studies is the construction of a reliable heterojunction model that accurately represents active sites while remaining computationally feasible. In this work, we propose a method for developing a periodic model of the $\text{Co}_3\text{O}_4|\text{CeO}_2$ interface based on well-defined nanograins of both oxides. We further examine the electronic structure and stability of the model under interaction with oxygen molecules, including adsorption, activation, lattice oxygen release, and vacancy formation. The computational findings are complemented by catalytic measurements performed on heterojunctions prepared via sonication.

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The Polish National Science Centre supported this work within the framework of the OPUS-28 project (grant no. 2024/55/B/ST4/01383).

This work was also supported by the strategic program Excellence Initiative - Jagiellonian University.

Gold-metal phosphate catalysts for microwave-assisted glucose oxidation: effects of preparation method and support composition

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Keywords: metal phosphate, gold, glucose oxidation, gluconic acid, H₂O₂

The present study contributes to ongoing efforts to develop and understand the reactivity of heterogeneous gold-based catalysts addressed to selective oxidation of biomass-derived substrates into valuable chemicals. Despite extensive research, the current literature does not provide a complete explanation of the activity of gold nanoparticles in oxidation processes using H₂O₂ as an oxidant, nor does it fully clarify the possible reaction pathways, especially when considering the microwave-assisted selective oxidation processes. In this context, the aim of this study was to elucidate the influence of the gold deposition method and support composition on surface properties of gold catalysts and their catalytic activity in microwave-assisted oxidation of glucose using H₂O₂ as an oxidant. In addition, special attention was devoted to elucidating the reaction pathways and identifying the nature of the active species and sites responsible for the oxidation process.

Supports for gold, namely cerium phosphate (CePO₄), aluminum phosphate (AlPO₄) and zirconium phosphate (ZrPO₄) were synthesized by a facile hydrothermal method according to the procedure described in [1,2]. Gold nanoparticles (2 wt.% of Au) were loaded on the surface of CePO₄ support using three different procedures: deposition-reduction (DR), deposition-precipitation with urea (DPU) and anchoring of gold species on the support functionalized with (3-aminopropyl)trimethoxysilane (grafting - GR) [1,2]. In the case of AlPO₄ and ZrPO₄ supports, gold was deposited only using the grafting method. All materials were characterized by ICP-OES, XRD, N₂ adsorption/desorption, NH₃-TPD, STEM with EDS analysis, as well as DR UV-Vis, FT-IR, and XPS spectroscopies. Catalytic activity of the prepared materials was evaluated in base-free glucose oxidation in a microwave synthesis platform MicroSYNTH (from Milestone, Italy), with the use of H₂O₂ as an oxidant. Products of glucose oxidation were identified and quantified using UHPLC.

The efficiency of gold deposition on the support surfaces was close to or reached 100%, regardless of the modification method or the type of metal phosphate used. UV-Vis, XPS spectroscopies and STEM imaging evidenced the presence of metallic gold in all catalysts. The gold nanoparticles were well dispersed over the surface of all metal phosphates; however, their average particle size differed, increasing in the sequence: Au/AlPO₄-GR (4.4 nm) < Au/Zr-PO₄-GR (5.5 nm) ≈ Au/CePO₄-GR (5.6 nm) < Au/CePO₄-DR (6.0 nm) = Au/CePO₄-DPU (6.0 nm).

All obtained gold catalysts showed 100% selectivity for the oxidation of glucose to the desired product, gluconic acid, although they differed in activity in the studied reaction. The results obtained in this study clearly show that the gold deposition method plays a determinant

role in controlling the surface properties and catalytic activity of gold catalysts supported on CePO_4 in microwave-assisted oxidation of glucose. It was demonstrated that Au/CePO_4 prepared via the grafting method ($\text{Au/CePO}_4\text{-GR}$) exhibits superior catalytic activity and efficiency in both H_2O_2 decomposition and glucose oxidation compared to catalysts supported on CePO_4 prepared by deposition-reduction (DR) or deposition-precipitation with urea (DPU). Considering the composition of the support, catalytic tests showed that cerium(III) phosphate is the most promising support among studied phosphates (Figure 1).

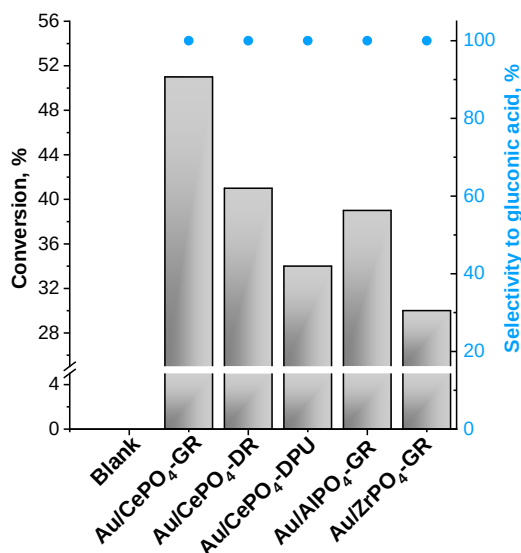


Fig. 1: Results of glucose oxidation with H_2O_2 and microwave heating over studied gold catalysts. Reaction conditions: 8 mL of 0.2 M glucose solution, glucose/Au (molar ratio) = 2140/1, $T = 90^\circ\text{C}$, 2.2 equiv. H_2O_2 , time = 20 min.

$\text{Au/CePO}_4\text{-GR}$ enabled very efficient conversion of glucose to gluconic acid in a very short reaction time (90 % glucose conversion in just 20 min, at 120°C) and could be successfully reused without any significant deactivation. The enhanced reactivity of $\text{Au/CePO}_4\text{-GR}$ originated from its strong surface acidity and the optimal gold particle size from among all synthesized materials. Concerning the analysis of reaction pathways, it was evidenced that the main oxidizing agent responsible for the efficient transformation of glucose into gluconic acid was molecular oxygen formed upon catalytic activation of H_2O_2 .

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ID-UB (UAM) Project Excellence Initiative - Research University financial support (project no 140/04/POB3/0007) is gratefully acknowledged.

We acknowledge the Czech Science Foundation for the project no. 23-08031K.

Engineering $\text{Co}_3\text{O}_4(100)/\text{CeO}_2$ Heterojunctions for Enhanced DOR and N_2O Decomposition: A Combined Synthesis, AI-Driven Modeling, and Experimental Study

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Keywords: DFT molecular modeling, ceria, ab initio thermodynamics, surface reconstruction

The (100) surface of cobalt spinel (Co_3O_4) is recognized as a highly efficient catalytic interface, particularly for the deep oxygen reduction reaction (DOR) and nitrous oxide (N_2O) decomposition. While surface modification via bulk or surface doping can enhance activity [1], such strategies often introduce undesirable changes in crystal morphology, potentially compromising structural integrity. To overcome this limitation, this study presents an alternative approach based on the formation of heterojunctions with cerium oxide ($\text{Co}_3\text{O}_4|\text{CeO}_2$) [2]. This strategy, based on sonication of both oxides, effectively modifies the electronic structure of the active surface while preserving the original crystal morphology, thereby optimizing catalytic performance without the structural drawbacks associated with traditional doping methods.

An efficient way to synthesize cobalt spinel and ceria-based heterojunction exposing the most active and stable (100) facets was developed. Nanocubes of Co_3O_4 and CeO_2 were synthesized by means of hydrothermal methods and combined together by sonication and subsequent calcination. The samples were characterized by means of XRD, RS, SEM/TEM/STEM/EDX, and XPS techniques. Oxygen isotopic exchange experiments were conducted to investigate surface and bulk oxygen mobility, followed by N_2O decomposition studies in the TPSR mode.

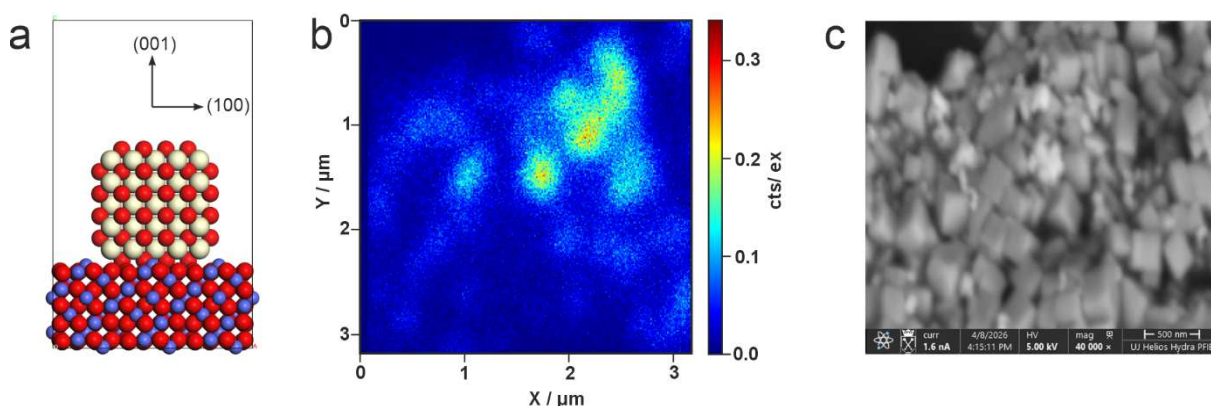


Figure 1. (3×3) Co_3O_4 (100) slab with $\text{Ce}_{62}\text{O}_{124}$ nanocluster (a), $^{18}\text{O}_2$ TOF-SIMS 2D FIB map (b), SEM BSE image of FIB profiling area before experiment (c)

Complementary molecular modeling was performed to elucidate the interface structure using cluster models of ceria supported on a cobalt spinel substrate (described within a slab model). To investigate the effect of CeO_2 cluster size, a large number of models (differing in both size and shape) were constructed. From this set, three optimal configurations containing 72, 186, and 405 atoms (**Fig. 1a**) were selected. Using Machine Learning Force Fields (MLFF), the potential energy surface for the mutual alignment of the Co_3O_4 slab and nanoclusters was scanned to identify global energy minima. These structures were further refined using a custom-developed Rigid-Body Relaxation algorithm at the GGA-DFT+U level. Analysis of Density of States (DOS) profiles revealed that interfacial electron flow is governed by surface defect states, regulated by the presence of oxygen vacancies. The theoretical results regarding charge transfer and defect mediation were conclusively corroborated by experimental data from X-ray Absorption Spectroscopy (XAS) and high-

resolution FIB-ToF-SIMS depth profiling (**Fig.1b,c**), establishing a definitive structure-activity relationship for this novel heterojunction system.

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Acknowledgements

This work was supported by the the Polish National Science Centre within the framework of the OPUS-28 project (grant no. 2024/55/B/ST4/01383).

Authors acknowledge the Polish high-performance computing infrastructure PLGrid for awarding this project access to the LUMI supercomputer, owned by the EuroHPC Joint Undertaking, hosted by CSC (Finland) and the LUMI consortium through PLL/2024/06/017087.

Authors acknowledge the Polish high-performance computing infrastructure PLGrid (HPC Center: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2025/018472.

This work was also supported by strategic program Excellence Initiative - Jagiellonian University.

Effect of preparation method on the catalytic properties of hydrotalcite-derived CuZnAl mixed oxides supported on SiO₂ for the hydrogenolysis of methyl butyrate to butanol

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Keywords: hydrotalcite-derived, CuZnAl oxides, SiO₂, composite, hydrogenolysis

Introduction. Catalytic upgrading of biomass-derived oxygenates to renewable fuels and chemicals is essential for carbon-neutral energy systems. Hydrogenation and hydrogenolysis convert oxygen-rich molecules into energy-dense alcohols such as butanol [1], an important fuel additive and platform chemical [2]. Copper-based catalysts are attractive due to their high C=O hydrogenation selectivity and low cost compared to noble metals [3]. Hydrotalcite-derived CuZnAl mixed oxides are versatile catalysts with tunable composition, highly dispersed metal species [4], and favorable redox and acid–base properties [5]. Upon calcination, layered double hydroxides form mixed oxides of CuO [6], ZnO, and Al₂O₃ [7]. These provide Cu⁰ sites for hydrogenation, while ZnO and Al₂O₃ stabilize the Cu nanoparticles [9]. However, their relatively low surface area and copper sintering at high temperature reduce performance [10]. Adding high-surface-area SiO₂ improves dispersion, and enhances mesoporosity. The preparation method is crucial for metal dispersion, metal–support interaction, and active-site accessibility: chemical mixing (CM) during co-precipitation yields more homogeneous composites, and physical mixing (PM) was also used as a reference to confirm the enhancement achieved by CM method. We synthesized SiO₂-supported CuZnAl hydrotalcite-derived catalysts by CM and PM, examining two compositions with different preparation and Cu loadings (CuZnAl-1: 53.8 wt.% Cu and CuZnAl-2: 7.7 wt.% Cu).

Methodology. CuZnAl hydrotalcite precursors were synthesized by co-precipitation at pH 10 (60 °C, 300 rpm), followed by ageing, filtration, drying (60 °C), and calcination in air at 350 °C for 3 h. For the CM composite, commercial SiO₂ (Sipernat®50, 1:1 wt. ratio) was added directly to the precipitation medium; for the PM composite, the calcined oxide was mechanically mixed with SiO₂ in a mortar. Catalysts were characterized by XRD, N₂-sorption, H₂-TPR, XRF, and SEM. Methyl butyrate (MB) hydrogenolysis was performed in a stainless-steel batch reactor (Parr) at 250 °C, 60 bar H₂, using 1 g catalyst in 10 mL MB + 140 mL decalin + 200 µL octane (internal standard). Catalysts were reduced in situ at 300 °C under pure H₂ for 40 min before each test. Liquid products were analysed by GC-FID (Agilent 7890A, HP-5 column).

Results and discussion. XRD patterns (Fig. 1) confirmed layered double hydroxide formation in all precursors, with reflections at 2θ: 11.8°, 23.6°, 38.9°, 60.3°, and 61.7° corresponding to the (003), (006), (009), (110), and (113) planes. After calcination at 350 °C, these reflections disappeared and CuO (tenorite) peaks appeared at 2θ: 35.6 and 38.7°, while ZnO and Al₂O₃ remained amorphous or beyond the detection limit of XRD. SiO₂ incorporation broadened CuO reflections and produced a broad hump at ~22° (amorphous silica), indicating improved CuO dispersion. Catalytic performance in MB hydrogenolysis of CuZnAl-1 (Cu 53.8 wt.-%) and CuZnAl-2 (Cu 7.7 wt.-%) is shown in Fig. 2. Pristine CuZnAl-1_350 exhibited the highest hydrogenolysis activity, attributed to a higher density of accessible Cu⁰ sites. At 800 °C, copper is increasingly incorporated into the stable (Cu_xZn_y)Al₂O₄ spinel phase [8]. This copper species is strongly bound and difficult to reduce, limiting active copper species under reaction conditions. SiO₂ addition lowered MB conversion for both CM and PM composites, consistent with partial dilution of active copper, while butanol selectivity was preserved. This, together with the performance of pristine CuZnAl-1_350, indicates that SiO₂-modified acid–base properties affect both hydrogenolysis and side reactions [11].

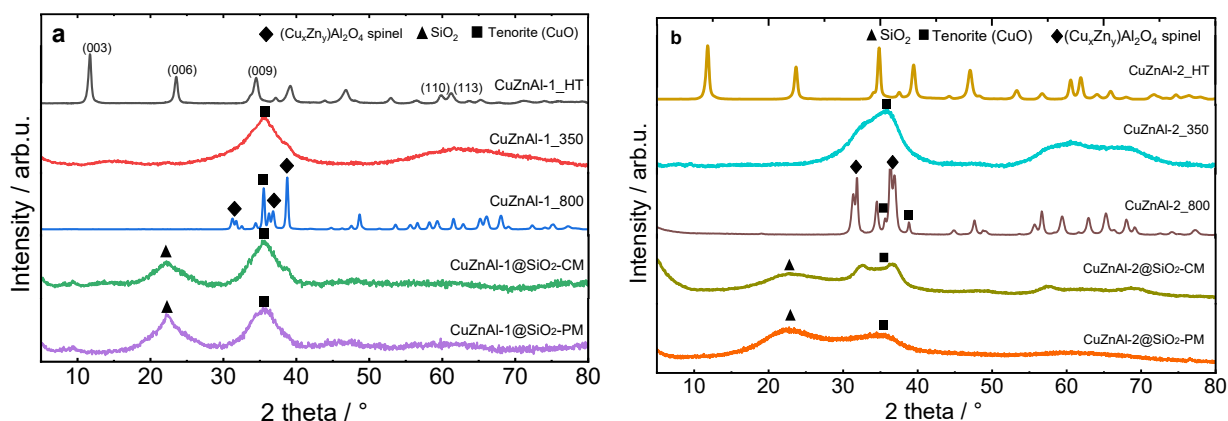


Fig. 1: XRD Patterns of the CuZnAl-1 (a) and CuZnAl-2 (b) hydrotalcite-derived based composites with SiO₂ support.

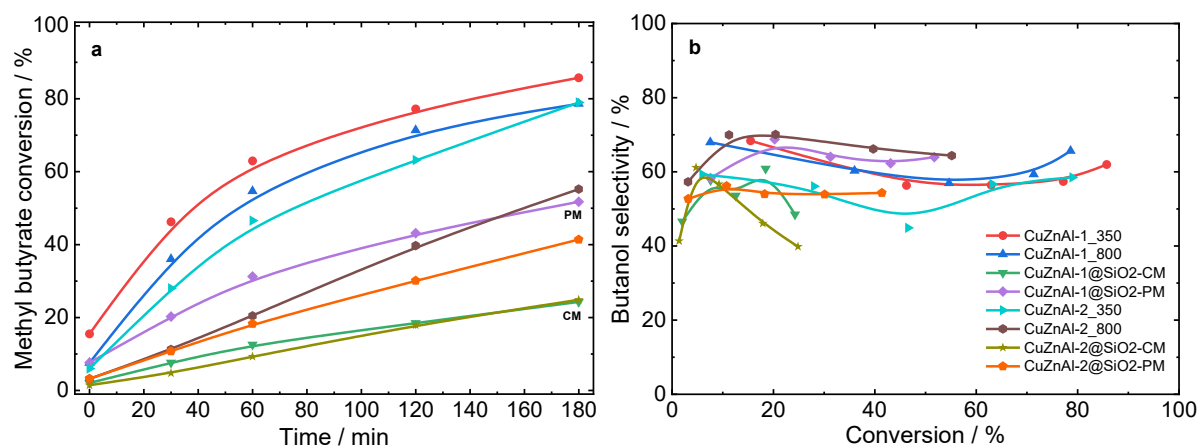


Fig. 2: Methyl butyrate conversion over time of CuZnAl catalysts (a) and selectivity towards butanol (b). Reaction conditions: 250 °C, 60 bar H₂, 10 ml Methyl Butyrate (MB) + 140 ml decalin + 200 µl octane.

Conclusions. CuZnAl hydrotalcite-derived catalysts with varying copper contents and SiO₂ incorporation via chemical (CM) and physical mixing (PM) were systematically investigated for the hydrogenolysis of methyl butyrate to butanol. Pristine CuZnAl exhibited the highest apparent hydrogenolysis activity (~80% conversion), while SiO₂-supported composites showed lower overall conversion, primarily due to dilution of active copper sites, but maintained butanol selectivity. Notably, the CM-prepared catalysts exhibited lower activity than their PM counterparts, suggesting that the incorporation method affects the composite structure and the accessibility of active sites, which requires further investigation. Overall, these results highlight the importance of considering copper content when comparing catalytic performance and demonstrate that the preparation route plays a key role in tuning Cu⁰ dispersion and reducibility in CuZnAl@SiO₂ composite catalysts for hydrogenolysis.

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From Flames to Stability: Perovskite-type oxides via Flame Spray Pyrolysis

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Keywords: Catalysis, Flame Spray Pyrolysis, Synthesis, Perovskite-Type Oxides

Introduction

Perovskite-type oxides have gained considerable interest as catalysts for energy conversion reactions due to their structural flexibility and ability to exhibit **exsolution** (growth of nanoparticle on the surface, activated by e.g. reduction). By incorporating A- and B-site doping of the complex oxides the catalytic performance can be readily enhanced [1]. In order to deliberately modify the catalysts, increased control over the synthesis parameters is necessary). In this regard, **Flame Spray Pyrolysis** (FSP) presents a promising synthesis approach. Due to its precise control over synthesis conditions, it allows for regulating the **precursor and material composition**, as well as **tunability of particle size** [2].

Methodology

The perovskite-type oxide (ABO_3) with the formula $Nd_{0.6}Ca_{0.4}Fe_{0.9}Cu_{0.1}O_3$ (NCF-Cu10) was investigated as a proof of concept for the synthesis of complex oxides with FSP. XRD measurements of the pristine materials were conducted to determine their phase purity after synthesis. Their **macrostructural properties** - specifically the specific surface area and particle size distribution - were characterised using Brunauer-Emmett-Teller (BET) and Particle Size Analysis (PSA) methods. Furthermore, the **flame behaviour** and **spray characteristics** under varying synthesis conditions and precursor compositions were evaluated using high-speed imaging.

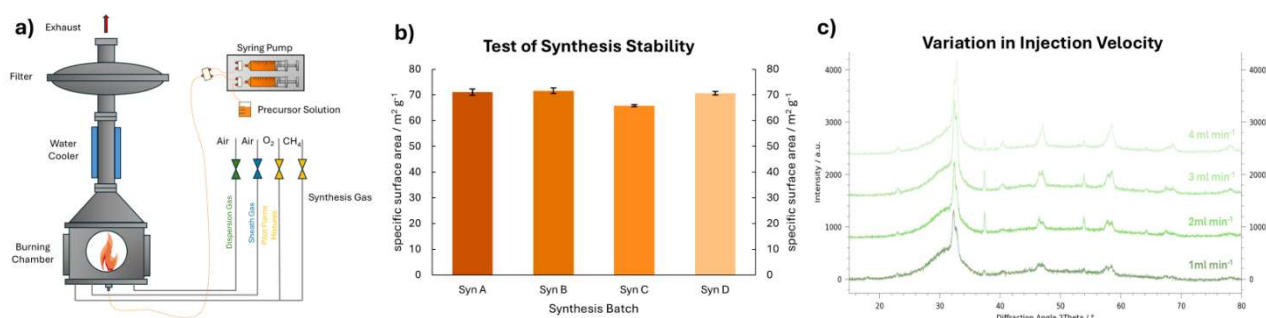


Fig. 1: a) Schematic illustration of a FSP unit b) BET averaged specific surface area of four synthesis repetitions of the pristine material NCF-Cu10 c) Ex-situ x-ray (XRDs) diffractograms of four synthesized materials (NCF-Cu10) at four different precursor injection flow rates

Results & Discussion

Analysis of the obtained data shows that a higher liquid-to-gas ratio decreases the specific surface area. This effect is independently occurring with either the variation of the injection velocity or dispersion gas flow rate. Additionally, humidity in the system also leads to lower specific surface areas. Moreover, the precursor composition influences the phase purity of the

synthesised material. It is shown, with an RSD of 4%, that the Flame Spray Pyrolysis is a stable, **reproducible synthesis** method.

Conclusion

The results show that complex oxides with specific **surface areas** up to **70 m² g⁻¹** can be obtained via FSP. Our optimal operating parameters were a flow rate of 10 slm dispersion gas, 2 ml min⁻¹ injection rate and a precursor composition of 35% ethyl hexanoic acid and 65% Ethanol.

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Acknowledgement

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Influence of distinct synthesis protocols for tungsten-incorporated mesostructured cellular foams on their performance in extractive catalytic oxidative desulfurization

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Keywords: MCF, tungsten, oxidative desulfurization

Owing to increasingly stringent environmental regulations, one of the principal challenges in refining remains the reduction of sulphur content in petroleum-derived fuels to ultralow levels. Consequently, the development of novel strategies for the removal of organosulfur compounds from gasoline is required. Among the most effective approaches proposed for this purpose is extractive catalytic oxidative desulfurization (ECODS). This method enables, for example, the efficient removal of dibenzothiophene (DBT), 4-methyldibenzothiophene (4M-DBT), and 4,6-dimethyldibenzothiophene (4,6DM-DBT) via their oxidation to the corresponding sulfoxides and sulfones under mild reaction conditions, combined with the simultaneous extraction of the oxidation products. Catalysts that are highly active in this process generally possess strong Brønsted acid sites (BAS) and metal centers capable of forming peroxo complexes with hydrogen peroxide, which is employed as the oxidizing agent [1].

The objective of this study was to develop an efficient catalyst for the ECODS process. To this purpose the MCF (mesoporous cellular foam) was synthesized according to the procedure described in [2] and subsequently modified with tungsten species via two distinct methods: (i) incorporation during the synthesis of the mesoporous silica framework and (ii) post-synthetic wetness impregnation. In addition, to enhance the stability of tungsten species deposited on the silica support, a third catalytic synthesis route was employed. In this procedure, titanium species were first introduced by wetness impregnation, and tungsten species were then deposited onto the resulting Ti-containing support using the same modification method. In all cases, the Si/W or Si/Ti molar ratio was maintained at 30. The resulting catalysts were characterized by N₂ adsorption–desorption isotherms, X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FT-IR) combined with pyridine adsorption. The catalytic performance was preliminarily evaluated in the decomposition of 2-propanol and in the dehydration and cyclization of 2,5-hexanedione, and subsequently the catalysts were applied in the ECODS process.

The mesoporous structure of the synthesized MCF support was confirmed by low-temperature N₂ adsorption–desorption isotherms, whereas the XRD patterns verified its amorphous character. Modification of the silica with metal precursors did not alter the morphology of the MCF. Only in the wide-angle XRD pattern of the W/MCF sample reflections attributable to monoclinic WO₃ were detected, while for the other samples impregnated with metal precursors no diffraction peaks were observed. This latter observation can be attributed to the high dispersion of the modifying species on the support. Both probe reactions, namely the decomposition of 2-propanol and the dehydration–cyclization of 2,5-hexanedione, confirmed the acidic nature of the catalysts, which was most pronounced for the W/Ti/MCF sample. For this material, FT-IR measurements combined with

pyridine adsorption also revealed the highest number and strength of Brønsted acid sites (BAS).

The catalytic performance of the materials obtained was evaluated in extractive catalytic oxidative desulfurization (ECODS) using H_2O_2 as the oxidant and acetonitrile as the extraction solvent. The highest desulfurization efficiency toward DBT (**Figure 1A**) was achieved for the W/Ti/MCF catalyst, for which approximately 92% DBT removal was obtained after 120 min at 40 °C. This catalyst also exhibited outstanding activity in the oxidation of more sterically hindered sulphur compounds (**Figure 1B**), such as 4M-DBT and 4,6DM-DBT, under mild reaction conditions. The stability of the synthesized catalysts was assessed based on their performance in DBT removal. As shown in **Figure 1C**, W/Ti/MCF demonstrated the highest stability among all investigated samples. The superior catalytic activity of W/Ti/MCF in sulphur compound removal can be attributed to the highest concentration and strength of acid sites on its surface. In turn, the enhanced stability is likely related to the beneficial effect of titanium incorporation into the mesoporous support, which contributes to the stabilization of tungsten species and mitigates their leaching into the liquid phase during reaction.

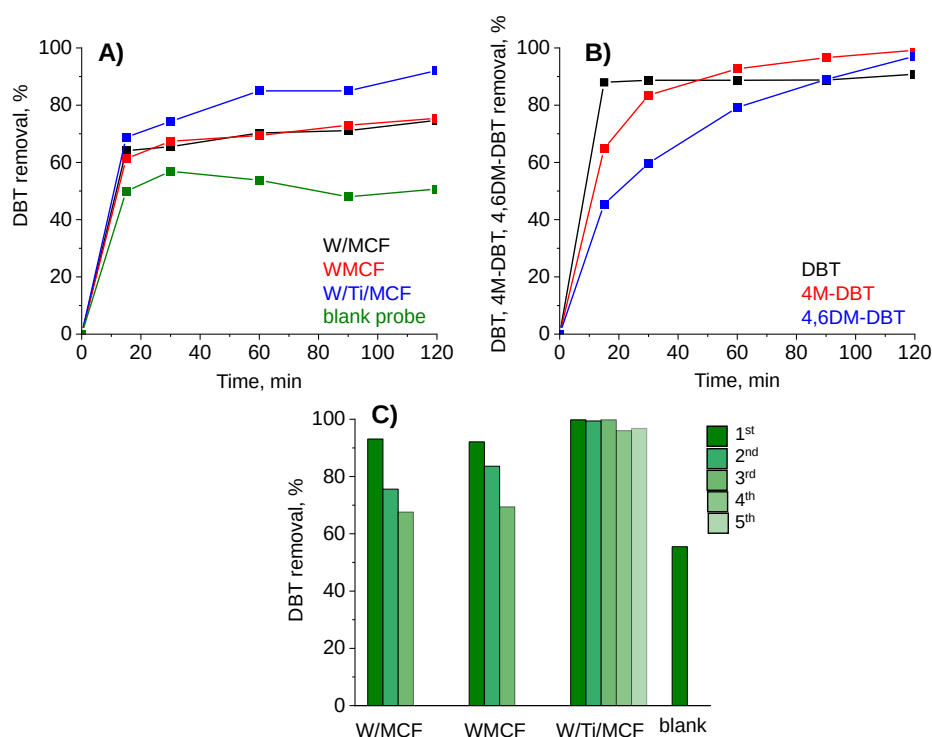


Fig. 1: The efficiency of DBT removal in the presence of the synthesized samples (A); the efficiency of the simultaneous removal of a mixture of DBT, 4M-DBT, and 4,6DM-DBT over the W/Ti/MCF catalyst (B); and the recyclability assessment conducted for the W/Ti/MCF material (C). The reaction conditions: (A) 0.5 wt.% of catalyst, 40°C, O:S=2:1; (B) 0.5 wt.% of catalyst, 40°C, O:S=6:1; (C) 0.5 wt.% of catalyst, 40°C, O:S=6:1, 60 min.

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Interplay of Acid Sites and Surface Hydrophobicity in Metal Silicate Catalysts

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Keywords: nonhydrolytic sol-gel; surface grafting; hydrophobicity; epoxide ring opening; ethyl lactate

Introducing organic groups into metal silicate catalysts and thus supposedly changing the surface hydrophobicity has been shown to enhance the catalyst performance in various reactions. However, the organic groups introduction does not unambiguously guarantee hydrophobicity control.¹ Therefore, a thorough characterization is necessary to provide a complete view of the interaction between the catalyst surface, reactants, and products

Herein, we have prepared aluminosilicate² and tin silicate³ catalysts with high specific surface areas (up to 900 m² g⁻¹, without requiring the use of any pore-generating agent), uniform metal dispersion, and high Lewis acid site numbers via the non-hydrolytic sol-gel method. These materials were post-synthetically modified with trimethylsilyl groups; their number on the catalyst surface was controlled via a temperature vacuum pretreatment. In such a way, we have obtained metal silicate materials with similar porosity, structure, and acid site strength and quality. The surface hydrophobicity has been thoroughly studied via water adsorption and water contact angle measurements.

The turnover frequency (TOF) in epoxide ring opening and ethanol dehydration scaled up with the number of trimethylsilyl groups grafted on the catalyst surface. Particularly, the heavily trimethylsilylated samples achieved three to five times higher TOF in styrene oxide aminolysis than parent metal silicate materials (Fig. 1 and 2). While hydrophobization markedly improved apparent TOFs in styrene oxide aminolysis, excessive silylation was detrimental to dihydroxyacetone conversion to ethyl lactate, underscoring the dual role of Si-OH and Si-OSiMe₃ groups in catalytic performance.

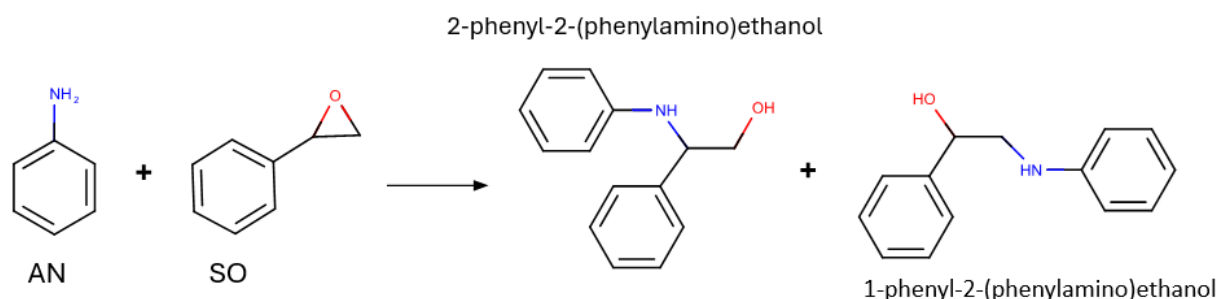


Fig. 1: Styrene oxide aminolysis with aniline.

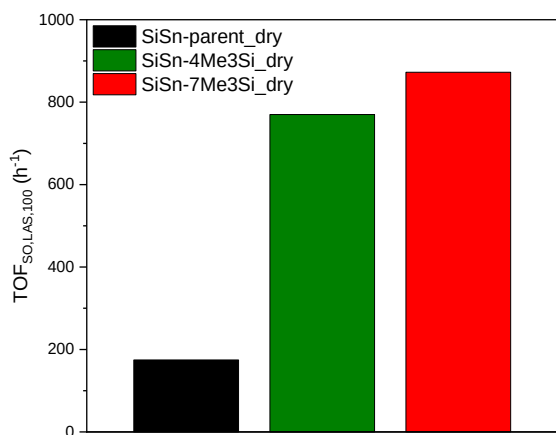


Fig. 2: Turnover frequency over parent tin silicate and trimethylsilylated tin silicates during aminolysis of styrene oxide (TOF expressed as mol of converted styrene oxide per mol of Lewis acid sites per hour)

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Acknowledgement

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Support-Controlled Hydrocracking of n-Hexadecane over Ni-Based Bimetallic Catalysts toward Jet-Range Hydrocarbons

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Keywords: hydrocracking; n-hexadecane; Ni-based bimetallic catalysts; zeolite Beta; jet-range hydrocarbons

Introduction

The selective hydrocracking of long-chain hydrocarbons into jet-range liquid products requires a careful balance between metallic and acidic catalytic functions. Strong acidity can promote C-C bond cleavage, but excessive cracking may lead to gas formation and loss of liquid yield. On the contrary, weakly acidic catalysts may preserve the liquid phase but leave a large fraction of the unconverted feed.

In this work, n-hexadecane was used as a model compound to study the influence of support properties and metal composition on Ni-based bimetallic catalysts. FeNi, MoNi and WNi catalysts were prepared on γ -Al₂O₃ and zeolite Beta-38 to directly compare the same metal combinations on supports with different acidity and textural properties.

Methodology

FeNi, MoNi and WNi catalysts with nominal loadings of 5 wt.% Ni and 5 wt.% second metal were prepared by sequential wet impregnation of γ -Al₂O₃ and zeolite Beta-38 using the corresponding metal precursors. Fresh catalysts were characterized by ICP-OES, N₂ physisorption, pyridine-FTIR, H₂-TPR, XRD and TEM, while spent catalysts were analyzed by N₂ physisorption and TEM.

Catalytic experiments were performed in a continuous down-flow fixed-bed reactor using n-hexadecane as feed. All catalysts were tested under identical conditions: 30 bar total pressure under H₂, H₂/feed molar ratio of 15, liquid feed flow rate of 0.04 mL min⁻¹ and 0.3 g catalyst with a particle size of 150-180 μ m. The temperature program was 250, 275 and 300 °C, followed by a return to 250 °C, with 15 min stabilization and 1 h reaction time at each temperature. Liquid products were analyzed by GC-FID, while gaseous products were monitored by online microGC as detected C₁–C₄ hydrocarbons on a carbon basis.

Results

The fresh Beta-38 supported catalysts showed higher BET surface areas, 483-532 m² g⁻¹, and larger micropore volumes, 0.171-0.210 cm³ g⁻¹, than the γ -Al₂O₃ supported catalysts, which had surface areas of 244-310 m² g⁻¹ and micropore volumes of 0.014-0.020 cm³ g⁻¹. Pyridine-FTIR confirmed stronger acidity for the Beta-38-based catalysts. FeNi/Beta-38 contained 98 μ mol g⁻¹ Brønsted and 227 μ mol g⁻¹ Lewis acid sites, while MoNi/Beta-38 showed the highest total acidity. On the contrary, the alumina supported catalysts had much lower total acidity, 18–53 μ mol g⁻¹. TEM showed nanosized metal-containing particles on Beta-38, with average sizes of 5.16 nm for WNi/Beta-38, 4.80 nm for FeNi/Beta-38 and 3.32 nm for MoNi/Beta-38.

At 300 °C, γ -Al₂O₃ supported catalysts showed only moderate conversion: 33.6% for FeNi/Al₂O₃, 32.7% for WNi/Al₂O₃ and 35.8% for MoNi/Al₂O₃. They maintained high total

liquid yields, around 75-91%, but the liquid phase was dominated by unreacted C16 hydrocarbons, usually around 86-93%, with only minor formation of lighter products.

The Beta-38 supported catalysts showed much higher conversion. At 300 °C, WNi/Beta-38, FeNi/Beta-38 and MoNi/Beta-38 reached 98.9, 100 and 100% conversion, respectively. Their liquid products shifted from unreacted C16 toward lighter hydrocarbons. FeNi/Beta-38 produced a C9-C15-rich liquid fraction with a strong contribution of isomeric hydrocarbons, reaching up to 44.96% of the liquid phase at 275 °C and remaining high after returning to 250 °C, at about 61.7-69.5%. WNi/Beta-38 and MoNi/Beta-38 also formed significant light liquid fractions, but shifted more strongly toward C5-C12 hydrocarbons and gaseous products at higher temperature.

At 300 °C, the total liquid yield over Beta-38 supported catalysts dropped to approximately 0-8%, indicating severe overcracking. Gas-phase analysis confirmed this trend: alumina supported catalysts produced only limited C₁-C₄ hydrocarbons, mainly CH₄ and C₂H₆, whereas Beta-38 supported catalysts generated much larger amounts of C₃-C₄ gases. WNi/Beta-38 and MoNi/Beta-38 showed particularly strong formation of i-C₄H₁₀ and n-C₄H₁₀.

Discussion

The results show that support acidity and textural properties strongly controlled the balance between conversion and liquid product preservation. The low acidity and low micropore volume of γ -Al₂O₃ supported catalysts limited C-C bond cleavage, so these catalysts preserved high liquid yields but mainly produced unconverted C16-rich liquids. This indicates that their metal function alone was not sufficient to promote effective hydrocracking under the applied conditions.

The Beta-38 supported catalysts, on the contrary, combined higher surface area, significant microporosity and stronger acidity, which promoted hydrocracking and formation of lighter liquid products. However, the same cracking function also increased gas formation and reduced total liquid yield at high temperature. This trade-off shows that maximum conversion alone is not sufficient for catalyst selection, therefore total liquid yield, gas formation, jet-range distribution and selectivity to individual hydrocarbon products must also be considered.

Conclusions

Replacing γ -Al₂O₃ with zeolite Beta-38 strongly enhanced the hydrocracking activity of FeNi, MoNi and WNi catalysts, but also increased the risk of overcracking, especially at 300 °C. The higher acidity and microporous character of Beta-38 promoted C-C bond cleavage and the formation of lighter hydrocarbons, while the alumina supported catalysts remained too mild and produced liquid phases dominated by unreacted C16. Among the Beta-38 supported catalysts, FeNi/Beta-38 showed the most pronounced formation of a broader C8-C15/C9-C15 jet-range liquid fraction. On the contrary, MoNi/Beta-38 and WNi/Beta-38 were highly active but shifted more strongly toward lighter C5-C12/C8-C12 liquid fractions and C₃-C₄ gaseous products with increasing temperature. This highlights FeNi/Beta-38 as the most interesting catalyst for jet-range liquid formation, while MoNi/Beta-38 and WNi/Beta-38 represent more severe cracking systems.

Acknowledgement



Funded by the European Union (Grant Agreement 101120389). YAF has also received funding from UK Research and Innovation, EPSRC (Grant reference: EP/Y031881/1).

MOF-derived Co and Ni containing catalysts for flow selective hydrogenation of α,β -unsaturated aldehydes

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Keywords: MOF-derived catalysts, flow hydrogenation, α,β -unsaturated aldehydes

The central objective of catalysis research is to achieve near-perfect selectivity toward the desired product. This is particularly critical in the synthesis of pharmaceuticals, vitamins, and fine chemicals, where even minor by-products can significantly impact efficiency, cost, and safety. Such transformations demand precise control over reactivity, enabling the suppression of side reactions while selectively addressing specific functional groups within multifunctional molecules. These requirements are especially pertinent to catalytic hydrogenation, a key transformation in the production of fine chemicals and pharmaceutical intermediates. Consequently, the design and development of cost-effective, well-defined, highly efficient, and environmentally benign catalytic systems for hydrogenation reactions remain essential for advancing sustainable chemical manufacturing.



Figure 1. Schematic illustration of catalyst synthesis and the hydrogenation process.

The aim of this study was to synthesize a new class of Co- and Ni-containing MOF-derived catalysts and evaluate their performance in the continuous-flow hydrogenation of α,β -unsaturated aldehydes (3-methyl-2-butenal and cinnamaldehyde) (Figure 1). The research focused on chemoselective hydrogenation to obtain value-added products, including 3-methylbutanol and 3-methyl-2-buten-1-ol, as well as 3-phenylpropionol and 3-phenyl-2-propen-1-ol, which are important intermediates in the pharmaceutical, fragrance, and cosmetic industries [1].

The catalysts were prepared via thermal transformation of MOFs under controlled conditions and characterized using XRD, XPS, XRF, TEM, magnetization measurements, and Raman spectroscopy. Hydrogenation reactions were carried out in isopropanol (0.1 M) over a temperature range of 45-100°C and pressures of 10-30 bar using a ThalesNano H-Cube Pro continuous-flow system.

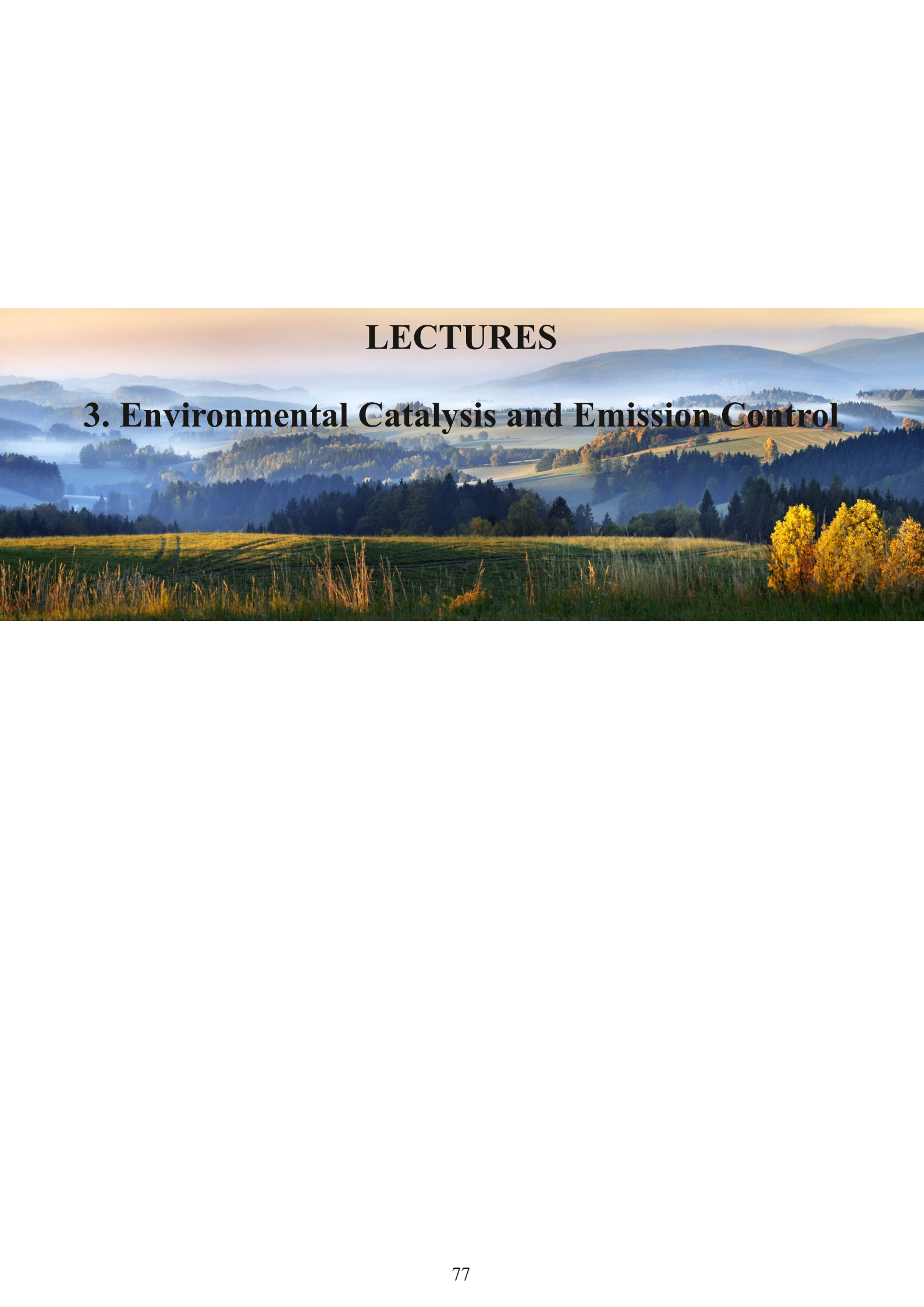
Our investigations demonstrate that cobalt- and nickel-based MOF-derived, nitrogen-doped catalysts exhibit high activity and selectivity in the flow hydrogenation of 3-methyl-2-butenal and cinnamaldehyde. Notably, all obtained products are value-added chemicals, highlighting the attractiveness of this process. Furthermore, this study provides important insights into the interplay between reaction conditions and the physicochemical properties of MOF-derived materials in determining catalytic performance.

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Acknowledgement

This work was financially supported by the National Science Centre in Poland within the project OPUS 25 no. 2023/49/B/ST8/00872.



LECTURES

3. Environmental Catalysis and Emission Control

TiO₂ – material for special applications

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Keywords: TiO₂, photocatalysis, environment

Titanium dioxide is well known for excellent pigment properties and is widely used in paints, coatings, plastics, and ceramics. However, titanium dioxide is also available in ultrafine form, which exhibit unique photocatalytic properties.

This photocatalytic type of TiO₂ can be used as an active ingredient for smart use = in a variety of environmental applications, including air purification, water treatment, and the degradation of organic pollutants. Our project is focused on application properties ultrafine form TiO₂ which leads to functional and designed solutions.

Removal of hydrocarbons by non-thermal plasma combined with catalysis, regeneration and re-use of catalysts

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Keywords: non-thermal plasma, heterogeneous catalysts, plasma catalysis, volatile organic compounds

Non-thermal plasma generated by atmospheric pressure electric discharges in combination with various catalysts is gaining an increasing interest. It utilizes high plasma reactivity, high catalyst selectivity and as such is often characterized by synergistic effects, when the combined effect of plasma and catalysis may be stronger than their individual. The synergy may lead to higher conversion of reactants, higher selectivity as well as higher energy efficiency. Thanks to this, plasma catalysis has found use in many environmental applications particularly in air pollution control technologies, including removal of nitrogen oxides, volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH), conversion of carbon dioxide CO₂, etc. The use of plasma catalysis in the VOC and PAH removal processes has been investigated by many authors and extensive and comprehensive reviews about the topic have been published in several papers. As a model VOC/PAH usually toluene, benzene and naphthalene are being used.

We have investigated removal of VOC/PAH by atmospheric pressure discharges in combination with pellets/beads of various properties and catalytic activities [1,2]. Typically tested materials were glass, Al₂O₃, Pt/Al₂O₃, TiO₂, and ZrO₂. They were characterized by distinct shape (spherical and cylindrical), size (3–5 mm in diameter, 3–8 mm in length), dielectric constant (5–200), and specific surface area (SSA) (37–150 m²/g). In addition, various materials of high dielectric constant (>1000) were tested as they can significantly enhance electric discharge through stronger local electric fields, higher micro discharge density, and improved plasma stability. Among them BaTiO₃, relaxor ferroelectrics such as PZN and calcium copper titanate (CCTO) were investigated to assess the role of dielectric response. The results showed the removal efficiency depended on the properties of the catalysts. An improvement was observed with increasing SSA, while the shape of catalyst pellets was found to be even more important. Higher efficiency was also found with smaller size pellets. The products of VOC/PAH decomposition were found both in the gas phase as well as solid deposits (coke) on surfaces of pellets. The absorption spectroscopy (FTIR) and gas chromatography (GC) were used for their identification. In addition to main gaseous products (CO, CO₂, H₂O and HCOOH), several other complex gaseous and solid by-products were also identified (anhydrides, quinones, carboxylic acids, etc). Surface analysis carried by scanning electron microscopy (SEM/EDS) revealed significant differences in the distribution of deposits on the surface of pellets as the result of different discharge regime (surface discharges vs. filamentary microdischarges) that form depending on the used material.

The experiments also showed that activity and selectivity of the catalysts decreased over time due to gradual accumulation of solid deposits on their surface and their replacement or regeneration was required. Therefore, we also investigated potential of non-thermal plasma regeneration of coke-deactivated pellet catalysts [3]. The plasma regeneration was tested for various catalysts (TiO₂, Al₂O₃, Pt/Al₂O₃, Pd/Al₂O₃) and compared with ozone and thermal regenerations. The results indicated that oxygen plasma regeneration, although not spatially non-uniform, exhibited the highest coke removal efficiency. The effect of ozone and heat

(100°C) was negligible. GC–MS analysis revealed that coke composed of long-chain alkanes and oxygen- or nitrogen-substituted aromatics was significantly reduced after plasma regeneration, unlike other regeneration techniques. To resolve non-uniform and partial regeneration of the catalyst surface plasma exposure was combined with intermediate pellet mixing and compared to plasma exposure without mixing. The mixing turned out to be effective and lead to enhanced spatial uniformity of regeneration. Despite incomplete coke removal after plasma generation catalysts maintained relatively high removal efficiencies over three repeated removal-deactivation-regeneration cycles. Plasma regeneration was also found strongly catalyst-dependent. Results indicates that primary effect of plasma regeneration is not only the coke removal and restoring the original active sites, but also modifications of catalyst surface. This may include adsorption of oxygen-containing surface species and modifications of the surface properties, which can either enhance or inhibit catalytic performance depending on the catalyst. Overall, our findings highlight the importance of catalyst surface evolution and regeneration strategy in plasma-catalytic systems, and can be implemented when designing systems of cyclic operation of catalyst use, regeneration and reuse.

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Acknowledgement

The work was supported by Slovak Research and Development Agency grant APVV-20-0566 and the EU NextGenerationEU through the Recovery and Resilience Plan project 09I03-03-V03-00033.

Plasma-catalytic decomposition of toluene over Ni-Co binary metal oxide catalysts on honeycomb monolith

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Keywords: *non-thermal plasma, plasma catalysis, volatile organic compounds, binary metal oxides*

Car exhaust treatment is essential for mitigating harmful environmental and health effects caused by emissions from car engines. Traditionally their treatment is done by three-way or oxidation honeycomb catalysts. Honeycomb catalysts have structured porosity, high surface area and support efficient surface reactions with high reaction rate and high selectivity. Non-thermal plasma (NTP) presents a promising strategy in targeting air pollution, including VOC and car exhaust. It generates highly reactive species, and supports efficient gas-phase reactions for their oxidative decomposition under ambient conditions. When honeycomb catalyst and plasma are integrated in one system thanks to their mutual interaction, high reaction rate, high selectivity, good carbon balance and possible synergy can be observed [1,2].

Commercial catalytic converters for VOC and hydrocarbon abatement predominantly rely on noble metals such as Pt, Pd, and Rh. However, recent studies have demonstrated that transition metal-based materials, including Ni, Co, and La, exhibit competitive catalytic performance, making them promising cost-effective alternatives for plasma-catalytic oxidation applications. [3,4]. In the present study, Ni-Co binary metal oxide coatings are employed to honeycomb monolith (cordierite). The introduction of Ni and Co-Ni oxide coatings increased the dielectric capacitance of the monolith, which in turn enhanced the discharge power generated within the plasma reactor. FTIR spectroscopy shown a corresponding increase in reactive species generation, evidenced by increased ozone concentrations. It was found that coated monolith promote more active plasma discharge conditions compared to uncoated ones. Toluene was selected as a model VOC at an inlet concentration of 834 ppm to evaluate plasma-catalytic decomposition performance. At an inlet gas flow rate of 1 L/min, both Ni and Co-Ni oxide-coated monoliths achieved up to 80% toluene removal efficiency, significantly outperforming uncoated cordierite, demonstrating that Ni, Co metal oxide coatings enhances plasma-assisted oxidation through improved discharge characteristics and increased reactive species availability. However, FTIR analysis of the outlet gas revealed the presence of partially oxidised byproducts, including acetic acid and formic acid, indicating incomplete mineralisation of toluene and highlighting the need for further optimisation of the plasma-catalytic system to improve CO₂ selectivity and suppress byproduct formation.

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Tailored Perovskite Catalysts for Efficient VOC Oxidation: Effect of Composition and Morphology

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Keywords: Volatile organic compounds, Oxidation, Perovskites, Electrospinning, Morphology

Volatile organic compounds (VOCs) represent a major class of air pollutants originating from industrial processes, solvent use, and petrochemical operations. Their removal is of significant environmental importance due to their toxicity, contribution to photochemical smog formation, and role as precursors of secondary organic aerosols. Among the available abatement technologies, catalytic oxidation is considered one of the most effective and energy-efficient methods, particularly at low VOC concentrations. While noble metal-based catalysts exhibit excellent activity, their high cost and susceptibility to poisoning motivate the search for alternative materials. In this context, perovskite-type oxides with the general formula ABO_3 have emerged as promising candidates due to their structural flexibility, tunable redox properties, and high thermal stability.

In this work, a series of cobalt-based perovskite catalysts with systematically varied composition and morphology were prepared and evaluated for the catalytic oxidation of representative VOCs, namely ethanol, acetone, and toluene. The studied materials included $LaCoO_3$ and $LaSrCoO_3$ synthesized via the sol–gel method, their manganese-modified analogues prepared by impregnation, and electrospun $LaSrCoO_3$ nanofibers. In addition, selected multicomponent perovskites ($LaSrCuFeO_x$, $LaSrMnNiO_x$, and $PrBaCeSrCoO_x$) were included for comparison to evaluate the influence of complex compositions on catalytic performance.

The catalysts were comprehensively characterized using X-ray diffraction (XRD), nitrogen physisorption (BET), scanning electron microscopy (SEM), temperature-programmed reduction (H_2 -TPR), and X-ray photoelectron spectroscopy (XPS). XRD analysis confirmed that the dominant crystalline phase in most samples corresponded to the perovskite structure, although minor secondary phases such as $SrCO_3$ were occasionally detected. Strontium substitution led to structural changes from rhombohedral to cubic symmetry, reflecting lattice distortion and the formation of oxygen vacancies. The electrospinning method resulted in nanofibrous materials with significantly higher specific surface area compared to sol–gel-derived bulk catalysts. SEM observations revealed that electrospun catalysts form a highly porous network of interconnected fibres, whereas sol–gel samples consist of irregular agglomerates.

Catalytic performance was evaluated in a fixed-bed reactor under conditions relevant for VOC abatement (1000 ppm VOC in air, GHSV = 20 L g_{cat}⁻¹h⁻¹, temperature range 50–400 °C). The activity was assessed using T_{50} values, while selectivity toward complete oxidation was evaluated based on T_{90} (CO_2). The results showed that cobalt-based perovskites exhibit the highest catalytic activity among all tested materials. In particular, Mn-modified $LaSrCoO_3$ catalysts demonstrated the lowest T_{50} values in ethanol oxidation, indicating enhanced redox properties and improved oxygen mobility. The activity followed the general trend ethanol >

acetone > toluene, which reflects the increasing stability of the molecules and the higher activation energy required for C–C bond cleavage and aromatic ring oxidation.

The influence of catalyst composition was found to be significant. Partial substitution of La^{3+} by Sr^{2+} enhances catalytic activity by creating oxygen vacancies and improving lattice oxygen mobility. Similarly, manganese modification further improves redox behaviour and promotes the oxidation of intermediate species. In contrast, multicomponent catalysts such as LaSrCuFeO_x and LaSrMnNiO_x exhibited moderate activity, while the Pr-containing catalyst showed the lowest performance, which can be attributed to its low specific surface area and the presence of multiple segregated phases.

The effect of morphology was particularly pronounced in catalytic activity. Electrospun nanofibrous catalysts exhibited higher activity compared to their bulk counterparts due to increased surface area, improved accessibility of active sites, and enhanced mass transport properties. These features facilitate faster adsorption and activation of reactant molecules, leading to lower T_{50} values.

In contrast, the selectivity toward CO_2 was found to be primarily governed by the intrinsic redox properties of the catalysts rather than morphology. Nevertheless, electrospun catalysts exhibited slightly improved selectivity, achieving lower $T_{90}(\text{CO}_2)$ values compared to sol–gel samples. This behaviour can be attributed to more efficient secondary oxidation of intermediate species within the porous nanofibrous structure, which reduces their desorption and promotes complete oxidation.

The oxidation of VOCs over perovskite catalysts is generally described by the Mars–van Krevelen mechanism, in which lattice oxygen participates directly in the oxidation of the organic molecule and is subsequently replenished by gaseous oxygen. Ethanol oxidation proceeds via acetaldehyde as an intermediate, which is readily oxidized to CO_2 . In contrast, acetone oxidation involves C–C bond cleavage and the formation of surface acetate species, while toluene oxidation requires activation and subsequent breakdown of the aromatic ring, making it the most demanding reaction in terms of both activity and selectivity.

The results demonstrate that both chemical composition and morphology play key roles in determining catalytic performance. Strontium substitution and manganese modification enhance oxygen mobility and redox properties, while electrospinning provides a favourable morphology that improves accessibility of active sites and mass transport. These findings highlight the potential of tailored perovskite catalysts as efficient and cost-effective materials for VOC abatement.

Acknowledgement

This work was supported by the Technology Agency of the Czech Republic within the project TN02000044.

Cu- and V-doped cryptomelane for enhanced catalytic activity in the simultaneous removal of soot and VOC

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Keywords: cryptomelane, oxidation, soot, volatile organic compounds, doping

Air pollution remains one of the major challenges faced by both developed and developing countries. The presence of particulate matter (especially soot) and volatile organic compounds (VOCs) in ambient air is directly associated with adverse environmental and health consequences. Catalytic total oxidation is considered one of the most efficient routes for their removal, particularly if both pollutants can be eliminated simultaneously. However, the concurrent oxidation of soot and VOCs is challenging due to fundamentally different reaction mechanisms and temperature requirements for catalytic removal of solid and gaseous pollutants. Therefore, the development of multifunctional oxide systems capable of operating efficiently under mixed-pollutant conditions has attracted increasing interest.

For soot combustion, catalytic systems based on alkali metals, particularly potassium, are known to be highly effective [1]. A representative potassium-based catalyst considered here is cryptomelane ($\text{KMn}_8\text{O}_{16}$), also referred to as K-OMS-2 [2]. Owing to its tunnel structure and high oxygen mobility, cryptomelane can also be applied in VOC combustion, especially when modified by transition-metal doping [3]. This study aimed to directly compare the effect of Cu and V doping on the structural and redox properties of cryptomelane and to identify optimal dopant loadings for enhancing the low-temperature oxidation of both soot and selected VOCs.

Parent cryptomelane was synthesized via the reduction of KMnO_4 with MnSO_4 in an acidic solution under reflux for 24 h. The resulting solid was filtered, dried, and calcined ($500\text{ }^\circ\text{C}/4\text{ h}$). Copper and vanadium dopants were introduced by dry impregnation using aqueous solutions of $\text{Cu}(\text{NO}_3)_2$ and NH_4VO_3 , respectively, followed by drying and calcination ($400\text{ }^\circ\text{C}/4\text{ h}$). The samples were characterized using complementary bulk and surface-sensitive techniques (XRF, XRD, RS, FTIR, XPS, UV/Vis-DR, H_2 -TPR, TEM) in order to correlate structural and redox properties with catalytic performance. Catalytic activity was evaluated in soot, ethylene and methane separate combustions, and in the simultaneous combustion of soot with these hydrocarbons.

Structural analysis confirmed that the cryptomelane framework was preserved after impregnation with aqueous solutions of V and Cu precursors. At higher copper loadings, the formation of nanocrystalline CuO domains was observed, indicating partial segregation of the dopant phase. Copper doping significantly enhanced the reducibility of cryptomelane, whereas vanadium doping resulted in an opposite effect.

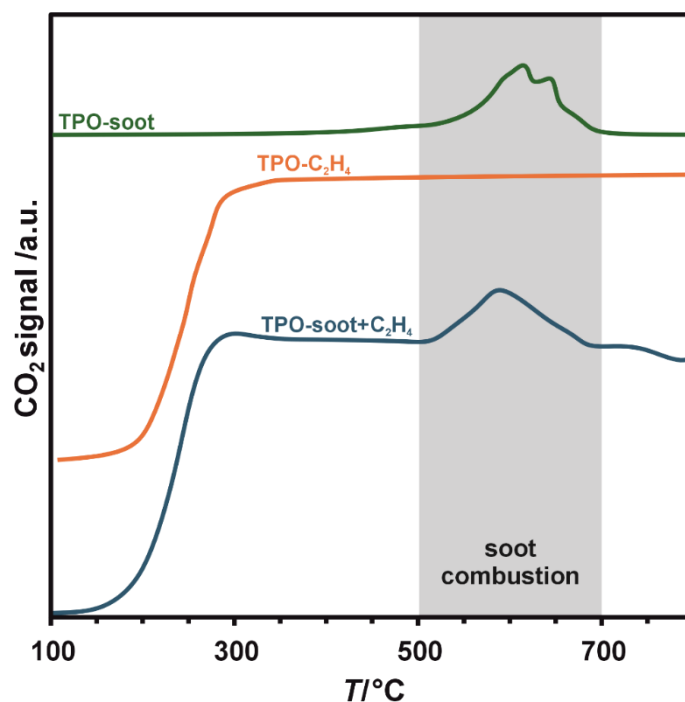


Fig. 1: Temperature evolution of the CO₂ signal during soot and ethylene combustion over a Cu-doped cryptomelane catalyst, including simultaneous removal conditions.

Parent cryptomelane exhibited high activity in both ethylene and methane combustion. The introduction of copper led to a pronounced enhancement of ethylene combustion activity. In contrast, its effect on methane oxidation was relatively weak and rather ambiguous, reflecting the higher activation barrier associated with activation of this specific pollutant. In contrast, vanadium doping decreased catalyst activity in methane combustion, and only a moderate improvement was observed in ethylene oxidation, compared to that observed for the bare cryptomelane catalyst. Overall, copper doping proved to be more effective than vanadium in promoting low-temperature VOC oxidation without compromising soot combustion performance. The observed trends in catalytic activity correlated well with changes in reducibility, indicating that oxygen mobility is crucial for activity, suggesting that a Mars–van Krevelen-type mechanism governs VOC oxidation. Importantly, all investigated catalysts retained activity under simultaneous soot and VOC combustion conditions (Fig. 1), indicating the absence of strong competitive inhibition between solid and gaseous reactants.

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Acknowledgement

This work has been supported from the Anthropocene Priority Research Area budget under the program "Excellence Initiative – Research University" at the Jagiellonian University

Kinetic modeling and selectivity analysis of C₃H₆ reactions over Cu/SSZ-13 catalysts for NH₃-SCR

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Keywords: SCR; kinetics; selectivity; mathematical modeling; exhaust gas aftertreatment

Cu/SSZ-13 catalysts are used for selective catalytic reduction of NO_x (SCR). A close-coupled SCR not preceded by an oxidation catalyst is being considered to meet stringent emission regulations during cold start. However, the influence of hydrocarbon oxidation on the SCR catalyst remains unclear. Our work extends current understanding by incorporating new oxidation reactions in a mathematical model of an SCR catalyst. The propylene oxidation leads to two major products – carbon monoxide (CO) and carbon dioxide (CO₂) – but other undesired byproducts may be detected in the outlet stream as well – acrolein (CH₃CH₂CHO), acetaldehyde (CH₃CHO), formaldehyde (HCHO) and, in the presence of NH₃, also acrylonitrile (CH₂CHCN) and HCN produced via ammoxidation. The ammonia consumption in these side reactions may lead to NH₃ scarcity that further degrades SCR performance. The aim of this work is to elucidate the reaction pathways leading to the formation of these by-products, and to build a kinetic model capable of predicting the propylene conversion and selectivity depending on operating conditions and concentration of active sites present in the catalyst.

2 wt.% Cu/SSZ-13 catalysts were synthesized via incipient wetness impregnation of copper acetate solution into HSSZ-13 with Si/Al ratios of 5.5 and 15 (ACS Materials). Powder samples were examined in a lab microreactor in the fresh state and after mild hydrothermal aging, resulting in a varying distribution of ZCuOH and Z₂Cu sites [1,2], Fig. 1. To characterize the active sites, the total copper content was quantified through NO + NH₃ titration performed at 175 °C with 200 ppm of NH₃ and 200 ppm NO. The specific concentration of ZCuOH sites was isolated and measured using NO₂ adsorption followed by temperature-programmed desorption (NO₂-TPD) with a 500 ppm NO₂ feed at 200 °C. Measurements of NH₃ adsorption and TPD revealed the amount of unexchanged Brønsted acid sites ZH.

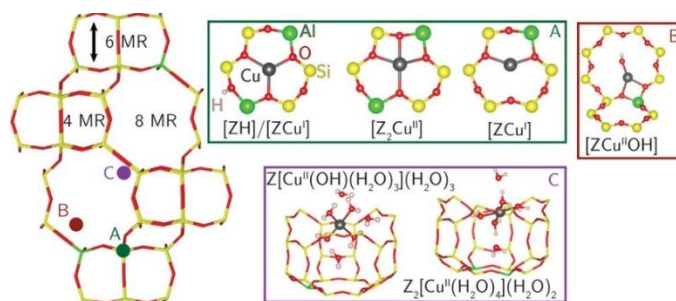


Fig. 1: Ion exchanged Cu species in SSZ-13 zeolite [1].

Steady-state propylene oxidation performance was evaluated across a temperature range of 175 °C to 500 °C in discrete steps, using a mixture of 1000 ppm C₃H₆, 10 % O₂, 7.6 % H₂O, and 0 or 200 ppm NH₃ to separate reactions with just O₂ and NH₃+O₂. Based on the experimental data, a kinetic model for propylene and ammonia oxidation on Cu/SSZ-13 was

developed, including partial oxidation of propylene to aldehydes. HCHO is considered as the key precursor for HCN formation in the reaction with ammonia, through the dehydration of formamide intermediates. The ZCuOH sites, the occurrence of which closely related to the Si/Al ratio of the zeolite, promote total oxidation of the undesired by-products with increasing temperature, Fig. 2. During mild hydrothermal aging, however, ZCuOH is gradually transferred to Z_2Cu , decreasing the oxidation activity [2,3].

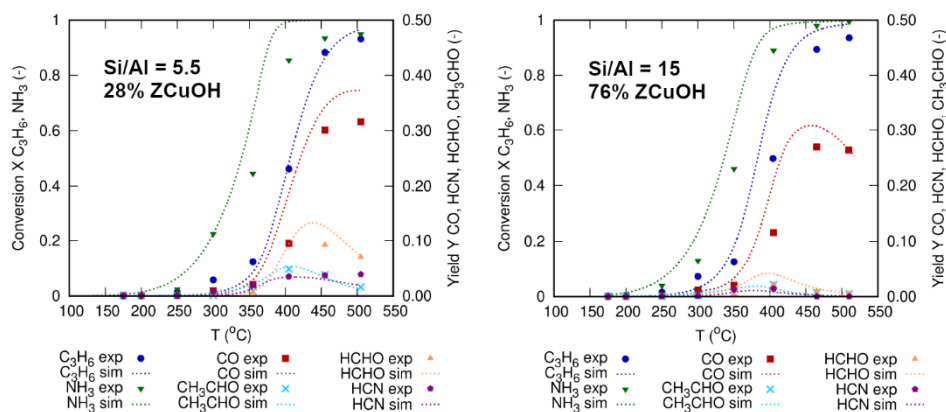


Fig. 2: Impact of Si/Al and ZCuOH fraction of Cu sites on $C_3H_6+O_2+NH_3$ conversion and selectivity. The same kinetic parameters were used for both catalysts, effect of ZCuOH concentration considered.

Extended hydrothermal aging further induces dealumination and formation of extra-framework Al moieties. These species are occluded within micropores and have been shown to restrict void space, leading to a decrease of the effective diffusivity of propylene into zeolite. The transport limitation translates into a milder increase in the propylene conversion and product yields with temperature compared to the fresh sample.

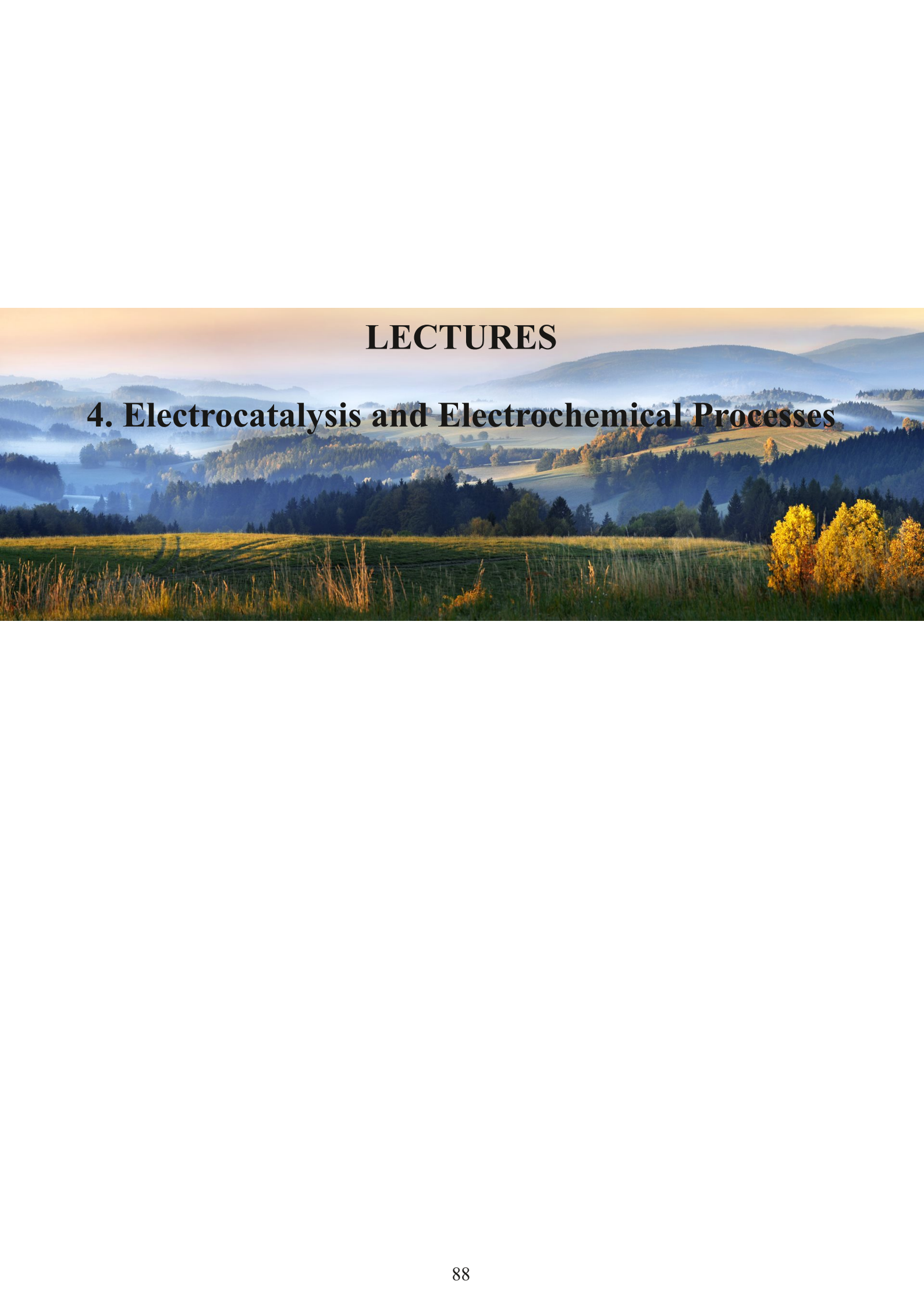
In conclusion, the developed kinetic model can predict propylene conversion and selectivity on a Cu/SSZ-13 SCR catalyst depending on Cu sites speciation and catalyst aging state. The new insights help optimize the SCR catalyst formulation and performance under realistic operating conditions.

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Acknowledgement

Czech Science Foundation (GAČR 23-07137L) and the National Science Foundation (NSF 2227016).



LECTURES

4. Electrocatalysis and Electrochemical Processes

2D metal clusters on 2D MoS₂, properties and activity in hydrogen evolution reaction

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Transition metal chalcogenides are broadly investigated catalysts, limited by the relative inertness of their pristine basal plane. MoS₂ single layers modified by substitutional oxygen can harvest the synergistic benefits of stably anchored single-atom sites and activated MoS₂ basal planes. [1] These oxygen sites lower the hydrogen adsorption barrier and also act as vertical electron channels. MoS₂ single-layer substrates with embedded non-metal heteroatoms also offer the benefit of site densities that are much higher than generally reported in the literature for metal SACs on various substrates [2] These sites might be suitable not only for hydrogen evolution, but also for anchoring metal atoms. We have shown that small Pt clusters (1 nm) anchored to MoS₂ defect sites shown orders of magnitude higher intrinsic activity in HER than Pt nanoparticles (5-10 nm) or even Pt single atom catalysts. By optimizing the deposition conditions, we were able to achieve a high-density decoration of the whole MoS₂ basal plane with small Pt clusters. The interaction of Pt atoms and MoS₂ creates ultra-fine (~1nm), bilayer (~3 Å height), semiconductor (E_g~250 meV) Pt clusters. [3].

Methods

A simple, rapid and scalable electrochemical technique was employed to deposit small Pt clusters all over the basal plane of the MoS₂ support, consisting of single- and few-layer MoS₂, grown by CVD on top of a graphite (HOPG) crystal. As metal (Pt, Pd, Au, Cu) source, we used a 0.5 M H₂SO₄ electrolyte solution, comprising of auxiliary ligand-free Pt ions.

The electrocatalytic properties of our samples were characterized by linear sweep voltammetry (LSV), impedance spectroscopy (EIS) and controlled potential electrolysis (CPE) in a three-electrode cell (ref. el.: Ag/AgCl, counter el.: Pt). The amount of H₂ was quantified by gas chromatography. To determine how the size of metal clusters formed on the surface of molybdenum sulfide can be controlled, and thereby tune their catalytic properties, we varied the growth conditions and methods. The formation process of the clusters was monitored by ellipsometry, and their size and morphology were further characterized using scanning tunneling microscopy and scanning electron microscopy. chromatography. The chemical nature of small clusters has been identified as Pt by energy dispersive spectroscopy (EDS) in a transmission electron microscope, while X-ray photoelectron spectroscopy (XPS) measurements. In addition to platinum, palladium, gold, and copper (copper oxide) clusters were grown on the MoS₂ surface. The formation conditions, morphology, and catalytic activity of these clusters in the electrochemical hydrogen evolution reaction were found to vary significantly.

Results and Discussion

By optimizing the deposition conditions, we were able to achieve a high-density decoration of the whole MoS₂ basal plane with small metal clusters. The interaction of Pt atoms and MoS₂ creates ultra-fine (~1nm), bilayer (~3 Å height). The observation of ultra-fine Pt clusters by STM indicates a remarkable stability, since the aggregation of Pt clusters is suppressed, even though the average distance between the clusters is only a few nanometres, a clear indication of strong support adhesion. After the formation of the Pt clusters, additional metal clusters were generated on the MoS₂ surface. Different metals form clusters with distinct morphologies. For example, gold forms monolayer-high clusters with diameters ranging from 3 to 5 nm.

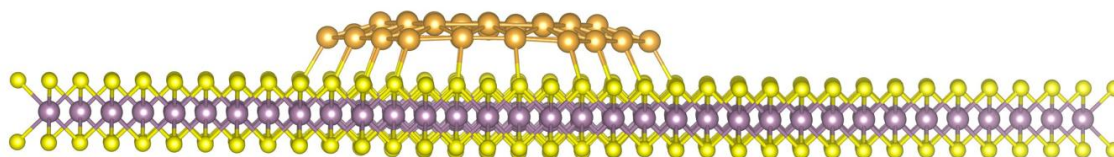


Figure 1. Simulated (DFT) structure of gold cluster on MoS₂

Conclusion

To determine how the size of metal clusters formed on the surface of molybdenum sulfide can be controlled, and thereby tune their catalytic properties, we varied the growth conditions and methods. The formation conditions, morphology, and catalytic activity of these clusters in the electrochemical hydrogen evolution reaction were found to vary significantly.

Keywords: 2D MoS₂, metal clusters. Pt, Pd, Au, Cu, Hydrogen Evolution Reaction

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From Materials Development to Pilot-Scale Electrocatalysis Testing with BioLogic Electrochemical Instruments

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Keywords: Electrocatalysis, electrochemistry, hydrogen, electrolyzers, fuel-cells, CCS

This short presentation introduces BioLogic instrumentation for electrocatalysis and electrochemical process research, covering workflows from material development to pilot-scale testing. The presentation will briefly present premium potentiostat platforms, including the SP-300 series and RRDE systems, together with selected electrochemical techniques used for catalyst and electrode characterization.

Main application areas will include:

- electrocatalyst activity and stability testing,
- hydrogen evolution and water electrolysis,
- CO₂ reduction and electrochemical synthesis,
- battery and energy materials research,
- impedance spectroscopy (EIS) for interface characterization,
- upscale and pilot-scale electrochemical testing.

The goal is to provide a concise overview of how BioLogic instruments support electrochemical research from fundamental studies to applied process development.

Fig. 1: SP-300 Bi-stat with RRDE accessory



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The pivotal role of carbon-sourced functional groups in promoting CO-tolerance of electrocatalysts for PEM fuel cells

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Keywords: PEM fuel cell, anode catalyst, CO-tolerance, composite support, mixed oxide

Stability and CO-tolerance are the must-have properties for a polymer electrolyte membrane fuel cell (PEMFC) anode catalyst. Presence of even trace amount of CO in H₂ fuel may block electrochemically active Pt sites making them unavailable for the hydrogen oxidation on anodic electrode. This in turn would decrease overall performance of the cell and make the whole process insufficient. The most commonly used carbon supported Pt catalysts are prone to this CO poisoning. Therefore, finding new solutions by designing and manufacturing catalysts with better CO tolerance is as important as their intrinsic activity to improve the efficiency of PEMFCs. We have already developed a Mo-incorporated TiO₂-C mixed oxide-carbon containing composite supported catalyst possessing higher stability and CO-tolerance in a standard three-electrode cell. In this system the strong interaction between rutile titania on carbon and Pt nanoparticles inhibits the corrosion and agglomeration of the active metal nanoparticles. The oxophilic dopant (Mo) of TiMoO_x mixed oxide in turn provides oxygen-containing groups at lower potentials than Pt helping oxidize carbon monoxide to CO₂ via bifunctional mechanism.

Our previous studies have already shown that replacing the traditional carbon materials in TiMoO_x-C composite materials with graphene-derived materials (graphene nanoplatelets (GNP), graphite oxide (GO)) [1, 2] and functionalized carbon (FC) [3–5] offer additional benefits (e.g. improving the characteristics of the composite supports by helping the dispersion of metal oxides on the carbon layer). The architecture of these supports ensures that Pt nanoparticles are dispersed evenly, maximizing the density of oxide-metal-carbon triple phase boundaries as it was verified by TEM (see Fig. 1).

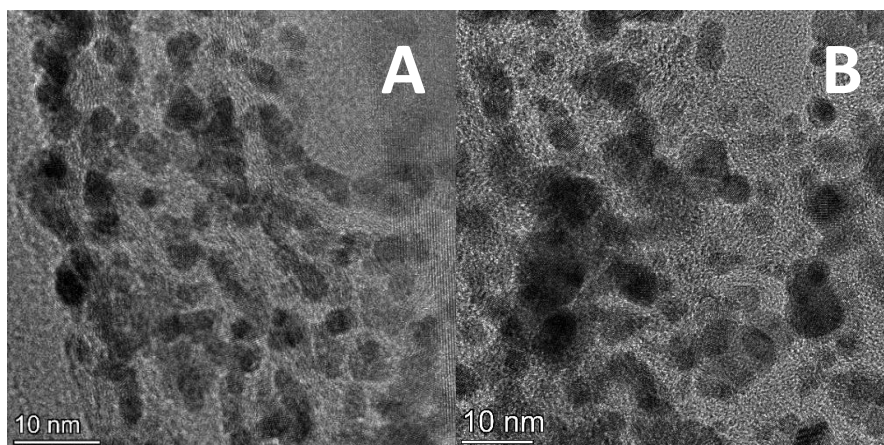


Fig. 1: TEM images of Pt/Ti_{0.8}Mo_{0.2}O₂-C (C: GNP-GO (A) and FC (B))

Advantageous metal–support interactions formed at the oxide–Pt–carbon triple junctions promote higher activity and improved stability for the catalysts.

TiMoO_x-C supported electrocatalysts, performing the best in three-electrode cell, were chosen to be assessed in fuel cell. These catalysts contained (1) HNO₃–glucose–functionalized carbon or (2) GNP and GO mixture as carbon component. The catalyst containing the former was exposed to reductive pre-treatment under H₂ atmosphere at 350°C to facilitate the formation of strong metal-support interactions (SMSI). Membrane electrode assemblies (MEAs) fabricated with composite-supported Pt electrocatalysts were evaluated in a PEMFC under practical operating conditions. To assess CO tolerance, the anodes were fueled with both pure hydrogen and a 100 ppm CO-in-H₂ mixture, with performance benchmarked against commercial Pt/C and Pt-Ru/C catalysts. While all MEAs exhibited comparable performance under CO-free conditions, those utilizing the composite supported catalysts significantly outperformed the commercial standards in the presence of CO, demonstrating markedly lower losses in voltage and power density.

This superior tolerance is attributed to a synergistic effect originating from the Mo-containing composite support. Specifically, molybdenum promotes the formation of OH_{ads} species at lower potentials, facilitating a bifunctional CO oxidation pathway. Simultaneously, SMSI electronically modify the Pt surface, effectively weakening the CO binding strength. In addition to CO tolerance, these catalysts have demonstrated exceptional electrochemical long-term stability during 10,000 polarization cycles [1, 5]. These results highlight that mixed oxide–carbon composites offer a promising strategy for the design of advanced PEMFC anode catalysts. Crucially, the carbon-sourced functional groups play a pivotal role in this architecture: they not only provide high specific surface area but also anchor the mixed-oxide phase and facilitate the uniform Pt dispersion to create the dense network of triple-phase boundaries necessary for efficient CO oxidation. By optimizing these surface interactions, these electrocatalysts maintain high performance under impure hydrogen feeds, reinforcing the importance of support functionalization in achieving robust CO tolerance.

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Acknowledgement

This research was funded by Project no. RRF-2.3.1-21-2022-00009, titled the National Laboratory for Renewable Energy, and has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus and by Project no. 2024-1.2.1-HE_PARTNERSÉG-2025-00042, titled European partnerships in Horizon Europe, announced by the National Research, Development and Innovation Office.

Electrooxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid on Nickel-Based Catalysts Supported on Lignin-Derived Biochars

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Keywords: biomass valorization, lignin-derived carbon, 5-hydroxymethylfurfural electrooxidation, 2,5-furandicarboxylic acid, nickel oxyhydroxide catalysis

Introduction

The electrochemical oxidation of biomass-derived platform molecules offers a sustainable route toward value-added chemicals. Among these, the conversion of 5-hydroxymethylfurfural (5-HMF) to 2,5-furandicarboxylic acid (FDCA) is particularly attractive due to FDCA's role as a renewable alternative to terephthalic acid in polymer production. Nickel-based catalysts, especially nickel oxyhydroxides (NiOOH), are known to be active for electrooxidation reactions in alkaline media.¹⁾ In this work, we investigate the performance of nickel catalysts derived from nickel hydroxide and nickel dithiooxamide precursors, supported on lignin-derived biochars, for 5-HMF electrooxidation.

Methodology

Lignin-derived biochars were prepared at different pyrolysis temperatures (550 and 1000 °C) from sugarcane bagasse (B) and straw (S) lignin obtained via kraft (K) or soda (S) processes. Nickel catalysts were introduced either as nickel hydroxide, Ni(OH)₂ or via nickel dithiooxamide precursors, Ni(dto). Catalyst inks were prepared by dispersing lignin-derived carbon and nickel precursors in a PVDF/NMP binder system, followed by stirring and sonication to obtain a homogeneous slurry, which was then deposited onto the electrode substrate and dried. Before electrochemical measurements, the electrodes were preconditioned in alkaline solution to form the catalytically active γ -NiOOH phase.²⁾ Electrochemical oxidation of 5-HMF was performed in 0.1 M KOH under controlled potential (1.47 V vs RHE), and reactions were conducted for 6 h to evaluate each Ni/biochar system activity. Product distribution and conversion were quantified using high-performance liquid chromatography (HPLC) analysis.

Results

Catalytic performance strongly depended on both the precursor chemistry and biochar properties. Electrodes derived from Ni(dto) exhibited significantly higher activity compared to those prepared from Ni(OH)₂. Among the tested samples, high-temperature biochars (1000 °C) showed improved performance relative to 550 °C counterparts.

The electrooxidation of 5-HMF proceeds through consecutive oxidation of the hydroxymethyl and aldehyde groups, forming typical intermediates such as DFF, HMFCa, and FFCA, before producing the final diacid product FDCA. The UV–Vis spectra (Fig.1) show a clear decrease of the 5-HMF absorption band around 280–285 nm with reaction time, confirming progressive 5-HMF depletion. At the same time, a new/increasing bands appear around 260–275 nm, consistent with the formation of oxidized furan products, including intermediates (DFF, FFCA) and FDCA. After longer reaction times, the spectrum becomes dominated by the lower-wavelength FDCA band, indicating substantial conversion of 5-HMF. These UV–Vis results are consistent with the HPLC data, which confirmed FDCA formation and allowed quantification of 5-HMF conversion and FDCA yield. The highest activity was observed for the Ni/AB (acetylene black) reference electrode, achieving 94% HMF conversion and 94% FDCA yield. Among biochar-supported catalysts, ST-S-1000 and BS-S-1000 showed the best performance, reaching FDCA yields of 54–55% with conversion up to 68%.

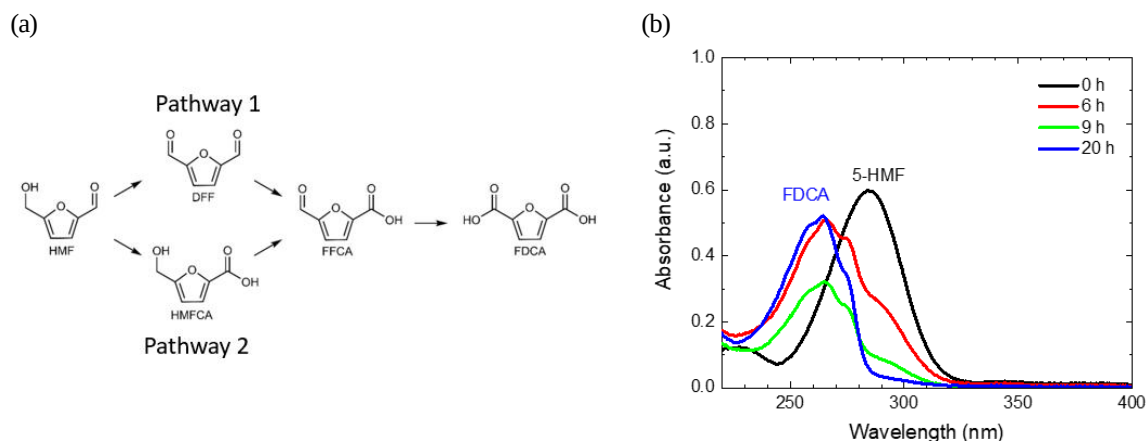


Fig. 1 (a) Reaction pathways for the electrooxidation of 5-HMF to FDCA in alkaline media, (b) time-dependent UV–Vis spectra for the electrooxidation of 5-HMF over Ni/ST-K-550 catalyst.

In contrast, several samples (e.g., ST-S-550, BS-K-550) exhibited negligible activity, correlating with extremely low current densities (< 0.01 mA).

Nickel hydroxide-derived catalysts overall showed significantly lower catalytic activity, with only the AB sample achieving notable conversion (83%) and FDCA yield (77%).

Discussion

The results indicate that catalytic activity is closely linked to the formation of electroactive γ -NiOOH species, which is facilitated by both precursor chemistry and carbon support properties. Ni(dto)-derived catalysts likely promote more efficient formation of the active Ni^{3+} phase, contributing to enhanced electrooxidation performance.²⁾

The superior performance of high-temperature biochars suggests that increased conductivity, structural ordering, and surface chemistry play key roles in electron transfer. Conversely, low-temperature biochars and certain feedstock-derived carbons appear insufficiently conductive, resulting in poor catalytic performance.³⁻⁴⁾

Despite high HMF conversion, FDCA yields remain moderate (~50–55%) for biochar-supported systems. This behavior is attributed to the rate-limiting oxidation of FFCA to FDCA, competing side reactions in alkaline media, and insufficient formation of the active γ -NiOOH phase on certain carbon supports, which limits the availability of high-valent Ni sites required for complete oxidation.

Conclusions

Nickel-based catalysts supported on lignin-derived biochars show promising activity for the electrooxidation of 5-HMF to FDCA. Catalyst performance is strongly influenced by precursor type and biochar properties, with Ni(dto)-derived systems and high-temperature biochars yielding the best results. This study highlights the potential of integrating lignin valorization with electrocatalytic biomass conversion toward sustainable chemical production.

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This work was supported by the Japan Science and Technology Agency, Strategic International Collaborative Research Program (SICORP), Grant Number JPMJSC2302, Japan. A.K. Chandel gratefully acknowledges the financial support from FAPESP (Project number: 2022/13184–1) and CNPq for the scientific productivity program (Process number: 304451/2025–8). Rzeznicka thanks Shibaura IT for providing travel grant.

Developing a Magnetic Rotating Disk Electrode for Mechanistic Investigations of Oxygen Electrochemistry

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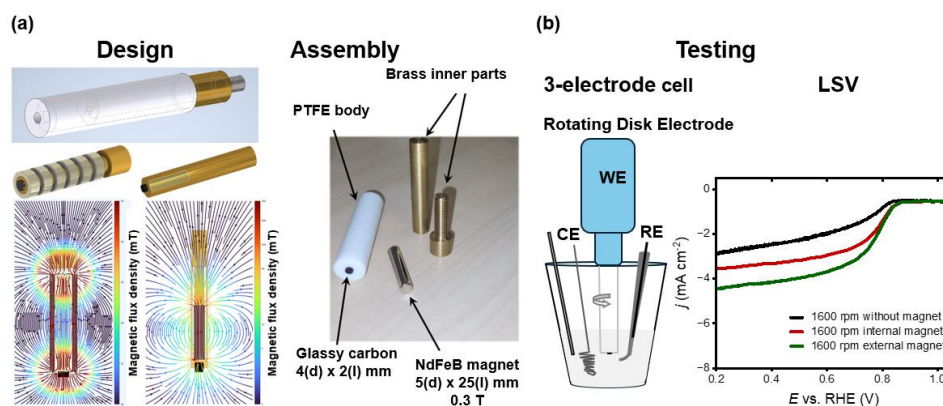
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Keywords: Magnetic electrocatalysis, oxygen reduction reaction, oxygen evolution reaction, rotating disk electrode

The urgent need to mitigate rising atmospheric CO₂ levels has accelerated the demand for sustainable energy conversion and storage technologies. While green hydrogen produced via electrochemical water splitting offers a carbon-neutral alternative to steam methane reforming (SMR), overall efficiency is heavily constrained by the sluggish kinetics of the anodic oxygen evolution reaction (OER) in electrolyzers and the cathodic oxygen reduction reaction (ORR) in fuel cells. Recent advancements indicate that applying an external magnetic field can lower reaction overpotentials by modulating mass transport and spin-selective charge transfer dynamics. However, systematic investigation of these phenomena requires specialized, custom-built instrumentation [1]. In this study, we report the design, fabrication, and validation of a novel magnetic Rotating Disk Electrode (RDE) setup developed via 3D CAD modeling. The rotating PTFE electrode body is designed to house either coaxially mounted NdFeB ring magnets or an axially positioned 5x25 mm NdFeB bar magnet. To ensure structural integrity and prevent magnetic interference, the internal conductive assembly was machined from diamagnetic brass, providing electrical contact to a 3.0 mm glassy carbon disk substrate. The setup was validated by evaluating the catalytic performance of drop-casted benchmark Pt/C and magnetically responsive CoNi@NC heterostructures. Electrochemical measurements, including linear sweep (LSV) and cyclic voltammetry (CV), were conducted in a standard three-electrode cell. Our results validate the custom RDE configuration and demonstrate that the localized external magnetic field effectively modifies OER and ORR reaction kinetics, highlighting the potential of magnetic-field-assisted electrocatalysis in optimizing next-generation green hydrogen technologies.

Fig. 1:



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Enhancing Platinum ORR Catalysts Through Carbon Support Modification

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Keywords: Fuel Cells, Electrocatalysis, Oxygen Reduction Reaction, Carbon Nanotubes, Platinum

A major obstacle to decarbonizing the transportation sector is the lack of high-energy-density energy-storage technologies capable of replacing internal combustion engines. Polymer electrolyte membrane fuel cells (PEMFCs) are among the leading candidates for this purpose; however, their scalability is hindered by the reliance on platinum (Pt) as a cathode catalyst, owing to its high cost and limited availability. Although Pt-free alternatives—such as transition-metal spinels, doped carbon materials, and metal–nitrogen (Me–N_x) systems—have been widely investigated, they often suffer from insufficient catalytic performance, limited durability, or complex synthesis protocols. An alternative strategy is to reduce Pt loading while enhancing catalyst stability and selectivity through rational materials engineering. This can be achieved by optimizing the carbon support and incorporating redox-active metal oxides that suppress undesirable oxygen reduction reaction (ORR) byproducts, particularly hydrogen peroxide (H₂O₂).

In this study, multi-walled carbon nanotubes (MWCNTs) were co-doped with iron (Fe) and nitrogen (N) through pyrolysis of the [Fe(1,10-phen)₃]Cl₃ complex under a nitrogen atmosphere. Pt nanoparticles were synthesized by solvothermal reduction of H₂PtCl₆ in ethylene glycol. Structural, morphological, and compositional characterization was performed using X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM) combined with EDX and EELS elemental mapping, elemental analysis, and X-ray photoelectron spectroscopy (XPS). The resulting catalysts contained Pt nanoparticles approximately 2–3 nm in diameter, as confirmed by XRD. XPS spectra of Fe,N-doped MWCNTs confirmed successful N-doping and indicated the presence of Fe–N_x moieties, while XRD patterns and TEM micrographs showed no evidence of crystalline iron species (Fig. 1). These results suggest the possible formation of atomically dispersed Fe–N centers.

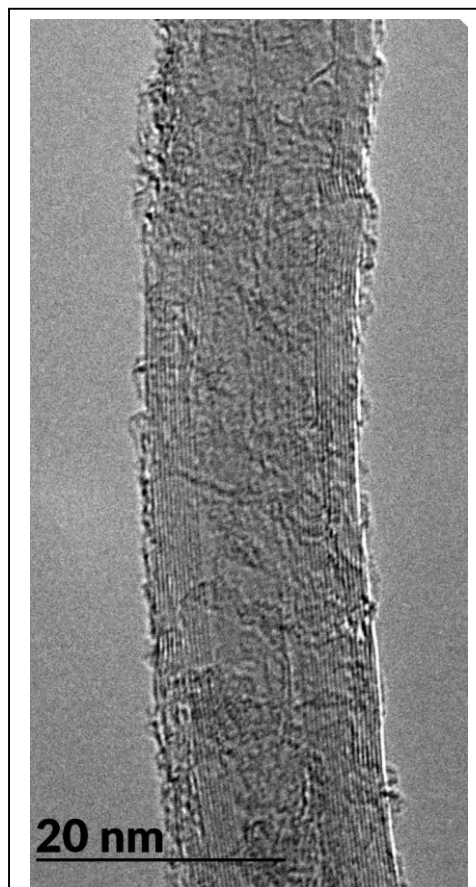
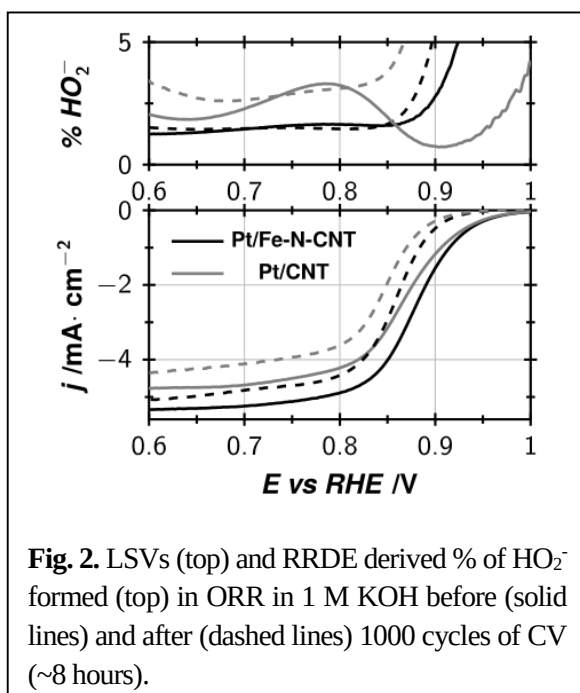


Fig. 1. HR-TEM microphotograph of Fe-N-MWCNT sample.



The ORR activity of the synthesized catalysts was evaluated using the rotating ring–disk electrode (RRDE) technique, with the most promising materials further tested in a fuel cell. The onset potential of Fe,N-doped MWCNTs reached 0.97 V vs. RHE, while the average number of electrons exchanged during ORR was close to 4.0, indicating high selectivity toward the four-electron pathway. Although Fe,N co-doping did not enhance the catalytic activity of the Pt-based catalyst, it improved both selectivity and long-term stability. After 1000 cyclic voltammetry (CV) cycles between 0 and 1.3 V vs. RHE, the two-electron H_2O_2 yield for the 10%Pt/MWCNT catalyst increased by 75%, whereas Fe,N-doped 10%Pt/MWCNT systems showed only a 33% increase in H_2O_2 yield (Fig. 2).

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Acknowledgement

The research was funded by the Ministry of Science and Higher Education of Poland, under the programme “Pearls of Science”, project “High-performance electrocatalyst for oxygen reduction reaction with low platinum content”, PN/01/0109/2022.

Unlocking Alkaline Oxygen Evolution Activity in Magnetite via ZnO Co-Catalytic Promotion

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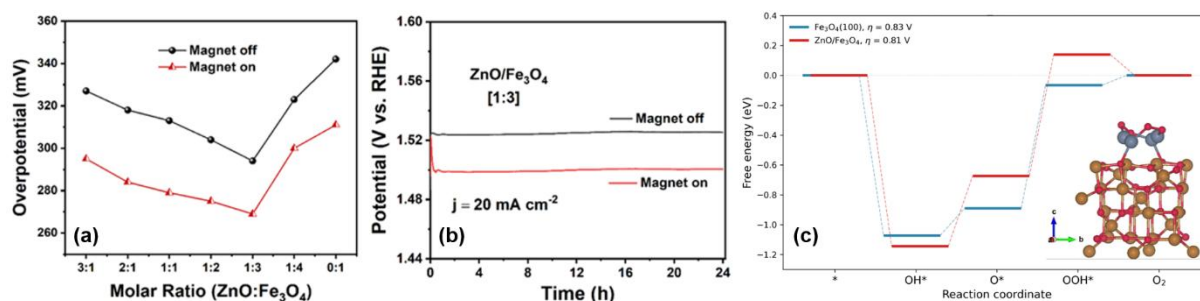
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Keywords: ZnO, magnetite, magnetic electrocatalysis, oxygen evolution reaction

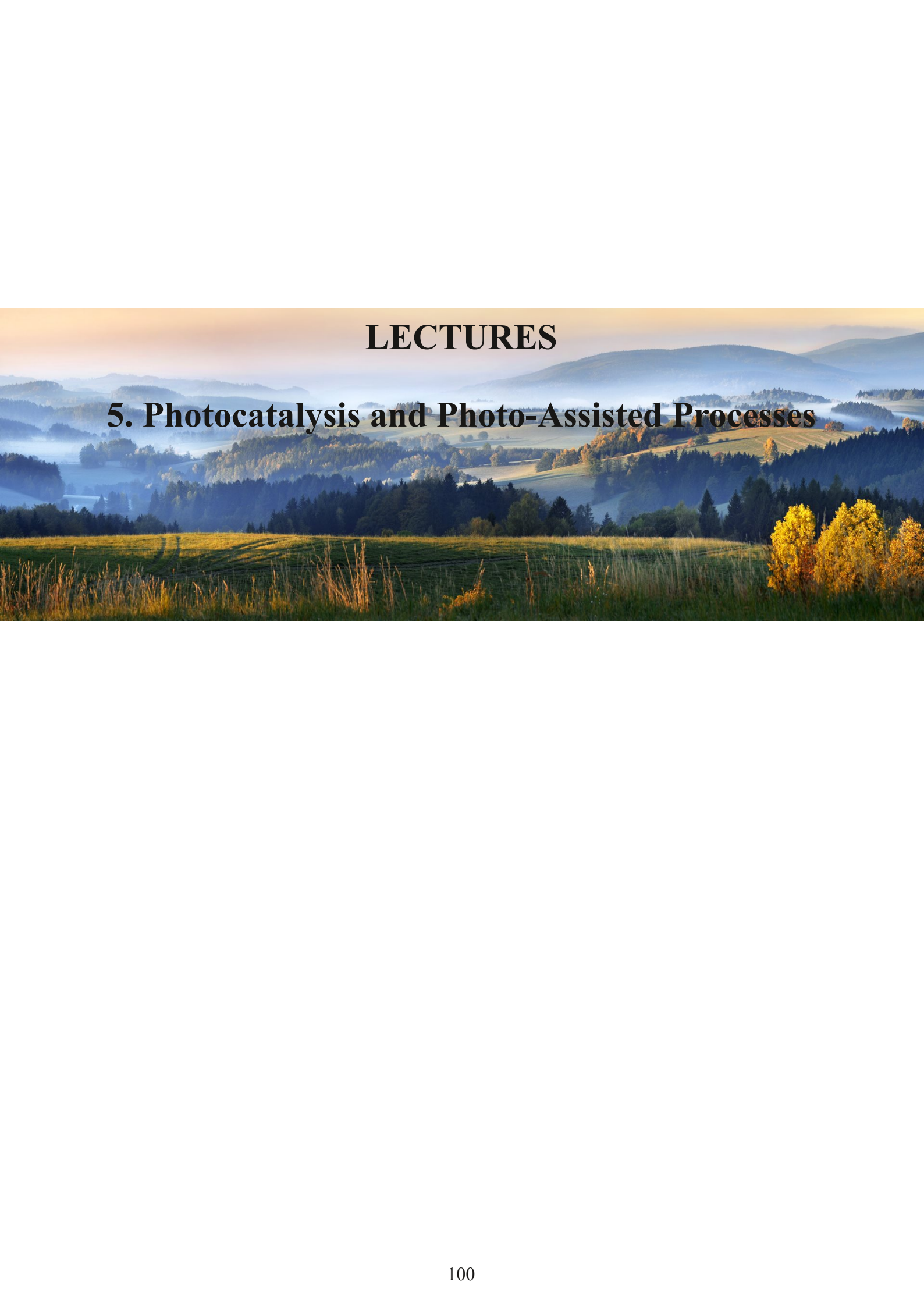
Driven by the accelerating global transition toward sustainable energy, water electrolysis has emerged as a pivotal technology for efficient energy storage. However, the Oxygen Evolution Reaction (OER) remains a major barrier due to the inherently sluggish kinetics of its four-electron pathway. To address this, we synthesized a series of ZnO/Fe₃O₄ heterostructures via a cyanometallate precursor route, followed by wet chemical processing and thermal annealing [1]. Both ZnO and magnetite are particularly attractive for large-scale applications as they are earth-abundant, non-toxic, and highly cost-effective inorganic materials. Structural and microscopic analyses confirmed the successful integration of high-purity ZnO and Fe₃O₄ phases, forming clustered nanoparticles with a uniform elemental distribution. Optical spectroscopy indicated that increasing the magnetite content narrows the energy band gap, suggesting a robust electronic interaction at the heterointerface. Electrochemical evaluations in 1 M KOH revealed that while ZnO is typically inactive for OER, it acts as a co-catalyst that promotes the activity of magnetite. To the best of our knowledge, this is the first report of such an enhancement in this binary oxide system. The optimized ZnO/Fe₃O₄ [1:3] composition exhibited a low overpotential of 214 mV at 20 mA cm⁻² with a Tafel slope of 97 mV dec⁻¹. To elucidate the origin of the enhancement, DFT calculations were employed, providing a theoretical framework by mapping the adsorption energies of reaction intermediates. Furthermore, the application of an external magnetic field led to an additional reduction in overpotential, demonstrating that magnetic field effects can further boost catalytic activity. These findings, supported by electrochemical impedance spectroscopy and stability tests, indicate that interfacial modulation of ZnO/Fe₃O₄ represents a robust and scalable approach to designing high-performance catalysts for alkaline water splitting.

Fig. 1: The (a) composition-dependent overpotential, the (b) long-term stability, and the (c) DFT results.



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LECTURES

5. Photocatalysis and Photo-Assisted Processes

Photocatalytic stability of the silver-modified TiO₂/ACF filtering felts determined by air deNO_xification

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Keywords: photocatalysis, titanium dioxide, activated carbon fibre felt, air treatment, denoxification

Introduction: Most outdoor NO_x originates from combustion-related emissions sources of human origin, primarily fossil-fuel combustion in electric utilities, high-temperature operations at other industrial sources, and the operation of motor vehicles. In indoor conditions, the primary sources of NO_x are tobacco smoke and unvented or poorly maintained gas-, wood-, oil-, kerosene- and coal-burning appliances such as stoves, ovens, space and water heaters. Moreover, outdoor NO_x from natural and anthropogenic sources can also influence indoor levels. Several studies [1, 2] have confirmed that indoor NO_x concentrations can often exceed outdoor air levels. This fact has led to many efforts to develop effective technologies for removing NO_x from indoor environments. Most indoor air pollution purification methods originate from industrial gas treatment technologies. The activated carbon-based filtration remains the most common approach.

Aim of research: The main goal of the study was to obtain a series of TiO₂-loaded activated carbon fibre (ACF) composites that act as indoor air filters, demonstrating superior air-purifying properties. The development of the filter materials strived to combine the advantages of two phenomena: adsorption and photocatalysis. The TiO₂ photocatalysts used to prepare the composites were further modified with silver nanoparticles (AgNPs) to enhance the photocatalytic properties of the final AgNPs/TiO₂/ACF-based air filters.

Methodology: The preparation of ACF/TiO₂ composites involved the utilisation of commercial ACF felt "CARBOPON-ACTIVE" (provided by OJSC «SvetlogorskKhimvolokno» company) and three types of titanium dioxide materials: AEROXIDE® P25 TiO₂, AEROXIDE® P90 TiO₂ (Evonik Industries AG, Germany), and TiO₂ slurry, supplied by sulphate technology from Grupa Azoty Zakłady Chemiczne POLICE S.A. chemical plant (Poland). In addition, the TiO₂ photocatalysts were modified with silver nanoparticles (AgNPs) using AgNO₃ as the silver precursor and NaBH₄ as the reducing agent. Appropriate concentrations of AgNO₃ solution were used to obtain AgNPs/TiO₂ photocatalysts containing the desired amount of Ag NPs (ca. 3, 5 or 10 wt.%). A 1 g of the photocatalyst was mixed with 50 cm³ of ethanol and dispersed onto the surface of ACF felt fragments (4 x 4 cm) via spraying process. The amount of applied TiO₂ was constant for all the samples (ca. 75 mg). The pure ACF and the obtained composites were characterized by XRD and N₂ adsorption-desorption methods. The air purifying properties of the materials were assessed by conducting multi-cycle photocatalytic oxidation tests using NO (1 ppm) as a model air pollutant.

Results and Discussion: All the titania-impregnated materials exhibited significantly higher NO removal rates, exceeding 80% (Table 1). Still, the composites have exhibited limited stability, as reflected in the ongoing deterioration of their photoactivity towards NO after each UV irradiation cycle. Compared with the unmodified titania-containing ACF materials (TiO₂/ACF, P25/ACF and P90/ACF), the NO removal rates were generally higher for the Ag NPs-loaded composites. This feature was particularly relevant for the materials containing approximately 5 wt.% of silver nanoparticles (AgNPs-4.85%/TiO₂/ACF, AgNPs-5.24%/P25/ACF, AgNP-5.16%/P90/ACF). The same composites also showed generally lower NO₂

selectivity values, ranging from ca. 2 to 18% (depending on the sample and UV irradiation cycle). The results indicate that the presence of Ag NPs is a vital factor in enhancing NO removal and limiting NO₂ emission during the photocatalytic oxidation process. This effect can be associated with (1) partial adsorption of generated NO₂ by the microporous ACF material (2) presence of supported Ag NPs, which can contribute to the number of active sites and enhance the separation of photogenerated charge, thus facilitating the conversion of NO₂ into other species (i.e. NO₂⁻ or NO₃⁻) [3]. It was additionally confirmed that the NO removal rate was limited under UV light alone and did not exceed 10%. Furthermore, the NO oxidation was followed by the simultaneous generation of NO₂, which, in terms of NO₂ selectivity values, exceeded approximately 52-55%. In the case of the pure ACF material, the overall NO removal rate was between ca. 27-33% (Table 1). It should be noted that, based on the progression of the presented NO removal profile, approximately 17% of removed NO was attributed to the adsorption effect. Since, approx. 10% of the NO removal rate was previously ascribed to direct photolysis; the actual impact of the pure ACF material of the NO photooxidation process was deemed negligible.

Table 1: Textural properties of pristine ACF and obtained AgNPs/TiO₂-loaded composites

Sample code	Textural parameters				NO removal rate (NO ₂ selectivity) [%]				
	SSA [m ² /g]	V _{total} [cm ³ /g]	V _{micro} [cm ³ /g]	V _{meso} [cm ³ /g]	1 cycle	2 cycle	3 cycle	4 cycle	5 cycle
Pure ACF felt	854	0.60	0.43	0.17	33 (38)	31 (42)	29 (43)	28 (45)	27 (47)
TiO ₂ /ACF	551	0.44	0.27	0.17	85 (14)	84 (15)	82 (16)	82 (17)	92 (18)
AgNPs-3.28%/TiO ₂ /ACF	501	0.42	0.24	0.18	96 (6)	94 (8)	93 (9)	92 (10)	92 (11)
AgNPs-4.85%/TiO ₂ /ACF	509	0.40	0.25	0.15	99 (2)	98 (4)	98 (7)	97 (10)	96 (12)
AgNPs-10.03%/TiO ₂ /ACF	500	0.41	0.24	0.17	97 (5)	95 (9)	92 (11)	89 (13)	86 (14)
P25/ACF	457	0.39	0.23	0.16	87 (16)	85 (20)	84 (21)	82 (23)	81 (24)
AgNPs-3.36%/P25/ACF	395	0.33	0.19	0.14	91 (10)	88 (14)	85 (17)	82 (18)	79 (20)
AgNPs-5.24%/P25/ACF	405	0.41	0.20	0.22	98 (6)	97 (9)	95 (13)	93 (15)	92 (18)
AgNPs-9.92%/P25/ACF	406	0.42	0.22	0.22	93 (8)	92 (11)	91 (14)	89 (17)	87 (19)
P90/ACF	494	0.54	0.24	0.30	91 (12)	88 (14)	87 (14)	86 (14)	85 (15)
AgNPs-3.14%/P90/ACF	481	0.49	0.23	0.26	95 (8)	94 (12)	92 (14)	91 (15)	89 (17)
AgNPs-5.16%/P90/ACF	478	0.47	0.23	0.24	97 (6)	96 (8)	96 (10)	95 (13)	94 (14)
AgNPs-10.03%/P90/ACF	477	0.48	0.23	0.25	92 (9)	91 (13)	90 (13)	87 (16)	83 (18)

Conclusions: A series of AgNPs/TiO₂-loaded ACF composites was prepared by immobilising AgNPs-modified commercial TiO₂ additives onto the surface of ACF. The presence of AgNPs in the materials was confirmed by the XRD method. The photocatalytic properties of the studied composites were evaluated by performing multi-cycle NO photocatalytic oxidation tests. In contrast to pure ACF, all of the AgNPs/TiO₂/ACF materials have proven to remove NO from air while simultaneously maintaining the NO₂ generation at moderated levels. In addition, the presence of Ag NPs was an important factor influencing the removal of NO and limiting the NO₂ formation.

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Acknowledgement: This work was supported by the National Centre for Research and Development, Poland under project No. LIDER/31/0115/L-9/17/NCBR/2018.

Development of Advanced Functional Quinone-based Materials and Metal-Organic Frameworks (MOFs) for Efficient Visible-Light-Driven CO₂ Reduction

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Keywords: Metal-Organic Frameworks (MOFs), Quinone-based materials, CO₂ reduction, Photocatalysis, Visible light

The escalating concentration of atmospheric CO₂ represents one of the most pressing environmental challenges of our time, driving urgent demand for sustainable carbon capture and conversion technologies. Photocatalytic reduction of CO₂ into value-added fuels and chemicals using visible light offers a promising route toward a carbon-neutral energy cycle. However, the development of efficient, stable, and visible-light-active photocatalysts from earth-abundant elements remains a critical challenge. In this work, we report the design, synthesis, structural characterization, and photocatalytic evaluation of three distinct copper-benzoquinoid coordination compounds derived from the redox-non-innocent organic building block 1,4-dicyano-2,3,5,6-tetrahydroxybenzene (LH₄): (A) the one-dimensional coordination polymer [CuL(DMF)₂]_n [1], (B) the three-dimensional mixed-valence metal-organic framework NCKU-52 ([Cu₄L₃]_n) [2], and (C) its isoquinoline pore-filled analogue NCKU-52-Cu(iq)₃ ([Cu₄L₃.Cu(iq)₃]_n) [2]. By systematically varying dimensionality, copper oxidation state, and pore environment across this series, we establish clear structure-activity relationships for visible-light-driven CO₂ reduction.

Compound A, [CuL(DMF)₂]_n, is a one-dimensional (1D) coordination polymer in which Cu^{II} adopts a distorted octahedral geometry: four oxygen atoms from two bridging benzoquinoid ligands L occupy the equatorial plane, while two oxygen atoms from coordinated DMF molecules fill the axial positions. The -C=N groups remain non-coordinating and instead engage in unusual supramolecular C=N...π and C=N...H interactions that stabilize the chain packing. Phase purity was confirmed by PXRD, and the compound is thermally stable to ca. 240 degrees C [1]. Importantly, LH₄ features electron-withdrawing nitrile groups that enable charge delocalization, a suitable redox potential, and strong visible-light absorption - properties equally critical for photocatalytic CO₂ activation.

Compound B, NCKU-52 ([Cu₄L₃]_n), is a three-dimensional (3D) MOF containing two crystallographically distinct Cu sites in a 1:3 ratio [2]. The minority Cu^{III} node is coordinated by four oxygen atoms from three bridging L ligands in a near-square-planar geometry. The majority Cu^I node is coordinated by four nitrogen atoms from the -C=N groups of four distinct ligands in a tetrahedral arrangement - the first time the -C=N groups of LH₄ coordinate to a metal center. This dual O/N binding mode generates a formal Cu^I/Cu^{III} mixed valency, unprecedented in any metal-organic extended solid, confirmed by high-resolution Cu K-edge XANES (pre-edge at 8981.4 eV), XPS (no Cu^{II} satellite at ca. 942 eV), temperature-dependent EPR (valence tautomerism below 298 K), and DFT Bader charge analysis. The resulting d-π conjugation along the Cu-O-C=N-Cu pathway confers semiconducting behavior (σ = 1.0

$\times 10^{-8} \text{ S.cm}^{-1}$; DFT band gap $E_g = 2.34 \text{ eV}$) and visible-light absorption. The BET surface area of $572 \text{ m}^2 \text{ g}^{-1}$ and three-dimensionally interconnected ca. $7 \text{ \AA}$ pore channels enable facile mass transport of CO_2 to the active Cu sites, making NCKU-52 an intrinsically photocatalytically active material.

Compound C, NCKU-52-Cu(iq)₃, retains the identical Cu^I/Cu^{III} mixed-valence 3D host framework of NCKU-52, but its ca. $7 \text{ \AA}$ pore channels are partitioned by encapsulated $[\text{Cu}(\text{iq})_3]^+$ guest cations. The planar isoquinoline rings of the guest engage in face-to-face pi-pi stacking (interplanar distance ca. $3.5\text{--}4.0 \text{ \AA}$) with the benzoquinoid walls of the host framework in all three crystallographic directions [2]. This supramolecular reinforcement raises the thermal decomposition temperature to ca. 470 degrees C (vs. ca. 280 degrees C for NCKU-52), reduces the effective pore aperture to ca. $3.5 \text{ \AA}$, and imparts molecular-sieving selectivity (CO_2 kinetic diameter $3.3 \text{ \AA}$ vs. N_2 $3.6 \text{ \AA}$), translating into enhanced CO_2 -to-CO selectivity.

The photocatalytic performance of all three compounds has been evaluated under visible-light irradiation ($\lambda > 420 \text{ nm}$) with TEOA as a sacrificial electron donor. The multielectron redox capacity of the Cu/quinone system was harnessed for the multi-electron reduction of CO_2 to value-added products (CO, formate, methanol). NCKU-52 delivers the highest CO_2 -to-CO turnover frequency owing to its open pores and optimal electrical conductivity, while NCKU-52-Cu(iq)₃ achieves superior selectivity attributable to CO_2 molecular sieving by the pi-pi stacked $[\text{Cu}(\text{iq})_3]^+$ guests and the best long-term stability.

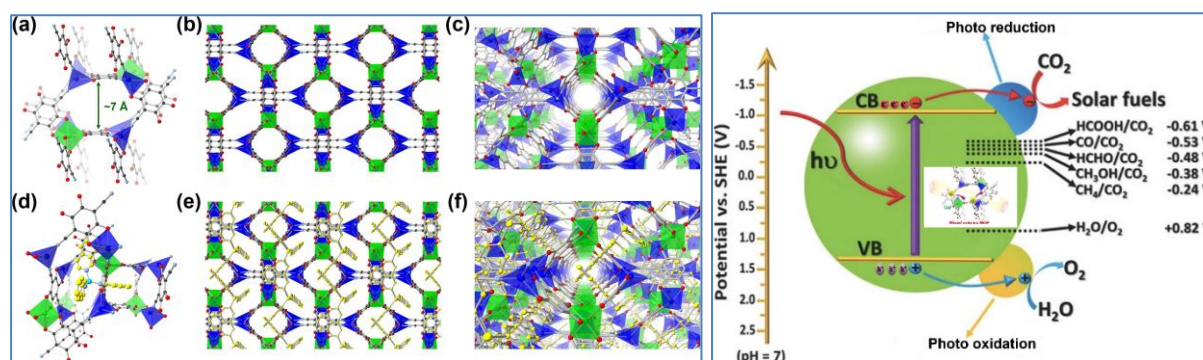


Fig. 1: Crystal structures of NCKU-52 and NCKU-52-Cu(iq)₃ showing 3D pores, mixed-valence Cu environments (a-f), and CO_2 photoreduction scheme.

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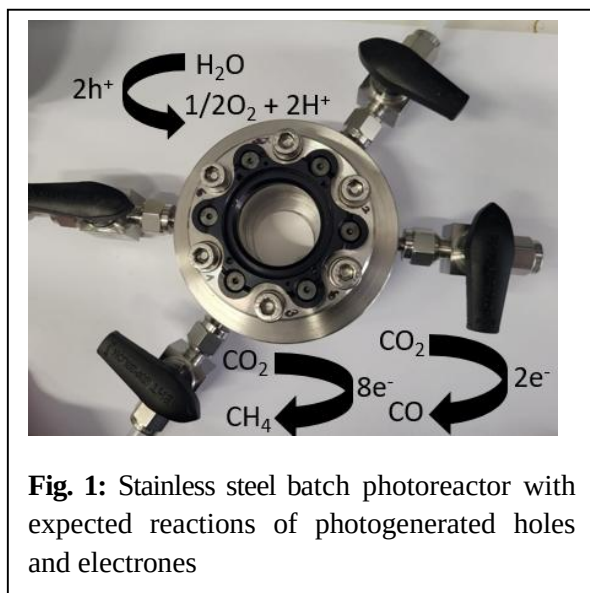
Gas phase photocatalytic reduction of CO₂ on composite TiO₂

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Keywords: CO₂ reduction, TiO₂, CO, CH₄

Although photocatalytic processes are typically associated with the oxidation of organic substances to CO₂ and water, in the presence of a suitable electron donor it is also possible to utilize photocatalysis for reduction processes [1]. The objective of this work was to evaluate the photocatalytic activity of TiO₂-based composite materials in terms of the reduction of CO₂ in the gaseous phase. For this purpose a batch photoreactor defined recently by DIN 91457 [2] was used (Fig. 1).



As a photocatalyst, TiO₂ (CG100, Precheza), consisting of the anatase phase with a crystal size of approximately 12 nm (XRD) in the form of pellet was used. Some of pellets were modified by spray coating of g-C₃N₄ dispersed in LiQUion™ solution. The deposited amount of g-C₃N₄ was about 34 mg cm⁻². The experimental procedure of photocatalytic CO₂ reduction can be described as follows. Using pure CO₂ and humidified nitrogen (50% relative humidity) a gas mixture with an initial CO₂ concentration of approximately 1700 ppm was introduced into the photoreactor (initial overpressure of about 1.2 bar). Irradiation was carried out using UV LED lamp (365 nm, irradiance 15.5 mW/cm²). Samples were collected at given times of irradiation using a

Hamilton syringe and analysed by GC-FID to determine the concentrations of the reduction products, CO and CH₄ and by GC-TCD to determine H₂ and O₂ concentrations. In control experiment (photocatalyst without irradiation), no traces of CO and CH₄ were recorded during 20 hours. Under UV irradiation in the presence of photocatalyst, CO, CH₄, H₂ and O₂ were found in the reaction mixture, the concentrations are summarised in Table 1.

Table 1: Concentrations of CO, CH₄, H₂ and O₂ after 6 and 20 hours of irradiation

Photocatalyst	C _{6HR} CO (ppm)	C _{6HR} CH ₄ (ppm)	C _{6HR} H ₂ (ppm)	C _{6HR} O ₂ (ppm)	C _{20HR} CO (ppm)	C _{20HR} CH ₄ (ppm)	C _{20HR} H ₂ (ppm)	C ₂₀ O ₂ HR (ppm)
TiO ₂	19	3	-	619	52	6	-	1439
TiO ₂ /g-C ₃ N ₄	17	24	29	592	55	46	45	1059
TiO ₂ /g-C ₃ N ₄ Fe	15	39	334	783	56	282	1993	1290

In the case of pure TiO₂, the concentration of CO as a reduction product of CO₂ predominates after 6 and 20 hrs of UV irradiation. Contrary to CO, the concentration of CH₄ is much lower (about 3 and 6 ppm respectively). It seems that the 2 electron reduction (eq.1) is favoured instead of 8 electron reduction to methane (eq. 2). Similar results were observed for TiO₂ P25 [3] where after 25 hours of irradiation higher yield of CO comparing to methane was observed.



Hydrogen was not found even after 20 hrs of irradiation; contrary to it, oxygen concentration gradually increases. This indicates that photogenerated holes oxidise water and photogenerated electrons do not reduce water but reduce CO₂ although produced CO is very small and CH₄ concentration is almost negligible. The commonly accepted assumption that CO is formed as an intermediate in the reduction pathway from CO₂ to methane is in conflict with observation that CO is not further reduced when present in the gas phase instead of CO₂ [4]. It means that methane has to be formed via an alternative mechanism.

In the case of TiO₂ modified by g-C₃N₄, produced CO is similar as in the case of pure TiO₂ but produced CH₄ is much higher and hydrogen can be detected. In fact the concentrations of CO, H₂ and CH₄ are very similar, 20-30 ppm after 6 hours and 45-55 ppm after 20 hours of irradiation. This indicates the positive role of g-C₃N₄ on the efficiency of CO₂ reduction comparing to pure TiO₂. The situation dramatically changes when TiO₂ is modified by Fe doped g-C₃N₄. Comparing to undoped g-C₃N₄ the concentration of hydrogen is 10 times higher reaching almost 2000 ppm after 20 hours of irradiation. The concentration of methane is also higher, especially after 20 hours of UV irradiation (282 ppm, 6 times) while the concentration of CO is similar as in the case of bare TiO₂ and TiO₂ modified by g-C₃N₄ (15 and 56 ppm after 6 and 20 hours of UV irradiation, respectively).

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Acknowledgement

The authors would like to thank the Grant Agency of the Czech Republic (project number 24-12812S) for financial support.

Programming Biomass Valorization with Sound and Light: Sonophotocatalytic Control of Oxidation, C–C Coupling, and Solar H₂O₂ Production

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Keywords: Biomass Valorisation, Biopolymers, H₂O₂ Production, Sono-PhotoCatalysis, Flow Chemistry

Lignin valorisation demands catalytic platforms able to transform recalcitrant phenolic motifs into defined high-value molecules while preserving the principles of green chemistry. Across the presented case studies, a coherent sonophotocatalytic strategy emerges: acoustic cavitation, photon-driven charge separation, and rational catalyst architecture are coupled to control oxygen activation, radical generation, and product selectivity [1]. Ultrasound-engineered chitosan–lignin carbon materials demonstrate that the synthesis field itself is catalytic design space; a 22 kHz/2h solvo-hydrothermal treatment yields a metal-free photocatalyst that converts coniferyl alcohol into ferulic acid under visible light while co-generating H₂O₂, with parallel formation of lignin-like dimers revealing a tuneable oxidation–coupling manifold. In continuous flow, CuBi₂O₄/TiO₂ heterostructures extend this concept toward scalable operation, where visible-light absorption, improved charge separation, and ultrasound-enhanced mass transfer deliver selective coniferyl alcohol oxidation to coniferyl aldehyde and ferulic acid [2]. The same acoustic logic becomes a selectivity switch in coniferyl alcohol dimerization: hydrophone pressure mapping, luminol sonochemiluminescence, online mass spectrometry, and TEMPO inhibition show that moderate acoustic energy produces the radical concentration window required for complete conversion and selective dehydroconiferyl alcohol formation while suppressing over-coupling to trimers [3]. Extending the platform to acetovanillone, a frequency-controlled chitosan–lignin catalyst (Syn-340) exploits primary amine-rich, mesoporous surfaces to drive metal-free C–C coupling to diapocynin with exceptional selectivity under ambient sonophotocatalytic conditions. Finally, atmosphere-engineered carbon nitride nanotubes with a heptazine–triazine homojunction establish a complementary metal-free route in water, where carbon-vacancy shallow traps, enhanced O₂ adsorption, and spatial charge separation enable simultaneous photosynthetic H₂O₂ production and selective benzyl alcohol oxidation. Together, these results define sonophotocatalysis not merely as process intensification, but as a programmable reaction environment. By matching catalyst electronic structure with acoustic energy distribution and light wavelength, biomass-derived aromatics can be directed toward acids, aldehydes, pharmacologically relevant dimers, and solar H₂O₂ under mild conditions. This integrated framework advances a circular biorefinery paradigm in which sound, light, and defect-engineered materials replace harsh oxidants, precious metals, and multistep synthesis.

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Acknowledgements: This work is supported by National Science Centre (NCN) of Poland under the research projects OPUS 20 No. 2020/39/B/ST5/00076 (<https://www.photo-catalysis.org/projects/nanoengineering-of-multicomponent-metal-free-carbonaceous-materials-for-bio-oil>) and OPUS 26 No. 2023/51/B/ST5/00752 (<https://www.photo-catalysis.org/projects/novel-method-for-the-transformation-of-natural-polymers-into-valuable-porous>).

Beyond the Spectra: Interpreting Reactive Species by Indirect Electron Paramagnetic Resonance Spectroscopy

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Keywords: Indirect EPR techniques, (Photo)catalysis, Hydroxyl radical, Sulfate Radical

Advanced oxidation processes (AOPs) have emerged as one of the most promising strategies for addressing pressing environmental challenges associated with the accumulation of persistent organic pollutants and contaminants of emerging concern (CECs) in water and air. Conventional wastewater treatment technologies are often insufficient for the complete removal of such compounds, leading to their continuous release into natural ecosystems and posing risks to human health and biodiversity. In this context, AOPs represent an advanced class of treatment technologies capable of mineralizing organic pollutants into harmless end products through the generation of highly reactive transient species.

Building on the fundamental role of AOPs and reactive oxygen species (ROS) generation, our recent studies provide detailed mechanistic insight into these processes through the application of electron paramagnetic resonance (EPR) spectroscopy. Given the transient nature of reactive intermediates, EPR-based approaches such as spin trapping, spin scavenging, oxidation of sterically hindered amines, and photoreduction – an indirect EPR techniques – were systematically employed to detect and identify the radical species formed under photocatalytic and AOP conditions.

Although these techniques offer powerful tools for the detection and identification of transient species, careful interpretation of the results is essential. In the case of spin trapping, utilizing the nitron-based spin traps (e.g., DMPO, BMPO), the generation of hydroxyl radicals ($\text{HO}^\bullet$), sulfate radicals ($\text{SO}_4^{\bullet-}$) and, depending on the system, superoxide radical anions ($\text{O}_2^{\bullet-}$) can be monitored *via* their corresponding spin-adducts. However, alternative pathways must be considered, such as the well-known transformation of superoxide-derived adducts or sulfate-based spin-adducts into hydroxyl-type signals, which may lead to misinterpretation if not properly addressed.

In parallel, the oxidation of sterically hindered amines, particularly the conversion of diamagnetic Temp to the stable free radical Tempone, was employed as a complementary approach. This method, often associated with singlet oxygen detection, is not selective. The observed formation of Tempone should therefore not be interpreted as unambiguous evidence of singlet oxygen, but rather as a general indicator of oxidative conditions, since sterically hindered amines can be oxidized by multiple reactive species, including both radical and non-radical oxidants. This distinction is crucial to avoid overinterpretation of experimental data and to correctly identify the dominant reactive pathways.

Our EPR investigations further demonstrated that the nature and relative contribution of reactive species strongly depend on the (photo)catalyst composition, surface properties, and

reaction conditions. Overall, these results highlight the critical role of indirect EPR techniques in elucidating complex AOP mechanisms. By integrating spin trapping with carefully selected spin trapping agents, it is possible to obtain a nuanced and reliable picture of reactive species generation, which is essential for the rational optimization of advanced (photo)catalytic systems for environmental remediation [1-8].

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Acknowledgement

This study was financially supported by the Slovak Research and Development Agency under the contract No. DS-FR-24-0027 and Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0422/24).

Artificial intelligence tools were used in the preparation of this abstract (for language editing and stylistic refinement).

Titanate nanotubes for the selective cleavage of lignin inspired β -O-4 linkages towards value-added aromatics under low-power light irradiation

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Keywords: photocatalysis; biomass valorization; titanate nanotubes; lignin-inspired β -O-4 linkages; mechanistic insights

Rising global demand for chemicals, materials, fuels, and energy necessitates the development of innovative and sustainable technologies [1]. In this context, significant research efforts have been directed toward the catalytic valorization of renewable feedstocks, particularly biomass waste, to produce value-added chemicals. Additionally, harnessing solar energy to drive selective chemical transformations is widely regarded as a promising green approach [2]. Therefore, the design of novel nanomaterials with enhanced photocatalytic performance, especially under visible light, is critical for efficient biomass valorization.

Titanium dioxide-based materials have been extensively investigated as photocatalysts; however, they are typically associated with non-selective conversion and complete mineralization of organic compounds [3]. Achieving controlled and selective photocatalytic activity requires precise tuning of their physicochemical properties [4].

In this study, novel one-dimensional titanium oxide nanomaterials (TiNPs-400) were synthesized from commercially available TiO₂-Anatase nanoparticles and evaluated for the selective oxidative cleavage of lignin-inspired β -O-4 linkages, using 2-phenoxy-1-phenylethanol (PP-ol) as a model compound, to produce value-added aromatic chemicals. The physicochemical properties of the studied materials were characterized by X-ray diffraction (XRD), nitrogen adsorption, and diffuse reflectance spectroscopy (DRS-UV-Vis), while transmission electron microscopy (TEM) was employed to examine their morphology.

The synthesized material consists of nanotubes with external diameters of 6-10 nm, inner channel diameters of 3-7 nm, and lengths ranging from 90 to 200 nm. These nanotubes exhibit a significantly enhanced specific surface area ($S_{\text{BET}} = 154 \text{ m}^2/\text{g}$) and total pore volume ($V_{\text{total}} = 0.80 \text{ cm}^3/\text{g}$) compared to the commercial TiO₂-Anatase precursor ($S_{\text{BET}} = 10 \text{ m}^2/\text{g}$, $V_{\text{total}} = 0.03 \text{ cm}^3/\text{g}$). The band gap of the nanotubes was estimated at 3.1 eV, coamparable to that of TiO₂-Anatase (3.2 eV).

Photocatalytic performance was evaluated under low-intensity UV-A irradiation (370 nm), as well as under visible light using monochromatic wavelengths (427, 440, and 525 nm),

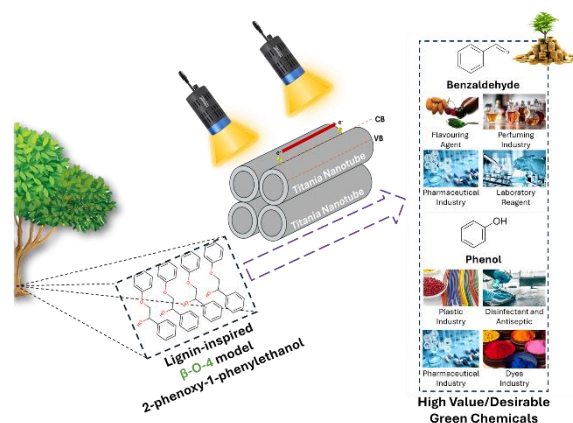


Fig. 1. Schematic illustration of the photocatalytic valorization of lignin-derived 2-phenoxy-1-phenylethanol (PP-ol) using titanium oxide nanotubes towards value-added chemicals, benzaldehyde (Ph-CHO), and phenol (Ph-ol).

both individually and in combination. It is worthy to point out that the no additives/oxidants were used while the photocatalytic reactions took place at ambient/lab conditions. The goal was to achieve the controlled and cleavage of the β -O-4 bonds of the lignin-inspired 2-phenoxy-1-phenylethanol (PP-ol) either via the C_{α} - C_{β} or the C_{β} -O as can be seen in the **Figure 2** [5].

Under UV irradiation for 3h, TiNPs-400 exhibited approximately 50% higher conversion of PP-ol compared to the TiO₂-Anatase precursor. The photocatalytic results highlight the cleavage of the C_{α} - C_{β} bond of the diaromatic compound and the production of benzaldehyde (Ph-CHO) and phenol (Ph-ol). The achieved yields for these two compounds were 29% and 24% accordingly, values similar % compared to Anatase, respectively.

To go a step forward, mechanistic studies were conducted under the influence of UV radiation. The scavenger tests showed that the cleavage reaction proceeds via a multi-mechanistic pathway, with photo-induced holes (h^+) acting as the primary active species, while superoxide radicals ($O_2^{\bullet-}$) play a key role in the selective and efficient production of the products. Additionally, the role of dissolved molecular oxygen was tested. The results showed that the presence of oxygen enhanced the yield of Ph-CHO for all photoactive materials, whereas the absence of oxygen was linked to higher yields of Ph-ol. The photocatalytic reactivity of potential intermediate products was also examined, revealing that most of them undergo further photocatalytic conversion to a significant extent.

Photocatalytic tests under visible light irradiation demonstrated that TiNPs-400 can be effectively photoexcited within the visible spectrum, except for 525 nm. Under combined visible-light irradiation, the synthesized nanotubes exhibited markedly enhanced activity, achieving a 2.4-fold increase in benzaldehyde (Ph-CHO) yield compared to commercial TiO₂-Anatase nanoparticles

Overall, these findings highlight the potential of engineering one-dimensional titanium oxide nanostructures for selective photocatalytic biomass valorization under visible light irradiation and demonstrate that TiNPs-400 is a promising candidate for sustainable and "green" industrial applications.

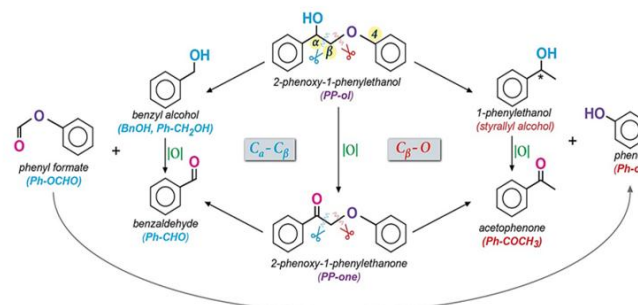
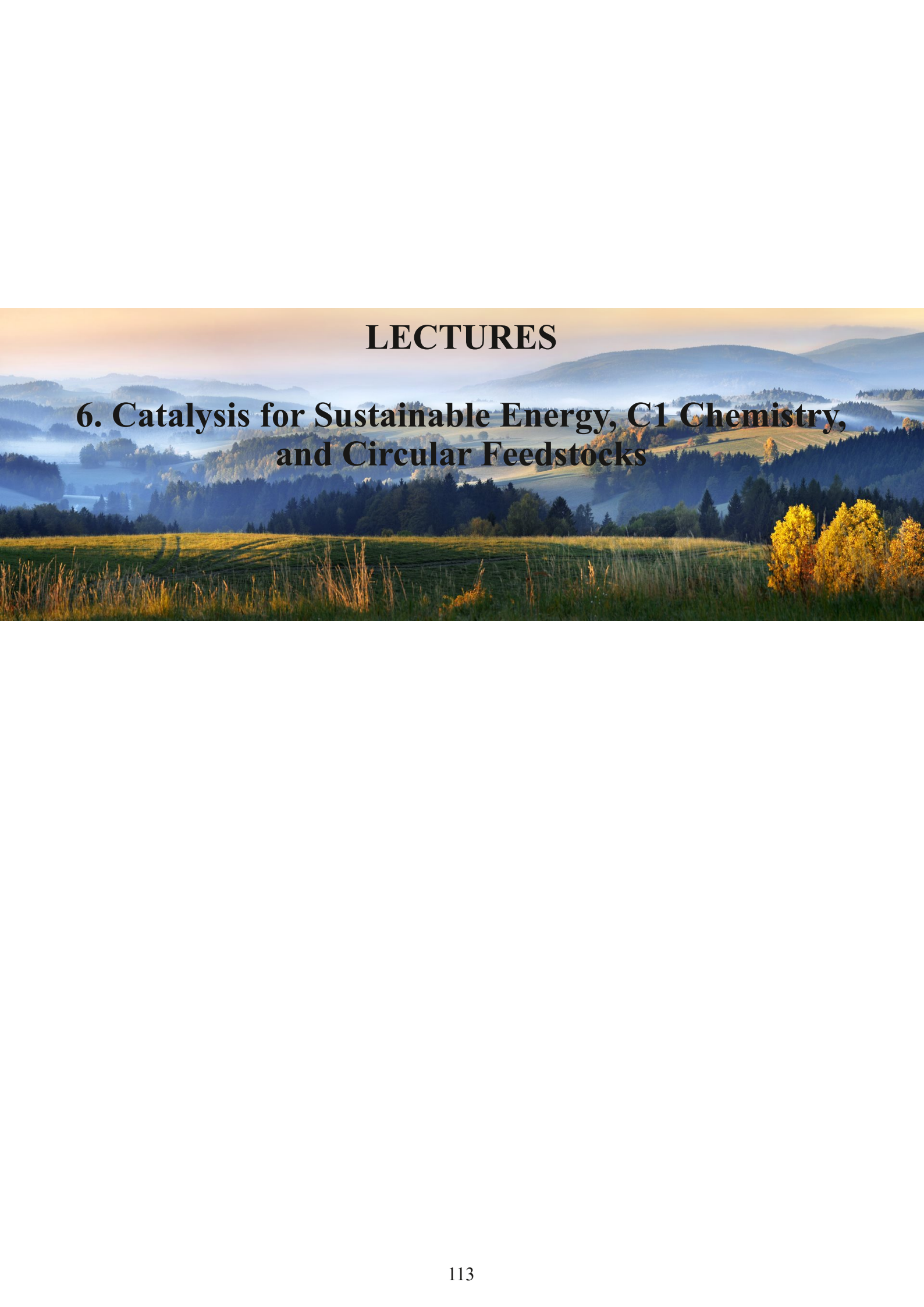


Fig. 2. All the possible reaction pathways for the oxidative cleavage of β -O-4 linkage of the lignin-inspired model compounds 2-phenoxy-1-phenylethanol (PP-ol) towards the selective formation of the desired monoaromatics (adapted from [5]).

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LECTURES

6. Catalysis for Sustainable Energy, C1 Chemistry, and Circular Feedstocks

Development of Cu-catalysts for valorization of lignin biomass towards high-value chemicals

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Keywords: lignin, deoxygenation, phenolics, carbon economy

Introduction. Biomass valorization is key to shifting from fossil to bio-based economy. Fossil fuels (coal, oil, gas) scarcity and CO₂ output — powering climate change, pollution, eco-system damage, threats to human well-being — highlight biomass' role in this transition. Lignocellulosic biomass from crops and wood — composed of cellulose, hemicellulose, and lignin — is abundant, renewable, non-edible, and can provide low-carbon fuels and chemicals without major infrastructure changes [1]. Lignin — an aromatic polymer rich in phenolic units (p-hydroxyphenyl, guaiacol, syringyl) linked by ether and C–C bonds — holds strong aviation potential, as its upgrading yields polyalkylated cycloalkanes and aromatics that match jet fuel's density, energy content, seal-swelling, and combustion requirements [2]. Lignin's complexity, low C/H ratio, and high oxygen content challenge processing compared to crude oil. Hydrodeoxygenation (HDO) with bifunctional metal/acid catalysts overcomes this by removing oxygen as CH₃OH, H₂O, CO, and CO₂. Yet typical systems — supported Pt, Pd, Ru, or Ni on oxides/zeolites — often drive rapid aromatic ring hydrogenation and demethoxylation (–OCH₃ loss) towards cycloalkanes, resulting in carbon loss as CH₄/CH₃OH byproducts, which lowers HDO atom economy [3]. In turn, Cu/Al₂O₃ catalysts show potential for improved atom economy by preserving terminal methyl groups on aromatic rings via demethylation, methylation pathways in anisole/guaiacol HDO (lignin models) [4]. Yet the effects of support properties (acidic, textural), Cu sites' role in demethylation/methylation, and high-conversion performance are unclear. Here, we examine Cu catalysts on Al₂O₃ and other oxide/zeolite supports — plus supports' intrinsic activity — to assess and optimize methyl retention from aromatic methoxy groups during lignin upgrading (using anisole as model) to fuels and chemicals (Fig. 1).

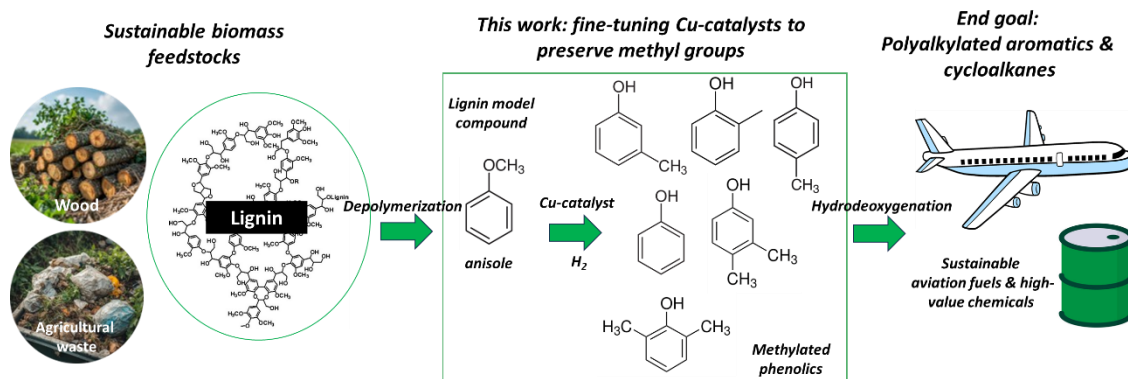


Fig. 1: Scheme of proposed lignin processing towards aviation fuels & chemicals

Methodology. Cu catalysts were prepared by wet impregnation on commercially available, industrial supports (Al₂O₃, TiO₂, SiO₂, and Beta, USY zeolites) from Euro Support, Sasol,

Saint-Gobain, and Zeolyst, followed by drying at 120 °C, calcination at 350 °C, and reduction at 200 °C. Catalytic tests of both bare supports and Cu catalysts (diluted with SiC) were conducted in a Vinci Tech flow reactor, with products analyzed by GC-FID and GC-MS.

Results&Discussion. Prior to Cu catalytic tests, SiC inert (blank test) and bare supports – SiO₂, TiO₂ anatase, γ -Al₂O₃, H⁺/Beta (Si/Al=20), H⁺/USY (Si/Al=30) – were in-situ activated at 250 °C under H₂ and studied using anisole feed (WHSV=12 h⁻¹, 5 bar H₂, 240–300 °C) to mimic Cu study conditions. SiO₂ and inert SiC were inactive. Zeolites gave the highest conversion (X) above all supports at 300 °C (USY: X=17 %, Beta: X=20 %), but mainly catalyzed anisole disproportionation (~80 % selectivity), yielding phenol (S=41–46 %) and methylanisole (S=36–39 %) in ~1:1 ratio. In contrast, at similar conditions, Al₂O₃ (X=16 % at 300 °C) was more selective towards phenol and methylated phenolics: phenol (S=60 %), methylphenols (S=25 %), dimethylphenols (S=13 %). TiO₂ gave only 1 % anisole X at 300 °C, forming minor amounts of phenol, methylphenols. These results suggest that combined Brønsted/Lewis acidity in zeolites promotes disproportionation and higher yields of undesired methylanisole (preserved O-CH₃), whereas purely Lewis-acidic oxides favor methylated phenols. Cu/Al₂O₃ (10 wt. % Cu) at WHSV=12 h⁻¹ and 300 °C achieved 100 % anisole conversion (**Fig. 2**), while preserving high selectivity to phenol (39 %), methylphenols (29 %), and dimethyl phenolics (18 %). Thus, careful choice of Cu catalysts supports is crucial to direct selectivity to methylated phenolics, which can then be deoxygenated to aviation fuel-range polyalkylated aromatics. Further study of catalyst acidity (py-FTIR) and Cu speciation (XPS) will help fine-tune these Cu systems.

Conclusions. This work highlights that different Cu-supports create distinct acidic sites, leading to different pathways during anisole conversion – altering product distribution. Such insights enable stepwise strategies to improve lignin HDO carbon atom economy using green Cu catalysts.

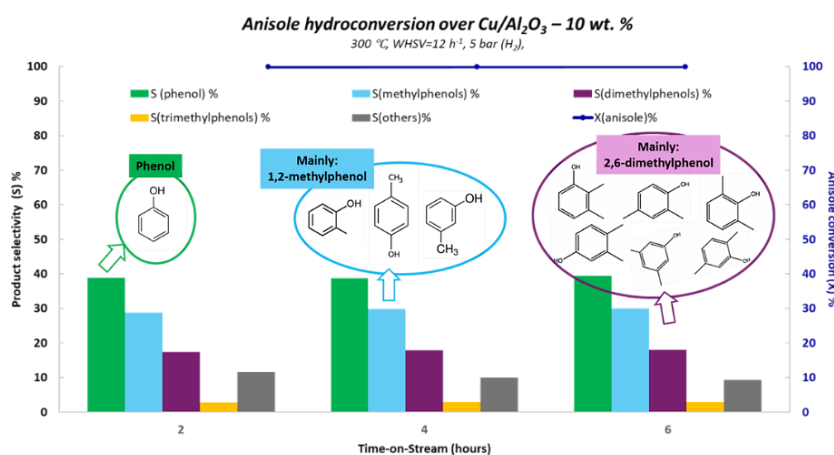


Fig. 2: Catalytic performance of Cu/Al₂O₃ – 10 wt. % Cu

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Acknowledgement. The authors acknowledge TAČR (TS02030246) grant for financial support.

Catalyst-Dependent Pathways in D-Glucose Isomerization

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Keywords: D-glucose, D-fructose, isomerization, biomass, base

Introduction

The transition from fossil feedstocks to renewable resources is accompanied by a growing importance of heterogeneous catalysis in the liquid phase. However, the design of heterogeneously catalyzed liquid-phase processes is hindered by the comparatively limited understanding of phenomena at liquid-solid interfaces, especially relative to the well-established knowledge of solid-gas reactions widely used in petrochemical applications. Literature data,¹ together with our previously published results,² strongly suggest that OH⁻ species generated in aqueous media act as catalytically active entities for molecular catalysts, including buffers^{2,3} and amines,⁴ as well as for sparingly soluble bases (e.g., hydroxides, carbonates, phosphates, and hydrotalcites).^{5,6,7} In many cases, the rate of isomerization correlates with the OH⁻ concentration.^{2, 4-7} At the same time, the presence of additional species influences reaction outcomes, affecting both selectivity and reaction rate.^{1,3,7}

Methodology

In this work, we investigated two case studies.

(i) D-Glucose isomerization in phosphate versus glycine buffers at pH 11

(ii) D-Glucose isomerization in the presence of unsupported MgO compared to MgO supported on various materials

To elucidate how catalyst nature (phosphate vs. glycine buffers; supported vs. unsupported MgO) affects catalytic performance, we employ a combination of experimental and computational approaches. Kinetic modeling (Fig. 1)⁸ is used to determine rate constants and activation energies for both isomerization and degradation pathways. Isotopically labeled substrates enable kinetic isotope effect studies and clarification of degradation mechanisms. NMR spectroscopy provides insight into interactions among soluble species, while GC-MS, HPLC, NMR, and GPC are used to identify and quantify side products. Experimental data further support computational mechanistic studies. In addition, solid catalysts are thoroughly characterized before and after reaction. Catalytic tests are conducted under both batch and continuous-flow conditions.

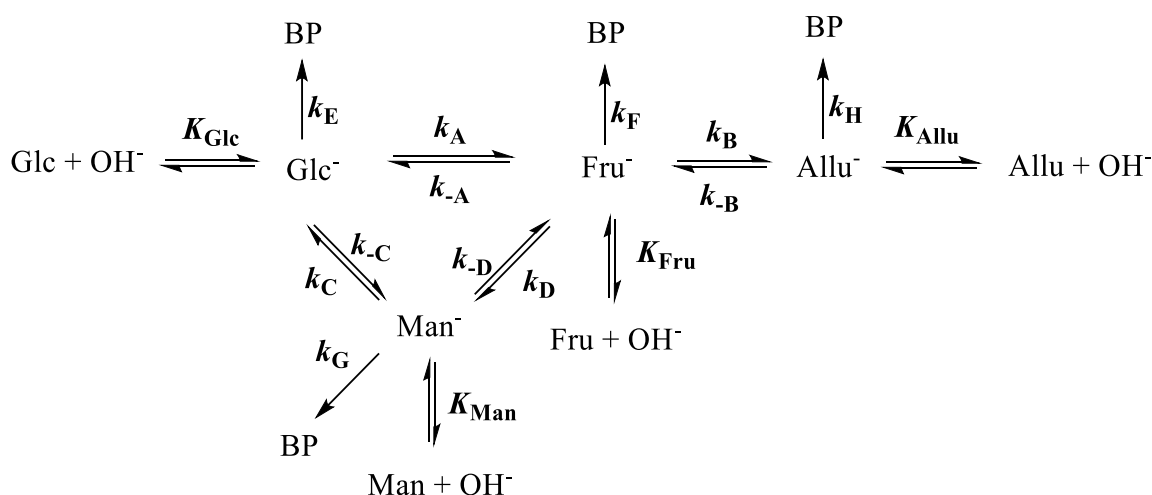


Fig. 1: Kinetic model used in this work. Glc refers to D-glucose, Fru is D-fructose, Man is D-mannose, Allu is D-allulose. BP refers to by-products.

Results and discussion

The main results obtained during the study can be summarized as follows:

(i) D-Glucose isomerization in phosphate versus glycine buffers at pH 11: despite similar pH values, the isomerization rate is approximately twofold higher in phosphate buffer than in glycine. Moreover, the D-fructose yield in phosphate buffer is about twice that obtained with glycine.

(ii) D-Glucose isomerization in the presence of unsupported MgO compared to MgO supported on various materials: under identical conditions, the D-fructose yield increases from 24% with unsupported MgO to 34% over MgO/biochar, highlighting the critical role of the catalyst support.

Currently, the work on getting molecular-level insight into catalytic isomerization processes the observed results is in progress.

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Acknowledgement (optional)

Financial support of the FWF (grant DOI 10.55776/PIN9945024.) is greatly acknowledged.

From CO₂ to Gasoline: Bridging Catalyst Design and Process Scale-Up toward C₅+ Hydrocarbon Production

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Keywords: CCU, CO₂, design of catalysis, scale up, industrialization

The catalytic conversion of CO₂ into value-added hydrocarbons represents a key pathway toward sustainable carbon utilization and synthetic fuel production. In this contribution, we present an integrated approach to transforming CO₂ into C₅+ hydrocarbons, bridging fundamental catalyst design with process-scale implementation. Starting from atomistic insights, we discuss the rational development of Na-promoted Fe-based catalysts, focusing on phase evolution, active site formation, and selectivity control toward long-chain hydrocarbons.

Beyond laboratory-scale investigations, we demonstrate the successful upscaling of the catalytic system to TRL 5 conditions, where CO₂ hydrogenation was carried out under industrially relevant parameters. At this scale, we achieved the continuous production of syncrude, which was subsequently processed into gasoline-range products, highlighting the practical feasibility of the approach.

The presentation addresses the full chain of challenges, from atomic-level phenomena—such as catalyst phase dynamics and surface reactions—to engineering aspects including catalyst shaping, stability, reactor operation, and process integration. By linking catalyst structure, synthesis, and performance across scales, we provide insights into how laboratory discoveries can be translated into industrially meaningful solutions.

This work demonstrates that CO₂ can be efficiently converted into liquid hydrocarbon fuels and emphasizes the importance of coupling catalyst design with scalable engineering strategies for real-world applications.

Zeolites as efficient catalysts for the preparation of diesel fuel additives

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Keywords: unsymmetric ethers, zeolites, ion-exchange resins, biofuels, heterogeneous catalysis

Ethyl tetrahydrofurfuryl ether (ETFE) is emerging as a promising candidate for use as a renewable diesel fuel additive. With a high cetane number in the range of 80-90, ETFE significantly enhances ignition quality. Engine tests of fuel blends containing ETFE and conventional diesel have demonstrated improved combustion behavior accompanied by reduced emissions of nitrogen oxides, sulfur oxides, and particulate matter [1]. These properties position ETFE as an attractive component in the ongoing transition toward cleaner and more sustainable fuel formulations.

A particularly appealing aspect of ETFE lies in its potential for fully biomass-based production. It can be synthesized via the etherification of tetrahydrofurfuryl alcohol (THFA) and ethanol (EtOH), both of which can be derived from lignocellulosic biomass. THFA is accessible through hydrogenation of furfural, itself obtained from hemicellulose, while ethanol is widely produced via fermentation of biomass-derived sugars. This creates a conceptual pathway where agricultural residues are gradually refined into high-performance fuel additives, linking waste valorization with energy applications.

In this study, we explore the catalytic synthesis of ETFE via the formation of unsymmetrical ethers from mixtures of alcohols over heterogeneous acid catalysts. This approach builds on our previous work, where similar catalytic systems proved effective for the selective synthesis of ethers from structurally diverse alcohol substrates [2,3]. The challenge resembles a selective pairing at the molecular level: among several possible etherification pathways, the system must favor the formation of the cross-ether (ETFE) over symmetrical by-products.

The reaction was investigated in a batch reactor configuration. A mixture of ethanol and THFA in a mass ratio of 5:1 was reacted at 140 °C for 5 hours in the presence of 0.3 g of a heterogeneous catalyst.

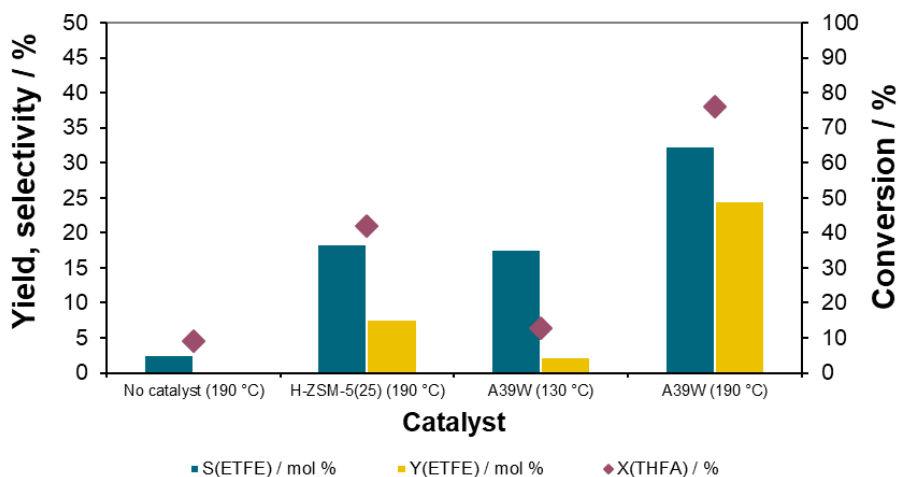
A range of commercially available heterogeneous acid catalysts was evaluated, including zeolites with varying framework topologies and acidity, as well as ion-exchange resins of the Amberlyst type. The catalysts differ not only in acid strength but also in pore architecture, which plays a crucial role in shaping selectivity by influencing molecular diffusion and confinement effects.

Among the tested materials, the zeolite H-ZSM-5 exhibited the best overall performance in both reactor configurations. In the continuous-flow system, a maximum ETFE selectivity of 18.3% was achieved at a THFA conversion of 41.9 %. The superior performance of H-ZSM-5 can be attributed to its balanced acidity and medium-pore structure, which appears to promote the formation of the desired unsymmetrical ether while suppressing side reactions such as

dehydration or oligomerization.

In contrast, ion-exchange resins showed lower selectivity toward ETFE, reduced stability under reaction conditions, and more challenging regeneration. These limitations may be associated with their lower thermal resistance, and differences in acid site strength and accessibility compared to crystalline zeolites (Fig. 1).

Fig. 1: Comparison of ETFE preparation in a batch system without a catalyst, in the presence of a zeolite, and in the presence of an ion-exchange resin at two different temperatures



The results highlight the potential of zeolite-based catalysts, particularly H-ZSM-5, for the efficient synthesis of ETFE from biomass-derived feedstocks. At the same time, the moderate selectivity indicates that further optimization is needed. Future work will focus on tailoring the acidity and pore structure of zeolitic catalysts, as well as exploring reaction engineering strategies to steer selectivity toward the desired product.

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Acknowledgement: The authors acknowledge the financial support to this research from the Grant Agency of Slovakia (project No. VV-MVP-24-0331).

Tuning performance of Ni catalyst in co-pyrolysis of biomass and plastic by selecting appropriate support

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Keywords: hydrogen-rich gas, aluminosilicates, nickel, lignocellulose, polymer

Co-pyrolysis of biomass and plastic is one of the promising routes for producing renewable fuels, including hydrogen. It turns out that thermal degradation of both types of feedstock results in the increase in the efficiency of the formation of gaseous products due to synergy effect related to enhancing decomposition of lignocellulose and limiting repolymerization of formed reaction intermediates [1]. Despite that, the effectiveness of this process is still questionable. Its competitiveness can be increased through the use of suitable catalyst that combines high activity, selectivity to the desired products, stability under reaction conditions, and reasonable cost. Based on previous research [2], we decided to study nickel-based systems and tune their catalytic performance by selecting appropriate support, focusing primarily on various types of aluminosilicates.

Synthesized Ni catalysts were subjected to catalytic tests in a quartz flow reactor using cellulose (as a model sample), spruce biomass, and low-density polyethylene. The gaseous products (hydrogen, methane, carbon monoxide, and carbon dioxide) were analyzed using a gas chromatograph equipped with a TCD detector. The physicochemical properties of the prepared catalysts were primarily determined using X-ray diffraction (XRD), temperature-programmed reduction (TPR), temperature-programmed desorption of ammonia and carbon dioxide (TPD-NH₃ and TPD-CO₂), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric (TG) methods.

Executed experiments confirmed that the presence of nickel catalyst increases the efficiency of high-temperature conversion of lignocellulosic feedstock. The highest hydrogen yield was obtained with the use of Ni supported on montmorillonite. This catalyst allowed for the formation of 30% more hydrogen than the reference Ni/ZSM-5 sample. Analysis of the surface properties of the studied materials indicated that high acidity does not necessarily correlate with improved catalytic activity. It is suggested that excessive acidity may promote the formation of more complex molecules and deposition of carbonaceous species (for example, the acidity of nickel catalyst introduced onto ZSM-5 was four times higher than of Ni supported on montmorillonite). On the other hand, the decomposition of the reaction substrates is facilitated by the greater availability of Ni on the catalyst surface. Activity tests also confirmed the beneficial effect of the addition of polymer to spruce biomass on the amount of gaseous products formed.

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Circular Upcycling of Spent Batteries into High-Performance Catalysts

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Keywords: Upcycling, Spent batteries, CO₂ hydrogenation, *Operando* DRIFTS, Circular Economy

Introduction

Power-to-Methane (PtM) technology¹ offers a promising route for renewable energy storage and CO₂ utilization through catalytic methanation. However, conventional Ni-based catalysts rely on virgin raw materials and energy-intensive synthesis routes². Simultaneously, hazardous waste streams such as spent Ni–MH batteries and aluminium foil continue to accumulate³. This work presents a circular-economy strategy in which waste-derived nickel and aluminium are transformed into high-performance Ni/η-Al₂O₃ nanocatalysts for CO₂ methanation⁴.

Methodology

Nickel sulfate was recovered from spent Ni–MH batteries by mild acid leaching and converted into Ni(OH)₂ hydrogel using L-glutamic acid and NaOH. Waste aluminium foil was processed into Al₂O₃ and combined with Ni precursors to synthesize 4 wt% and 8 wt% Ni/η-Al₂O₃ catalysts (Figure 1). The catalysts were characterized using XRD, HRTEM, STEM-EELS, BET, and H₂-TPR analyses. CO₂ methanation was evaluated in a fixed-bed reactor at 250–550 °C, while *operando* DRIFTS coupled with GC + MS was used to study the reaction mechanism.

Results and Discussion

Structural characterization confirmed the formation of disordered cubic η-Al₂O₃ with uniformly dispersed Ni nanoparticles. TEM analysis revealed Ni particle sizes in the range of 18–39 nm with no significant agglomeration. BET analysis showed a substantial increase in specific surface area after Ni incorporation, reaching 226.82 m² g^{−1} for the 8-Ni/η-Al₂O₃ catalyst.

Among the synthesized catalysts, 8-Ni/η-Al₂O₃ exhibited the best catalytic performance for CO₂ methanation. At 400 °C, the catalyst achieved 99.8% CH₄ selectivity and a space–time yield (STY) of 80.3 mmol_{CH₄} g_{cat}^{−1} h^{−1}. The catalyst also demonstrated excellent thermal stability under prolonged reaction conditions and repeated temperature cycling without observable deactivation.

The enhanced catalytic performance is attributed to the synergistic interaction between Ni nanoparticles and the disordered η-Al₂O₃ support. The η-Al₂O₃ phase promotes CO₂ adsorption and stabilization of reaction intermediates, while highly dispersed metallic Ni provides active hydrogenation sites. H₂-TPR analysis indicated relatively low reduction temperatures (<500 °C), facilitating catalyst activation.

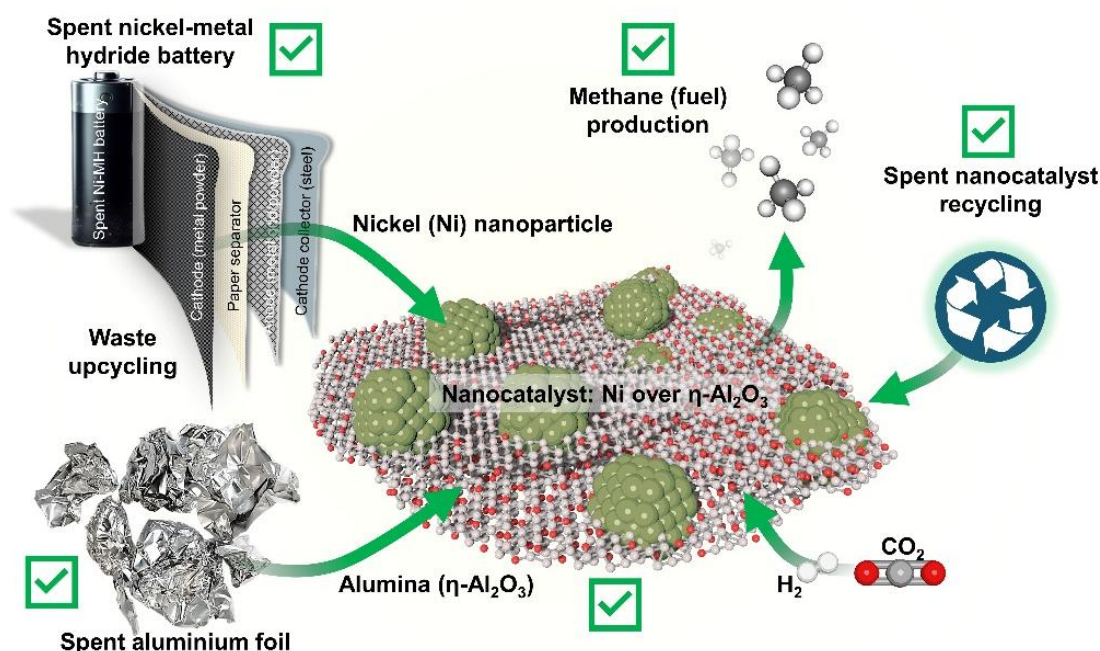
Operando DRIFTS studies revealed that CO₂ methanation proceeds predominantly through an associative pathway involving sequential formation of hydrogen carbonate, formate, and methoxy intermediates before methane generation. Surface bicarbonate species formed on η-Al₂O₃ were progressively hydrogenated on adjacent Ni sites, ultimately producing CH₄. At temperatures above 450 °C, the reverse water-gas shift (RWGS) reaction became thermodynamically favourable, increasing CO formation.

To complete the circular process, spent catalysts were recycled through acid/base leaching and selective precipitation to recover Ni and Al precursors, demonstrating the feasibility of catalyst regeneration and resource recovery.

Conclusions

This study demonstrates a sustainable approach for converting hazardous e-waste into efficient CO₂ methanation catalysts. Waste-derived Ni/ η -Al₂O₃ catalysts exhibited high methane selectivity, strong stability, and effective CO₂ conversion. The work highlights the integration of e-waste upcycling, catalyst recycling, and CO₂ utilization within a circular-economy framework.

Fig. 1: Transforming battery/aluminium waste into nanocatalysts for methane (fuel) production and recycling spent nanocatalysts into catalyst precursors⁵.



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Zinc-Modified Zeolites with Different Topologies for Methane and CO₂ Transformation

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Keywords: zinc, zeolites, FTIR spectroscopy, methane, carbon dioxide

1. Introduction

Increasing industrial activity contributes to climate change, while methane and CO₂ are among the major greenhouse gases. Their valorization into products such as methanol, acetic acid, or olefins is an important research direction; however, the high thermodynamic stability of both molecules remains a significant catalytic challenge. In this context, the literature highlights the key role of zinc centers in methane activation, leading to the formation of reactive Zn²⁺-CH₃ species that can undergo CO₂ insertion.^{1,2} This process enables C-C bond formation and represents a promising strategy for concurrently activating and coupling methane and carbon dioxide.

2. Methodology

In this study, BEA (Si/Al = 9.5), ZSM-5 (15), and FER (9) zeolites were modified via ion exchange with Zn(NO₃)₂ to achieve a Zn/Al ratio of about 0.24. The resulting materials were characterized by UV-Vis DRS and FTIR spectroscopy, using CO and pyridine as probes to determine zinc speciation and location. Catalytic performance was evaluated in the stepwise conversion of CH₄ with CO₂.

3. Results and discussion

Spectroscopic analysis revealed that ZnH-FER and ZnH-ZSM-5 are dominated by isolated Zn²⁺ species with small contributions from [ZnOH]⁺ and binuclear [Zn-O-Zn]²⁺ sites, whereas ZnH-BEA contains mainly aggregated ZnO species (Fig. 1A). Methane activation (RT-200°C) over ZnH-FER leads to the formation of methoxy species (bands at 1445-1421 cm⁻¹, Fig. 1B), accompanied by water evolution and an increase in the number of Brønsted acid sites. This confirms C-H bond cleavage in the CH₄ molecule via hydrogen transfer to the framework. These intermediates are characteristic of Zn²⁺ cations placed in 8-membered rings capable of methane activation. Upon introduction of CO₂, a rapid consumption of methoxy species and CO₂ is observed together with the formation of acetic acid (m/z = 60), indicating effective coupling of CH₃- and CO₂-derived species. In contrast, ZnH-ZSM-5 and ZnH-BEA (dominated by zinc oxo-species) show negligible CO₂ conversion and no formation of additional hydroxyl groups. In these systems, methane-derived intermediates undergo mainly C-C coupling and dehydrogenation, leading to olefin formation (Fig. 1C and D).

Time-resolved FTIR-MS experiments at 250°C combined with 2D correlation spectroscopy (2D COS) provided detailed insight into the reaction pathways. For ZnH-FER, negative correlations between bands at 1636, 1505, and 1475 cm⁻¹ with the 1420-1365 cm⁻¹ region indicate transformation of

methane-derived or methoxy species into more oxygenated intermediates, such as carboxylate-type species. Simultaneously, positive correlations between 1636 cm^{-1} and $1505/1475\text{ cm}^{-1}$ suggest concurrent formation of oxygenated species interacting with Zn sites and/or water. In ZnH-ZSM-5, only positive correlations are observed, indicating stable accumulation of acetate species without further transformation. In ZnH-BEA, only a single negative correlation between methane consumption and water formation is observed, confirming that only the initial activation of CH_4 occurs.

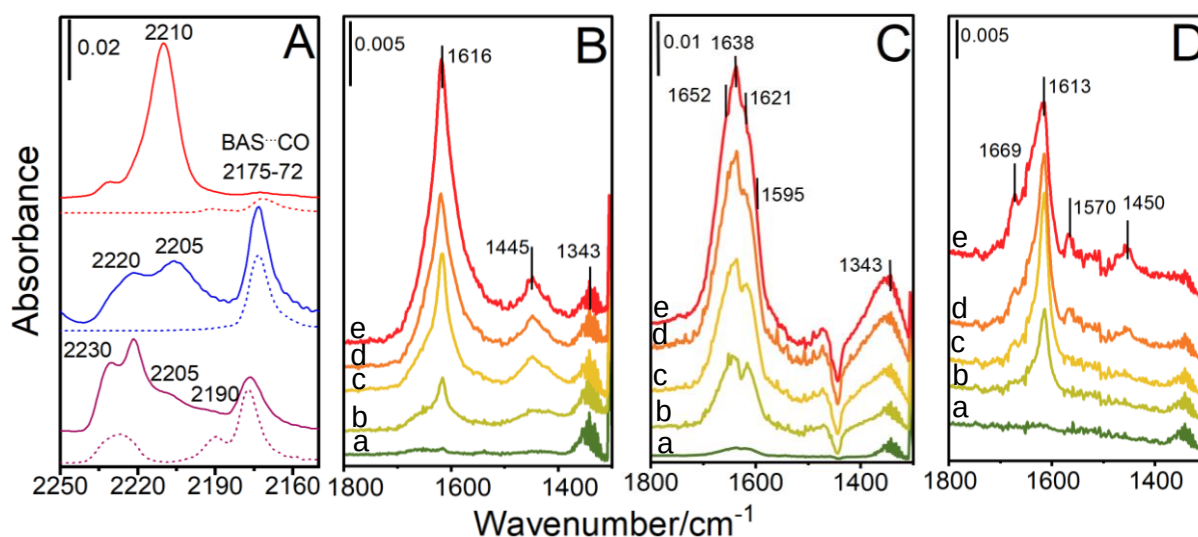


Fig. 1: A-FTIR spectra of CO interacting with Zn-materials: ZnH-FER (red line), ZnH-ZSM-5 (blue line), ZnH-BEA (purple line), parent zeolites (dashed line), B,C,D-FTIR spectra recorded for ZnH-FER, ZnH-ZSM-5 and ZnH-BEA during methane activation from RT to $200\text{ }^{\circ}\text{C}$, a-shows difference spectra collected at RT after CH_4 adsorption and after heating to $50\text{--}200\text{ }^{\circ}\text{C}$, followed by cooling to RT (b-e).

4. Conclusions

The activation and co-conversion of methane and carbon dioxide was experimentally verified over Zn-exchange zeolites. The zeolite topology and zinc speciation strongly influence catalytic performance, even at identical Zn loading. In particular, zinc species located in 8-MR pores facilitate the initial C-H bond activation in methane.

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Acknowledgement: The research was funded by the National Science Centre, Poland [2022/47/I/ST4/00607] and the Czech Science Foundation [project no. 24-14387L].

NiMo/MgO Catalysts for Methane Pyrolysis: Sol-Gel Preparation Method versus Impregnation to Enhance Stability

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Keywords: nickel, molybdenum, methane pyrolysis, hydrogen

Introduction

Methane decomposition, or in other words, methane pyrolysis ($\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$), represents a temporary solution for producing clean hydrogen until the water electrolysis becomes economically viable for green hydrogen production. The pyrolysis reaction produces clean (turquoise) hydrogen and valuable nanostructured carbon when using appropriate catalysts [1]. Nickel is often the primary choice as the active metal component, but it is prone to deactivation unless modified with a second metal. Indeed, a strong synergistic effect was reported for Mo-modified nickel catalysts. We investigated the primacy of a Ni/Mo~1/1 composition compared to Mo-lean catalysts when the adsorption-deposition synthesis method was applied on a magnesia support. The less pronounced partial segregation of bimetallic particles during reaction was found as an explanation for the better stability in the case of the equimolar metal composition [2]. In the present work, the same metal loadings and atomic Ni/Mo=1 ratio were set using two synthesis methods to study differences in the formation of alloyed phases and their performance in hydrogen and carbon production during methane decomposition.

Methodology

Two samples with a metal loading of 1.2 mmol/g_{cat} and Ni/Mo atomic ratios of 1 and 0.5 were prepared by wet impregnation on commercial MgO using aqueous solutions of nickel nitrate and ammonium molybdate precursors (denoted as WI and WI_0.5, respectively). A third sample (SG) with the same metal loading and a Ni/Mo ratio of 1 was produced by the sol-gel method: the aqueous precursor solutions were added to a 1:1 methanol-toluene solution of Mg-methoxide, followed by an aging step. The dried samples were calcined in air at 550 °C and subsequently reduced by H₂ at 800 °C. Methane pyrolysis tests after different pretreatments (with reduction, without reduction, and pre-carburization) were conducted under isothermal conditions at selected temperatures in a 50% CH₄/Ar feed, and the gaseous products were analyzed by quadrupole mass spectrometry (QMS) and gas chromatography (GC). The carbon formed was estimated from CH₄ conversion and also measured by thermogravimetry (TG). Structural characterization of the fresh and spent catalysts was performed using temperature-programmed reduction (TPR), X-ray diffraction (XRD) using synchrotron radiation with Rietveld refinement, transmission electron microscopy (TEM coupled with STEM-EDS), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy.

Results and Discussion

TPR measurement up to 800 °C showed complete reduction of the SG sample, but only 65-70% reducibility for the catalysts prepared by wet impregnation. XRD measurements of the reduced samples detected the same fcc NiMo alloys (~28 % Mo), with the highest fraction in the SG sample. The Rietveld refinement suggested the existence of some bcc NiMo crystallites with about 15-30 % Ni content for the equimolar samples, while almost pure Mo for the WI_0.5 catalyst. Moreover, part of the molybdenum was found to be in the amorphous phase in all the reduced samples. TEM analysis resulted in somewhat larger average particle sizes than XRD. The surface Ni/Mo concentration by XPS was close to unity for the SG sample, whereas it was around 0.5 or lower for the WI catalysts in both calcined and reduced states. This suggests that a surface NiMoO₄ layer was obtained on the simultaneously formed MgO surface in the SG catalyst, while the Mo excess and the lower Ni concentrations of the impregnated samples may indicate that Ni and Mo are located at different places on the support: the Ni-containing entities may be in the pores, while part of the molybdenum must be finely dispersed. Pyrolysis tests revealed different catalytic activities for the SG and WI samples. Increasing the reaction temperature increased the initial activity but accelerated deactivation in all cases. The SG sample exhibited higher CH₄ conversion and significantly lower deactivation rates over 3 h, and produced much higher carbon yields than the WI samples. Contact of methane with the calcined catalysts resulted in higher initial conversion but faster deactivation and thinner carbon nanotubes, with different trends in carbon production depending on the catalyst. The highest carbon yield was achieved on the SG sample when reduced and pre-carburized at low temperature. The carbon products were multiwalled carbon nanotubes in all cases, with similar structural quality as reflected by the Raman D/G intensity ratios. XRD analysis of the spent catalysts showed that the specific fcc NiMo alloy became leaner in Mo during reaction, indicating Mo escape with the parallel formation of nanosized Mo-carbide crystallites for all the samples. Based on the Rietveld fitting of the spent samples, the existence of a little metallic Mo was seen in the impregnated samples, whereas a bcc NiMo alloy phase with about 60 % Ni content was identified in the SG sample. This difference must have been further strengthened by the stronger interaction and a larger interface with the support particles, having the smallest MgO crystallite size for the spent SG catalyst.

Conclusions

The SG sample significantly outperformed the catalysts prepared by wet impregnation in both stability and activity under all conditions. This can be explained by its higher reducibility and the highest concentration of the active NiMo alloy phases with an appropriate particle size. The results indicate that bimetallic alloy particles in strong interaction with the MgO particles, rather than in situ-formed carbides (in the absence of reduction pretreatment), contribute to the enhanced stability.

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Acknowledgement

The financial support of the NRDI Fund (OTKA K143216 and K146032) is acknowledged.

Methane decomposition on nickel-iron catalysts

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Keywords: catalytic methane decomposition, Ni-Fe/Al₂O₃

Hydrogen production is one of the most important issues of our time. This raw material is primarily used in chemical production (e.g., ammonia synthesis, methanol production, and petrochemical processes) and is considered a pure fuel/energy carrier for the waste-free economy. Nowadays, hydrogen is primarily produced from natural gas via steam methane reforming (SMR). This technology emits large amounts of carbon dioxide but remains one of the most profitable. Catalytic methane decomposition (CMD) is much less energy-intensive, and during CH₄ splitting, only nanostructured carbon materials are produced. Moreover, using biogas as a feedstock allows for net-negative CO₂ emissions. However, the main disadvantage of the CMD industrial application stems from problems with the destruction of the catalyst structure during the process and the subsequent separation of carbonaceous materials.

The most active catalytic materials proposed for CMD are nickel-based catalysts [1-3]. These catalysts enable the splitting of methane molecules below 500 °C, with satisfactory H₂ yields. On the other hand, iron-based catalysts require a slightly higher temperature, but iron is more abundant, cheaper, and more environmentally friendly [3-4]. Both types of catalysts are prone to destruction of the active phase during CMD. This is associated with the so-called tip-growth mechanism, in which carbon nanofibers form between metallic nanoparticles and the support, thereby destroying the catalyst structure [5]. One solution is to obtain catalysts with a strong interaction between the active phase and the support, which prevents tearing of the catalyst structure, and to appropriately modify the properties of the active phase, thereby altering the course of the elementary steps of the CMD reaction. Therefore, the aim of this study was to evaluate the effect of the composition of nickel-iron bimetallic catalysts on the course of methane decomposition reactions and the properties of the resulting carbonaceous materials.

The catalytic systems with different Ni/Fe ratios were prepared by impregnation of a commercial support, γ -Al₂O₃. To begin, powdered aluminum oxide was immersed in the aqueous solution of nickel nitrate and iron nitrate. After water evaporation, the precursors were dried at 110 °C for 24 hours and calcined at 400 °C for 1 hour. Before testing, the catalysts were reduced with H₂ at 600 °C for 2 hours. The physicochemical properties of catalysts were characterized, among other techniques, by X-ray fluorescence (XRF), N₂ adsorption/desorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR), hydrogen desorption (H₂-TPD), oxidation (TPO), and transmission electron microscopy (TEM). The activity of the catalysts was evaluated by temperature-programmed methane decomposition at a rate of 5 °C/min from 200 °C to 900 °C in a reaction mixture containing 5 vol.% methane in an inert gas. The stability of the catalysts (time-on-stream) was studied at 550 °C for 2 hours. Carbon deposits from spent catalysts were analyzed using TPO and TEM. Studies have shown that the composition of the active phase of catalysts significantly affects their activity and the structure of the resulting carbonaceous materials. The nickel and nickel-iron catalysts exhibit active-phase crystallites in the 3-5 nm range, whereas the iron catalyst has much larger crystallites, about 38 nm. The Ni/Al₂O₃, Ni_{0.8}Fe_{0.2}/Al₂O₃ and Ni_{0.75}Fe_{0.25}/Al₂O₃ catalysts initiate methane decomposition at temperatures as low as 300 °C (Fig. 1a), while Ni_{0.5}Fe_{0.5}/Al₂O₃, Ni_{0.33}Fe_{0.67}/Al₂O₃ and Fe/Al₂O₃ catalysts require higher temperatures.

Nonetheless, above 400 °C, $\text{Ni}_{0.5}\text{Fe}_{0.5}/\text{Al}_2\text{O}_3$ and $\text{Ni}_{0.33}\text{Fe}_{0.67}/\text{Al}_2\text{O}_3$ show higher hydrogen yields than other nickel-iron catalysts. Also noteworthy is the high $\text{Fe}/\text{Al}_2\text{O}_3$ activity near 540 °C. The presence of iron altered the structure of carbonaceous materials. The CO_2 signals (Fig. 1b) recorded during TPO studies show that oxidation of carbon deposits on nickel and high-nickel-content nickel-iron catalysts begins at lower temperatures than on iron and high-iron-content nickel-iron catalysts. Moreover, these TPO signals can be resolved into a few maxima, indicating the presence of various types of carbonaceous materials on the catalyst surface, a finding that is also confirmed by TEM images. On the other hand, the observed oxygen consumption (Fig. 1c) at lower temperatures, especially for nickel and nickel-iron catalysts (immediately after the start of the experiment), suggests that, before the oxidation of carbon deposits, the catalyst surface is oxidized.

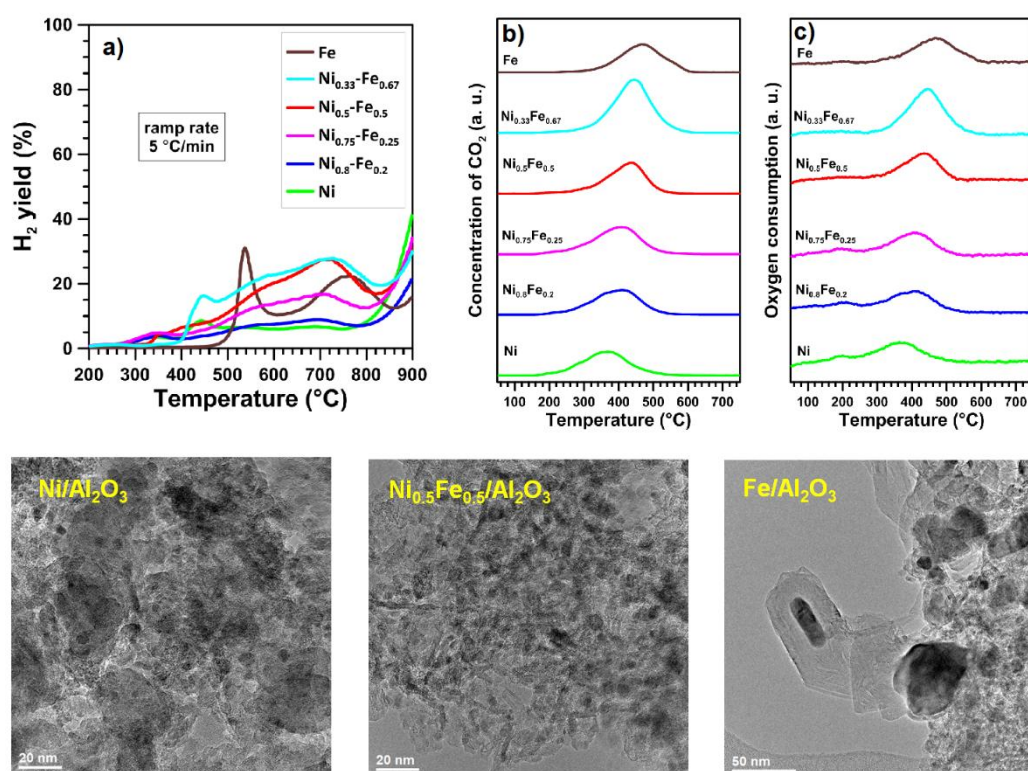


Fig. 1: Catalyst activity in methane decomposition (a) and analysis of carbon deposits by TPO (b, c) and TEM.

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Acknowledgment for financial support from the NAWA PROM program no. BPI/PRO/2025/1/00013/U/00001.

Influence of Zn, In, and Cu Modification on Ni/ γ -Al₂O₃ Catalysts in the MCM–TOL LOHC System

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Keywords: LOHC, dehydrogenation, methylcyclohexane, bimetallic catalyst, nickel/zinc/indium/copper catalysts

Methylcyclohexane (MCH)–toluene (TOL) represents a promising industrial candidate for an economical and safe liquid organic hydrogen carrier (LOHC) system. Platinum-based alumina catalysts exhibit high activity and selectivity in the hydrogenation–dehydrogenation cycle. Replacement of noble metals with transition metals offers a cost-effective alternative. However, nickel catalysts suffer from lower selectivity due to their high hydrogenolysis activity, as well as rapid deactivation caused by extensive carbon deposition.

The modification of nickel catalysts with non-precious transition metals has emerged as an effective strategy to enhance their catalytic performance. Bimetallic systems are expected to improve activity, selectivity, and stability, while minimizing undesired side reactions and catalyst deactivation. The introduction of a second metal can modulate surface active sites via electronic and geometric effects, thereby altering the adsorption energies of reactants and intermediates and suppressing C–C bond cleavage. Copper and zinc are well-established promoters for nickel-based catalysts, enhancing selectivity in MCH dehydrogenation [1, 2]. In Ni–Cu systems, interfacial interactions, preferential occupation of C–C bond cleavage sites by Cu, and/or the formation of Ni–Cu solid solutions are considered responsible for suppressing side reactions. In contrast, the accepted perception is that zinc does not form bulky alloy with nickel; instead, it preferentially occupies low-coordination sites, such as edges and corners, primarily associated with C–C bond cleavage.

So far, investigations of indium as a promoter in Ni-based catalysts for MCH dehydrogenation have remained limited. Introducing In into a Ni catalyst has a positive effect on selectivity in other types of dehydrogenation reactions [3]. Systematic investigations comparing different secondary metals under identical conditions are still lacking. Therefore, we investigated bimetallic nickel compositions containing Cu, Zn, or In as secondary metal, as well as the surface structural features responsible for the differences in activity, selectivity, and stability. Mono- and bimetallic Ni–Me/ γ -Al₂O₃ (Me= Zn, In, or Cu) catalysts were prepared and studied in the hydrogenation–dehydrogenation cycle of TOL–MCH at WHSV = 1 g_{MCH} g_{cat}^{–1} h^{–1} in a flow-through reactor system with H₂ as the carrier gas. The alumina support was loaded with 10 wt.% metal (either monometallic Ni or 6–7 wt.% Ni combined with 3–4 wt.% Zn, In, or Cu) by incipient wetness impregnation. Textural investigations showed that the alumina support, with its bimodal pore system, has favorable surface properties and allows the formation of finely dispersed metal particles of 5–7 nm. The H₂-TPR measurements revealed that the reducibility of nickel is hindered by the addition of Zn, whereas promotion with In or Cu has a favorable effect. Raman spectroscopy supported the strong interaction of Ni with the alumina support, along with the formation of ZnO-rich segregated domains in the NiZn catalyst. The absence of Raman features of crystalline CuO or In₂O₃ suggests that these oxides are highly dispersed and/or intimately associated with the nickel phase rather than forming separate oxide domains. The CO chemisorption experiments revealed that only 3–4 % of the reduced metal

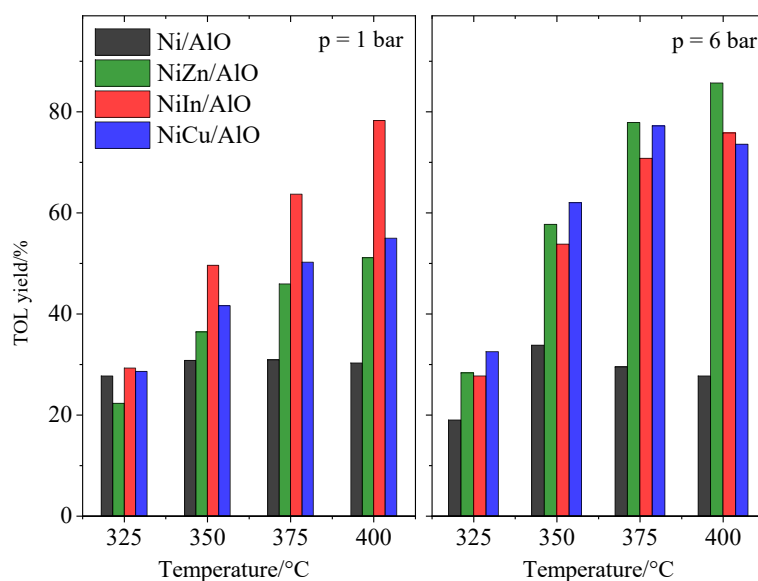


Fig. 1: TOL yield vs. reaction temperature in dehydrogenation of MCH to TOL over mono- and bimetallic nickel alumina catalysts at 1 bar (left panel) and 6 bar (right panel) total pressure; WHSV = 1 g_{MCH}g_{cat}⁻¹h⁻¹; H₂/MCH molar ratio of 1.25. Catalysts were pre-reduced at 450 °C in H₂.

acts as catalytically active centers. FT-IR investigation of adsorbed CO showed the presence of only linearly bound CO species on the NiCu and NiIn catalysts, which is characteristic of isolated Ni atoms in intermetallic and/or alloyed metal particles. In contrast, on the Ni–Zn catalyst, bridging carbonyl species in twofold coordination (Ni₂–CO) were also observed, indicating that Zn atoms tend to replace Ni atoms on the surface by occupying low-coordination sites rather than incorporating into the unit cell of the nickel phase.

The NiZn, NiCu, and NiIn catalysts were more active and stable in the MCH dehydrogenation reaction compared to the Ni/Al₂O₃ catalyst, reaching high conversion and selectivity (Fig. 1), i.e., suppressing hydrodealkylation by modifying the electronic properties of the nickel phase. Among the catalysts, the NiIn/Al₂O₃ system exhibited outstanding activity and over 90% selectivity at atmospheric pressure. The NiZn and NiCu catalysts approached or exceeded this performance only at higher pressures, which can be attributed to lower coverage or formation of less dense and encapsulating types of carbonaceous deposits due to the higher partial pressures of H₂ and MCH during the reaction. Investigation of the spent catalysts confirmed that the bimetallic systems are highly resistant to metal nanoparticle sintering, maintaining high dispersion throughout extended catalytic runs. Raman spectroscopic analysis of the spent catalysts further confirmed the relationship between the amount and nature of carbon deposits and catalytic performance.

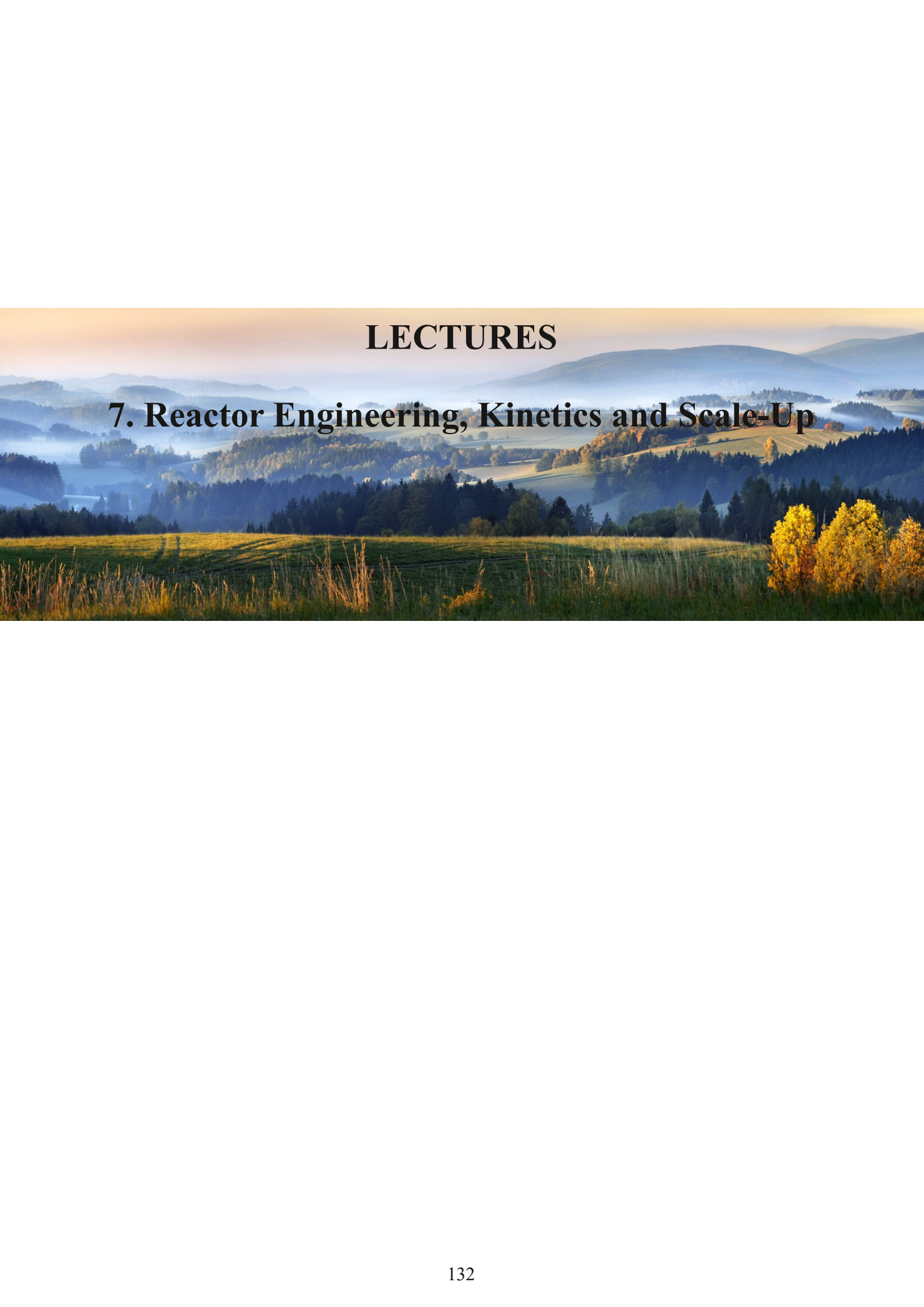
Based on our studies, the three investigated dopant metals show distinct surface structures: zinc tends to occupy corner and edge sites of nickel nanoparticles, whereas promotion with indium leads to the formation of intermetallic compounds, and copper readily forms alloys with nickel.

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Acknowledgements

Authors thank the financial support provided by the European Regional Development Fund and the National Research, Development and Innovation Office, under the Interreg V-A Slovakia–Hungary Cooperation Program SKHU/1902, (Project No: SKHU/1902/4.1/001).



LECTURES

7. Reactor Engineering, Kinetics and Scale-Up

MgO and Sm₂O₃ supported on carbon extrudates for catalysis of 1-butanol condensation reaction

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Keywords: bioalcohols, heteroatom elimination, C-C condensation, scale-up, macro-kinetics effects

The presence of sulfur or oxygen heteroatoms makes the processing both fossil and renewable feedstocks difficult, as they lead to equipment corrosion, catalyst poisoning, or reduced fuel energy value. While traditional hydrodeoxygenation (HDO) is common in fatty-acid-rich feed engineering, the oxygen-rich sources like monosaccharides or bioalcohols make HDO impractical due to the consumption of large amount of hydrogen.

Direct C-C condensation of bioalcohols including 1-butanol is a promising alternative, enabling simultaneous carbon chain extension and oxygen removal as water. Although homogeneous catalysis is already used industrially for fine chemicals, its extensive application is limited. Research is now shifting towards heterogeneous catalysis and full-scale plant modeling. However, a significant knowledge gap exists regarding the understanding of macro-kinetic effects mutually interconnected with the scale of catalyst particles (extrudates) and reactor parameters. Current literature [1,2] focuses mostly on small sphere particles (grain less than 0.5 mm) and a kinetic regime without limitation of external and internal diffusion. Our research thus represent a unique contribution to assessing process feasibility.

The catalysts MgO/C and Sm₂O₃/C, perspective according to our previous work [3], were newly synthesized and characterized (Table 1, Fig. 1) in 20 g batches in the form of extrudates (Norit RX, cylinders of 3.2 mm diameter and 5 mm length). SEM-EDX analysis confirmed the homogeneous 30 wt.% concentration profiles of the oxides trough the extrudates. XRD analysis confirmed X-Ray amorphous character of Sm₂O₃/C (both fresh and used catalyst) while MgO/C exhibits Periclase (PDF 01-075-0447) with diameter 14.5 and 19.5 nm by Scherrer equation, for the fresh and used catalyst respectively. We found that MgO/C exhibited slightly developed secondary mesopores due to the presence of a three-dimensional phase of the deposited MgO. Figure 2 shows 1-butanol condensation to C₈ hydrocarbons (alkenes and alkanes, 2n pathway), mostly over MgO/C extrudates, and 1-butanol condensation to C₇ hydrocarbons (alkenes/alkanes) and 4-heptanone (2n-1 pathway), mostly over Sm₂O₃/C extrudates. We have previously observed that the intrinsic activity of the Sm₂O₃/C catalyst, i.e. the activity in the kinetic regime determined over grains (0.16-0.32 mm) defined as a pseudo-first-order rate constant of the formation all C-C condensed C₇+C₈ products (k_{C-C}), was more than 2.5 times higher than the activity of MgO/C. In contrast, the apparent activity of Sm₂O₃/C extrudates was found to be just 1.7 times higher than the apparent activity of MgO/C in Fig. 2. This relative activity drop, from 2.5 to 1.7, was explained by the high activity of Sm₂O₃ species. The macro-kinetics effects were calculated in Table 2. The influence of the macro-kinetics effects during the studied reaction over the high activity Sm₂O₃/C extrudates is thus 60% higher than that over the MgO/C extrudates. Particularly, the strongly laminar flow inside the semi-pivotal reactor influences the external efficiency factor (η_{ext}).

In conclusion, the results indicate the macrokinetic effects as key aspects for successful industrial implication. Increasing the catalyst size from lab-scale to industry-scale shows that the less active but 2n pathway selective MgO/C may appear perspective if high C₈ selectivity is desirable. If a high

production is prerequisite indifferently on the C₇/C₈ selectivity, the Sm₂O₃/C still provides higher activity.

Table 1: Specific surface area S_{BET} , S_{meso} and micropore volume V_{micro} by Ar physisorption and relative porosity ε calculated from Hg porosimetry and He pycnometry

Sample	S_{BET} (m ² g ⁻¹)	S_{meso} (m ² g ⁻¹)	V_{micro} (mm ³ liq g ⁻¹)	ε (-)
C – Norit	1051	418	269	0.75
MgO/C extrudates	558	270	117	0.63
Sm ₂ O ₃ /C extrudates	543	236	128	0.65

Table 2: computed external ($\eta_{\text{ext.}}$), internal ($\eta_{\text{int.}}$) and overall (η) efficiency factor for studied catalyst in form of extrudates in semi-pivotal reactor at 400 °C and 1 bar

Sample	$\eta_{\text{ext.}}$	$\eta_{\text{int.}}$	η
MgO/C extrudates	0.91	0.52	0.48
Sm ₂ O ₃ /C extrudates	0.69	0.42	0.29

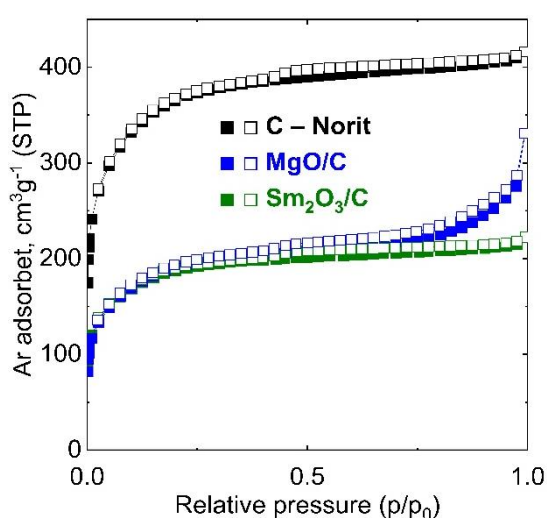


Fig. 1: Ar physisorption over the extrudates of activated carbon C – Norit, and synthesized catalysts MgO/C and Sm₂O₃/C

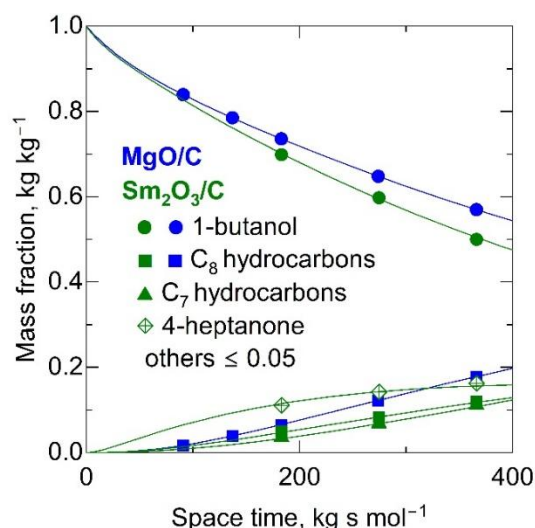


Fig. 2: The main products of 1-butanol condensation at 400 °C and 1 bar over the extrudates in semi-pivotal reactor (i.d. 21 mm)

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Acknowledgement: This work was supported by the Technology Agency of the Czech Republic (BIOCIRKL Project No. TN02000044).

Enantioselective membranes fabricated via ionic interactions between ion-exchange membranes and charged cyclodextrins

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Keywords: membrane, separation, enantioselective, chiral, selectivity

Enantiomers are mirror-image forms of chiral compounds that share identical chemical structures but can behave differently in interactions with other chiral systems, such as those found in human metabolism. These stereoselective interactions may lead to significantly different biological effects, which is particularly important in pharmaceuticals. Despite this, many drugs are still marketed as racemates-equimolar mixtures of both enantiomers-because large-scale separation remains technologically complex and costly. Developing efficient enantioseparation methods is therefore crucial, not only to improve drug safety and efficacy but also to reduce environmental impacts associated with inactive enantiomers. Membrane-based approaches offer a promising route, though conventional fabrication of chiral-selective membranes is often complicated and expensive. This study presents a simple method for preparing chiral membranes by exploiting strong ionic interactions between a charged chiral selector and an oppositely charged membrane. A homogeneous anion-exchange membrane (TailorMem Hollex ADL 911 NR) was modified via dip-coating with the polyionic chiral selector sulfobutylether- β -cyclodextrin (SBE- β -CD). The resulting coverage was $0.68 \mu\text{mol}\cdot\text{cm}^{-2}$ ($130 \mu\text{mol}\cdot\text{g}^{-1}$), with the selector distributed both on the surface and within the membrane matrix. The modified membrane's separation performance was evaluated using N-Boc-tryptophan in a diffusion cell. The system exhibited sorption-selective behavior, driven by preferential inclusion complex formation between SBE- β -CD and the L-enantiomer. Sorption decreased with increasing methanol content in the solvent. Lower feed concentrations and a temperature of 8 °C improved selectivity over time but reduced flux. Performance declined gradually due to saturation of the chiral selector; however, regeneration in pure methanol restored selectivity. The modification remained stable after both operation and regeneration.

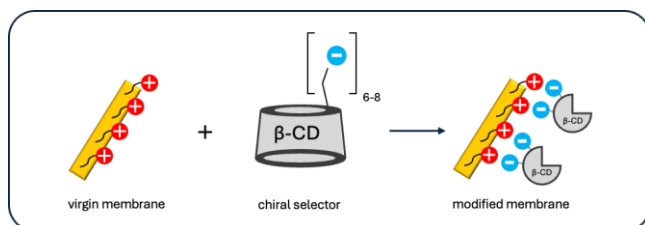


Figure 1. Functionalization of anion exchange membrane with polyionic chiral selector

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Acknowledgement: The study was funded by the GACR, project number 25-15195S

Bridging catalyst development and reaction engineering: Kinetic modeling and scale-up of a novel catalyst for the reverse water-gas shift reaction under industrially relevant conditions

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Keywords: Reverse water-gas shift reaction, Power-to-Liquid, Experimental Setup, Syngas Production, Kinetic study

The reverse water-gas-shift (rWGS) reaction catalytically converts CO₂ into CO and represents a key step in Power-to-Liquid (PtL) processes, where syngas (CO + H₂) serves as feedstock for downstream synthesis routes, such as the Fischer-Tropsch synthesis (FTS) or methanol synthesis. The objective of the reaction is to maximize the CO₂ conversion and CO selectivity while suppressing the formation of undesired by-products, particularly CH₄. From a thermodynamic perspective, the rWGS reaction is favored at high temperatures (typical operation up to 950 °C) and low pressures (less than 10 bar_a). However, such conditions are not necessarily compatible with PtL downstream processes, which are typically operated at lower temperatures (550 °C) and higher pressures (up to 20 bar_a). In addition, side reactions such as methanation and carbon formation become relevant and negatively affect the overall process efficiency. [1, 2]

Optimizing the rWGS performance under the mentioned process-relevant aspects requires adjustments to the operating conditions and the selection of highly active and selective catalysts. A fundamental understanding of the underlying reaction kinetics is therefore essential for describing and predicting the catalyst and reactor performance. While the current state of research focuses on non-selective nickel-based catalysts [3–8], only a limited number of studies address kinetic modeling of novel catalyst materials, especially those that operate selectively at elevated pressures combined with comparatively low temperatures. This represents a critical gap, as process integration with downstream units favors operating conditions that deviate from the thermodynamically optimal conditions of the rWGS reaction.

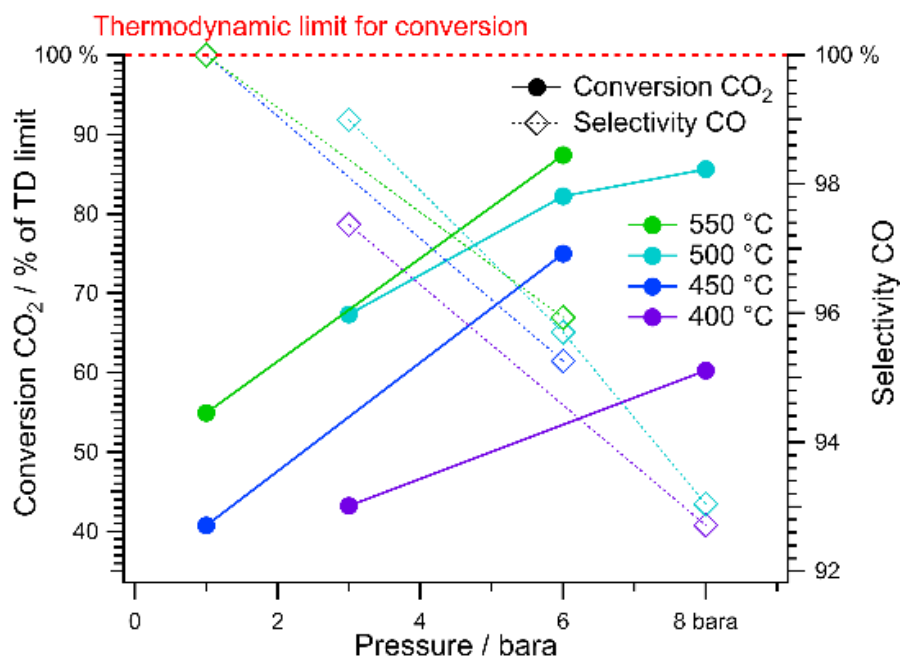


Figure 1: Relationship of CO₂ conversion and CO selectivity as a function of changes in temperature (400-550 °C) and pressure (1-8 bar_a)

In a previous work, a novel selective catalyst was investigated in a laboratory-scale setup demonstrated promising performance under moderate conditions [9]. In the temperature range of 400 to 550 °C and at pressures up to 8 bar_a, methane selectivity was less than 8% at all conditions. While the selectivity for CO was best at low pressures, the conversion increased with higher pressures due to favorable kinetics, presenting a sweet spot behavior with regards to pressure. These findings highlight both the potential of the catalyst and the challenges of operating rWGS at higher pressures and lower temperatures, particularly regarding finding optimal operation windows. Here, detailed kinetic studies can also provide further insights.

To investigate these aspects under industrially relevant conditions and to provide a scalable description of catalytic performance, the catalyst is studied in an advanced miniplant-scale reactor setup at pressures up to 25 bar_a. The work includes kinetic characterization, focusing on the determination of observed reaction rates while accounting for mass and heat transport limitations. The experimental and modeling framework is first established using a commercial nickel-based catalyst, for which validated kinetic models from the literature are available. The resulting approach is implemented in an one-dimensional, steady-state, isothermal plug flow reactor model. This approach enables the quantification of mass and heat transport limitations and their influence on the measured kinetics in the reactor setup. The methodology is then applied to the novel catalyst using macrokinetic approaches, such as the power-law model, and empirical correlations from the experimental campaign to describe the observed reaction rate.

With this work, we present a transferable methodology for the kinetic investigation of novel catalytic systems under industrially relevant conditions. It enables the identification of intrinsic kinetics, the quantification of transport limitations, and the development of predictive reactor design models. The approach is applicable to related catalytic processes, describes a novel catalyst system, and provides practical guidance for operating a reaction under non-ideal conditions.

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Case study: Construction of a 300W fuel cell stack with Al-TiN bipolar plates for a light-weight vehicle

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Keywords: PEMFC, fuel cell electric vehicle, bipolar plates, TiN

Shell EcoMarathon is a sustainability competition for universities [1]. Goal of the race is to plan and build a vehicle (max. 140 kg), which is able to run a determined distance (15 km) within a level time (45 min), with the lowest fuel consumption. Team of the Mechanical Engineering Faculty of the Budapest University of Technology and Economics (BME SHARK TEAM) took part in that competition more times in diesel category. This year a fuel cell electric vehicle (FCEV) was planned by them for the Shell EcoMarathon. Speciality of that racing car is that its FC stack is not a commercial one, but is designed and built by the Renewable Energy Research Group of the HUN-REN Research Centre for Natural Sciences, with collaboration of the BME SHARK TEAM and the ArtTECHNICS Bt. 3D model of the FC stack can be seen on **Figure 1**. Its most important parameters are the following: min. 250 W operating power, 30 cell/stack, 45.5 cm² gas diffusion layers, parallel serpentine flow field pattern on bipolar plates (BPPs), closed cathode, water cooling. Cathode gas supply is provided by an air blower. Anode side is humidified and humidifier is tempered by the cooling water of the stack. Goal of this development was to verify, that building of an FC stack with lower (100-500 W) power range is possible and feasible independently from the great FC manufacturers, relying on national industrial companies and universities as much as possible.

Most important technical challenge was the manufacturing of bipolar plates. Industry applies pressed BPPs, made of 0.05-0.075 mm thick stainless steel or titanium sheets, which are usually coated to decrease the bulk interfacial contact resistance (ICR) and to protect them against corrosion. This solution is economic above larger (> 10000 pc) seria because of the expensiveness of pressing tools. Milling was the only manufacturing method, which was available for us and because of that, minimum 3-4 mm material thickness was necessary. Choosing of the suitable BPP material was crucial. Stainless steel, graphite, titanium and aluminum were the possible structural materials. Stainless steel has excellent mechanical stability, but it is hard to mill and its density is too much. Graphite has very good electric properties (good conductivity, corrosion resistance), but it is very fragile. Titanium seems to be the ideal material, because of its mechanical stability, resistance against corrosion, and its acceptable density. In this case price and the difficulty of milling are the most important issues. Aluminum is light, easy to mill and it has very good electric and thermal conductivity. Strongest argument against Al is its weak resistance against corrosion. That problem can be solved by coating of the BPPs [2,3]. For this, galvanic coating, Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) were possible available techniques.

Based on the idea of the work of Yan *et al.* [3], who tested Al bipolar plates with TiN coating in a 30.25 cm² lab scale single cell with promising results, milled Al BPPs with a 2 micron TiN coating deposited by PVD were designed for the ShellEcoMarathon FCEV. It is important to emphasize, that in case of Al PVD coating is much more difficult, than in case of Ti, because the temperature of the procedure is lower. That problem was solved, coatings were even, and the complete development was carried out by Hungarian industrial partners.

Most important technical challenge was to go from TRL3 (first FC measurements with 16 cm² cell) to TRL7 (testing of the ready FCEV prototype). In the beginning, Pt loading of MEA and working conditions were optimized. Manufacturing method of MEAs was standardized. In case of every development stage, polarization curve was taken from the cell/short stack. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) was also applied for cell characterization.

Preliminary experiments were successful. Short stack experiments under real working conditions showed, that 11-13 W/MEA power is possible, which provides enough power (>300 W) for the FCEV. Additionally, FC stack is decomposable and suitable for high-throughput experimental technique.



Fig. 1: 3D model of the 300 W PEM fuel cell stack

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Acknowledgement

This research was funded by Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus and by Project no. 2024-1.2.1-HE_PARTNERSÉG-2025-00042, titled European partnerships in Horizon Europe, announced by the National Research, Development and Innovation Office. I want to say thanks for the LAUFENBERG GmbH.



LECTURES

8. Operando, In Situ and Computational Approaches in Catalysis

Catalytic activity distribution of individual catalyst particles in one catalyst batch

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Keywords: particle-to-particle heterogeneity; single-particle catalysis; fluorescence microscopy; correlative SEM-EDS; furfural disproportionation

Introduction

A catalyst batch is rarely a uniform material, but rather an ensemble of individual particles differing in local composition, morphology, surface properties, and catalytic activity. Conventional catalytic testing and bulk characterization provide only averaged information and cannot distinguish whether the measured performance originates from a large population of similarly active particles or from a small fraction of highly active “champion” particles accompanied by weakly active or inactive ones [1]. Resolving particle-to-particle heterogeneity is therefore essential for establishing reliable structure–activity relationships in heterogeneous catalysis.

In this work, hydrotalcite-derived Mg–Al materials were used as a model system to demonstrate a particle-resolved approach. Hydrotalcites are suitable for this purpose because their catalytic behavior as solid base catalysts depends sensitively on Mg/Al ratio, calcination history, hydration state, and reconstruction through the memory effect [2,3]. The aim was to map catalytic activity distributions of individual particles within one catalyst batch and correlate them with local elemental composition.

Methodology

The catalytic activity of individual hydrotalcite particles was investigated using fluorescence-based chemical labelling. The approach relies on the base-catalyzed disproportionation of furfural, producing furfuryl alcohol and furoic acid, followed by formation of fluorescent polymeric species derived from furfuryl alcohol. The fluorescence signal was therefore used as an apparent descriptor of local catalytic activity. Two Mg–Al hydrotalcite-derived materials with different Mg/Al ratios, approximately 5:1 and 25:1, were studied. The samples were prepared by impregnation of MgO with aluminum isopropoxide [3] borovceand investigated after different treatments, including pre-calcined, freshly re-calcined, and rehydrated states. The labelling reaction was performed in furfural/isopropanol at 50 °C for 1 h with a catalyst loading of 1 mg per 5 mL of reaction mixture. After reaction, the particles were analyzed by confocal fluorescence microscopy using optimized acquisition conditions, with excitation at 488 nm. Fluorescence images were processed to determine particle-resolved intensity descriptors, including an amplification factor used as a proxy for apparent catalytic activity. The same particle ensembles were subsequently characterized by SEM-EDS to correlate activity with morphology and local Mg/Al ratio. The influence of EDS acquisition time and data processing workflow was evaluated because particle-level Mg/Al determination is semi-quantitative and sensitive to measurement conditions. Selected compositional trends were further compared with complementary elemental information obtained from XRF and TOF-SIMS measurements.

Results and discussion

The developed correlative microscopy workflow revealed pronounced heterogeneity in catalytic activity among individual particles within the same catalyst batch. Even particles originating from the same material and subjected to the same treatment exhibited broad distributions of fluorescence intensity. This confirms that bulk catalytic measurements may obscure a substantial degree of inter-particle variability and that particle-resolved analysis is necessary to identify highly active, weakly active, and nearly inactive particles within one catalyst sample.

A clear influence of sample treatment was observed. Freshly calcined and pre-calcined materials showed generally low apparent activity under the applied liquid-phase reaction conditions. In contrast, rehydrated samples exhibited markedly higher fluorescence response. This behavior is consistent with partial reconstruction of the hydrotalcite-

derived mixed oxide phase and reformation of weak basic sites associated with hydroxyl groups and interlayer species. These sites appear to be particularly relevant for the furfural disproportionation reaction under mild conditions.

The correlation between catalytic activity and local Mg/Al ratio was found to depend on the composition range. For the material with lower Mg/Al ratio, rehydrated particles showed a positive trend between apparent catalytic activity and Mg/Al ratio, suggesting that Mg-rich particles may possess a higher density or more favorable distribution of basic sites. However, this trend was not observed in the same way for the material with higher Mg content. At higher Mg/Al ratios, the activity appeared to reach a plateau, indicating that further increase in magnesium content does not necessarily lead to higher catalytic activity. This suggests the possible existence of an optimal compositional window rather than a simple linear relationship between Mg/Al ratio and activity.

The study also highlighted several methodological challenges. The reliability of particle-level Mg/Al determination by SEM-EDS was strongly affected by acquisition time and data processing mode. Short acquisition times enabled practical analysis of larger particle ensembles but introduced higher uncertainty, especially for particles with high Mg/Al ratios. Longer acquisition times improved counting statistics but reduced throughput. Therefore, the obtained activity–composition relationships should be interpreted primarily as qualitative or semi-quantitative trends. Nevertheless, the combination of fluorescence microscopy and SEM-EDS proved suitable for identifying heterogeneity patterns that are inaccessible to conventional bulk analysis.

Conclusions

This work demonstrates a particle-resolved methodology for mapping the catalytic activity distribution of individual particles within a single catalyst batch. Fluorescence labelling based on furfural disproportionation enables visualization of catalytically active particles, while correlative SEM-EDS provides information on particle morphology and local Mg/Al composition.

The results show that hydrotalcite catalyst batches are not catalytically uniform at the single-particle level. Rehydrated samples exhibited substantially higher apparent activity than calcined materials, emphasizing the importance of structural reconstruction and weak basic sites for the studied reaction. The relationship between activity and Mg/Al ratio was composition-dependent and suggests the existence of an optimal range rather than a monotonic increase in activity with magnesium content.

More broadly, the presented approach provides a practical tool for deconvoluting structure–activity relationships in heterogeneous catalysts at the level of individual particles. By distinguishing active, weakly active, and inactive particles within one batch, it can support rational optimization of catalyst synthesis and treatment procedures aimed at reducing particle-to-particle heterogeneity and improving overall catalytic performance.

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Acknowledgement

This project was supported by the Czech Science Foundation (GACR No. 23-08083M).

Insight into the redox dynamics of cryptomelane, K-OMS-2, using TP-XPS, O-XAS, *operando* S/TEM-EELS, and DFT – competitive defect- and tunnel-centred pathways

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Keywords: cryptomelane, redox reaction mechanisms, temperature-programmed spectroscopy, *operando* microscopy, DFT calculations

Introduction

Temperature-programmed (TP) and *operando* studies are essential for understanding the redox behaviour of transition-metal oxides, which underpin many catalytic and energy-related processes. Among these materials, tunnel-structured manganese oxides represent an important class due to their structural flexibility and multivalent manganese chemistry. Hollandite-type $K_xMn_8O_{16}$ (cryptomelane, K-OMS-2) is particularly attractive, as its framework of MnO_6 octahedra forms one-dimensional tunnels stabilised by alkali cations, enabling oxygen exchange and mixed-valence stabilisation.

Despite extensive investigation, the mechanisms governing redox transformations in $K_xMn_8O_{16}$ remain unclear, particularly the interplay between tunnel accessibility, defect structure, and morphology evolution under reaction conditions. Addressing these aspects requires a multi-technique approach combining TP, *in situ* and *operando* methods with theoretical modelling. In this work, we investigate the redox behaviour of K-OMS-2 nanorods using a combination of TP-XPS, *operando* XAS, *in situ/operando* electron microscopy, and DFT calculations, with the aim of identifying dominant redox pathways and their structural consequences.

Methodology

Euhedral cryptomelane nanorods were synthesised and characterised using complementary structural and spectroscopic techniques [1]. Temperature-programmed XPS (TP-XPS) tracked changes in manganese average oxidation state (AOS) and potassium speciation under controlled conditions, while *operando* Mn K-edge XAS provided bulk-sensitive insight into redox and coordination changes. *In situ/operando* S/TEM-EELS monitored structural evolution and spatially resolved valence variations. Redox conditions were tuned via temperature and reactive gases (H_2 , O_2) to identify stability windows. Density functional theory (DFT) calculations were used to evaluate oxygen vacancy formation, potassium mobility, and transformation energetics.

Results

TP-XPS revealed systematic changes in Mn average oxidation state during reduction and reoxidation, accompanied by evolving potassium speciation, indicating its active role. *Operando* XAS confirmed reversible changes in Mn oxidation state and coordination.

In situ and *operando* observations show that the reduction of $K_xMn_8O_{16}$ follows two pathways depending on tunnel accessibility. When small molecules (e.g., H_2) penetrate the tunnels, reduction proceeds in the bulk via a tunnel-centred mechanism, involving Mn reduction, potassium migration, and gradual tunnel destabilisation. When access is limited (e.g., thermal or solid reductants), reduction occurs at defects, where vacancies and voids act as active sites, leading to local phase transformations and, under harsher conditions, structural fragmentation.

Temperature-programmed experiments identified stability windows for reversible redox behaviour, beyond which irreversible structural changes dominate.

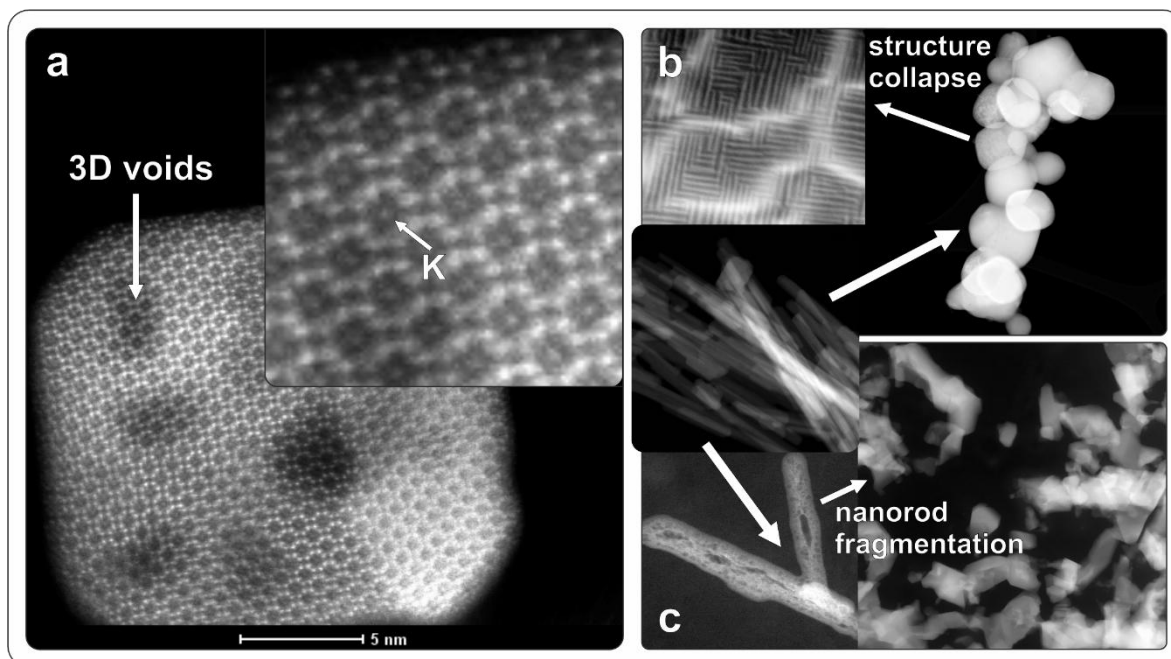


Fig. 1: High-resolution STEM image of a $K_xMn_8O_{16}$ nanorod cross-section showing the cryptomelane tunnels with confined K ions and structural defects (a). Schematic of competing redox pathways: tunnel-mediated reduction via diffusion through tunnels (b) and defect-mediated reduction at surface defects and voids (c).

Discussion and conclusions

The results show that the redox behaviour of cryptomelane is governed by competing tunnel- and defect-mediated pathways, controlled by reaction conditions and structural accessibility. Tunnel access enables efficient bulk reduction but drives potassium migration, structural rearrangement, and tunnel collapse, limiting reversibility. In contrast, defect-mediated pathways proceed more gradually at surface-accessible defects, enabling broader reversible regimes but potentially causing extensive degradation under aggressive conditions.

Temperature-programmed and *operando* measurements identify stability windows separating reversible and irreversible transformations. Complementary spectroscopy and DFT confirm strong coupling between manganese redox chemistry, oxygen vacancies, and potassium mobility, with vacancy formation favoured at defect sites.

Overall, combining TP, *in situ/operando* methods, and DFT provides a framework for understanding and optimising redox stability in tunnel-structured manganese oxides, guiding the design of more robust catalysts for thermochemical applications.

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Acknowledgement

The research is carried out within the OPUS 25 (grant number 2023/49/B/ST4/00740, PI: Dr Joanna Gryboś) project, funded by NCN, the Polish National Science Centre. Research at the National Synchrotron Radiation Centre SOLARIS was supported by the Ministry of Science and Higher Education, Poland, under contract no. 1/SOL/2021/2. Authors thank the Priority Research Area SciMat under the program Excellence Initiative – Research University at the Jagiellonian University and Materials Research Hub project for access to the XPS Nano-Peak laboratory.

New emerging technique of Raman spectroscopy: TIME-GATED RAMAN

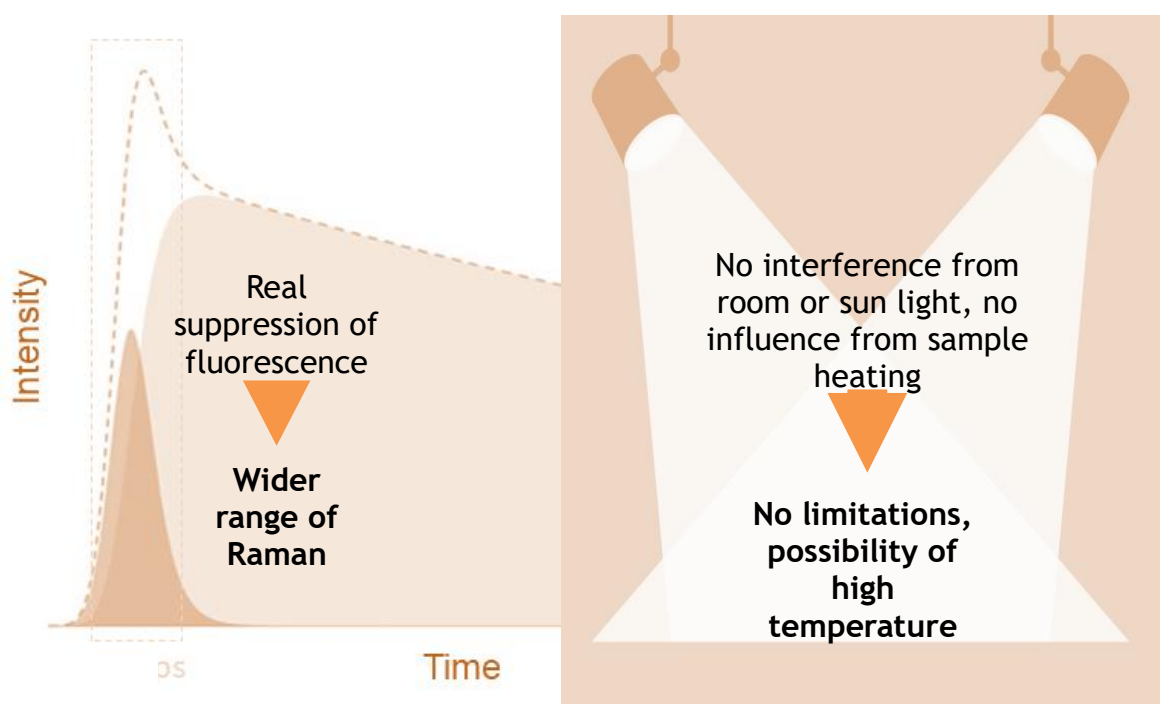
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Keywords: Raman spectroscopy, in-situ,

We will soon celebrate the 100th anniversary of the Raman effect [1]. After the discovery of lasers, Raman spectroscopy became a frequently used non-destructive analytical method. Unfortunately, it is not applicable for many samples because the focused laser radiation can change or destroy the sample. Many samples, especially colored ones, can emit very intense fluorescent radiation instead of a weak Raman spectrum.

The new TIMEGATE technology eliminates fluorescent radiation as well as the undesirable effects of ambient light and high temperatures. We present examples of its use in the chemical analysis of minerals and in the on-line study of the kinetics of biochemical processes and in the in-situ study of catalytic processes at temperatures above 1000°C.



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Reactant loading-dependent evolution of the hydrocarbon pool: insights into methanol conversion over zeolites from operando UV–Vis study with MCR-ALS analysis

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Keywords: methanol conversion, zeolite, hydrocarbon pool, heterogeneous catalysis, *operando*

The hydrocarbon pool mechanism is widely considered to govern the methanol-to-hydrocarbons (MTH) catalytic process, enabling the production of a range of hydrocarbons, including olefins [1]. Despite extensive study, its details remain the subject of ongoing scientific debate. Continued advances in experimental techniques and data analysis methods are providing new tools for better understanding of this process, which has been applied commercially for decades. In industrial practice, zeotype SAPO-34 with a CHA framework is commonly employed, offering high selectivity toward olefin production.

Operando UV–Vis spectroscopy was used to monitor the catalyst surface during three reaction cycles (2 hours each) of methanol conversion at different loadings over an SSZ-13 (CHA) zeolite catalyst. These measurements were complemented by GC and MS analysis to track the products released from the catalyst. The spectroscopic data were further analyzed using MCR-ALS, which enabled separation of the spectra into individual components and helped identify the different species contributing to the observed signals.

High loading led to faster deactivation, a rapid decline in methanol conversion, and an earlier dominance of aromatic growth and coke-forming species, whereas low loading sustained higher conversion for longer time and delayed the onset of deactivation pathways. UV–Vis, FTIR, and MCR-ALS analyses consistently showed that higher loading accelerated methylation, aromatic condensation, and the formation of polyaromatic coke precursors, while lower loading prolonged olefin production and slowed the evolution of the hydrocarbon pool. Overall, the reaction mechanism remained unchanged, but reactant loading governed the balance between olefin- and aromatics-driven cycles as well as the rate of catalyst deactivation.

The combined operando spectroscopic and following algorithmic analyses demonstrate that methanol loading plays a decisive role in governing both the evolution of hydrocarbon pool species and the deactivation pathway of H-SSZ-13 in the MTH reaction. Lower methanol feed delays the formation of aromatic and polyaromatic coke precursors, prolongs the induction period, and sustains olefin production over multiple cycles. The application of MCR-ALS proved particularly valuable in uncovering transient intermediates, such as cyclopentenyl cations, that are not directly evident from raw spectra. These findings provide deeper mechanistic insight into loading-dependent behavior and highlight the importance of controlled reaction conditions for optimizing catalyst lifetime and selectivity in industrial MTH processes.

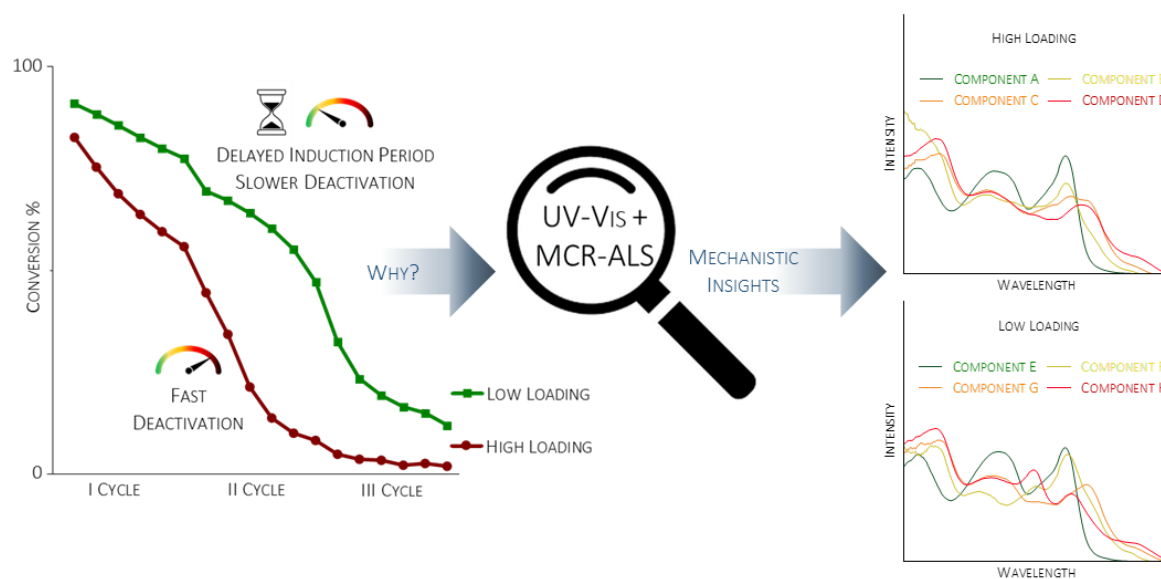


Fig. 1: Schematic representation of the study

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Acknowledgement

Financial support of the National Science Centre, Poland (2023/49/B/ST4/02340) is acknowledged

Semiquantitative electron spectroscopy method for characterization of the encapsulation state of supported Pt nanoparticles in strong metal-support interaction

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Keywords: Pt nanoparticle, oxide, strong metal-support interaction, encapsulation

In heterogeneous catalysis, the interaction between metal nanoparticles and their supports plays a crucial role in determining the performance and stability of the catalytic system. These metal-support interactions significantly influence both the geometric and electronic structure of the particles and often lead to formation of interfacial active sites with combined properties from the support and metal phases. One of the most spectacular manifestations of the metal-support interactions is the decoration of platinum group metal nanoparticles deposited onto reducible oxides by an ultrathin partially reduced oxide layer, which can be induced by reductive pre-treatment under mild conditions [1]. This strong metal-support interaction phenomenon modulates the activity/selectivity of the catalyst nanoparticles and enhances their stability, which is especially important in electrocatalytic applications [2,3].

In spite of its importance, characterization of the encapsulation layer is a challenging task. Its direct visualization is possible in model systems by scanning tunneling microscopy; otherwise, typically chemisorption experiments and low energy ion scattering spectroscopy measurements [4,5] provide information about its existence.

In this contribution a semiquantitative photoelectron spectroscopy method is proposed for identifying the decoration of platinum nanoparticles by support-originated species. The basic idea is comparison of the intensities of Pt spectral features with very different inelastic mean free paths (IMFPs, i.e. with very different kinetic energies) during treatments used for inducing encapsulation. Indeed, if the IMFP of the electrons from a given spectral feature is long with respect to the thickness of the decoration layer, encapsulation results only in a relatively slight attenuation of the signal intensity, so distinction between the uncovered and the covered states is difficult. On the other hand, if the IMFP is comparable or smaller than the thickness of the decoration layer, the attenuation of the intensity of the corresponding feature is much more pronounced or, in other words, a spectral feature with lower IMFP is suppressed to a much higher extent than another one with a higher IMFP if the surface is covered by a thin overlayer. Consequently, the intensity ratio of a low and high IMFP Pt feature can be a sensitive probe for the decoration state of the Pt particles, as it is much smaller for encapsulated particles than for uncovered ones. In the X-ray excited electron spectrum of Pt the NOO Auger transition at the low kinetic energy end of the spectrum (around 64 eV, with a corresponding mean free path of approximately 0.4 nm in both Pt and oxides) is suitable for the low IMFP feature, while the Pt 4f peaks (around 1180 eV kinetic energy for MgK α excitation with IMFP around 1.35 nm in Pt or 2.2 nm in oxides [5]) are available at the high kinetic energy end of the spectrum.

The feasibility of the above idea was tested by model calculations for different spatial arrangements and encapsulation states of supported Pt nanoparticles. According to the results, in case of particles on a flat surface, the suppression effect of the intensity ratio by a 0.3 nm thick overlayer was very pronounced (around 60%) with respect to the case of the non-covered particles. Somewhat less but still significant suppression (50%) was calculated for layers of support grains covered by encapsulated or non-encapsulated catalyst particles, which models the case of a realistic catalyst powder. As the next step, the calculation results were confirmed by model experiments performed on Pt particles grown on a flat $\text{TiO}_2(110)$ single crystal surface. Finally, the method was successfully applied for interpretation of the encapsulation state of reductively pre-treated $\text{Ti}_{0.8}\text{Mo}_{0.2}\text{O}_2\text{-C}$ and $\text{Ti}_{0.9}\text{Sn}_{0.1}\text{O}_2\text{-C}$ composite supported Pt electrocatalysts, for which other measurements, involving electrochemical tests, indicated fractional (for Mo-containing system [3]) or complete (for Sn-containing system [7]) encapsulation.

In conclusion, model calculations as well as validation experiments confirmed that the intensity ratio of the low and high kinetic energy Pt feature can consistently be used for judging the encapsulation state of the catalyst particles. Important feature of the proposed method is that it is designed for photoelectron spectrometers with conventional X-ray sources, so it can be implemented using widely accessible laboratory instruments.

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Acknowledgement: This research was funded by Project no. RRF-2.3.1-21-2022-00009, titled the National Laboratory for Renewable Energy, and has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus and by Project no. 2024-1.2.1-HE_PARTNERSÉG-2025-00042, titled European partnerships in Horizon Europe, announced by the National Research, Development and Innovation Office.

In-situ X-ray Structure Analysis under Non-Ambient Conditions

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Keywords: Raman spectroscopy, in-situ,

In-situ X-ray structure analysis under non-ambient conditions has become an important technique for understanding the structural changes of materials under non-ambient conditions such as elevated temperature, applied electric potentials, or reactive atmospheres. Compared to conventional ex-situ approaches, in-situ X-ray diffraction (XRD) and scattering methods enable direct observation of phase transitions and kinetic processes, thereby providing insight into structure–property relationships.

Recent advances in X-ray instrumentation have significantly improved the capabilities of these methods. As an example, high-power rotating anode sources provide sufficient photon flux to investigate even strongly absorbing materials while still achieving short acquisition times necessary for following fast processes. Furthermore, modern detector technologies offer high angular resolution, enhanced sensitivity, and improved energy discrimination, effectively suppressing background contributions from $k\beta$ and fluorescence radiation. The integration of specialized sample environments, such as the Rigaku Reactor X attachment, allows precise control of experimental parameters, including temperature and gas composition during XRD and small-angle X-ray scattering (SAXS) measurements.

As a result, in-situ X-ray techniques have become very important for a wide range of research fields, including catalysis, energy storage, and advanced materials synthesis. In this presentation, we demonstrate which structural information can be obtained from XRD and SAXS studies of various materials under reactive and non-ambient conditions.

Advanced Multimodal Characterization Approaches for Catalysis Research: From Bulk Structure to Surface Chemistry and Nanoscale Characterization

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Keywords: Atomic Force Microscopy–IR, Catalyst characterization; Electron microscopy; Surface analysis; Correlative microscopy

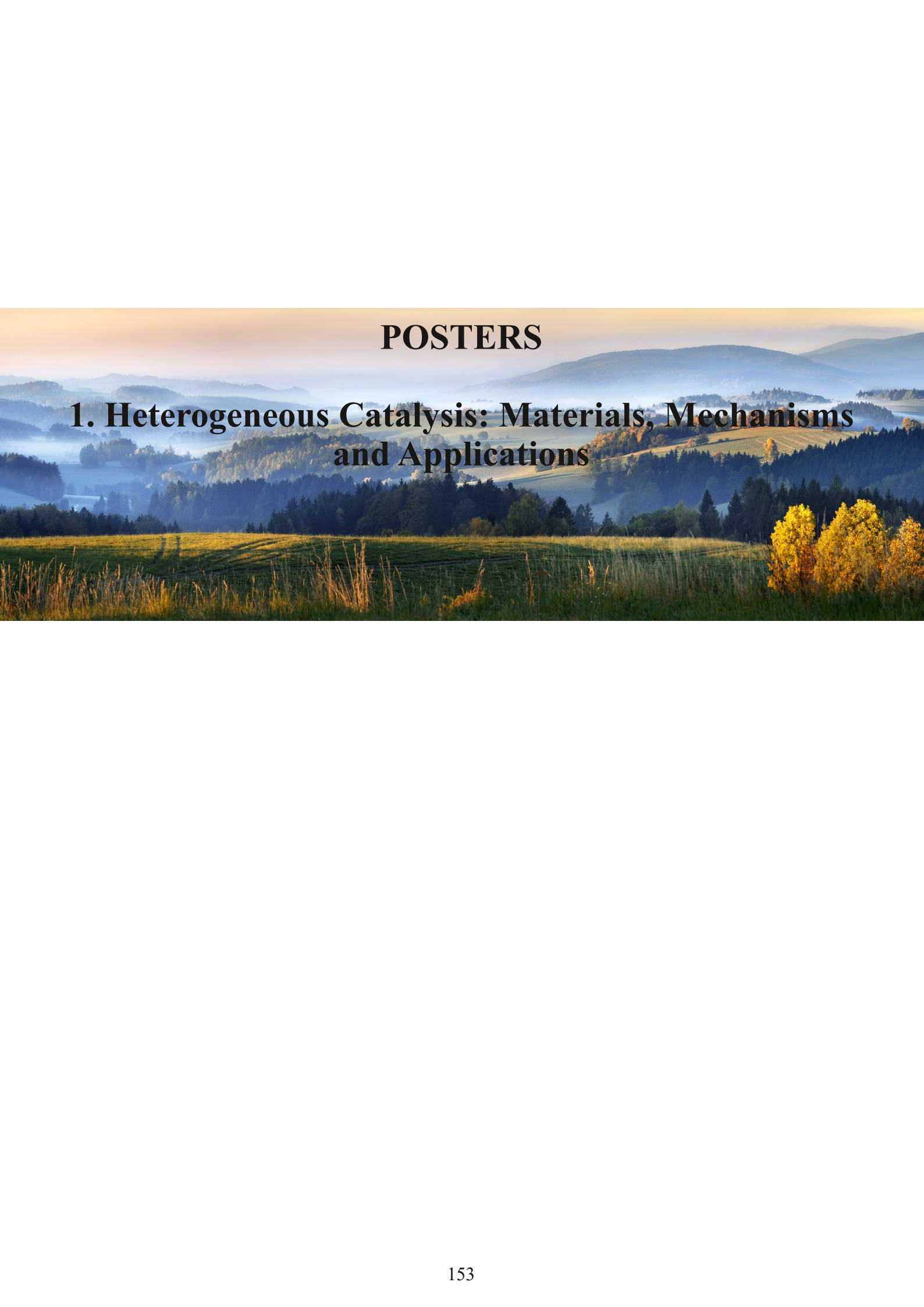
The development of modern catalytic materials requires increasingly comprehensive characterization approaches capable of correlating morphology, crystal structure, elemental composition, surface chemistry, and defect-related properties across multiple length scales. No single analytical method can provide all the information necessary to fully understand catalyst synthesis, activation, degradation, and reaction mechanisms. Therefore, multimodal and correlative characterization workflows are becoming essential tools in contemporary catalysis research.

This contribution presents just a few selected analytical and imaging techniques available within the portfolio of Měřicí technika Morava (MTM), with emphasis on their application in heterogeneous catalysis, electrocatalysis, photocatalysis, and advanced energy-related materials.

Special attention will be devoted to Atomic Force Microscopy and nanoscale infrared spectroscopy (AFM-IR), which enable simultaneous investigation of surface topography, nanomechanical properties, and localized chemical composition with spatial resolution well below the diffraction limit. These techniques provide unique insight into catalyst surface heterogeneity, adsorbate distribution, phase segregation, polymer-supported catalytic systems, and local physicochemical transformations under ambient or controlled environments.

Advanced electron microscopy, including scanning and transmission electron microscopy, enables nanoscale characterization of catalyst nanoparticles, interfaces, lattice defects, and structural transformations. Selected SEM and TEM workflows will be presented together with advanced analytical detector technologies, including energy-dispersive X-ray spectroscopy, electron backscatter diffraction, wavelength-dispersive spectroscopy, and micro-X-ray fluorescence. The combination of high-resolution imaging with elemental and crystallographic analysis enables detailed investigation of catalyst morphology, nanoparticle dispersion, phase composition, grain orientation, elemental segregation, and degradation processes.

Surface-sensitive analytical methods, including X-ray Photoelectron Spectroscopy and Time-of-Flight Secondary Ion Mass Spectrometry, enable detailed investigation of oxidation states, surface composition, adsorbed intermediates, and depth-dependent chemical changes. Modern XPS systems equipped with Scanning X-ray Imaging (SXI) further enable the acquisition of **SEM-like surface images** with lateral chemical sensitivity. In combination with quantitative XPS analysis, this approach represents a powerful tool for correlating surface morphology, chemical-state distribution, and local chemical heterogeneity in complex catalytic systems.



POSTERS

1. Heterogeneous Catalysis: Materials, Mechanisms and Applications

Partial oxidation of methane to syngas on perovskite catalysts

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Keywords: nickel catalyst, perovskites, partial oxidation of methane, synthesis gas, *operando* XRD

Compared to conventional steam reforming, partial oxidation of methane (POM) to synthesis gas (CO and H₂) is more energy efficient [1], furthermore yielding a H₂:CO ratio of 2 well suited for Fischer-Tropsch synthesis. Perovskites containing catalytically active elements can be used as precursors of supported metal catalysts, which form upon pretreatment in reductive environment or *in situ* via reduction of the perovskite by reaction gases. The synthesized perovskites lanthanum nickel oxide, lanthanum cobalt oxide and mixed lanthanum nickel/cobalt oxides have been characterized with XRD, SEM, BET and TPR and tested for POM reaction in a tubular flow reactor. Pretreatments with different atmospheres were tested and the effect on catalyst activation, performance and stability were investigated. The activation of the catalyst and the evolution of phases have been investigated with TEM/EDX and monitored during the POM reaction with *operando* XRD. The synthesis of the perovskites was carried out by different routes, such as the Pechini method, wet impregnation and flame pyrolysis to determine the effect of the different procedures on nanoparticle morphology/composition and catalytic performance. Additional characterization methods such as XPS, UPS and electron microscopy will be applied for more detailed understanding of the surface reactions. In the future, planned synchrotron-based *operando* XPS, XAS and XRD will enable to investigate the fast decomposition of the perovskite structure during the activation of the catalyst.

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Coupling Reactions of Ethanol and an Ethanol/Acetaldehyde Mixture over Mo/MgO-SiO₂ Catalysts

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Keywords: Ethanol, Acetaldehyde, Molybdenum oxide, MgO-SiO₂ catalysts, Butadiene

Currently, the production of butadiene is based on petrochemical basis, namely more than 99% of butadiene is produced from petroleum, natural and shale gas. The extensive use of fossil-origin carbon and energy resources contributes to severe economic and environmental problems. Concerns about the limited availability of petroleum resources, as well as climate change and global warming encourage the use of sustainable and renewable carbon sources. Bioethanol, as biological product, completely fulfills these requirements. The second and third generation bioethanol producing technologies are of sustainable nature. The increasing global demand for bio-derived chemicals enforces the biomass based production of butadiene. Efficient coupling reactions are also interesting topics for fundamental catalytic science and technology. The efficiency of the heterogeneous catalytic ethanol-to-butadiene process can be enhanced only in deep understanding of the origin catalytic activity, the chemistry of the process, i.e., the catalytic mechanism.

The present study is dealing with preparation/characterization of MgO-SiO₂ catalysts obtained by wet kneading method. The first step in an ethanol coupling reaction is the dehydrogenation of ethanol into acetaldehyde. It is known that molybdenum trioxide (MoO₃) exhibits high activity in this reaction. However, the ethanol to butadiene coupling reaction involving molybdenum oxide has not yet been studied in detail. Considering this, in our work we investigated the catalytic activity of molybdenum oxide impregnated on MgO-SiO₂ in ethanol coupling reaction.

Catalysts were characterized by means of XRD, N₂-physisorption, SEM and UV-vis measurements. The acidic/basic properties were investigated by NH₃/CO₂-TPD measurements. Catalytic test reactions were performed with pure ethanol and a 9/1 ethanol/acetaldehyde mixture between 300 and 425 °C at a space velocity of 1 h⁻¹. Reactions were also performed at 325 and 375 °C with a space velocity of 0.33 to 6 h⁻¹.

Structural studies have shown that as the molybdenum content increases, the isolated molybdate forms are replaced by the polymolybdate forms. The addition of molybdenum increased the acidity of the catalysts, while their basicity decreased compared to the pure MgO-SiO₂ samples. Due to the change in acid-base conditions, the selectivity of the coupled products decreased in the molybdenum-containing samples. Meanwhile, the selectivity of acetaldehyde increased and ethane appeared among the products due to the disproportionation of two adsorbed ethanol molecules on two adjacent active sites on a partially reduced molybdenum-containing catalyst. The products of the aldol condensation pathway, crotonaldehyde and crotyl alcohol, appear in the reaction of the ethanol/acetaldehyde mixture. These products can only be detected in trace amounts in the reaction of pure ethanol. Significant amounts of ethyl vinyl ether and ethyl acetate also appeared among the products at high space velocities and low temperatures. These products are formed in the condensation reactions of ethanol-acetaldehyde and acetaldehyde-acetaldehyde. Based on these results, mechanisms analogous to the formation of ethane have been proposed. These mechanisms achieve carbon-carbon coupling through the condensation of two acetaldehydes and a crotonaldehyde intermediate. It has also been suggested that

introducing acetaldehyde as a reactant could create new reaction pathways. This is because ethanol dehydrogenation would no longer be the rate-determining step in the consecutive reaction chain.

Acknowledgement

Authors thank the financial support provided by the National Research, Development and Innovation Office, grant number FK20 134332 and also acknowledge the support from the European Regional Development Fund and the National Research, Development and Innovation Office, under the Interreg V-A Slovakia - Hungary Cooperation Program, SKHU/1902, (Project No: SKHU/1902/4.1/001), as well as under the China – Hungary Cooperation Program (Project No: 2024.-1.2.8-TÉT-IPARI-CN-2025_00063). One of the authors (G.N.) thanks for the support provided by the EKOP-25 University Excellence Scholarship Program of the Ministry for Culture and Innovation from the source of the National Research, Development and Innovation Fund (ELTE Eotvos Lorand University, Budapest, Hungary).

Tuning the Selectivity of Ethanol Steam Reforming over Cobalt-Containing Commercial Beta Zeolite Catalysts

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Keywords: Cobalt catalyst, Beta zeolite, Ethanol dehydration, Ethanol dehydrogenation

Ethanol steam reforming (ESR), described by the reaction $\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 6\text{H}_2 + 2\text{CO}_2$, is an efficient and environmentally friendly route to hydrogen production and has been extensively studied in recent years. It is an equilibrium-limited process with a complex reaction network involving multiple parallel and consecutive reactions. As a result, a variety of products can form, including H_2 , CO_2 , CO , CH_4 , C_2H_4 , acetaldehyde, and carbonaceous deposits. The reaction pathway strongly depends on the acid–base properties of the catalyst. In the presence of catalysts with acidic sites, ethanol readily undergoes dehydration to ethylene, which can further polymerise, leading to severe coke formation and catalyst deactivation. Therefore, ethanol dehydration should be minimised. In contrast, on catalysts with basic or redox sites, ethanol preferentially undergoes dehydrogenation to acetaldehyde, which can subsequently decompose into CO and CH_4 . Methane may be further converted via steam reforming or dry reforming at higher temperatures, thereby contributing to hydrogen production. Efficient conversion of CH_4 to H_2 is essential for maximising hydrogen yield. Carbon monoxide can be converted to CO_2 via the water–gas shift (WGS) reaction, which is desirable because CO is toxic in downstream applications such as fuel cells. In contrast, methanation of CO and CO_2 is undesirable because it consumes hydrogen and reduces overall H_2 selectivity. Catalyst deactivation in ESR is primarily associated with coke formation, originating from side reactions such as ethylene decomposition, methane decomposition, CO disproportionation, and acetaldehyde transformation [1,2].

As highlighted in [3], the limited application of zeolites in ESR is mainly due to their high density of acid sites, which promotes ethanol dehydration to ethylene, thereby accelerating coke formation and catalyst deactivation. Nevertheless, the excellent textural properties of zeolites make them attractive candidates for developing efficient ESR catalysts. Their performance can be improved by reducing acidity, for example, through alkali modification or by increasing the Si/Al ratio of the zeolite support [4]. Accordingly, cobalt-containing catalysts supported on commercial Beta zeolites with different Si/Al ratios were evaluated in ethanol steam reforming to control reaction selectivity.

The Co-modified zeolitic catalysts were thoroughly characterised using N_2 adsorption–desorption, XRF, XRD, TEM/EDX, H_2 -TPR, and NH_3 -TPD. These techniques were employed to investigate the structural, textural, and morphological properties of the catalysts, as well as their acidity and reducibility. Their catalytic performance in ethanol steam reforming was evaluated at an ethanol/ H_2O molar ratio of 1:12 and at 500 °C, with a focus on hydrogen selectivity and the distribution of carbon-containing products.

As expected, the catalytic performance strongly depends on the Si/Al ratio of the zeolite support. For clarity, Fig. 1 presents ethanol conversion and product selectivity measured after 12 h of the ESR process as a function of the Si/Al ratio. As shown in Fig. 1A, under the applied conditions, complete ethanol conversion (100%) was achieved for all catalysts, regardless of the Si/Al ratio (12.5–150). However, significant differences in product selectivity were

observed (Fig 1A and B). The selectivity toward H_2 increases almost linearly with increasing Si/Al ratio, from approximately 27% to 81% (Fig. 1A). In contrast, the selectivity toward C_2H_4 decreases from about 69% for Co/Beta-12.5 to approximately 34% for Co/Beta-150. This behaviour can be attributed to the decreasing acidity of the zeolite with increasing Si/Al ratio, which suppresses ethanol dehydration to ethylene and promotes pathways leading to hydrogen formation. At the same time, lower acidity favours ethanol dehydrogenation to acetaldehyde, which can be further converted into reforming products, thereby enhancing H_2 selectivity.

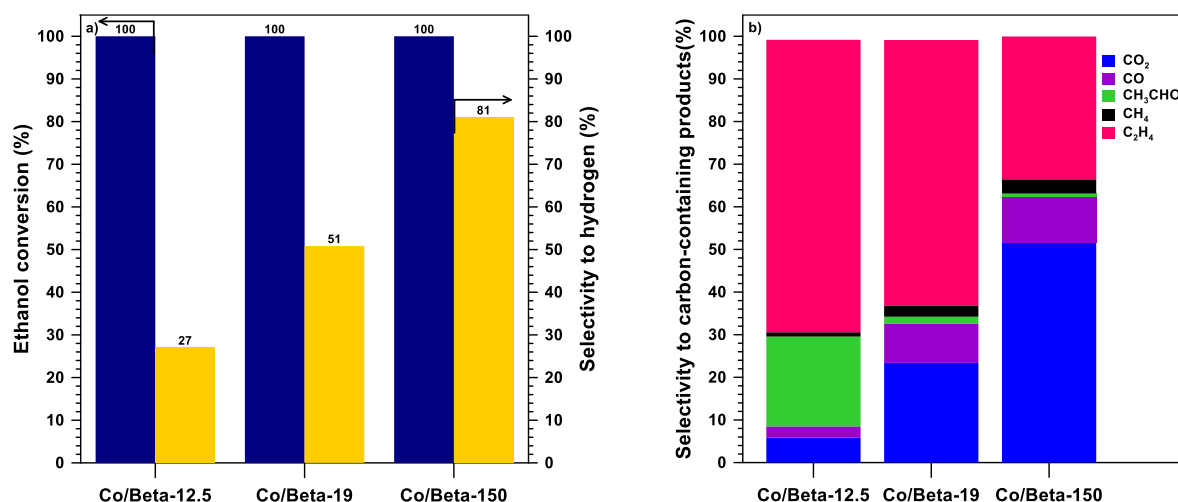


Fig. 1: The ethanol conversion (A) and selectivity to H_2 (A) and carbon-containing products in the 12th hour of the ESR reaction at 500 °C for ethanol/ H_2O molar ratio of 1:12 for the series of cobalt catalysts supported on Beta zeolite differing in Si/Al.

Post-mortem STEM-EDS characterisation confirmed the formation of carbonaceous deposits on the surface of all catalysts. These deposits are mainly associated with ethanol dehydration to ethylene on acidic sites, followed by its polymerisation and subsequent carbon formation.

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Tailoring Silanol Defects in Silicalite for Stabilization of Encapsulated Copper Nanoparticles

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Keywords: Silicalite, silanol defects, Cu nanoparticles, FTIR, CO adsorption

Copper nanoparticles (CuNPs) encapsulated within silicalite (pure-silica **MFI** zeolite) have attracted significant attention due to their high catalytic efficiency across a wide range of catalytic applications [1, 2]. However, their tendency to sinter or agglomerate, driven by the high surface energy, remains a major challenge, as it reduces the active surface area and alters the electronic properties imparted by the zeolite microenvironment.

Pure silica zeolites represent promising host matrices due to the presence of structural defects and silanol groups, which can act as anchoring sites for copper species. These silanol defects can be located either within the zeolite's internal framework or on its external surface. Internal silanol groups typically originate from framework imperfections or imbalances, whereas external silanols serve to complete the valence requirements of surface oxygen atoms. Three principal types of silanol defects are commonly identified: (i) isolated (terminal) silanols, (ii) connectivity defects, and (iii) silanol nests associated with T-site vacancies [3, 4]. The concentration and distribution of these defects can be finely tuned by adjusting synthesis parameters such as the organic structure-directing agent (OSDA)/silica ratio, crystallization temperature, and aging time. In the present study, synthesis conditions were specifically tailored to maximize the formation of internal silanol nests, which are expected to play a crucial role in stabilizing ultra-small CuNPs.

Under mild hydrothermal conditions, prolonged silica aging (18 h) in tetrapropylammonium hydroxide (TPAOH) (OSDA/SiO₂ = 0.24), combined with low-temperature crystallization at 90 °C, produced spherical silicalite (**S-1,1**) nanocrystals (~120 nm), as determined by SEM analysis. Nitrogen physisorption analysis revealed a high external surface area (165.5 m²·g⁻¹) along with significant microporosity. These mild hydrothermal conditions promote the generation of abundant framework defects, particularly silanol nests. Fourier-transform infrared (FTIR) spectroscopy confirmed a high concentration of silanol species, evidenced by a sharp absorption band at 3740 cm⁻¹ corresponding to isolated external silanols, and a broad band centered around ~3515 cm⁻¹ attributed to hydrogen-bonded hydroxyl groups. The latter is characteristic of internal silanol nests or Si–OH···O–Si clusters [3, 5]. Di-tert-butylpyridine (DTBP) adsorption, limited to the external sites due to the large size of the probe molecule, indicated that part of the silanol defects is located on the external surface.

In contrast, increasing the OSDA/SiO₂ ratio to 0.4 and the crystallization temperature to 170 °C led to the formation of larger well-defined irregular hexagonal crystals (~157 nm). This silicalite material (**S-1,2**) exhibited a slightly reduced external surface area (142.5 m²·g⁻¹) while maintaining well-defined microporosity, as confirmed by nitrogen physisorption. FTIR analysis indicated a lower concentration of external silanol groups than in nanocrystalline silicalite. Two distinct peaks at ~3726 cm⁻¹ and ~3690 cm⁻¹ were clearly observed and assigned to internal silanols (associated with connectivity defects) [6], while a broad band at ~3444 cm⁻¹ was

attributed to the hydrogen-bonded silanol species. Further modification by potassium incorporation (~ 0.25 wt%) significantly modified the silanol distribution (**K/S-1**). Potassium cations interact with silanol groups, reducing defect density and promoting crystal growth, resulting in larger particle sizes (~ 237 nm) and a progressive decrease in the intensity of the 3444 cm^{-1} band, confirming the reduction of hydrogen-bonded silanol nests.

To investigate the role of internal silanol defects in stabilizing CuNPs, copper was introduced either during the synthesis or *via* post-synthetic impregnation. For the direct synthesis route, polyamines of different sizes, ethylenediamine (En) and tetraethylenepentamine (TEPA), were used to form stabilized $[\text{Cu}(\text{En})_2]^{2+}$ and $[\text{Cu}(\text{TEPA})]^{2+}$ complexes, respectively. These complexes were incorporated into precursor gels containing silica, OSDA, and water, and the resulting gels were then used directly for hydrothermal synthesis under conditions identical to those used for the parent silicalite. Alternatively, copper was introduced by post-synthesis wet impregnation of the prepared silicalites using a copper nitrate solution.

The resulting Copper-encapsulated and impregnated silicalite samples were reduced *in-situ* under hydrogen flow and characterized by interaction with CO molecules. Titration of the Cu particle surfaces (performed by volumetric measurements of CO adsorption isotherms) was employed to estimate the nanoparticle size. Analysis of stretching frequencies of CO adsorbed on the surface of CuNPs (measured by FTIR spectroscopy) was used to determine their electronic properties. Characterization of CuNPs indicated that they were highly dispersed, with particle sizes below 2.0 nm for a **S-1,1** and around 3.7 nm for a **S-1,2**. A higher concentration of internal defects/silanols increases the positive charge on the CuNPs, thereby influencing their intrinsic catalytic activity in ethanol dehydrogenation.

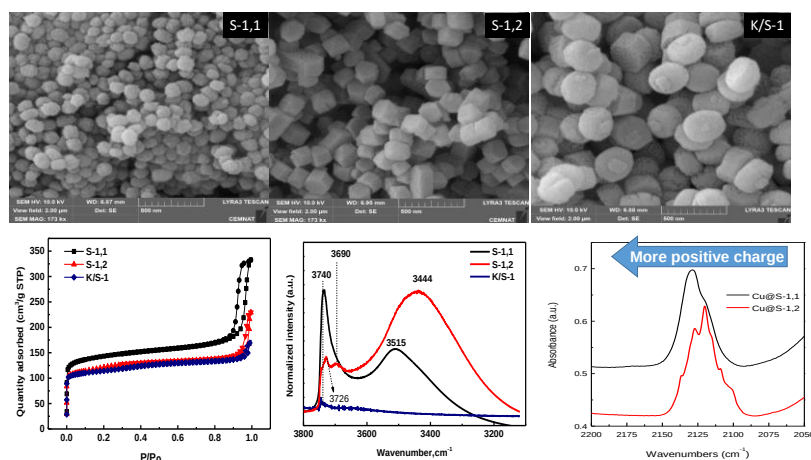


Fig. 1: Characterization of **S-1** zeolites, SEM images (top), N_2 adsorption isotherms (bottom left), FTIR spectra of SiO-H vibrations (bottom middle), and carbonyls at 3 mbar, 25°C , on reduced Cu@S-1 samples (reduction at 250°C in 25 mbar H_2 for 1 h)

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Acknowledgement

This study was financially supported by the Czech Science Foundation under the project no. 24-10766S.

Flame Spray Pyrolysis vs. Pechini Synthesis: Exsolution Behaviour Testing Done Twice Fold

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Keywords: Flame spray pyrolysis, Pechini, Perovskite, Exsolution

Introduction

Flame spray pyrolysis (FSP) serves as a novel method for synthesizing perovskite-type oxides. Perovskite type oxides are known for their capability to grow catalytically active metallic nanoparticles right from the lattice on the surface of the material, with the process being known as exsolution [1]. The advantage of the material is the on-demand production of said nanoparticles in reductive environments followed by the regeneration of the material in oxidizing atmospheres and its promising potential for the application in the global energy transition [2]. The chosen synthesis method stands out with its exceptional control over morphology, crystal size and specific surface area [3], resulting in an outstanding catalytic activity by addressing more active centers. The focus of this investigation is the reduction, thus the exsolution behavior, of the FSP perovskite type-oxides compared to the exsolution behavior of materials synthesized via a modified Pechini method.

Methodology

A- and B-site doped perovskite-type oxides with the formula $\text{Nd}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.9}\text{Cu}_{0.1}\text{O}_3$ (NCF-Cu10) were synthesized via FSP. For the evaluation of the reduction properties reactor treatments in oxidizing and reductive environments at different temperatures were performed. The macroscopic structure was characterized by the utilization of BET and PSA measurements, regarding the specific surface area and particle sizes. The exsolution properties were assessed using TPR measurements. Additionally, subsequent XRD measurements of the *ex-situ* reduction experiments were performed. Furthermore, *in-situ* pXRD measurements were conducted to corroborate the results.

Results and discussion

By comparing *in-situ* pXRD measurement of the Pechini synthesized material with the FSP synthesized material under a reductive environment, it becomes apparent that the operation window for exsolution of metallic nanoparticles for the FSP samples becomes significantly smaller and is by addition also shifted to higher temperatures. On the contrary TPR measurements uncover a shift to lower temperatures, indicating an early onset of reduction, indicating the growth of small metallic particles, which are undetectable in pXRD. On top of that, SEM images reveal the difference in morphology between both synthesis methods and BET measurements show a tremendous difference in specific surface area.

Conclusion

The investigated materials were proven to exhibit the same chemical structure but differ in the physical properties. The macroscopic structure was characterized by BET and SEM, revealing

differences in surface area and morphology. The influence of the synthesis method on the exsolution behavior was obtained by *in-situ* pXRD measurements obtained at DESY beamline P02.1. In conclusion, the introduction of a new synthesis method offers exciting possibilities in fine-tuning the properties of the material by deciding which synthesis is to be used determined by the use case of the material.

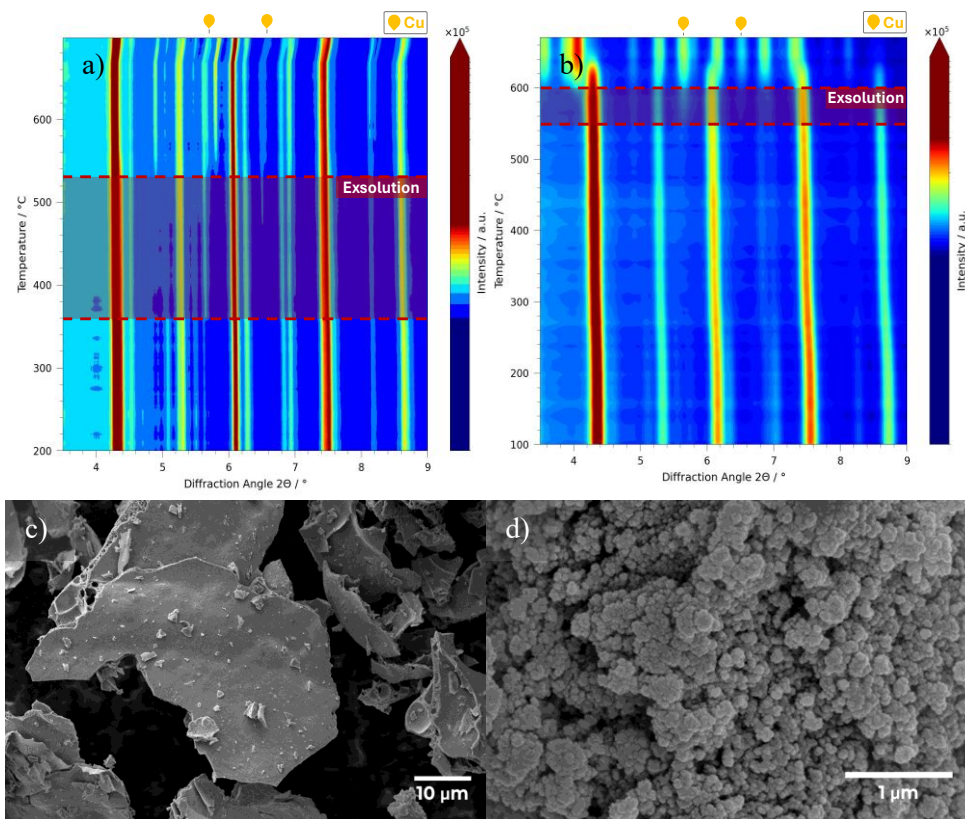


Fig. 1: a) *in-situ* pXRD study of the exsolution behaviour of Pechini synthesized NCF-Cu10; b) *in-situ* pXRD study of the exsolution behaviour of FSP synthesized NCF-Cu10; c) SEM image of Pechini NCF-Cu10 reveals a coarse flaky structure; d) SEM image of FSP NCF-Cu10 reveals a fine globular structure.

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Acknowledgement

This research was funded in part by the Austrian Science Fund (FWF) [10.55776/COE5] (Cluster of Excellence MECS)

We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III and we would like to thank Henrik Jeppesen and Martin A. Karlsen for assistance in using P02.1. Beamtime which was allocated for proposal I-20211526 EC and I-20240893 EC.

Influence of NO and H₂O on NH₃-SCO over calcined hydrotalcite–zeolite composites

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Keywords: zeolite acidity, ammonia oxidation, hydrotalcite, mixed oxides, copper

Ammonia (NH₃) is classified as an air pollutant leading to eutrophication and acidification of water systems, and can be effectively removed from waste gases by low-temperature selective catalytic oxidation of ammonia (NH₃-SCO, ≤ 400 °C) (1,2). Despite extensive research, achieving high selectivity toward dinitrogen (N₂) remains a significant challenge, highlighting the need for advanced catalyst design. This work presents six calcined hydrotalcite–zeolite composites prepared according to a previously reported synthesis protocol (3). Zeolite ZSM-5 with varying Si/Al ratios served as the support, while Cu-Mg-Al hydrotalcite acted as a precursor of the active phase. Upon *in-situ* thermal decomposition (550 °C), highly dispersed copper oxide species and mixed metal oxides (MMOs) were formed on the zeolite surface.

Composites were characterized by analytical methods (XRD, H₂-TPR, NH₃-TPD and by TPD-H₂O) and tested in NH₃-SCO. XRD confirmed the formation of desired hydrotalcite phase after the coprecipitation step and stability of the zeolite ZSM-5 support. However, CuO species and spinel phases were not detected by XRD after calcination, indicating high dispersion or amorphous character of copper species. On the other hand, H₂-TPR profiles exhibited reduction peaks below 250 °C, which can be attributed to the reduction of highly dispersed CuO species to metallic Cu (2) thus confirming CuO presence in the catalysts. The acidic properties of the prepared materials were investigated by temperature-programmed desorption of ammonia (NH₃-TPD), providing insight into both the strength and distribution of surface acid sites.

The catalysts with ZSM (6) and Y (5.2) exhibited very promising NH₃-SCO performance, with NH₃ conversion exceeding 80 % already at 300 °C (WHSV = 1000 ml·min⁻¹g⁻¹) and N₂ selectivity remaining above 90 % within the entire temperature range of 225–375 °C. For these samples, additional catalytic tests were performed in the presence of NO and H₂O to evaluate the effect on the NH₃-SCO performance. In the presence of NO, enhanced NH₃ conversion was observed at lower temperatures compared to the dry conditions. Selectivity remained stable around 98 % during the whole temperature range. This improvement might be attributed to the contribution of parallel reaction pathways, including selective catalytic reduction (SCR) - like interactions between NH₃ and NO, which promote more efficient NH₃ removal under these conditions (4).

On the other hand, the observed trends for tests with H₂O showed that the NH₃ conversion was lower compared to dry conditions. This might suggest competitive adsorption between NH₃ and H₂O, influenced by the surface acidity of the samples, which is determined by the support material used. Water induced a slight but partially irreversible modification of the catalyst, as the NH₃ conversion did not fully return to its initial level after switching back to dry conditions. Subsequent exposure to H₂O did not lead to further decline in conversion after its removal, suggesting that only a limited fraction of active sites was permanently affected, while the majority remains unaffected (**Fig.1**).

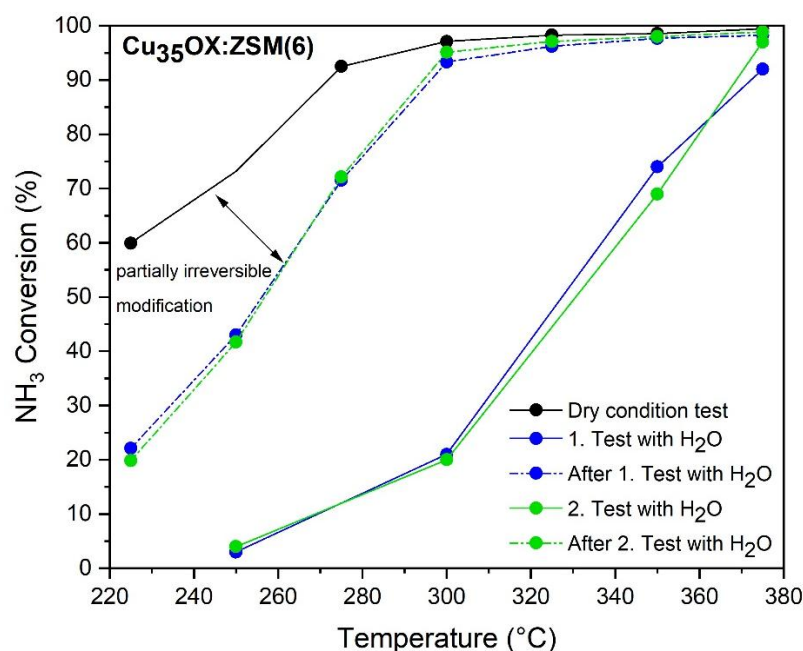


Fig. 1: NH₃ conversion of Cu₃₅OX:ZSM(6) in dry conditions and in the presence of H₂O. Composition of reaction mixture: 350 ppmv of NH₃, 10 mol.% of O₂, 2,8 mol.% of O₂, N₂ balanced. WHSV: 1000 mL·min⁻¹·g⁻¹.

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Acknowledgement (optional)

Experimental results were accomplished by using Large Research Infrastructure ENREGAT supported by the Ministry of Education, Youth and Sports of the Czech Republic under project No. LM2023056.

The work was supported by the OP JAK project "INOVO!!!", No. CZ.02.01.01/00/23_021/0008588 supported by the Ministry of Education, Youth and Sports and co-financed.

Glycerol oxidation catalysed by 3D-graphene supported Pt

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Keywords: glycerol oxidation, graphene, Pt catalysts

Introduction

Glycerol is obtained in large quantities as by product in the biodiesel production process and its management is considered an important issue, as the global biodiesel production is increasing. Also, glycerol with three carbon atoms and three hydroxyl groups, can be an important platform molecule for a large variety of useful compounds [1]. So, the identification of optimum catalysts and reaction conditions to transform glycerol in valuable compounds is an important and actual research area.

Graphene based catalysts were investigated in the recent years for a large variety of processes: oxidation, hydrogenation, reformation etc. [2]. One major disadvantage of these catalysts is their tendency to restack, losing the graphene structure's advantages. To avoid this process, one solution is to prepare 3D structured graphene based materials, which combine the stability of a meso-macro porous material and the specific properties of graphenes [3].

In this study Pt catalysts deposited on a 3D-reduced graphene oxide (3DG) support were prepared, characterized and tested in glycerol oxidation in mild conditions.

Methodology

The 3D graphene was prepared through hydrothermal synthesis. The GO-water mixture was sonicated with an ultrasonic processor for 2h, then placed in an autoclave and heated at 180°C, under autogenous pressure, for 24h. After cooling to ambient temperature, the resulted black monolith, was dried by freeze-drying to preserve the porous structure. The Pt/3D-rGO catalyst with platinum target concentration of 2 wt.% was prepared by incipient wet impregnation method, followed by thermal reduction in (H_2+Ar) (10 vol.% H_2) for 1h at 250°C.

The resulted catalyst was characterized by: (i) powder X-Ray diffraction to investigate the support crystallinity; (ii) N_2 adsorption-desorption isotherms to calculate the surface area and meso-porosity; (iii) electronic microscopy (SEM and TEM) to reveal the porous structure and metal nanoparticles size and dispersion.

Results

Following the preparation method described above, meso-macroporous catalysts with very highly dispersed Pt nanoparticles were successfully prepared (Fig 1).

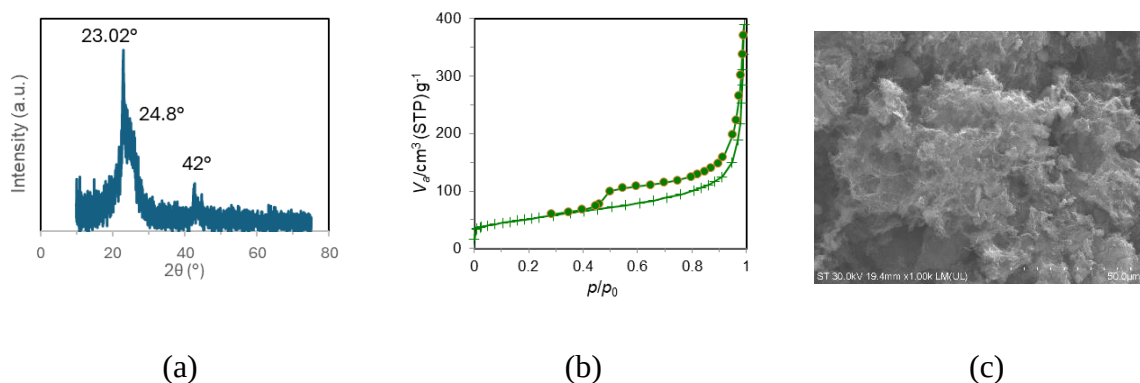


Fig. 1: Structural characterization of Pt/3DG (a) XRD pattern; (b) N_2 adsorption-desorption isotherm; (c) SEM image

The catalytic results are presented in Fig.2.

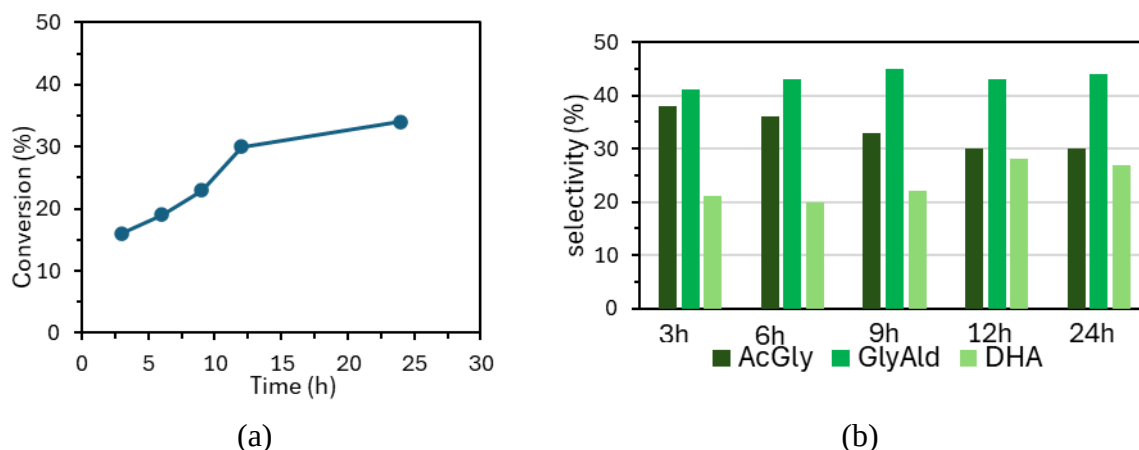


Fig. 2: Catalytic results in glycerol oxidation by Pt/3DG; variation of (a) conversion and (b) selectivity with reaction time (40°C, 2 bar)

Discussion

XRD pattern presents the specific peak of reduced graphene oxide situated at 23-24.8°. By deconvoluting the peak, two types of carbon was revealed, confirmed also by TGA investigation. The carbon is structured as mostly few layers graphene (5 C layers) with insertions of low number carbon layers graphite (25 C layers). The total surface area of catalyst is 80 m²/g with very large distribution of pore's size: from mesopores to macropores. The SEM investigation revealed the porous structure of support confirming the structuring of graphene layers in a 3D structure. The SEM investigation showed the presence of low dimension PtNPs (3-5 nm) well dispersed on the support.

The catalysts were investigated at low temperature (40°C) and pressure (2bar) in a glass reactor. The conversion of glycerol increased significantly in the first 12h of reaction and then with only few percents in the next 12 h. The identified reaction products were: glycolic acid (AcGly), glycolic aldehyde (GlyAld) and dihydroxyacetone (DHA). Fig. 2b shows that by increasing the reaction time the selectivity for AcGly decreases and for DHA decreases.

Conclusions

New catalyst with dispersed PtNPs deposited on 3D graphene were prepared and characterized. Their catalytic activity for glycerol partial oxidation in mild conditions (40°C and 2 bar) provide promising results in terms of activity.

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Acknowledgement

The authors acknowledge financial support from the "Nucleu" Program within the National Research Development and Innovation Plan 2022–2027, Romania, carried out with the support of MEC, project nr. 27N/03.01.2023, component project code PN 23 24 01 01.

Oxidative transformation of cellulose

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Keywords: formic acid, cellulose, oxidation, vanadium catalysts

Formic acid is an important raw material widely used in many industries such as chemical, leather, textile, pharmaceutical, and agricultural. In recent years, it has been proposed as a reversible hydrogen storage source, for example for proton exchange membrane fuel cells as a possible hydrogen generator [1]. Formic acid is currently produced mainly from fossil sources. An alternative is the oxidation of cellulose in water in the presence of soluble homogeneous catalysts (the Keggin-type structure of $\text{H}_4\text{PMo}_{11}\text{VO}_4$) using oxygen, which provides approximately 66 % yield of formic acid [2]. A limited number of papers describe the investigation of the transformation of cellulose to formic acid using oxygen over heterogeneous catalysts. Over micellar Mo-V-P heteropoly acids catalysts the yield of formic acid 40 mol % was reached [3].

In our work, we investigated the catalytic performance of vanadium catalysts based on silica in the transformation of cellulose to formic acid with molecular oxygen in an aqueous system. The influence of the used support and the amount of vanadium on the activity of the vanadium catalyst based on silica and selectivity to formic acid, as well as glucose and acids with higher carbon chains, e.g. acetic and lactic acid, was studied.

Commercial SiO_2 , Aerosil 200 and Sylobloc 700, were used for preparation of vanadium catalysts. Supported metal oxide catalysts were prepared by the wet impregnation method. The oxidation experiments were carried out in a stirred batch reactor lined with glass at temperature of 180 °C and pressure of oxygen 0.8 MPa. The reaction mixture was analyzed by means of HPLC and GC methods.

A significant effect of vanadium on cellulose transformation was observed in the presence of prepared vanadium catalysts on silica. It was found that cellulose conversion and the yield of formic acid, glucose and acetic acid depended on the amount of vanadium. The addition of molybdenum to the vanadium supported catalyst had only a small effect on the formation of formic acid and acetic acid compared to the pure vanadium catalyst. Over this catalyst, the conversion of cellulose reached 100 % with formic acid yield of 34 %. Increasing the reaction temperature from 150 °C to 180 °C greatly enhanced the reaction rate of cellulose conversion and formic acid formation. However, increasing the temperature to 200 °C had a negative effect on the yield of formic acid, which is consistent with literature data. The Mo-V catalyst was easily separated from the reaction mixture by filtration and used in subsequent runs.

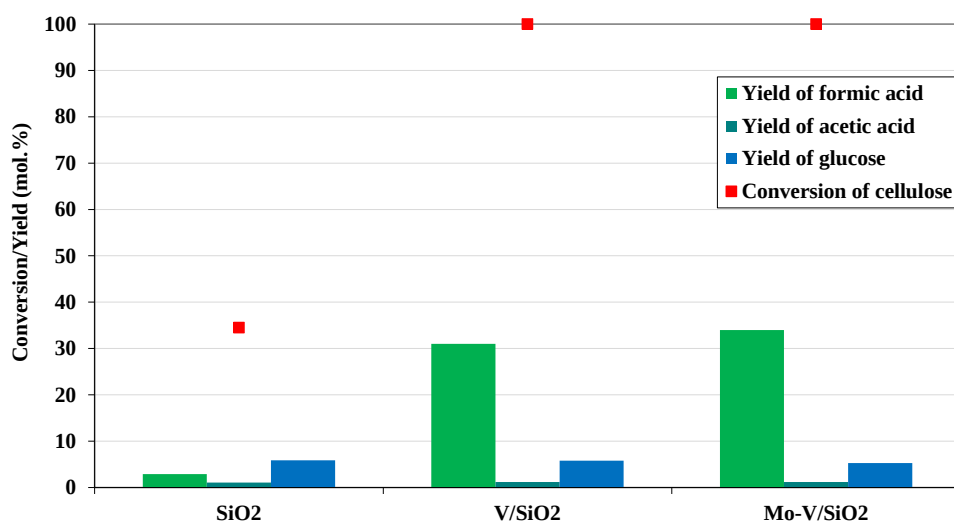


Fig. 1: Oxidative transformation of cellulose in experiments carried out over vanadium catalysts based on silica

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Acknowledgement

This work was supported by the Slovak Research and Development Agency under the Contract no. VV-MVP-24-0331

A Bio-Based Polymer Designed for Cars as a Tool for Organic Chemistry

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Keywords: polymer support, heterogeneous catalysis, palladium, copper, carboxylic acid activator

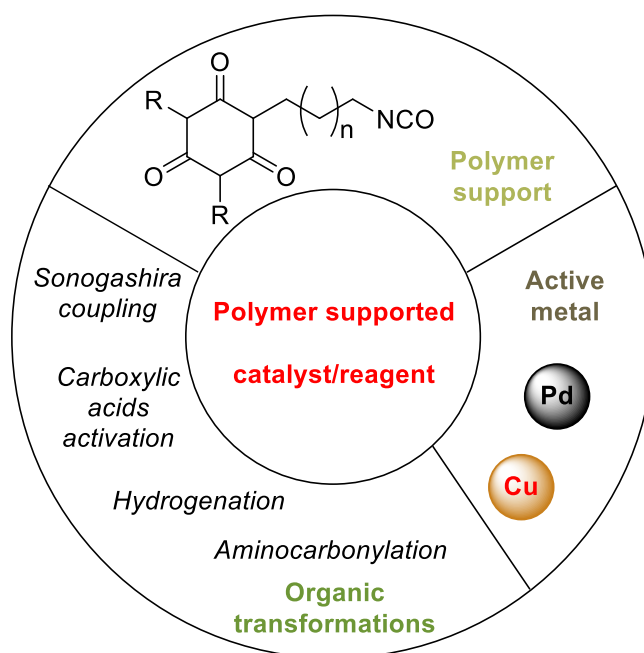
Heterogeneous polymer-supported catalysts have attracted considerable interest as sustainable alternatives to classical homogeneous catalytic systems in organic synthesis [1]. Their major advantages include facile separation from reaction mixtures, catalyst recyclability, reduced metal contamination of products, and improved compatibility with green chemistry principles. Compared with their homogeneous analogues, polymer-supported systems often simplify downstream purification while maintaining high catalytic efficiency and chemical stability. In addition, polymeric matrices provide tunable architectures, adjustable porosity, and high densities of functional groups suitable for catalyst immobilization or direct chemical reactivity.

Recent advances in functional polymer chemistry have enabled the exploration of unconventional industrial polymers as catalytic platforms. In this context, polyisocyanate-based materials are particularly attractive due to their highly reactive isocyanate functionalities, crosslinking capability, and ability to generate durable three-dimensional polymeric networks [2]. Although polyisocyanates are predominantly employed in polyurethane materials for automotive coatings, adhesives, and lightweight composites, their intrinsic chemical reactivity suggests significant untapped potential in heterogeneous organic synthesis.

In this work, we present the development of a novel group of bio-based polyurea-supported metal catalysts derived from a naturally occurring cadaverine-based scaffold, which were subsequently functionalized using various chemical modifiers [3]. The prepared catalysts demonstrated high catalytic activity together with excellent structural stability of the polyurea matrix. Moreover, the presence of nitrogen-containing functional groups within the polymer network effectively stabilized the metal species, leading to suppressed metal leaching even after repeated catalytic cycles under demanding reaction conditions.

These supported catalysts were successfully applied in the aminocarbonylation of aryl halides using a CO surrogate [4], in the hydrogenation of nitrobenzenes, in Sonogashira coupling employing bimetallic catalyst, and also as polymer-supported equivalents of DCC in activation of carboxylic acids.

Fig. 1:



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This work was supported by the Slovak Research and Development Agency under the Contract no. VV-MVP-24-0331.

Hydroconversion of cresol over Ni/Al₂O₃ based catalysts

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Keywords: Hydrodeoxygenation, Cresol, Heterogeneous catalysis, Ni/Al₂O₃

The irreversible effects of climate change and the efforts of the global energy industry have made the urgent need for a quick switch to a sustainable and environmentally friendly, low-CO₂ energy system. This transition, together with the implementation of circular economy principles, increases the importance of using plant waste as a raw material. Although using lignocellulosic biomass often results in CO₂ emissions, it is still considered a green energy source because the same amount of CO₂ is released during natural decomposition processes. Converting lignocellulose yields oxygen-rich compounds. One method of converting these oxygenates into renewable fuels and chemicals is catalytic hydrodeoxygenation (HDO) [1].

Cresol (CRE) is widely used as model feedstock for HDO of bio-oxygenates. The HDO reaction of CRE can lead to a variety of fully or partially deoxygenated products. Saturated hydrocarbons (methylcyclohexane, cyclohexane) can be used as fuels or non-polar solvents. Aromatic products like toluene and benzene are important precursors of many commercial chemicals and polymers. The partially reduced products like cyclohexanone and cyclohexanol are industrial precursors of nylons, while phenol serves as a precursor to a large array of drugs, herbicides, and plastics [1,2].

Our previous results show that the support acidity and the hydrogenation activity of the metal play a key role in the activity and stability of the catalysts in the HDO of phenolic compounds. We have demonstrated that Lewis and Brønsted acid sites on the catalysts are essential for producing oxygen-free liquid products as they facilitate the cleavage of phenolic OH groups. However, the strong Brønsted acid sites are unfavorable due to their high activity in aromatic condensation reactions leading to coke deposition and rapid loss of activity. Alumina-supported Ni catalyst shows excellent activity and stability in HDO of phenolics producing saturated and unsaturated hydrocarbons as well as cyclohexanol depending on the reaction conditions. However, the strong interaction between the small NiO clusters and the alumina leads to a very low degree of reduction and small number of active metallic sites [3,4].

This study aims to improve the reducibility of the nickel by modifying the alumina support with different oxides (CeO₂, ZnO, ZrO₂), thereby increasing the activity of the catalyst. The catalyst was modified using a simple wet impregnation method. First, the metal oxide precursor was impregnated onto the Al₂O₃ support. Then, the Ni precursor compound was impregnated. The Ni and metal oxides contents were 5 and 20 wt%, respectively. The reducibility and the H₂ adsorption capacity of the catalysts was studied using H₂-TPR and H₂-TPD methods, respectively. The structure of the catalysts was characterized using XRD, in situ XRD, TEM, SEM, XPS, and N₂ adsorption/desorption methods. The acid-base properties of the catalysts was studied by the FT-IR spectroscopic examination of adsorbed pyridine.

The activity of the catalysts was tested in the HDO reaction of the CRE model compound using a fixed-bed, flow-through, high-pressure microreactor system. The effect of surface modification and the reaction conditions on the catalyst activity and selectivity was studied.

The XRD patterns of the calcined catalyst precursors shows that γ -Al₂O₃ is the only detectable phase in the Ni/Al₂O₃, Ni/CeO₂/Al₂O₃ and Ni/ZrO₂/Al₂O₃ catalysts. This indicates that the NiO, as well as CeO₂ and ZrO₂ are highly dispersed on the alumina support. The XRD pattern of the Ni/ZnO/Al₂O₃ catalyst shows the reflections of ZnAl₂O₄ and ZnO phases. Prior to the catalytic runs, the catalysts underwent in situ reduction in the reactor at 450 °C for 2 hours. H₂-TPR results show that the reduction degree of the Ni/Al₂O₃, Ni/CeO₂/Al₂O₃, Ni/ZnO/Al₂O₃ and Ni/ZrO₂/Al₂O₃ catalysts were 0.5 %, 6 %, 24 % and 14 %, respectively, when reduced under the same conditions. Pyridine adsorption revealed that the γ -Al₂O₃ support contains strong and medium-strong Lewis acid sites. Modifying the alumina with metal oxides slightly reduced the Lewis acidity of the support.

The activity of the catalysts in the CRE hydrodeoxygenation was studied at 225 °C, 10 bar total pressure, and a space time of 0.05 (g_{cat}/g_{CRE})*h. Under these reaction conditions, methylcyclohexanol (MCHL) and methylcyclohexane (MCHA) were formed as main products. The activity of the Ni/CeO₂/Al₂O₃ and Ni/ZnO/Al₂O₃ catalysts were stable during the 25 h time-on-stream (TOS), while the CRE conversion was around 95 %. In contrast, the activity of the Ni/Al₂O₃ and Ni/ZrO₂/Al₂O₃ catalysts decreased from 95 % to 64 and 74 %, respectively after 25 h TOS. These results demonstrate that modifying the alumina surface with CeO₂ or ZnO could significantly improve the activity and stability of the Ni/Al₂O₃ catalyst, whereas ZrO₂ was found to be a less effective modifier. Catalytic experiments that varied the space time revealed that CRE hydroconversion to MCHA occurs through the intermediates methylcyclohexanone, MCHL, and methylcyclohexene.

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Acknowledgement (optional)

Supported by the EKÖP-25 University Research Scholarship Program of the Ministry for Culture and Innovation from the Source of the National Research, Development and Innovation Fund. Authors also thank the financial support provided by the National Research, Development and Innovation Office, grant number FK20 134332 and acknowledge the support from the European Regional Development Fund and the National Research, Development and Innovation Office, under the Interreg V-A Slovakia - Hungary Cooperation Program, SKHU/1902, (Project No: SKHU/1902/4.1/001), as well as under the China - Hungary Cooperation Program (Project No: 2024.-1.2.8-TÉT-IPARI-CN-2025_00063).

CO₂ cycloaddition to styrene oxide over silica-based catalysts containing CTAB

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Keywords: CO₂ cycloaddition, Styrene oxide, Mesoporous silica, MCM-41, CTAB

Carbon dioxide is one of the main components of greenhouse gases and its increasing emissions are considered one of the major causes of global warming and ongoing climate change.[1] At the same time, CO₂ represents an abundant, non-toxic and economically attractive C1 building block for the synthesis of value-added chemicals.[2] Among the available approaches, the cycloaddition of CO₂ to epoxides is one of the most efficient routes for the preparation of cyclic carbonates [1], which are widely used as solvents, electrolytes and intermediates in the chemical industry.[3, 4] Although the reaction can proceed without a catalyst under harsh conditions [5], efficient conversion and selectivity are typically achieved only in the presence of suitable catalytic systems.

A non-calcined mesoporous silica-based catalyst MCM-41/CTAB was prepared, in which cetyltrimethylammonium bromide (CTAB) was intentionally retained within the porous structure. For comparison, CTAB-impregnated materials (MCM-41/CTAB_i) were also prepared. The prepared catalysts were characterized using range of analytical techniques, such as UV-Vis and FTIR spectroscopy, elemental analysis and nitrogen physisorption, to determine their composition, presence of CTAB and textural properties. The catalytic performance was evaluated in the cycloaddition of CO₂ to styrene oxide (Fig. 1) in a stainless-steel autoclave at 120 °C and 1.2 MPa. The influence of catalyst loading, co-catalyst type (KI, KBr, KCl, ZnBr₂), solvent (toluene, 1-methyl-2-pyrrolidone, *N,N*-dimethylformamide) and catalyst reusability was systematically investigated. Reaction mixtures were analyzed by GC-MS to determine conversion of styrene oxide and selectivity toward styrene carbonate.

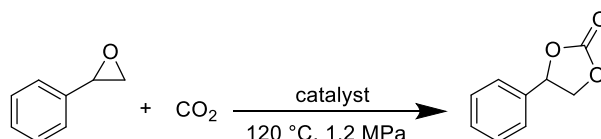


Fig. 1: Cycloaddition of CO₂ to styrene oxide

In the first stage, the non-impregnated MCM-41/CTAB catalyst was studied and reaction conditions were optimized. The presence of CTAB in the structure was confirmed by FTIR spectroscopy and elemental analysis. The highest styrene oxide conversion (97 %) was achieved in 1-methyl-2-pyrrolidone (NMP) using KI as a co-catalyst and 75 wt% catalyst loading, corresponding to a styrene carbonate yield of 19 %. The highest selectivity towards styrene carbonate (32 %) was obtained in dried *N,N*-dimethylformamide (DMF) under the same conditions, with a corresponding yield of 16 %, while similar selectivity (31 %) was observed in toluene (both dried and non-dried). Subsequently, CTAB-impregnated catalysts (MCM-41/CTAB_i) were investigated. These materials exhibited slightly lower conversion but significantly higher selectivity toward styrene carbonate. The best performance was obtained in presence of NMP, KI and 75 wt% catalyst loading, reaching 48% conversion of styrene oxide and 98% selectivity, corresponding to a styrene carbonate yield of 58 %.

The lower conversion observed for the impregnated catalysts is consistent with their lower CTAB content, as confirmed by FTIR spectroscopy and elemental analysis. In contrast,

nitrogen physisorption revealed differences in pore structure between non-impregnated and impregnated materials, with higher specific surface area, pore volume and larger pore diameter observed for the impregnated catalysts. This indicates that the pores are not blocked by CTAB, unlike in the non-impregnated material. The larger pore diameter and volume reduce steric hindrance, allowing the bulkier styrene carbonate molecule to fit more easily within the pore system, which probably leads to higher selectivity. As expected, increasing catalyst loading led to higher conversion. Among the tested solvents, NMP provided the highest conversion, which can be attributed to its low vapor pressure at the reaction temperature, ensuring a high partial pressure of CO₂ in the system and its favorable CO₂ solubility under reaction conditions. The use of KI as a co-catalyst resulted in the highest conversion, which can be explained by the high nucleophilicity of the iodide anion, facilitating the ring opening of the epoxide. Reusability tests showed a decrease in conversion after the first catalytic cycle, which can be attributed to a combination of pore blocking and partial leaching of the active species. Under the given reaction conditions, the extent of CTAB leaching was approximately 6 %, indicating that both loss of active sites and reduced pore accessibility contribute to the observed decline in catalytic performance. Drying of the solvent led to a slight increase in selectivity; however, this effect was not significant and comparable selectivity values were obtained across different solvents. Non-calcined MCM-41/CTAB represents an effective catalyst for achieving high styrene oxide conversion in CO₂ cycloaddition, while CTAB-impregnated materials provide significantly improved selectivity toward styrene carbonate. The balance between activity and selectivity can be tuned by catalyst design, contributing to a better understanding of factors influencing CO₂ cycloaddition processes.

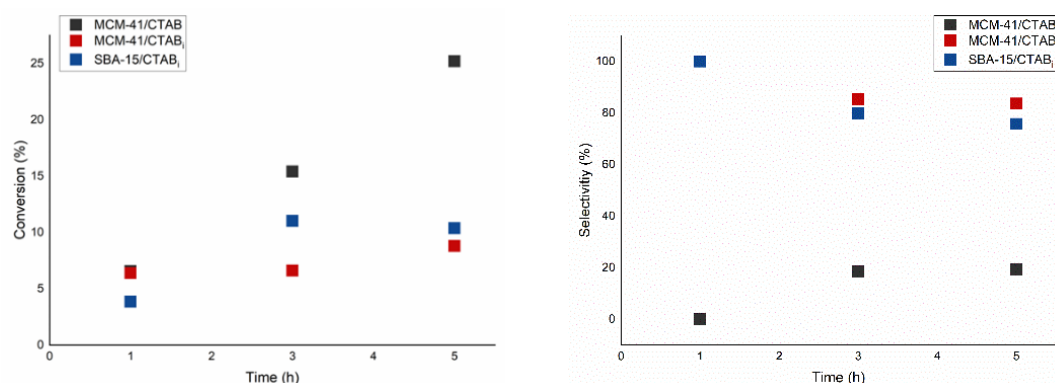


Fig 2: Comparison of reactions with different heterogeneous catalysts

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Limitations of zeolite supports for K-promoted Co–Mn–Al oxide catalysts in NO decomposition

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Keywords: mixed oxide, zeolite, NO decomposition, potassium

Co–Mn–Al mixed oxide catalysts modified with potassium are known to exhibit significant activity for the direct decomposition of NO in bulk form, where intimate contact between potassium and cobalt creates active sites and enhances surface basicity and facilitates key reaction steps [1]. In this work, we investigate the impact of dispersing such active phases onto a zeolite support (Beta, ZSM-5), with the aim of enhancing surface area and catalytic efficiency. Catalysts were prepared via hydrotalcite-like co-precipitation directly on the zeolite, followed by calcination. Potassium was introduced using three different approaches: co-precipitation, washing of the filter cake, and post-synthesis impregnation and compared with unsupported reference sample, where K was deposited on the Co-MnAl spinel by wet impregnation (referred as bulk).

Comprehensive characterization was performed using AAS, H₂-TPR, NO-TPD, CO₂-TPD, NH₃-TPD, XRD, and *in situ* FTIR spectroscopy. XRD analysis confirmed the formation of the spinel phase on the zeolite support, while AAS verified that the Co:Mn molar ratio corresponded to the intended composition. The specific surface area of the supported catalysts was 2–4 times higher than that of the corresponding bulk materials, indicating a beneficial effect of dispersion on textural properties. Catalytic performance was evaluated in NO decomposition between 500–800 °C. While reference bulk catalyst showed expected activity [2], all zeolite supported systems were inactive regardless of potassium incorporation method.

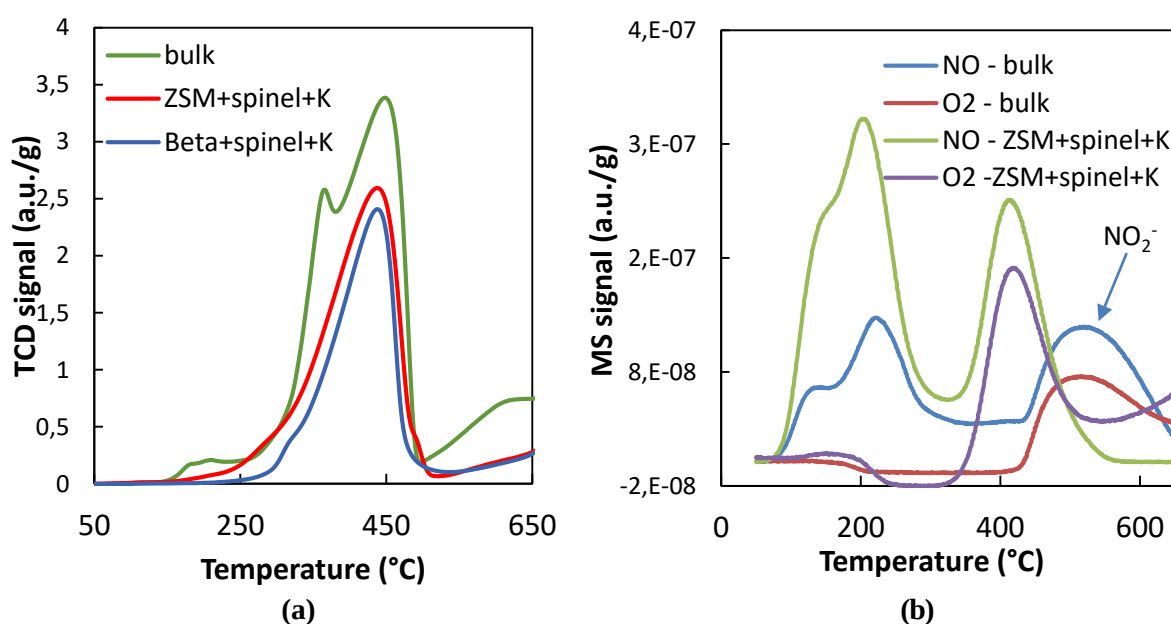


Fig. 1: (a) H₂-TPR results, **(b)** NO-TPD results, NO signal: $m/z = 30$, O₂ signal: $m/z = 32$.

The absence of catalytic activity is attributed to the lack of effective interaction between potassium and cobalt sites. Unlike bulk systems, where potassium increases surface basicity and promotes the formation and decomposition of key NO_2^- intermediates, supported catalysts did not exhibit corresponding features. H_2 -TPR results showed no modification of cobalt reducibility upon potassium addition (Fig. 1a), while NO-TPD profiles lacked desorption peaks associated with NO_2^- species (Fig. 1b). Similarly, CO_2 -TPD analysis revealed the absence of medium-strength basic sites typically induced by potassium, indicating that the promoter is not present in the vicinity of the active phase.

Although literature reports that, potassium can be stabilized in proximity to cobalt active sites even on zeolite supports [3, 4], this behaviour was not observed in the present system. The results suggest that potassium preferentially interacts with the zeolite framework and becomes incorporated into ion-exchange positions, even in the impregnated samples. This behaviour is likely enhanced by partial dealumination of the zeolite during co-precipitation of the hydrotalcite precursor resulting in the structure degradation, which generates additional exchange sites. Although this process may improve textural properties and accessibility of the active phase, it simultaneously promotes potassium sequestration within the support, leading to its spatial separation from cobalt oxide sites.

These findings highlight a fundamental incompatibility between ion-exchange supports and alkali-promoted oxide catalysts that rely on close promoter–metal interaction. To mitigate this limitation, several strategies can be considered, including the use of supports with low ion-exchange capacity, pre-saturation of zeolite exchange sites with competing cations, optimization of synthesis conditions to minimize desilication and dealumination, increasing potassium loading, or higher oxide phase coverage to partially shield the support surface. Such approaches may help maintain the necessary promoter–active phase interaction and restore catalytic performance.

Overall, the present results demonstrate that the beneficial effect of potassium promotion in Co–Mn–Al mixed oxides cannot be straightforwardly translated to zeolite-supported systems, as support–promoter interactions may dominate and lead to complete catalyst deactivation.

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Acknowledgement

This research was funded by the European Union under Research Excellence For REgion Sustainability and High-tech Industries (REFRESH) project No. CZ.10.03.01/00/22_003/0000048 via the Operational Programme Just Transition.

Experimental results were accomplished by using Large Research Infrastructure ENREGAT supported by the Ministry of Education, Youth and Sports of the Czech Republic under project No. LM2023056.

Pilot Scale Hydrogenation of Acetone to Isopropanol Using a Fixed Bed Raney-type Nickel Catalyst in Continuous Flow

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Keywords: Hydrogenation, Raney-type nickel, Fixed-bed, Pilot scale

The catalytic hydrogenation of acetone is a key process for producing isopropyl alcohol, a widely used industrial chemical [1]. Bio-produced acetone from CO₂ is intended for such transformation [2]. It offers an alternative to the common cumene process utilizing hydrocarbons from fossil sources. Acetone hydrogenation was carried out using a Raney-type nickel catalyst in a fixed bed continuous flow reactor. In large-scale applications, the utilization of the fixed-bed Raney-type catalysts is not very common. The current study focuses on optimization of this process at a pilot-scale. From there, it is intended to be further transferred to an industrial production level. Results from our previous lab scale experiments were taken as a starting point for the upscale-process optimization [3]. Our focus was directed towards optimized conversion, selectivity and overall throughput of the process. Main challenges were to handle relatively high exothermicity of the reaction and to maintain the reaction in the liquid phase. Finally, by using a cascade reactor setup (5L and 3L) with space velocity of LHSV=0.5 h⁻¹, both the conversion and the selectivity exceeded 99.5 % and a daily production of up to 30 L of isopropyl alcohol was achieved. Hence, the transfer of technology from the lab scale to the pilot scale was successful. These encouraging results suggest that the production of isopropyl alcohol from renewably sourced acetone using fix-bed Raney-type nickel catalyst exhibits high potential for industrial applications.

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Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 101037009.

Effect of Preparation Method on Cu/SiO₂ Catalysts for the Selective Hydrogenation of Cinnamaldehyde

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Keywords: Selective hydrogenation, Cinnamaldehyde, Cu supported catalysts, Catalyst preparation methods

3-Phenylprop-2-enal (cinnamaldehyde) is an important aldehyde widely used in the perfume, food, and pharmaceutical industries. In addition to its practical applications, cinnamaldehyde serves as a model substrate in studies of selective hydrogenation due to its molecular structure containing a conjugated C=C bond, a carbonyl (C=O) group, and an aromatic ring.

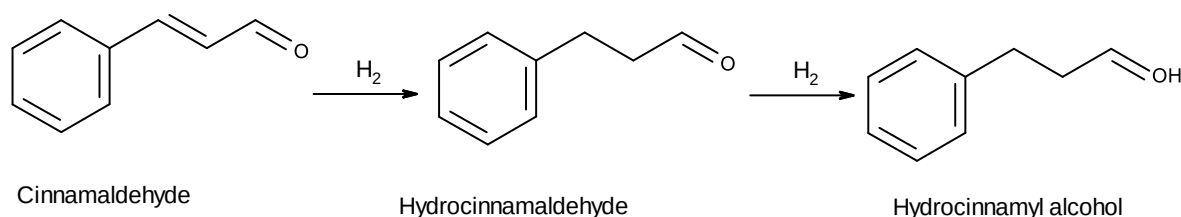


Fig. 1: Hydrogenation of cinnamaldehyde over Cu-supported catalysts

This combination enables detailed evaluation of catalyst selectivity toward different functional groups and provides valuable insights into structure–activity relationships in catalytic systems. Copper-based catalysts are commonly employed for the selective hydrogenation of cinnamaldehyde, as reported for various Cu/SiO₂ systems and modified catalysts in the literature. The catalytic performance has been shown to strongly depend on the preparation method, copper dispersion, particle size, and the nature of the support, with reported variations in activity and selectivity among Cu-based systems prepared by impregnation, ion exchange, or deposition techniques.¹⁻⁴ Despite extensive research, optimization of catalyst preparation routes remains essential to achieve high selectivity at high conversion.

The aim of this work was to investigate the effect of the preparation method on the physicochemical properties and catalytic performance of Cu/SiO₂ catalysts in the selective hydrogenation of cinnamaldehyde. Four different preparation methods were compared, including wet impregnation (WI), incipient wetness impregnation (IWI), chemisorption–hydrolysis (CH), and deposition–precipitation (DP). The catalysts were characterized using BET surface area analysis, XRD, TPR, and N₂O chemisorption in order to correlate textural properties, copper dispersion, and particle size with catalytic behavior.

Among the investigated catalysts, the DP-prepared Cu/SiO₂ catalyst exhibited the highest specific surface area, the smallest copper particle size, and the highest copper dispersion. These properties translated into superior catalytic performance, reaching 96 % cinnamaldehyde conversion with 96 % selectivity toward hydrocinnamyl alcohol after 5 hours of reaction. The high activity was attributed to the presence of finely dispersed copper nanoparticles and the thermal stability of the catalyst, allowing reduction at higher temperatures without significant

sintering.

For the DP-based catalyst, the influence of preparation parameters such as calcination temperature, calcination atmosphere, reduction temperature, and the type of silica support was further examined. While calcination temperature showed only a minor effect on selectivity, the type of silica significantly influenced surface area and product distribution. Catalysts prepared on Sipernat 50 silica exhibited increased selectivity toward the intermediate hydrocinnamaldehyde, whereas overall copper surface areas remained comparable across different supports.

The results demonstrate that the preparation method is a key factor governing the catalytic performance of Cu/SiO₂ catalysts. High copper dispersion and small particle size are critical for achieving high conversion and selectivity in the selective hydrogenation of cinnamaldehyde, providing guidance for the rational design of efficient copper-based catalytic systems.

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Ceramic Nanocarbon Composites for Application as Nanoparticle Catalyst Supports

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Keywords: Structured catalysts; carbon-coated ceramic foam; ruthenium nanoparticles; transfer hydrogenation; recyclability

Introduction

Structured ceramic foams are attractive catalyst supports because they combine mechanical robustness, open porosity, improved liquid handling, and facile catalyst recovery compared with conventional powder catalysts [1], [2]. This work investigates using biomass-derived tar as an adhesive coating for aluminium oxide based ceramic foams (CF, Lanik s.r.o) to adhere metal (ruthenium-based) nanoparticle catalysts for liquid-phase transfer hydrogenation. The study addresses a key practical challenge in heterogeneous catalysis: retaining the activity of Ru/C-type powder catalysts while improving separation, reusability, and operational handleability.

Methodology

Tar-derived carbon-coated ceramic foams were prepared by dip-coating, drying, and graphitisation, providing mechanically stable carbon-ceramic composites. Acetophenone transfer hydrogenation in isopropyl alcohol (IPA) was selected as the benchmark reaction [3]. Two catalyst-loading strategies were assessed: direct Ru₃(CO)₁₂ precursor decomposition onto tar-coated foams and IPA-assisted drop-casting of commercial Ru/C onto graphitised tar-coated foams. The resulting Ru/C@CF catalysts were evaluated for catalytic activity, product yield, ease of recovery, and recyclability over repeated reaction cycles.

Results and Discussion

Direct decomposition of Ru₃(CO)₁₂ on the structured foam was unsuitable for producing an active catalyst. In contrast, drop-casting commercial Ru/C from IPA onto graphitised tar-coated foams produced a recoverable structured catalyst with clear catalytic activity [1]. Although its activity per Ru mass was lower than that of the Ru/C powder control, this behaviour is consistent with diffusion limitations, inaccessible Ru sites, and non-uniform catalyst distribution within the porous carbon-coated support. Recyclability testing showed progressive but manageable deactivation, with acetophenone conversion decreasing by approximately 20% and product yield decreasing by approximately 33% over repeated cycles (Fig. 1). The decline suggests partial Ru/C loss, surface fouling, and active-site blockage, but the catalyst remained reusable and easily separable from the reaction medium.

Conclusions

This work demonstrates that carbon-coated ceramic foams can function as practical structured supports for immobilised Ru-based catalysts, bridging the gap between the high activity of powder catalysts and the operational advantages of structured catalytic materials. The findings highlight both the limitations of direct precursor decomposition on structured carbon supports

and the promise of Ru/C drop-casting as a simple route to recyclable catalysts. Future work will focus on second-generation ruthenium nanoparticles supported on graphene nanofibre (RuNPs@GNFs) architectures [4] immobilised on carbon coated-ceramic foams to improve metal (Ru) dispersion, coating stability, mass transfer, and long-term catalytic performance.

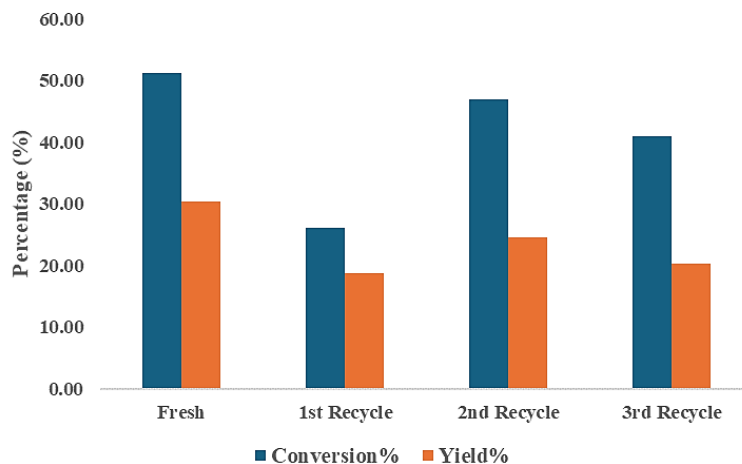


Fig. 1: Recyclability performance of the Ru/C@carbon-coated ceramic foam for acetophenone transfer hydrogenation in isopropanol, showing acetophenone conversion and 1-phenylethanol yield for the fresh catalyst and three consecutive reuse cycles.

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Acknowledgement

This work was supported by the Ministry of the Environment of Czechia under the LERCO project no. CZ.10.03.01/00/22_003/0000003.

Development and study of Rh- and Co-based h-BN catalysts for the hydroformylation of styrene

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Keywords: styrene hydroformylation, hexagonal boron nitride (h-BN), rhodium catalysts, cobalt catalysts, heterogeneous catalysts

Introduction

Hydroformylation is a key catalytic process widely employed in the chemical industry for the production of aldehydes from olefins.¹ These aldehydes serve as valuable intermediates in the synthesis of chemical specialties, including active pharmaceutical ingredients such as vitamins, antibiotics, and anti-inflammatory drugs. Despite the fact that most modern industrial catalytic processes rely on heterogeneous catalysts, hydroformylation is still predominantly carried out using homogeneous rhodium-based systems. Although highly active and selective, homogeneous catalysts suffer from inherent disadvantages related to catalyst separation, recyclability, and metal loss. Consequently, the development of efficient heterogeneous hydroformylation catalysts represents a long-standing challenge and an important research goal. Hexagonal boron nitride (h-BN) is an inorganic layered material composed of boron and nitrogen, crystallizing in a hexagonal structure analogous to graphite and therefore often referred to as “white graphite.” Unlike graphite, h-BN exhibits distinct physical properties, particularly at high temperatures and under electric fields. Owing to its high thermal stability, chemical inertness, and electrical insulation, h-BN has found broad application in materials chemistry, electronics, and catalysis. As a catalyst support, h-BN promotes high dispersion of metal species due to weak metal–support interactions and offers a large number of accessible active sites.² Its excellent thermal and chemical stability enhances catalyst durability, while the inert surface minimizes undesired interactions with reactants and products, contributing to improved selectivity and overall catalytic stability.

Styrene was selected as a model reactant in this study due to its electronic and steric complexity.³ Hydroformylation yields two aldehyde products, linear 3-phenylpropanal and branched 2-phenylpropanal, while undesired side reactions include hydrogenation to ethylbenzene and oligomerization to styrene dimers and trimers (Figure 1).

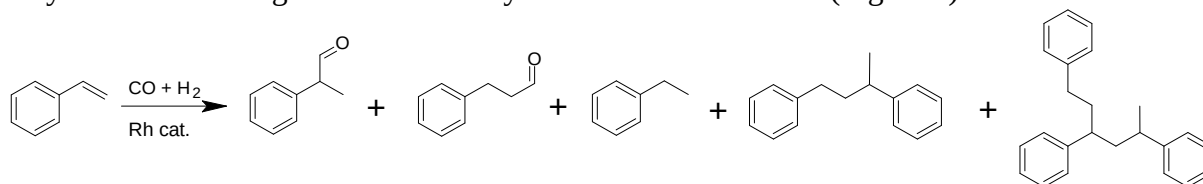


Fig. 1: Hydroformylation of styrene toward desired aldehydes and competing ethylbenzene, product of hydrogenation

Methodology

The aim of this work was the preparation, characterization, and catalytic evaluation of heterogeneous Rh- and Co-based catalysts using hexagonal boron nitride (h-BN) as a

two-dimensional support. A series of Rh/h-BN and Co/h-BN catalysts with different targeted metal loadings (0.5–10 wt%) was prepared using various impregnation approaches. Rhodium chloride and cobalt nitrate were used as metal precursors. The prepared catalysts additionally underwent calcination at 300 °C (12 h). Wilkinson's catalyst was employed as a homogeneous reference standard for benchmarking activity and selectivity. All catalysts were comprehensively characterized using N₂ physisorption, X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM), and FTIR spectroscopy. Catalytic performance was evaluated in the hydroformylation of styrene under controlled reaction conditions. Hydroformylation tests were performed in a 50 mL autoclave using syngas (CO:H₂ = 1:1) at a pressure of 3 MPa and a temperature of 100 °C for 6 h.

Discussion

Rh-based h-BN catalysts exhibited very high hydroformylation activity, with the most active samples achieving styrene conversions exceeding 90% and aldehyde selectivities above 90%, closely approaching the performance of the homogeneous reference catalyst. This behavior indicates that Rh species supported on h-BN remain highly accessible and catalytically efficient, suggesting favorable dispersion and stabilization of active Rh sites on the inert 2D support. The high selectivity toward aldehydes, combined with suppressed hydrogenation and oligomerization, points to a well-balanced catalytic environment that favors hydroformylation pathways over competing side reactions.

In contrast, Co/h-BN catalysts displayed significantly lower overall activity, with styrene conversions limited to 10–20%, while maintaining very high aldehyde selectivity (>90%). The lower activity of Co-based systems is consistent with the intrinsically lower hydroformylation activity of cobalt compared to rhodium under mild hydroformylation conditions. Nevertheless, the excellent selectivity observed for Co/h-BN catalysts highlights the ability of the h-BN support to suppress undesired hydrogenation and oligomerization reactions, even for less active metal centers.

For both catalytic systems, the minimal formation of ethylbenzene and oligomeric by-products demonstrates the beneficial role of h-BN as a chemically inert and non-acidic support, which limits side reactions commonly promoted on conventional oxide supports.

Conclusions

This study demonstrates that h-BN-supported Rh and Co catalysts represent promising heterogeneous systems for selective styrene hydroformylation. While Rh/h-BN catalysts provide high activity and selectivity, Co/h-BN systems offer excellent selectivity with reduced hydrogenation side reactions. These findings contribute to the development of more sustainable heterogeneous alternatives to conventional homogeneous hydroformylation catalysts.

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Acknowledgement: This project was funded by the Czech Science Foundation (GACR No. 23-08083M) and by the UCT Prague institutional support Dagmar Procházková Fund.

Novel Catalyst Materials for CO₂ Hydrogenation

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Keywords: energy conversion, materials design, catalytic testing, in-situ spectroscopy

The fight against the steadily increasing amount of greenhouse gases in our atmosphere is one of the defining challenges of our time. A possible solution may be reducing and converting CO₂, closing the carbon cycle. Therefore, catalysts that are highly active and exhibit long-term stability are needed.

Copper (Cu) containing materials (and Copper alloy materials) play a crucial role in CO₂ hydrogenation reactions, as they support CO₂ activation and facilitate the production of value-added products like e.g. methanol or formate [1]. However, for wide spread industrial application this activity has to be enhanced even further.

In this work we compare the reactivity of novel carbon supported catalysts with our doped perovskites. The two different approaches are highlighted and the respective strengths in CO₂ hydrogenation.

Perovskite-type oxides are catalysts with the general structure of ABO₃, allowing for a wide variety of elemental compositions. Through this flexibility, they are used in CO₂ utilisation reactions and can also be applied for methanol synthesis [2, 3]. Perovskite-type oxides are capable of forming nanoparticles on their surface, as B-site elements migrate there under reducing conditions (= exsolution) [4]. These nanoparticles are uniformly distributed and lead to increased catalytic activity.

Carbon-supported methanol synthesis catalysts offer compelling advantages for modern process intensification. Their high surface area and tunable micro-/mesoporosity enable ultra-fine dispersion of active phases, boosting turnover and lowering precious-metal loadings. Intrinsic electrical and thermal conductivity enhance heat management in exothermic conversion, mitigating hot spots and sintering. Hydrophobic surfaces modulate water at the interface, preserving active sites and favoring methanol selectivity, especially in CO₂ hydrogenation. Robust, corrosion-resistant carbons tolerate redox cycling, sulfur traces, and thermal stress, extending lifetime. Versatile surface chemistry allows anchoring promoters and defect engineering, while shaping into monoliths or porous pellets reduces pressure drop and improves mass transfer.

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Acknowledgement (optional)

This work has been funded by the Österreichische Forschungsförderungsgesellschaft (FFG) and is carried out under the Produktion und Material 2024 program with project nr. FO999922651

Role of Zn, Pd, Ni, Fe dopant in modifying Cu/CeO₂ catalyst properties for steam reforming of methanol (SRM)

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Keywords: copper catalysts, ceria support, steam reforming of methanol, hydrogen production

Steam reforming of methanol (SRM): $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$ has attracted substantial attention as one of the most promising catalytic routes for on-demand hydrogen production, particularly in distributed energy systems and proton exchange membrane fuel cells (PEMFCs). The growing demand for clean and sustainable energy carriers, driven by environmental concerns and the need to reduce greenhouse gas emissions, has intensified research on hydrogen as a key energy vector. Among hydrogen carriers, methanol is especially attractive due to its high hydrogen content, liquid state at ambient conditions, relatively low toxicity, and well-established production and transportation infrastructure, making it a practical medium for hydrogen storage and release. Furthermore, 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.

Compared to conventional hydrocarbon reforming processes such as steam reforming of methane, SRM offers important advantages, including lower operating temperatures (200–300 °C), reduced energy input, and higher selectivity toward hydrogen and carbon dioxide. However, its industrial application remains limited by challenges related to catalyst activity, selectivity toward CO₂, suppression of CO formation, and long-term stability. The SRM process involves a complex network of parallel and consecutive reactions, including methanol dehydrogenation, decomposition to CO and H₂, steam reforming to CO₂ and H₂, and the reverse water-gas shift (RWGS) reaction. CO formation is particularly problematic, as even trace amounts (10 ppm) can poison PEM fuel cell catalysts. Therefore, developing catalysts that promote complete conversion to CO₂ and H₂ while suppressing CO is crucial. Two main reaction pathways are generally accepted. In the formate pathway, methanol is dehydrogenated to methoxy species and then to surface formate intermediates (HCOO*), which decompose to CO₂ and H₂. In the decomposition pathway, methanol forms CO and H₂, followed by CO conversion via the water-gas shift reaction. The contribution of each pathway depends strongly on catalyst properties, especially the nature of active sites and metal-support interactions.

The most commonly used catalysts in the steam reforming of methanol are mainly copper-based systems, as well as metals of groups 8–10 of the periodic table. Traditional Cu/ZnO/Al₂O₃ catalysts have been widely studied due to their relatively high activity, but they suffer from copper sintering, structural instability, and limited resistance to redox cycling, leading to gradual deactivation. These limitations have driven the development of alternative catalyst systems with improved stability and stronger metal-support interactions. Among various supports, cerium oxide (CeO₂) has emerged as a promising candidate due to its unique physicochemical properties, including high oxygen storage capacity, reversible Ce⁴⁺/Ce³⁺ redox behavior, and the ability to form oxygen vacancies. These features allow ceria to actively participate in catalytic processes by facilitating oxygen transfer and enhancing redox reactions. Oxygen vacancies on ceria surfaces play a key role as active sites for water dissociation and intermediate transformations, while also enhancing adsorption of polar molecules. In addition, strong interactions between CeO₂ and supported metal nanoparticles stabilize highly dispersed metal species, prevent sintering, and promote the formation of highly active interfacial sites,

which often govern catalytic performance. Among ceria-based catalysts, Cu/CeO₂ systems have attracted significant attention due to their high activity and relatively low cost. The interaction between copper and ceria leads to the formation of active interfacial sites that enable synergistic activation of methanol and water. Methanol adsorbs on copper sites and forms methoxy and formate intermediates, which decompose into CO₂ and H₂, while water is activated on ceria vacancies. The oxidation state of copper plays a crucial role, with Cu⁰ associated with methanol activation and Cu⁺ with intermediate transformation toward CO₂. Maintaining an optimal Cu⁰/Cu⁺ balance is essential for catalytic performance.

Despite these advantages, Cu/CeO₂ catalysts still suffer from deactivation, structural changes, and CO formation via side reactions such as RWGS and methanol decomposition. To improve performance, secondary metals such as Zn, Pd, Ni, and Fe are introduced as promoters. These elements can influence copper dispersion, redox properties, oxygen vacancy concentration, and metal-support interactions. Zn improves dispersion and stabilizes copper, Pd enhances hydrogen activation and reducibility, Ni increases activity but may promote CO formation, and Fe can improve stability and suppress CO, although excessive amounts may reduce activity. Despite extensive research, most studies focus on individual promoters under different conditions, making direct comparison difficult. Therefore, understanding how different promoters influence the Cu-CeO₂ interface and catalytic performance remains incomplete. In this context, this work presents a systematic investigation of Cu-x/CeO₂ catalysts (x = Ni, Pd, Zn, Fe) under SRM conditions. The aim is to establish clear structure-activity relationships and better understand how promoter identity affects hydrogen production and CO₂ selectivity, providing insights for the rational design of efficient and stable SRM catalysts.

The Cu/CeO₂ catalysts modified with various elements, prepared by the impregnation method, were subjected to physicochemical analysis and catalytic tests in the steam reforming of methanol. Catalytic studies of modified catalyst conducted over the temperature range of 180-420 °C, showed that these systems are active and highly selective toward hydrogen and carbon dioxide in the SRM. Among all the studied systems, the highest conversions (in the temperature range of 240-380 °C) were observed for the Cu-Fe/CeO₂ catalyst. The Cu-Fe/CeO₂ catalyst produced the lowest amount of CO compared to the other catalysts, which may indicate that iron promotes the activation of the WGS reaction, in which CO is converted to CO₂ and H₂.

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Dynamics of Potassium Migration during Iron Oxide Reduction under Variable Reductant and Pressure Conditions: A Thermal Desorption Study

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Keywords: potassium promotion; iron oxide reduction; potassium dispersion; potassium stability; Fisher-Tropsch;

The study of promoter dynamics under industrial conditions is highly timely as it addresses a critical "pressure and material gap" in heterogeneous catalysis: while the structural promotion of iron catalysts is well-documented, the real-time migration and energetic stability of potassium (K) during the actual phase transition from oxides to active carbides or metals remain poorly understood [1]. By utilising thermal alkali desorption, this research fills a fundamental knowledge gap by providing quantitative activation energies (E_d) for potassium on specific iron phases, moving beyond qualitative visual dispersion to reveal how strongly the promoter is anchored under varying chemical potentials and high-pressure regimes of the reduction process [2]. Such data are essential for designing more stable catalysts for Fischer-Tropsch and ammonia synthesis, as they elucidate the precise conditions under which potassium migrates from "storage" oxide phases to active surface facets or is lost to the bulk [3].

The commercial iron oxides impregnated with potassium precursors are placed in the high-vacuum apparatus – TADEK (Thermal Alkali Desorption & Electronic Kelvin Probe) station. Therein, in the high-pressure reactor, the materials are reduced in 5% H₂/Ar and H₂/CO 2:1 mixtures under atmospheric pressure and 10 bar. The reduced and reference materials are then transferred *in situ* to the alkali desorption station to determine the potassium desorption flux and desorption activation energy, E_d . In addition, the influence of the reduction process and potassium desorption cycles on the materials' work function is determined using the Kelvin Probe station in the same apparatus. Phase composition changes are studied *ex situ* using X-ray diffraction, and surface chemical composition changes are studied using X-ray photoelectron spectroscopy.

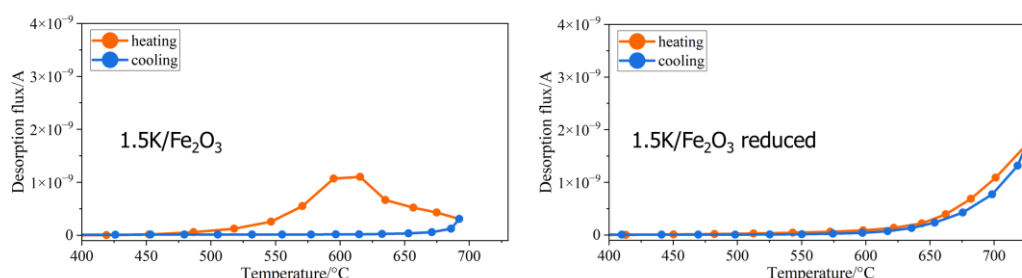


Fig. 1: Potassium desorption flux from hematite, Fe₂O₃, and hematite reduced under 5% H₂ flow, loaded with 1.5 wt.% K.

The effect of the reduction at ambient pressure of Fe₂O₃ loaded with 1.5 wt.% potassium on the K-desorption flux is presented in Fig.1. The initial maximum, assigned to the surface

segregation of potassium promoter, disappears. Possible explanations include a more uniform distribution of surface sites or enhanced surface diffusion of the potassium promoter, leading to preferential desorption from low-binding-energy sites.

The thermal desorption studies of materials obtained with varying gas feeds and reduction pressures, complemented with structural and surface characterisation, will allow to elucidate the fundamental interplay between reduction environments and promoter stability. Specifically, this multifaceted approach will clarify how the chemical potential of the gas feed and the total system pressure determine whether potassium transforms from its initial precursor state into stable surface phases or migrates into the bulk lattice. By correlating the E_d with phase evolution and work function changes, the study will define the energetic thresholds required to maintain optimal promoter dispersion. Ultimately, these insights will provide a mechanistic framework to bridge the gap between idealised surface science and industrial application, enabling the rational design of iron-based catalysts with enhanced structural and electronic stability under demanding operating conditions.

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Acknowledgement: We thank the National Science Centre, Poland, for funding the research (grant no. 2024/55/B/ST5/02291).

Synthesis and Catalytic Properties of Facet-Controlled $\text{Co}_3\text{O}_4|\text{Cu}_2\text{O}$ Heterojunctions

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Keywords: cobalt spinel, cuprous oxide, heterojunctions, redox catalysis

Cobalt spinel (Co_3O_4) is widely recognized as a promising redox catalyst mainly due to its mixed valence states and favorable surface oxygen mobility [1]. However, its intrinsic catalytic performance is often limited by insufficient activity and stability under reaction conditions, which restricts its broader practical application. To address these limitations, modification strategies such as doping with other metals have been explored [2], although these approaches frequently introduce challenges related to structural complexity, phase segregation, and limited control over active sites. A simpler and effective strategy was presented, which is based on the formation of heterojunctions with other metal oxides, to enhance the catalytic performance of cobalt spinel.

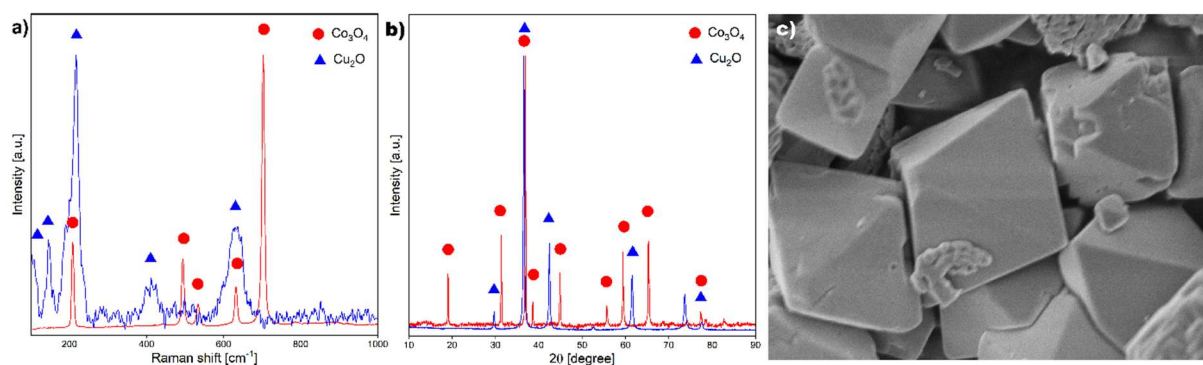


Fig. 1: Raman spectra (a) and XRD patterns (b) of synthesized Co_3O_4 and Cu_2O nanoparticles, SEM micrograph of synthesized Co_3O_4 (c) nanoparticles.

The enhanced catalytic performance of the heterojunction systems arises from interfacial electronic interactions between the two oxide components. The formation of a heterointerface promotes charge redistribution and facilitates directional charge transfer, which improves the separation of redox-active species and increases the availability of reactive sites [2]. Two types of nanoparticles were synthesized separately: Co_3O_4 and a secondary metal oxide Cu_2O . Special emphasis was placed on optimizing the synthesis of Co_3O_4 and Cu_2O nanostructures to obtain nanocubes and nanooctahedra exposing well-defined (100) and (111) crystal facets, respectively. All synthesized samples were characterized to confirm their structural and morphological properties. Phase composition and crystallinity were examined by X-ray diffraction (XRD, **Fig.1a**), while Raman (**Fig.1b**) and infrared (IR) spectroscopy were employed to probe vibrational features and verify chemical composition. Scanning electron

microscopy (SEM, **Fig.1c**) was used to assess particle morphology, confirming the formation of well-defined nanocrystals with the intended shapes and exposed facets. The heterojunctions $\text{Co}_3\text{O}_4|\text{Cu}_2\text{O}$ were fabricated via a facile sonication-assisted assembly process, ensuring intimate interfacial contact without complex chemical modification. The resulting hybrid systems was evaluated in catalytic redox reactions and compared directly with previously studied heterojunction of $\text{Co}_3\text{O}_4|\text{CeO}_2$ composition[3].

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Acknowledgement

This work was supported by the the Polish National Science Centre within the framework of the OPUS-28 project (grant no. 2024/55/B/ST4/01383).

Efficient Zeolite BETA-Catalyzed Route to a Fragrant Tetrahydropyranyl Acetate: Prins Reaction and Esterification Study

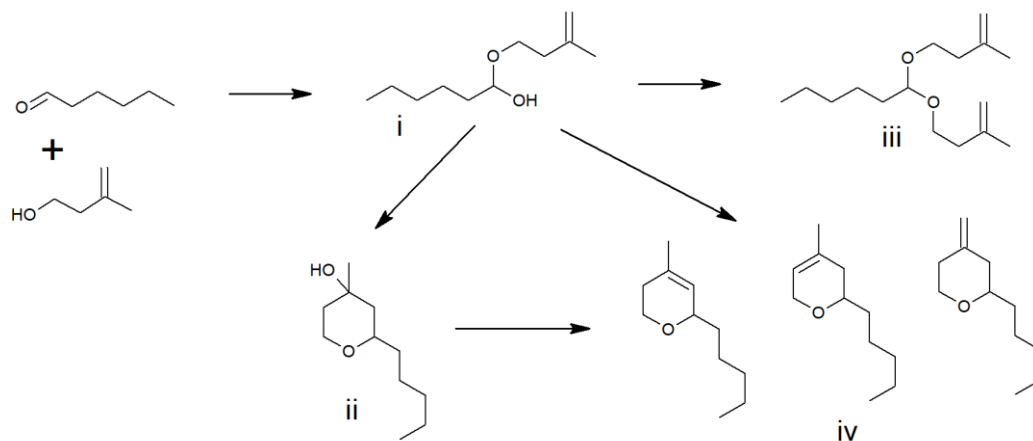
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Keywords: 4-Methyl-2-(1-pentyl)-tetrahydro-2*H*-pyran-4-ol; Prins reaction; esterification; zeolite BETA

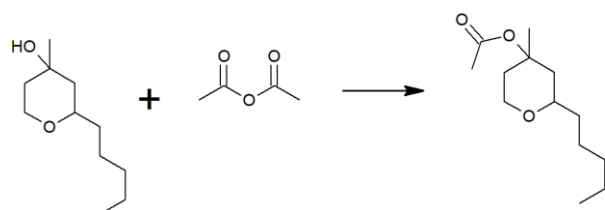
Substituted tetrahydropyransols and their esters show interesting olfactory properties and are often used as fragrances. 4-Methyl-2-(1-pentyl)-tetrahydro-2*H*-pyran-4-ol, which can be synthesized via Prins reaction of hexanal with isoprenol, is described to have fruity and floral scent. Its ester, 4-methyl-2-(1-pentyl)-tetrahydro-2*H*-pyran-4-yl acetate, is also fragrance with green, floral and amber-wood scent. This work focused on two-step synthesis of 4-methyl-2-(1-pentyl)-tetrahydro-2*H*-pyran-4-yl acetate, using zeolite BETA as catalyst. Mechanism of first step, Prins reaction of hexanal with isoprenol (Fig. 1) is proceeded via intermediate – hemiacetal (i), which can be converted to desired tetrahydropyranol (ii) or to products decreasing selectivity – acetal (iii) or dihydropyranes (iv). Influence of reaction conditions (catalyst amount, solvent, temperature and water addition) on Prins reaction of hexanal with isoprenol, with focus on selectivity to desired tetrahydropyranol was performed. Using 1,4-dioxane and temperature 80°C, 76% selectivity and total conversion of hexanal (5 h) was obtained.

Fig. 1: Prins reaction of hexanal with isoprenol



Second step, esterification of tetrahydropyranol with acetic anhydride (Fig. 2), was also optimized (solvent, catalyst amount, temperature, molar ration of reactants); In this case, total conversion of tetrahydropyranol and 90% selectivity to desired 4-methyl-2-(1-pentyl)-tetrahydro-2*H*-pyran-4-yl acetate was observed (zeolite BETA, RT, 24 h).

Fig. 2: Esterification of 4-methyl-2-(1-pentyl)-tetrahydro-2*H*-pyran-4-ol to acetate



Tuning the activity and selectivity of ceria supported nickel catalysts

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Keywords: carbon dioxide hydrogenation, CeO₂, nickel catalyst, selectivity changes, deactivation

In an era of growing demand for hydrocarbon resources, the efficient use of CO₂ and H₂ derived from the processing of waste or renewable raw materials for the production of the valuable chemical products is becoming a necessity. The widespread use of hydrocarbon resources as energy carriers and raw materials for the production of various consumer goods leads to CO₂ emissions. The development of effective methods for converting waste or biogenic CO₂ into basic chemical compounds is of paramount importance. These include carbon monoxide ($\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{H}_2 + 2\text{CO}$; $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$), methanol ($\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$; $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$), methane and higher hydrocarbons ($\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$; $(2n+1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$; $n\text{CH}_3\text{OH} \rightarrow (\text{CH}_2)_n + n\text{H}_2\text{O}$), as well as other valuable chemical products that could contribute to the development of a circular economy.

Cerium oxide is a unique material that was proposed as a support for various catalysts in many processes. Thanks to the presence of Ce^{4+/3+}-O²⁻ Lewis acid-base centres on the surface of CeO₂ lattice, the ability of the formation of hydroxyl groups and thus Brønsted centres, and above all the possibility of creating oxygen vacancies associated with the easy change in the oxidation state of Ce, this material enhances activation and transformation of various molecules, including CO₂, CO, H₂O, CH₃OH, and others. It may also induce appropriate changes in the electronic properties of the metal nanoparticles deposited on them or affect their morphology. Catalysts containing nanoparticles of metals such as Ni, Co or Ru dispersed on the surface of CeO₂ are highly active in reactions such as CO₂ methanation, dry reforming of methane or steam reforming of ethanol. On the other hand, the addition of metals such as Au, Pt, Pd and Cu facilitates the hydrogenation of CO₂ to CO (RWGS) or, under certain conditions, the production of methanol. The use of appropriate synthesis methods, the introduction of promoters and additives or the selective poisoning of catalysts can lead to significant changes in activity and selectivity.

The aim of our studies was to develop effective catalysts for the conversion of CO₂ to methane, as well as, to determine the scope for modifying the composition of the catalysts to achieve very high selectivity towards CO, which is advantageous for the subsequent production of methanol or liquid hydrocarbons.

The catalysts were synthesised using a wet impregnation method using nano-CeO₂ as a support [1-3]. The composition of the impregnation mixture was modified to achieve catalysts containing between 10 and approximately 40 wt% Ni in a similar way as described earlier [1-3]. At the same time, selected modifiers, such as Co, Mo, W and Nd, were introduced in different amounts.

The surface properties and porosity of the catalysts determined by using the low-temperature nitrogen adsorption/desorption method were primarily influenced by the properties of the cerium oxide support and the amount of modifiers used. In turn, the temperature-programmed reduction and oxidation (TPR/TPO) methods, X-ray diffraction and Raman spectroscopy revealed a strong influence of nickel content, the type of modifiers and treatment conditions on

the redox properties of catalysts, the size of Ni crystallites and the density of defects in the CeO₂ lattice. The results were confirmed by the application of the transmission electron microscopy (TEM) [1-3].

Studies revealed a synergistic effect of factors directly dependent on the features of the nickel crystallites, the properties of the modifiers, and the support. Consequently, the activity of the catalysts without the addition of modifiers increased gradually over a wide temperature range as the nickel content rose to around 20-30 wt%, and then decreased. Such effect was related to the changes in the active surface area and the size of Ni crystallites. In-situ DRIFTS studies of the hydrogenation of CO₂ by H₂, carried out using a Nicolet 6700 FTIR spectrometer equipped with a high-temperature DRIFTS reaction chamber (Harrick), indicated formation of differently coordinated intermediate carbonyl groups on Ni and carbonate species on the support, which were then transformed into the formate intermediates and methane. Therefore, the increase in the fraction of the metal-support border line by increase in Ni dispersion or Ni content, to some extent, facilitated the successive transformations of the species with hydrogen activated on the nickel nanoparticles [1]. It was found that the introduction of cobalt into the catalysts composition did not result in a significant change in their activity. This effect indicated the significant role played by the acid-base and redox properties of the support in the course of the methanation reaction. We have demonstrated that small amounts of Nd promoter led to an improvement in Ni dispersion and increase in activity. However, the introduction of larger amounts of Nd resulted in a decrease in activity, ascribed to partial coverage of nickel crystallites and CeO₂ surface, inhibiting activation and redox transformations of intermediate species [3]. Studies into the poisoning of catalysts by H₂S present in the reaction mixture stream have shown that the catalysts may not fully lose their activity, whilst almost completely driving the hydrogenation reaction towards CO [2]. We have observed that, in a similar manner but in a much more controlled way, the selectivity can be adjusted by adding appropriate amounts of Mo or W modifiers. As a result, an excellent RWGS catalysts can be achieved.

The results of the studies showed that the activity of ceria supported nickel catalysts can be improved by increasing their specific and active surface area, modification the nature of the sites located on the surface of the nickel nanoparticles, as well as by appropriate changes in the acid-base or redox properties of CeO₂. Such properties can be achieved by introducing an appropriate amount of nickel active phase, adding small amounts of promoters (e.g. Nd, Co) or applying suitable reduction or reaction conditions. A shift in the selectivity of catalysts in a direction other than methane, e.g. towards CO, can be achieved by inhibiting the processes leading to the deep hydrogenation of the resulting surface intermediate species. Such effects can be reached by limiting the ability to form strong bonds of intermediate carbonyl groups or hydrogen with metallic nanoparticles, e.g. by partial poisoning of nickel surface, altering its electronic properties following the introduction of modifiers (Co, Mo, W), changing the size of metallic nanoparticles to facilitate metal-support interactions. Furthermore, the selectivity can be altered by modifying the course of the surface reactions taking place with the involvement of the cerium oxide support, e.g. by appropriately changing its acid-base and redox properties through the introduction of suitable amounts of modifiers.

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POSTERS

2. Homogeneous, Organocatalysis and Biocatalysis

Synthesis and separation of (*R*)-1-phenylethyl acetate using enzymatic transesterification and deep eutectic solvent extraction

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Keywords: 1-phenylethanol; (*R*)-1-phenylethyl acetate; lipase; deep eutectic solvent; microfluidics

Continuous flow (CF) synthesis and purification have emerged as key enabling technologies in the pharmaceutical and fine chemicals industries. Compared to conventional batch processes, microfluidic CF systems offer significant advantages, including rapid prototyping, modular design, precise control of flow and temperature, improved reproducibility, and reduced processing times due to minimized transport limitations. These features make CF platforms particularly attractive for the production of low-molecular-weight active pharmaceutical ingredients (APIs), many of which are chiral and require efficient enantioselective synthesis and separation strategies.

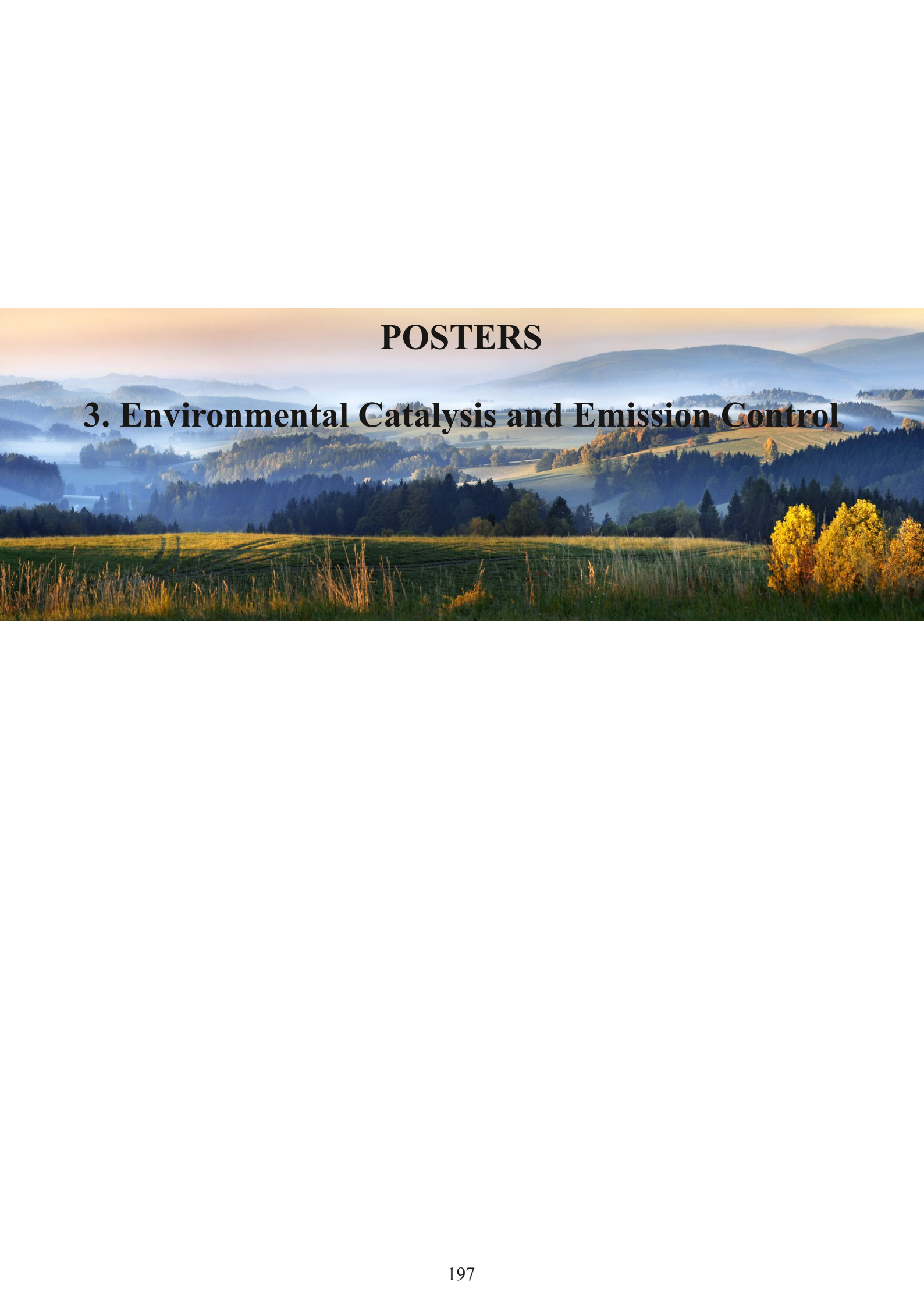
A widely used approach for the resolution of chiral alcohols is enzymatic enantioselective transesterification. In this work, we investigate the resolution of racemic 1-phenylethanol via transesterification with vinyl acetate, catalyzed by immobilized *Candida antarctica* lipase B (CALB). Owing to the high enantioselectivity of CALB, the reaction selectively converts one enantiomer, yielding (*R*)-1-phenylethyl acetate, while the (*S*)-1-phenylethanol remains unreacted.

To integrate reaction and downstream processing, we propose a modular continuous flow microdevice that combines a packed-bed reactor (PBR) containing immobilized CALB with microfluidic extraction units. For the separation step, deep eutectic solvents (DES) are employed as an alternative to conventional organic solvents. DES offer several advantages, including low volatility, tunable polarity, low toxicity, and potential for selective extraction of target compounds, making them promising candidates for sustainable separation processes.

The study is structured in two stages. First, the operational characteristics of the enzymatic reactor and the microfluidic extraction module are investigated independently, focusing on parameters such as substrate conversion, enantioselectivity, phase behavior of DES, and mass transfer performance of a slug-flow microextractor. Subsequently, both modules are integrated into a single CF platform, forming a continuous reaction-separation system. The resulting microfluidic “factory” produces two distinct outlet streams: an organic raffinate enriched in (*R*)-1-phenylethyl acetate and DES-based extract enriched in (*S*)-1-phenylethanol.

This work demonstrates a proof-of-concept for coupling enzymatic synthesis with green extraction techniques in a continuous flow environment. The proposed approach highlights the potential of modular microfluidic systems for efficient, scalable, and sustainable production of enantiomerically pure compounds, which are of high importance in pharmaceutical manufacturing.

Acknowledgement: The authors thank the Czech Science Foundation for grant no. 24-11480S.



POSTERS

3. Environmental Catalysis and Emission Control

Ti-functionalised dendritic fibrous nanosilica in the role of catalysts for dibenzothiophene oxidation with H₂O₂

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Keywords: DFNS, titanium, oxidative desulfurization, dibenzothiophene

Conventional hydrodesulfurization (HDS), widely used to remove sulfur from fuels, is less effective for refractory aromatic sulfur compounds and requires harsh operating conditions. Oxidative desulfurization (ODS) is seen as a promising alternative, operating under milder conditions. This process involves the selective oxidation of sulfur compounds to sulfones or sulfoxides, which can be easily removed via extraction or adsorption. The efficiency of ODS strongly depends on catalyst properties such as surface area and pore accessibility[1]. Mesoporous silica materials are attractive catalyst supports. Among them, dendritic fibrous nanosilica (KCC-1) exhibits a unique morphology with radially oriented silica fibers, providing high surface area and excellent accessibility of active sites [2]. Incorporation of titanium into KCC-1 yields Ti-KCC-1 catalysts, which can be active in oxidation reactions.

In the studies, we performed a synthesis to obtain titanium-modified fibrous silica nanospheres. The morphology of the obtained materials was confirmed by transmission and scanning electron microscopy. Textural properties were analyzed using low-temperature N₂ sorption. Metal form and aggregation were studied by UV-Vis-DR spectroscopy. The chemical composition was determined by ICP-OES measurements. The obtained catalysts were tested in the reactions of organic sulphide oxidation (e.g. dibenzothiophene) using hydrogen peroxide as an oxidant.

The obtained materials presented the desired morphology and textural properties. The titanium was incorporated mainly in the form of highly dispersed species. Analysis confirmed the incorporation of titanium into the silica framework, similar to the assumed value. Catalytic tests confirmed that Ti-KCC-1 materials are active in the oxidation of sulfur compounds. The high efficiency can be attributed to the combination of both accessible fibrous structure and well-dispersed titanium species, which enable effective diffusion of substrate and oxidation products.

In conclusion, Ti-KCC-1 materials exhibit promising catalytic performance in oxidative desulfurization processes. Their unique fibrous morphology provides high accessibility of active sites, while titanium incorporation is responsible for efficient oxidation. These results make Ti-KCC-1 a good catalyst candidate for sulfur removal in the ODS process.

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Comparative Study of COP and BP Preparation Routes: Stability and Resistance of K-doped Co-Mn-Al Catalysts against O₂ and CO₂

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Keywords: NO decomposition, Co-Mn-Al mixed oxide, inhibition, co-existing gases, *in situ* FTIR

Direct catalytic decomposition of nitric oxide (NO) into N₂ and O₂ represents an environmentally friendly route for NO_x abatement, as it eliminates the need for external reducing agents. Despite being thermodynamically favorable, the process faces significant challenges, primarily the competitive adsorption and poisoning by co-existing exhaust gases [1]. This study investigates the inhibition mechanisms of oxygen (O₂) and carbon dioxide (CO₂) on highly active potassium-promoted Co-Mn-Al mixed oxides, focusing on the stability of surface species and their impact on catalytic performance.

K-promoted Co-Mn-Al mixed oxide catalysts (molar ratio 4:1:1) were compared: one prepared by co-precipitation (3K/CoMn_COP) [2] and the other by impregnation of a "wet cake" (3K/CoMn_BP) [3]. Catalytic tests were performed at 700 °C in a stainless steel fixed bed reactor using a feed of 1000 ppm NO/ N₂, both in the absence and presence of O₂ and CO₂ (0-5 vol. %). The evolution of surface species and reaction intermediates was monitored using *in situ* DRIFTS (HTHP reaction cell Specac connected to FTIR spectrometer) at reaction temperatures of 600–700 °C to elucidate the inhibition mechanism at the molecular level.

While both catalysts exhibited high activity in an inert atmosphere, reaching NO conversions between 54% and 60%, the addition of co-existing gases led to a significant performance decline (Fig. 1 A, 1 B).

The presence of 0.5 vol. % O₂ resulted in a 50 % reduction in conversion (Fig. 1 A), which *in situ* DRIFTS analysis attributed to the O₂-promoted oxidation of adsorbed NO species into highly stable surface nitrates (NO₃⁻). These nitrates effectively block the Co³⁺/Mn³⁺ active sites, hindering further reaction. The inhibitory effect of oxygen was found to be fully reversible, as NO conversion returned to its initial values immediately after O₂ was removed from the feed.

An even more pronounced inhibitory effect was observed with CO₂. At a concentration of 0.5 vol. %, the catalytic activity dropped to quarter of its original value (Fig. 1 B). This degradation is linked to the massive formation of extremely stable surface carbonates on the potassium sites, identified in the *in situ* DRIFTS spectra at 1350–1550 cm⁻¹ region. Furthermore, the *in situ* DRIFTS analysis revealed that CO₂ at high temperatures triggers a deep 'corrosion' of the spinel lattice and the displacement of structural water. This suggests a more aggressive degradation of the active phase compared to the competitive adsorption of oxygen. The COP sample showed enhanced tolerance to these inhibitory effects, likely due to a more favorable potassium distribution which helps to stabilize the catalyst surface in the presence of coexisting gases. Similar to oxygen, the inhibition by CO₂ is a reversible process.

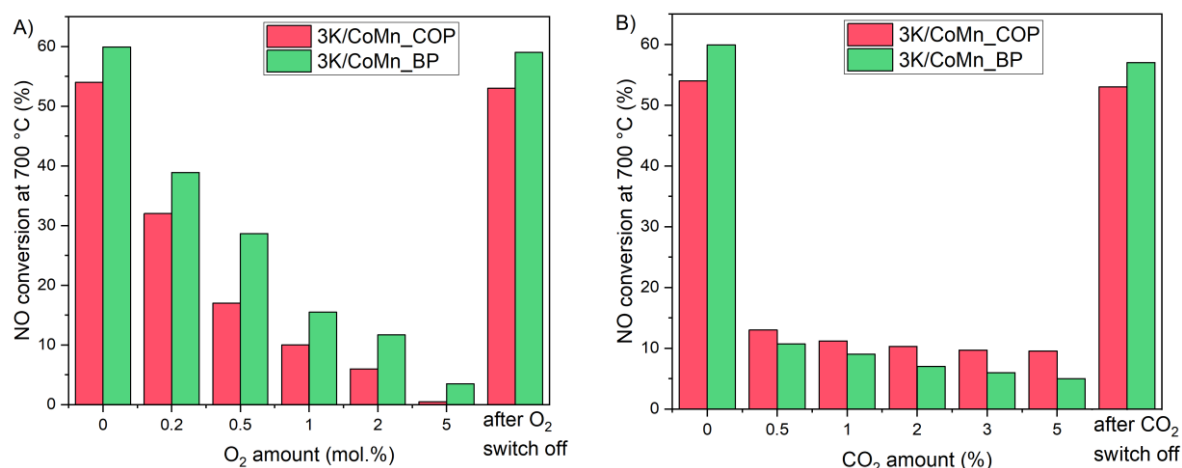


Fig. 1: Effect of O₂ (A) and CO₂ (B) on the NO conversion over K-doped Co-Mn-Al catalysts prepared by co-precipitation (3K/CoMn_COP) and impregnation of a "wet cake" (3K/CoMn_BP).

The study demonstrates that while O₂ acts primarily as a competitive inhibitor by forming nitrates, CO₂ induces a more fundamental restructuring of the catalyst surface. Understanding these interactions is crucial for designing the next generation of robust deNO_x catalysts for real-world applications.

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Acknowledgement

This work has been produced with the financial support of the European Union under the REFRESH – Research Excellence For REgion Sustainability and High-tech Industries project number CZ.10.03.01/00/22_003/0000048 via the Operational Programme Just Transition. The experiments were performed using the Large Research Infrastructure ENREGAT (No. LM2023056) supported by the Ministry of Education, Youth and Sports of the Czech Republic.

Removal of Sulfur and Chlorine Contaminants from Syngas

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Keywords: chemisorption, syngas, purification

The hot-gas cleaning of syngas is a critical step in advanced thermochemical conversion processes, such as the gasification of waste biomass, particularly when the downstream pathway involves catalytic hydrogenation for the production of methanol and dimethyl ether (DME). Trace contaminants, including hydrogen sulfide (H₂S) and hydrogen chloride (HCl), must be removed to ultra-low levels, as even ppm concentrations lead to rapid catalyst deactivation and irreversible loss of activity. Operation in the intermediate temperature range (300 - 400 °C) represents a compromise between energy efficiency and sorbent reactivity, while maintaining compatibility with downstream catalytic process integration.

The study investigates the removal of H₂S and HCl under reducing conditions using ZnO, Na₂CO₃-based sorbents, and commercial iron-based hydroxide/oxide materials. Sorbent performance is evaluated using breakthrough experiments in a fixed-bed configuration. The experimental data are interpreted using a shrinking core model, enabling the estimation of apparent reaction kinetics and identification of rate-limiting steps. ZnO and Fe-based sorbents show high efficiency for H₂S removal, while Na₂CO₃ provides effective HCl capture via acid - base reactions. In the case of sulfur sorbents, regeneration and reusability are also assessed to evaluate their potential for cyclic operation. Attention is given to the influence of temperature and gas composition on sorbent performance and kinetic parameters.

This work is co-financed from the state budget by the Technology Agency of the Czech Republic, within the project no. TQ06000004 "Gasification and Electrolysis Novel Integration Used for Sustainable Fuels" within the SIGMA program within the CET 2023 Partnership call.

Photocatalytic and Antimicrobial Performance of Direct-Written TiO₂ Thin Films Evaluated by a Resazurin-Based Assay

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Keywords: TiO₂; antimicrobial activity, resazurin assay, photocatalytic activity

Titanium dioxide (TiO₂) thin films represent an important class of photocatalytic materials with significant potential for antimicrobial surface applications, driven by their ability to generate reactive oxygen species under irradiation. In this study, TiO₂ layers were prepared using a brick-and-mortar strategy and deposited via a direct ink writing technique, enabling controlled structuring of the catalytic surface.

The structure and roughness of the prepared layers were studied using scanning electron microscopy and atomic force microscopy, and the layer thickness was determined by profilometric measurement. The photocatalytic activity of the prepared layers was tested for the degradation of the model dye resazurin.

The antimicrobial performance of the prepared coatings was evaluated using a resazurin-based assay, which provides a rapid and highly sensitive measure of microbial metabolic activity. The method is based on the reduction of resazurin to the fluorescent product resorufin, where the fluorescence kinetics correlates with the concentration of metabolically active microorganisms [1-2].

The activity was tested against representative microorganisms with distinct cell wall architectures, including Gram-negative *Escherichia coli*, Gram-positive *Enterococcus faecalis*, and the yeast *Candida glabrata*.

This work highlights the interplay between surface architecture, photocatalytic efficiency, and antimicrobial performance, and demonstrates the suitability of resazurin-based methods for rapid and comprehensive evaluation of functional TiO₂ coatings.

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Acknowledgement

This work was supported by the Czech Technology Agency through project: CZ.01.01.01/01/22_002/0000322

High Entropy Oxide deposited on potassium glass as catalysts for the simultaneous removal of soot and VOC

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Keywords: high entropy oxides, glass, catalytic oxidation, soot, volatile organic compounds

For years, air pollution containing carbonaceous particulate matter (soot) and volatile organic compounds (VOCs) has remained a serious environmental challenge. Although catalytic complete oxidation is regarded as an effective abatement strategy, the simultaneous removal of solid soot and gaseous VOCs using noble-metal-free catalysts is still strongly desired.

Alkali-metal-based materials, particularly potassium silicate glasses, have recently shown high potential in such applications as soot oxidation. In contrast, oxidation of VOCs usually requires the presence of redox-active catalytic centers.

In this study, a composite catalyst consisting of a high entropy oxide (HEO) – $\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O}_x$ supported on potassium silicate glass was developed for the simultaneous oxidation of soot and VOCs. Potassium silicate glass ($25\text{K}_2\text{O}-59\text{SiO}_2-16\text{CaO}$) was synthesized by melt-quenching, followed by deposition of an equimolar Mg–Co–Ni–Cu–Zn HEO phase using various methods: incipient wetness impregnation (IWI), solution combustion (SC), and controlled solution combustion (CSC) routes.

A comprehensive structural and spectroscopic characterization (XRF, XRD, RS, FTIR, UV/Vis-DR, H_2 -TPR, SEM/EDX) of the synthesized samples confirmed the amorphous nature of the glass matrix and the formation of a homogeneous high entropy oxide phase without any detectable crystalline single-metal oxides. The obtained HEO–K–glass composites exhibited noticeable catalytic activity in the oxidation of ethylene (Fig. 1) and propane, as well as promising performance in soot combustion. Importantly, the studied materials exhibited the capability for the simultaneous removal of soot and VOCs. This fact can advocate for the synergistic role of potassium-based glass in soot oxidation and redox-active HEO centers in VOC combustion.

The developed HEO–glass system represents a novel noble-metal-free catalytic system for multifunctional air pollution control applications.

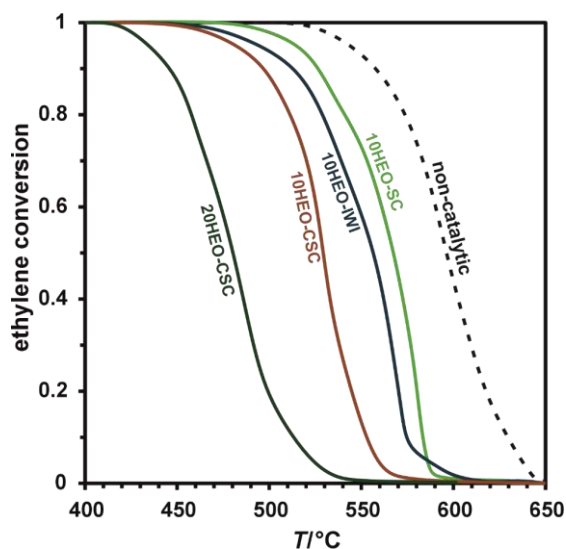


Fig. 1: Catalytic conversion of ethylene on HEO-glass composites as a function of temperature.

Acknowledgement: This work has been supported from the Anthropocene Priority Research Area budget under the program "Excellence Initiative – Research University" at the Jagiellonian University

Highly effective technology for ammonia abatement from industry operations

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Keywords: Advanced oxidation processes, Hydrogen peroxide Ammonia, Nitrogen recovery

Ammonia emissions represent a critical environmental and public health challenge, contributing significantly to ecosystem acidification, eutrophication, and the formation of secondary particulate matter. While agricultural activities remain the primary source of these emissions, industrial sectors also contribute to atmospheric ammonia levels. In response to increasingly stringent European Union regulations, there is a growing demand for innovative and cost-effective abatement technologies [1-3].

This study presents an advanced two-stage photochemical system utilizing UV/H₂O₂ advanced oxidation processes (AOPs) designed to efficiently remove gaseous ammonia from waste air. Recent technological improvements, including the addition of water vapor and optimized tubular reactor configurations, have further enhanced the system's performance, allowing for both high removal efficiency and the recovery of valuable nitrogen compounds as liquid fertilizers, thereby supporting circular economy principles.

The ammonia conversion rate in the dry photocatalytic reactor reached up to 24%, depending on the flow rate and initial concentration. The wet scrubber achieved an efficiency of around 98%. An aqueous hydrogen peroxide solution in combination with UV irradiation was used to convert the captured ammonia, with its concentration maintained above 100 mg/L. To oxidize ammonia into the desired nitrogen compounds, it was found necessary to maintain the pH within the range of 9.2 to 10.8, with the highest efficiency observed at values around 10.3. The technology, consisting of a photolytic reactor, a wet scrubber, and a tubular reactor with UV lamps, was capable of oxidizing approximately 45% of the absorbed ammonia. In the final stage of the project, the system was further optimized to increase the production of nitrogen compounds, particularly nitrates and nitrites, by increasing the number of tubular reactors from one to three and maintaining a constant hydrogen peroxide concentration through continuous dosing. At the same time, steam was introduced into the photolytic reactor. Through these modifications, we achieved a yield of 257 mg N/L in the form of nitrates and nitrites.

These results demonstrate the effectiveness of the proposed two-stage photochemical technology for ammonia abatement, achieving an ammonia removal rate of approximately 98% in the scrubbing stage. Process optimization including the water vapor addition, multi-stage tubular reactor configuration, controlled pH (9.2-10.8), and continuous H₂O₂ dosing significantly enhanced the conversion of absorbed ammonia into nitrates and nitrites. This transformation not only meets increasingly stringent EU emission regulations, but also supports circular economy principles by recovering nitrogen for use in liquid fertilizers. Ultimately, this cost-effective and scalable solution represents a significant advancement in industrial and agricultural air purification, offering a sustainable pathway toward a greener future.

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Acknowledgement (optional)

Experimental results were accomplished by using Large Research Infrastructure ENREGAT supported by the Ministry of Education, Youth and Sports of the Czech Republic under project No. LM2023056 and by the project OP TAK - Innovative technology for eliminating ammonia emissions from waste air using photochemical oxidation, reg. nr. CZ.01.01.01/01/22_002/0000762, Ministry of Industry and Trade of the Czech Republic.

Valorization of Pineapple Leaf Waste into Fe-Modified Biochar for Efficient H₂S Adsorption

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Keywords: Pineapple-leaf; Biochar; Fe-modification; Hydrogen-sulfide; Gas purification.

Thailand generates large amounts of pineapple leaf (PAL) waste that is often discarded or openly burned, causing environmental concerns. In this study, PAL waste was converted into Fe-modified biochar for hydrogen sulfide (H₂S) removal from gas streams. The adsorbents were prepared by FeCl₃ impregnation followed by pyrolysis under nitrogen atmosphere at different temperatures. The influence of Fe loading and pyrolysis temperature on pore development, iron phase composition, and adsorption performance was investigated.

The results showed that Fe modification significantly enhanced the surface area and pore structure of the biochar while promoting the formation of Fe₃O₄ active species. Among the prepared samples, 2Fe/PALC600 achieved the highest H₂S breakthrough capacity of 380.1 ± 15.4 mg H₂S g⁻¹ sample under 40 % relative humidity. The improved adsorption performance was attributed to the synergistic effect between developed porosity and accessible Fe₃O₄ species on the carbon surface. Humidity enhanced H₂S adsorption, whereas CO₂ slightly reduced the adsorption capacity because of competitive adsorption [1].

XPS analysis confirmed the formation of sulfur-containing species after adsorption [2], while density functional theory (DFT) calculations demonstrated stronger interaction of H₂S with Fe₃O₄ compared with metallic Fe [3]. These findings indicate that Fe-modified PAL-derived biochar is a promising and sustainable adsorbent for H₂S removal and biogas purification.

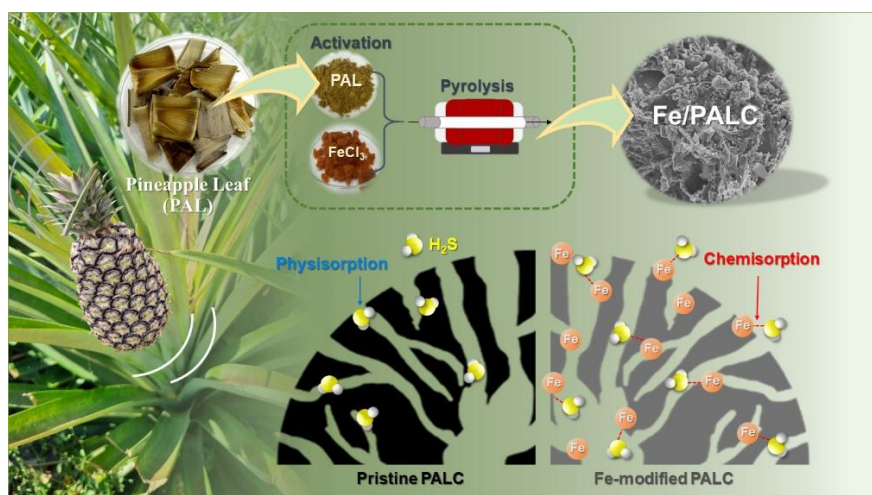
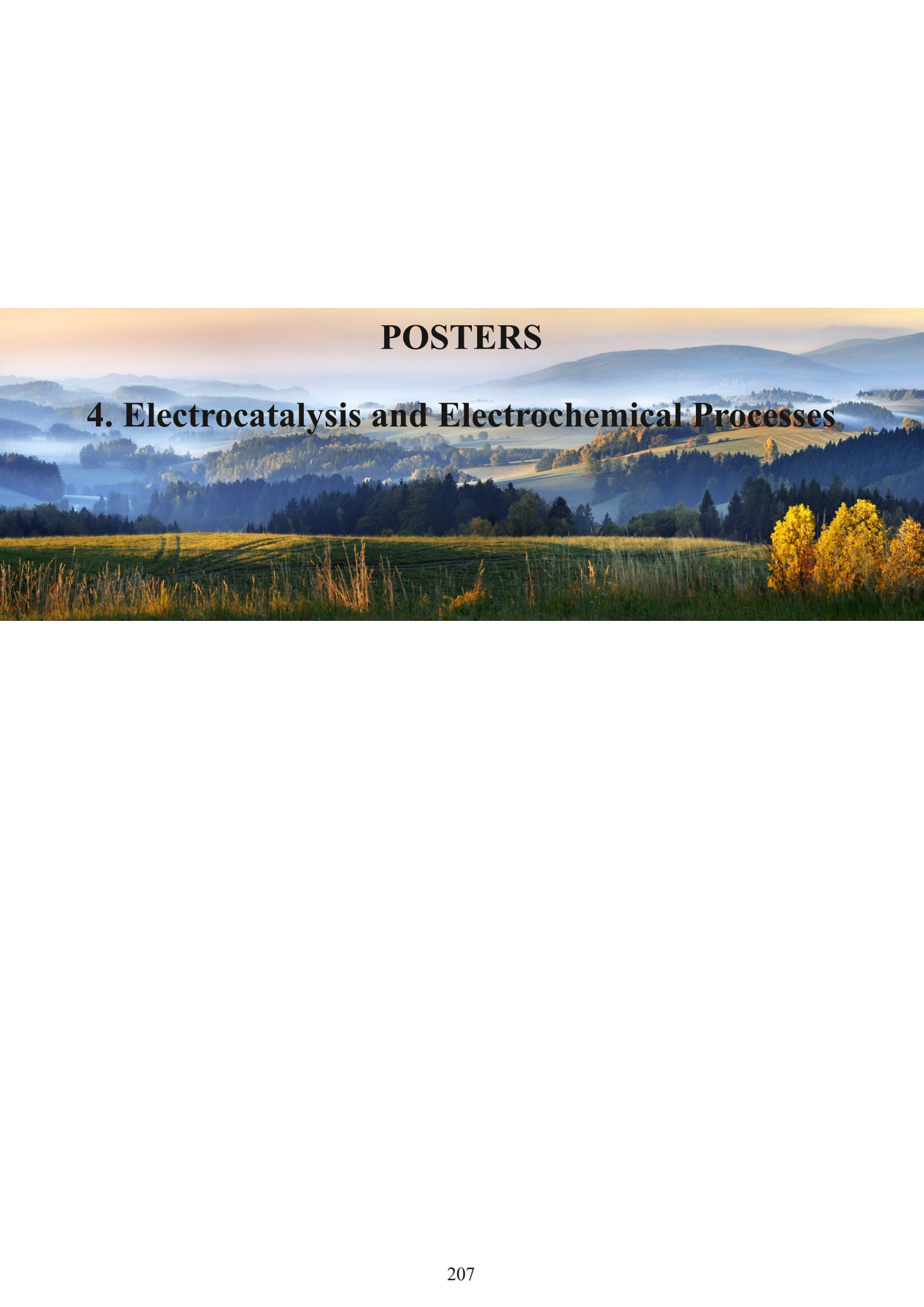


Fig. 1: Preparation route of Fe-modified PAL biochar and proposed H₂S adsorption mechanism.

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POSTERS

4. Electrocatalysis and Electrochemical Processes

Advancing directions for stability enhancement: the best results achieved on composite supported Pt electrocatalysts

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Keywords: TiMoO_x, functionalized carbon, composite material, Pt electrocatalyst, long-term stability

For the wide-range implementation of polymer electrolyte membrane fuel cells (PEMFCs), it is most essential to produce low-cost durable units. Composites of Mo-doped TiO₂ and carbon represent a new class of multifunctional supports proposed for Pt electrocatalysts in PEMFCs, in which the oxide component enhances corrosion resistance and the strong metal-support interaction (SMSI) at the Pt-oxide interface ensures high stability of Pt nanoparticles. Non-traditional carbons such as graphene nanoplatelets (GNPs), graphite oxide (GO) and their mixtures open new potential for use as support components, combining the advantageous properties of both materials in the composite supported Pt electrocatalysts. In this work, our efforts were aimed at clarifying the influence of (i) the functionalization of the carbonaceous component, (ii) the GO/GNP ratio in the mixture of GO and GNP, (iii) the mixed oxide/carbon ratio, and (iv) the reduction temperature that ensures the occurrence of the SMSI effect on the electrocatalytic performance of related Pt/Ti_{0.8}Mo_{0.2}O₂-C catalysts.

The Ti_{0.8}Mo_{0.2}O₂-C composites were synthesized using both a mixture of GO and GNP (denoted as GO&GNP with GO/GNP= 50/50 ratio [1]) as well as unmodified and HNO₃-glucose-functionalized Black Pearls 2000 carbon (denoted as BP and FBP, respectively [2]) as the carbon materials. In addition, the results obtained on the catalyst containing only GO as the starting carbonaceous material (requiring additional solvothermal (ST) treatment) are also included [3]. The samples are identified by a unique identifier, which contains the nominal composition of the composite materials denoted by the nominal weight percentage of the carbon with respect to the mixed oxide content, along with the type of carbon used (C: GO&GNP, BP, FBP or GO): e.g., 25GO&GNP means the composite consisting of 75 wt.% Ti_{0.8}Mo_{0.2}O₂ and 25 wt.% mixture of GO and GNP; in all cases the desired Ti/Mo atomic ratio was 80/20. To induce SMSI, 20 wt.% Pt electrocatalysts were pre-treated at 250 and 350 °C in H₂ stream (denoted as Pt/50FBP-250 and Pt/50FBP-350 [4] or Pt/25GO&GNP-250). Structural and surface chemical properties of the resulting catalysts were studied by N₂ physisorption, XRD, TEM, STEM/EDS and XPS completed with *in situ* H₂ exposure experiments. In the long-term stability test, the samples were submitted to cyclic polarization at a 100 mV s⁻¹ scan rate for 10,000 cycles between 50 and 1000 mV potential limits. Similar measurements on the 20 wt.% Pt/C (Quintech) reference catalyst were done for comparison.

Mo-containing composite supports were prepared by the same ideal structure in mind (i.e., good coverage of oxide crystals on the high surface area carbon). In all investigated catalyst systems, the interaction between the Mo and Pt was found to be decisive regarding either their electrocatalytic properties or the nature of SMSI developing after reductive pre-treatment.

Our best 10,000-cycle stability tests results obtained on 20 wt.% Pt/Ti_{0.8}Mo_{0.2}O₂-C catalysts prepared using different carbonaceous material and various pre-treatments are demonstrated in Figure 1. As can be seen from Figure 1, the most pronounced electrochemically active Pt surface

area (ECSA) decrease was observed on the reference Pt/C ($\Delta\text{ECSA}_{10,000} = 47.8\%$). Long-term stability tests showed improved performance of catalysts prepared using functionalized BP carbon and high carbon content (75 wt.%) compared to supports containing unmodified BP and lower carbon content (50 wt.%). These results suggest that catalysts with high carbon content may have a more uniform microstructure, which may be key to improved stability. A similarly high stability was achieved on the Pt/25GO-ST sample, thus demonstrating the importance of using non-traditional carbon materials. Among the catalysts used without reductive pre-treatment, the Pt/25GO&GNP catalyst demonstrated the best stability after 10,000 polarization cycles ($\Delta\text{ECSA}_{10,000} = 21.2\%$). As can be seen from Figure 1, the use of reductive pre-treatment leads to further improvement in catalyst stability; the result obtained on the Pt/25GO&GNP-250 catalyst ($\Delta\text{ECSA}_{10,000} = 17.0\%$) is the best of all those we obtained on the Pt/Ti_{0.8}Mo_{0.2}O₂-C catalytic system. According to the presented results, the combination of various unmodified, functionalized and non-traditional carbon materials with different treatments carried out during or after sol-gel synthesis resulted in the creation of innovative Pt electrocatalysts with excellent long-term stability.

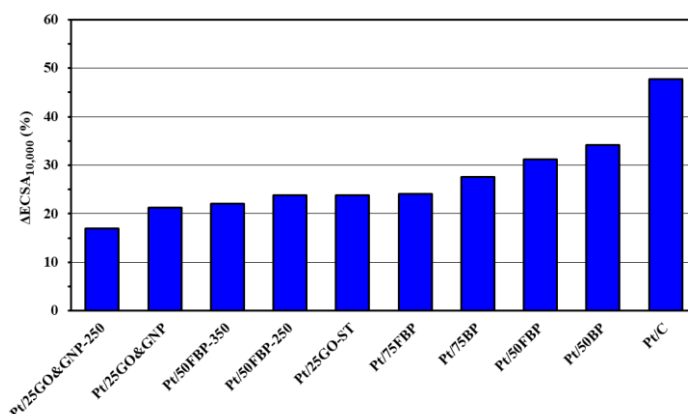
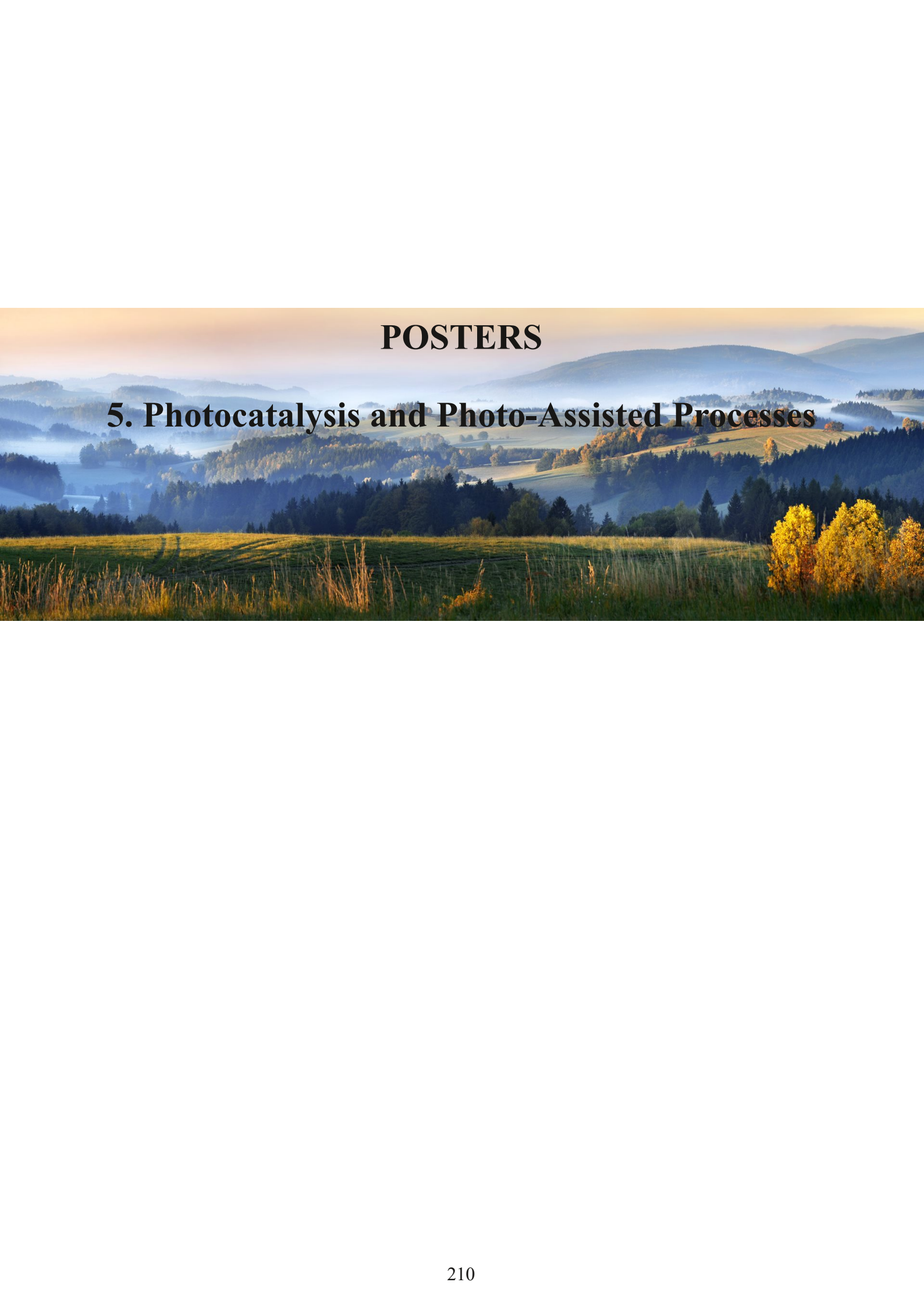


Fig. 1: The best results of the 10,000-cycle stability tests obtained on the Pt/Ti_{0.8}Mo_{0.2}O₂-C catalysts.

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Acknowledgement: This research was funded by Project no. RRF-2.3.1-21-2022-00009, titled the National Laboratory for Renewable Energy, and has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus and by Project no. 2024-1.2.1-HE_PARTNERSÉG-2025-00042, titled European partnerships in Horizon Europe, announced by the National Research, Development and Innovation Office.



POSTERS

5. Photocatalysis and Photo-Assisted Processes

Dry and Bi-reforming of Methane through TiO₂ Photocatalysis under Mild Conditions

María de los Milagros Ballari^a, Rudolf Ricka^a, Kamila Kočí^a

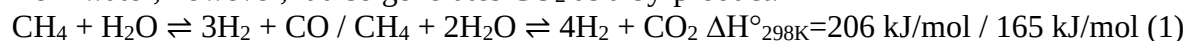
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Keywords: Greenhouse gases; CO₂, CH₄; Photocatalysis; Reforming

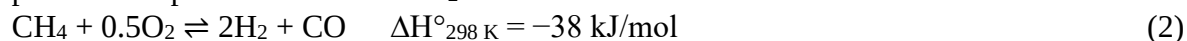
The increase in atmospheric greenhouse gas concentrations, particularly CO₂ and CH₄, is largely driven by anthropogenic activities, including fossil fuel combustion and agriculture [1]. Methane is an abundant energy source but a strong greenhouse gas, making its effective conversion into valuable products crucial for environmental and energy sustainability. Methane reforming enables the production of hydrogen, carbon monoxide, or hydrocarbons, with syngas (H₂/CO mixture) being a key feedstock for chemical synthesis and energy applications.

Conventional reforming methods involve three major oxidants [2]:

i) Steam reforming (SRM) produces the highest yield of H₂ due to the hydrogen contribution from water; however, it also generates CO₂ as a by-product.



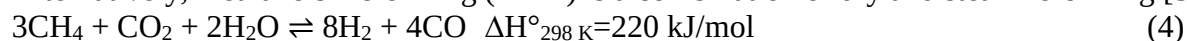
ii) Partial oxidation (POM), using oxygen as an oxidant, requires controlled conditions to prevent complete oxidation to CO₂ and water.



iii) Dry reforming (DRM) employs CO₂, offering an alternative route to syngas while mitigating CO₂ emissions.



Alternatively, methane bi-reforming (BRM) is a combination of dry and steam reforming [3].



This approach enhances the H₂/CO ratio, which is favorable for liquid fuel synthesis.

All these processes involve highly endothermic reactions and require elevated temperatures and significant heat input, often from fossil fuels, which reduces their environmental benefits. Additionally, catalyst deactivation due to carbon deposition (coking) remains a challenge, as solid carbon formation reduces efficiency and can damage reactors.

In contrast, photocatalytic methane reforming has emerged as a promising alternative. Inspired by early studies on photocatalytic water splitting, recent studies have explored the use of light energy to drive methane conversion reactions [1,2]. Although this field has gained traction only recently, interest in photocatalytic methods continues to grow due to their potential for sustainable methane utilization.

In this work, photocatalytic methane dry reforming was investigated using CO₂ as the main oxidant and TiO₂ as a nanostructured photocatalyst. In addition, the effect of water addition was also evaluated to explore the BRM as a hybrid method for CH₄ conversion.

Photocatalytic methane reforming experiments were conducted using TiO₂ (Evonik P25) immobilized on a glass plate (1.04 mg/cm²). The reaction was carried out in a batch reactor (V_R = 556 mL) with recirculation and filled with CO₂ or humidified CO₂ (50% RH), followed by CH₄ injection. After temperature stabilization at 25°C, the reactor was irradiated with a UV-C lamp (254 nm, 304 μW cm⁻²), and gas concentrations (H₂, CO, CH₄) were periodically analyzed by GC-BID (Barrier Discharge Ionization Detector). Control experiments were conducted with He, without photocatalysis, or under dark conditions.

Figure 1 shows CH₄ degradation and H₂/CO formation under UV-C irradiation for dry reforming (Fig. 1a) and bi-reforming (Fig. 1b). Under dry reforming conditions, the methane

degradation rate was lower than the CO formation rate, and the stoichiometry of Eq. (3) was not strictly followed. Notably, CO formation significantly exceeded H₂ production, suggesting that CO may partially originate from CO₂ photoreduction, while some CH₄ may undergo complete oxidation to CO₂ and H₂O. H₂ formation remained limited, reaching a maximum concentration of 0.21 $\mu\text{mol L}^{-1}$ after 4 hours. These results highlight the challenge of achieving selective photocatalytic H₂ production under mild temperature conditions.

For bi-reforming (Fig. 1b), the addition of water clearly enhanced CH₄ degradation, while CO formation proceeded at a lower rate. CO concentration initially increased, and then stabilized, indicating possible sequential CO₂ reduction followed by partial CO reoxidation. H₂ selectivity was only slightly higher than in dry reforming (0.22 $\mu\text{mol L}^{-1}$), and remained low relative to the extent of CH₄ conversion. Overall, the results suggest that a significant fraction of CH₄ is fully oxidized to CO₂ and H₂O, limiting the overall syngas yield.

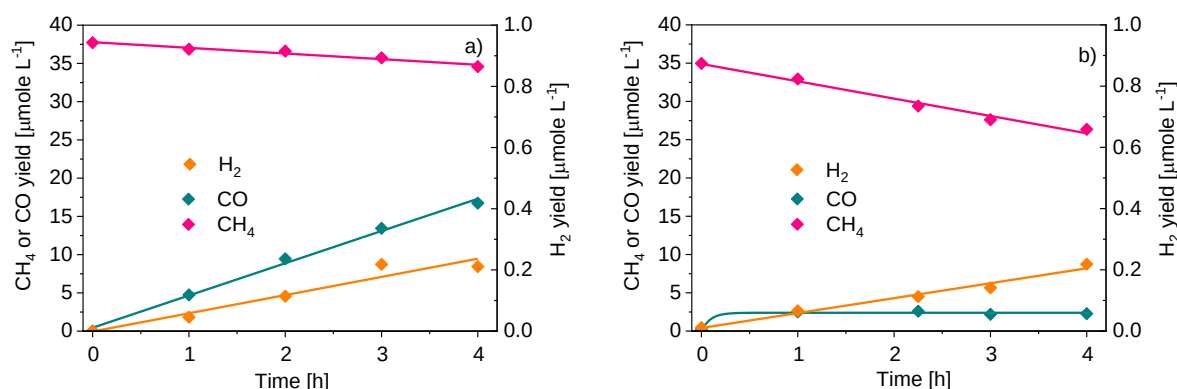


Fig. 1: H₂, CO, and CH₄ concentration profiles during CH₄ photocatalytic reforming at mild conditions and under UV-C irradiation. a) Dry reforming (DRM). b) Bi-reforming (BRM)

Control experiments using He instead of CO₂ showed similar CH₄ degradation but with negligible CO and H₂ formation, supporting the conclusion that, in the absence of CO₂, CH₄ undergoes complete oxidation rather than selective reforming. Photolysis experiments (UV-C without TiO₂) resulted in measurable CH₄ conversion, but the reaction rates for CH₄ disappearance and H₂ and CO formation were significantly lower than in the presence of irradiated TiO₂. No CH₄ conversion was observed in the absence of radiation.

Further work is needed to elucidate the reaction pathways in photocatalytic methane reforming. Future studies will focus on optimizing reaction parameters such as CO₂/CH₄/H₂O ratios, reactant concentrations, and temperature; testing alternative photocatalysts with improved selectivity toward syngas; and conducting kinetic studies to better understand the influence of key variables on methane conversion and product distribution.

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Acknowledgement

This research was financially supported by the Large Research Infrastructure ENREGAT (project No. 2023056), the European Union under the REFRESH – Research Excellence For Region Sustainability and High-tech Industries (Project No. CZ.10.03.01/ 00/22_003/0000048).

Atmosphere-dependent Work Function and Surface Photovoltage of Photocatalysts under Illumination

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Keywords: Work function; Surface photovoltage; Kelvin probe; Photocatalysis; Controlled atmosphere

This contribution presents ongoing work aimed at exploring how the work function (Φ) and surface photovoltage (SPV) of photocatalytic materials respond to changes in atmosphere, humidity, and illumination. The study focuses on two markedly different photocatalytic systems: TiO₂ (P25), a widely used oxide semiconductor, and graphitic carbon nitride (g-C₃N₄), considered here as a representative metal-free photocatalyst with distinct electronic and surface properties. In both cases, surface electronic behavior is strongly affected by adsorbates such as water and oxygen.

Introduction

The surface electronic structure of photocatalysts plays a key role in charge separation and recombination processes, directly impacting catalytic performance. In materials such as TiO₂ (P25) [1] and, graphitic carbon nitride (g-C₃N₄), the work function (Φ) and surface photovoltage (SPV) are highly sensitive to adsorbates, which can modify surface dipoles and band bending [2]. Due to their fundamentally different electronic structures and surface chemistries, these materials provide an attractive platform to investigate how atmospheric conditions and illumination influence surface electronic properties.

Methodology

Kelvin probe (KP) mapping is used to measure the work function and illumination-induced contact potential difference (Δ CPD). Measurements are performed on macroscopic pellets (~1 cm diameter) under controlled atmospheres (Ar, N₂, and dry air) with adjustable relative humidity. The experiments are carried out using a commercial Kelvin probe system (Instytut Fotonowy), equipped with LED-based discrete wavelength illumination (836, 727, 625, 591, 530, 464, 425, 394, and 370 nm), enabling wavelength-dependent surface photovoltage analysis, as demonstrated in recent Kelvin probe-based studies of photocatalytic systems [3]. The experimental approach is currently applied to TiO₂ (P25) and will be extended to other photocatalytic materials, including g-C₃N₄) to enable comparative analysis.

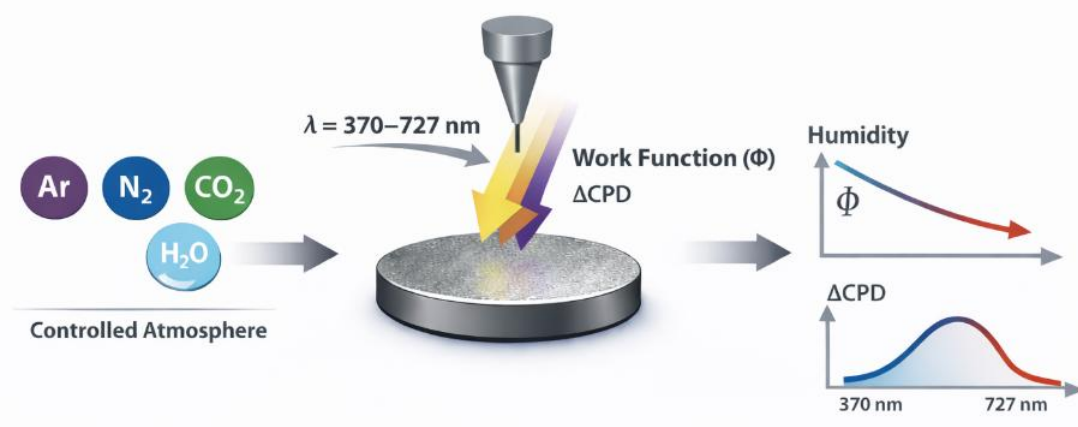


Fig. 1: Schematic representation of the Kelvin probe (KP) measurement setup under controlled atmosphere and illumination.

Results and Discussion

Preliminary results for P25 TiO₂ under Ar at low humidity show a decrease in Φ with decreasing humidity. Under near-bandgap illumination, a negative ΔCPD is typically observed, consistent with reduced band bending in this n-type semiconductor. However, for shorter wavelengths, a marked positive ΔCPD is also detected, suggesting the presence of additional photoinduced surface processes. The magnitude of the response strongly depends on the surrounding atmosphere. These results are preliminary and represent an initial stage of the study.

Conclusions

The preliminary results highlight the strong coupling between atmosphere, humidity, and surface electronic properties. The combination of controlled-atmosphere Kelvin probe measurements and wavelength-selective illumination provides a promising approach to probe adsorbate effects in photocatalysts. Further measurements are currently in progress.

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Acknowledgements

We acknowledge financial support from the European Union through the REFRESH – Research Excellence For REgion Sustainability and High-tech Industries project (No. CZ.10.03.01/00/22_003/0000048) via the Operational Programme Just Transition, and from the ENREGAT project (No. LM2023056) supported by MŠMT.

Tuning Textural Properties of DIW-Printed PHI Films via Drying Control and Porogen Engineering

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Keywords: PHI; precipitation; formulation; direct ink writing; morphology

Poly(heptazine imide) (PHI) represents a structurally well-defined subclass of polymeric carbon nitrides that has recently attracted significant attention due to its tunable electronic structure and promising performance in photocatalytic and photoelectrochemical applications. In contrast to conventional g-C₃N₄ materials, PHI can be processed from aqueous dispersions, opening a pathway toward the fabrication of binder-free thin films.[1] However, the practical implementation of PHI in structured coatings remains limited by challenges in controlling film formation, particularly with respect to wetting, drying behavior, and resulting morphology. Addressing these challenges requires a systematic approach that bridges material synthesis with controlled processing strategies, enabling the rational design of PHI-based functional layers.[2]

PHI dispersions were prepared via a salt-melt[3] synthesis followed by extensive dialysis to remove residual ions and low-molecular byproducts, yielding stable but highly dilute aqueous sols.[4] To enable film formation, the product was subsequently concentrated and separated using a controlled precipitation–centrifugation route based on a 3-factor screening (A×B×C): (A) precipitant composition (anhydrous EtOH; anhydrous EtOH/acetone 3:1; 96% EtOH/acetone 3:1), (B) precipitation regime (fast vs. slow addition under stirring), and (C) post-separation consolidation (single vs. re-centrifugation). Among the tested variants (S1–S12), the S12 formulation (96% EtOH/acetone 3:1, slow addition, re-centrifugation) was identified as the optimal baseline, providing homogeneous, readily redispersible pastes with reliable extrudability and laterally uniform tracks. Importantly, S12 also offers a practical advantage by avoiding the need for anhydrous ethanol, making the route more scalable while maintaining coating quality. This step establishes a reproducible and technologically relevant starting point for further processing while preserving the intrinsic chemical integrity of the PHI phase.

Building on this baseline, a systematic additive and porogen strategy was implemented to control film formation during wet deposition and to tailor the final texture after drying and thermal treatment. Three organic humectants with distinct physicochemical characteristics—glycerol (high viscosity, low volatility), ethylene glycol (moderate viscosity, hydrophilic), and ethylene glycol monopropyl ether (amphiphilic, higher volatility)—were selected to decouple the effects of viscosity, wettability, and evaporation kinetics. Each additive was evaluated both individually and in combination with ammonium bicarbonate (NH₄HCO₃) as a thermolabile porogen. This design enables independent assessment of (i) wetting, spreading, and consolidation behavior in the as-deposited state and (ii) pore formation induced upon thermal decomposition of the porogen. The resulting 2 × (3 + 3) matrix provides a mechanistically interpretable framework for linking formulation chemistry to film topology and, ultimately, to functional properties.

The formulated PHI pastes were deposited using direct ink writing (DIW), enabling controlled fabrication of well-defined coatings on FTO-coated glass substrates. The extrusion-based approach ensures precise placement of material and reproducible line geometry, while

minimizing uncontrolled spreading typical of drop-casting methods. By optimizing the deposition parameters, continuous and laterally uniform tracks were obtained, which coalesced into homogeneous coatings with a typical thickness of $\sim 1\ \mu\text{m}$ after drying. This strategy provides a robust route to prepare structured, binder-free PHI films suitable for subsequent photoelectrochemical characterization.

Ongoing work focuses on a detailed texture analysis of the as-prepared and thermally treated films, combining profilometry/AFM with electron microscopy to resolve topology, roughness, and pore formation across the additive/porogen matrix. These structural descriptors will be correlated with electrochemical and photocatalytic performance, including dye degradation as a model reaction, to establish quantitative structure–property relationships. This approach is expected to identify processing–texture–function links that guide the rational optimization of PHI coatings for photoelectrochemical applications.

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Acknowledgement

This work was supported by Czech Science Foundation through project 26-22262S.

Role of PEG in Tuning Structure and Photocatalytic Activity of MOF–Cellulose Acetate Membranes

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Keywords: cellulose acetate, sustainable membranes, copolymer, MOF

The development of functional polymer membranes with tailored properties is of increasing interest for environmental and catalytic applications. Cellulose acetate (CA) represents a widely used polymer due to its processability and biodegradability; [1–3] however, its performance can be further enhanced through the incorporation of functional additives. In this work, CA-based films are modified by the addition of polyethylene glycol (PEG) and metal–organic frameworks (MOFs) to investigate their combined influence on membrane structure and photocatalytic potential. [4–6]

Membranes are prepared via solution casting using selected conventional and green solvents, considering their polarity, volatility, and compatibility with the polymer–additive system. PEG is incorporated to influence hydrophilicity and phase separation behavior, while MOFs are introduced as functional fillers providing potential photocatalytic activity. The interplay between solvent properties and additive incorporation is expected to affect solution behavior, film formation, and resulting morphology.

The prepared membranes are characterized using Fourier-transform infrared spectroscopy (FTIR) to verify chemical structure, scanning electron microscopy (SEM) to evaluate morphology and porosity, and X-ray diffraction (XRD) to assess structural organization. The photocatalytic activity of the membranes is evaluated in terms of the removal of organic pollutants from water under irradiation, using methanol as a model compound, while simultaneously assessing hydrogen generation as a potential energy carrier.

The combination of PEG and MOFs within the CA matrix provides a versatile platform for tuning membrane properties. The study highlights the role of additive interactions in controlling membrane structure, functionality and influence on photocatalytic performance of the composite contributing therefore to the development of advanced materials with potential applications in water treatment and sustainable energy production.

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Acknowledgement

This work was supported by the Large Research Infrastructure ENREGAT (projects No. LM2023056 and LM2018098), by the European Union through the REFRESH—Research Excellence For REgion Sustainability and High-tech Industries project (No. CZ.10.03.01/00/22_003/0000048) under the Operational Programme Just Transition, COST Action EU4MOFs (COST Action CA22147) and by the Czech Ministry of Education, Youth and Sports under the project Metal-organic framework (MOF) Profiling for Cutting-Edge Wastewater Treatment: Characterization and Performance Assessment (LUC25056) and student project SP2026/080 of VSB–Technical University of Ostrava.

In situ grown sepiolite/UiO-66-NH₂ composites for photocatalytic hydrogen evolution from aqueous methanol

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Keywords: Sepiolite; UiO-66-NH₂; MOF–clay composite; Photocatalytic hydrogen evolution; Methanol photoreforming

Sustainable energy technologies have driven increasing interest in photocatalytic hydrogen production using tunable porous materials. Zr-based UiO-type MOFs, particularly UiO-66-NH₂, are attractive due to their porosity, stability and linker-dependent photoresponse. However, their performance may be affected by particle aggregation, restricted charge transport and limited accessibility of reactive sites. Hybridization with sepiolite, a fibrous magnesium silicate bearing silanol groups and channel-like porosity, offers a promising route to improve MOF dispersion, interfacial contact and exposure of active sites.

In this work, in situ grown sepiolite/UiO-66-NH₂ composites were prepared as hybrid MOF–clay materials and investigated for the photocatalytic removal of organic pollutants from water under UV-A irradiation, using methanol as a model compound, while simultaneously evaluating hydrogen generation as a potential energy carrier.

A series of composites with different nominal UiO-66-NH₂:sepiolite mass ratios was synthesized by an in situ solvothermal method using ZrCl₄ and 2-aminoterephthalic acid as MOF precursors, DMF as solvent and acetic acid as modulator. The resulting materials were recovered, washed, solvent-exchanged with methanol and dried, while pure UiO-66-NH₂ and process-treated sepiolite were prepared for comparison. The composites were systematically characterized by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy coupled with energy-dispersive spectroscopy, thermogravimetric analysis, N₂ physisorption, zeta-potential measurements, UV-Vis diffuse reflectance spectroscopy, photoluminescence spectroscopy and photocurrent response analysis. Photocatalytic performance was evaluated in terms of simultaneous methanol degradation and hydrogen evolution from aqueous solution under 365 nm irradiation in a stainless-steel batch photoreactor using a Thorlabs M365LP1 mounted UV LED source.

XRD and FTIR confirmed the formation of genuine sepiolite/UiO-66-NH₂ composite systems, with characteristic contributions from both the fibrous clay matrix and the Zr-based MOF phase. Increasing nominal UiO-66-NH₂ loading led to progressive strengthening of MOF-related diffraction and vibrational features, while sepiolite-associated signals remained detectable across the series, indicating that the main structural features of both parent components were preserved. SEM–EDS revealed a clear composition-dependent morphological evolution, from largely visible sepiolite fibres decorated by fine UiO-66-NH₂-derived domains at lower MOF loading to progressively more pronounced Zr-rich MOF coverage at higher UiO-66-NH₂ contents, as shown in Figure 1. Textural analysis showed a non-monotonic evolution of porosity, where low MOF loading may partially restrict access to the native

sepiolite pore/channel system, whereas higher MOF contents progressively introduce UiO-66-NH₂-derived microporosity and increase the accessible surface area. Zeta-potential measurements demonstrated that UiO-66-NH₂ growth substantially modifies the exposed surface chemistry of sepiolite, particularly in the acidic region, while maintaining negatively charged surfaces under near-neutral conditions relevant to photocatalytic testing. UV-Vis DRS, photoluminescence and photocurrent measurements enabled the optical response, charge-carrier recombination behaviour and photoinduced charge separation to be related to the observed photocatalytic performance.

The photocatalytic results show that the sepiolite/UiO-66-NH₂ architecture influences the combined process of pollutant degradation and hydrogen generation not simply through the amount of MOF present, but through the combined effects of MOF nucleation, clay surface coverage, accessible porosity, surface charge and photoinduced charge-carrier dynamics. Overall, the results demonstrate that sepiolite acts as a multifunctional structural and interfacial matrix rather than as a passive diluent or inert support. This work highlights in situ grown sepiolite/UiO-66-NH₂ composites as promising hybrid materials for photocatalytic water purification coupled with hydrogen production and, more broadly, demonstrates the potential of fibrous clay minerals as platforms for designing MOF-based photocatalysts with tunable morphology, surface chemistry, porosity and photoresponse.

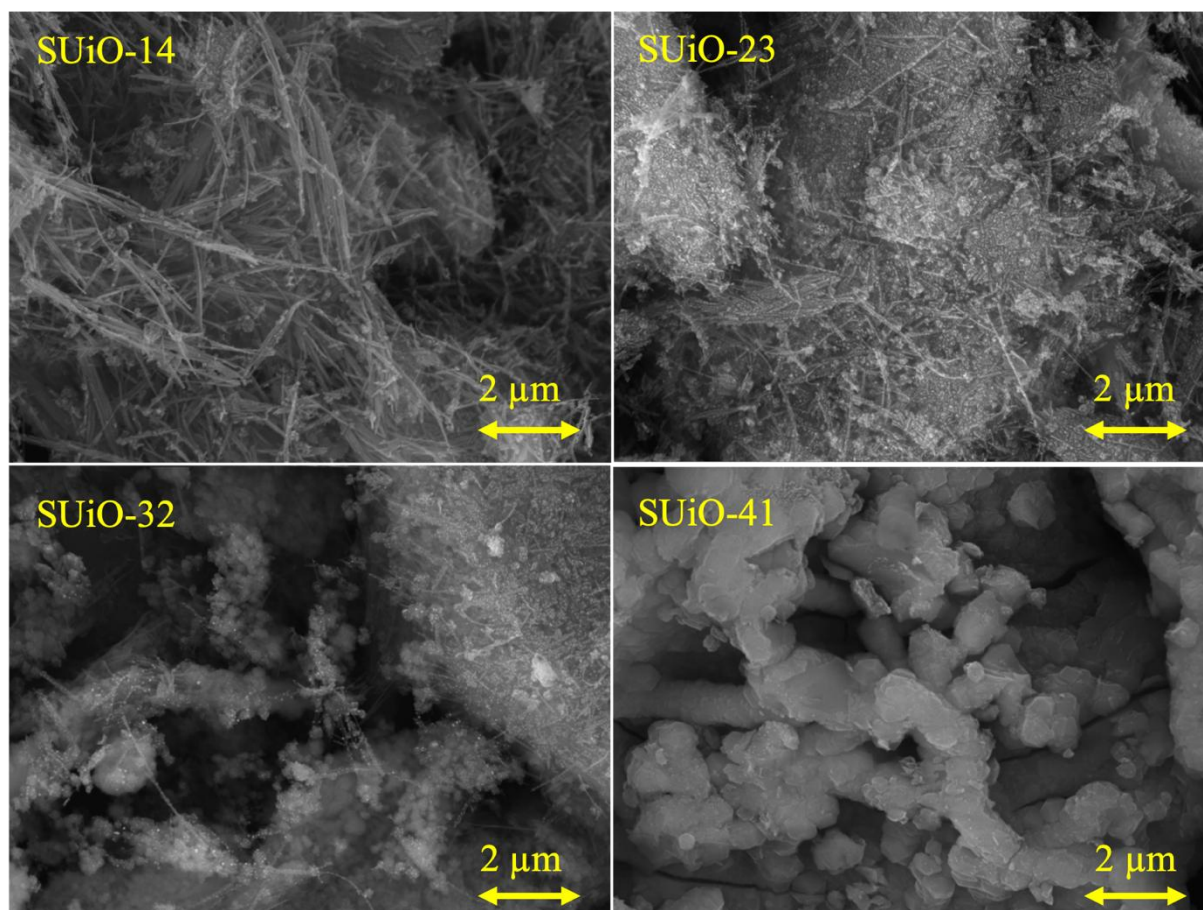


Fig. 1: SEM micrographs of SUiO-14, SUiO-23, SUiO-32 and SUiO-41.

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Acknowledgement (optional)

This work was supported by the Large Research Infrastructure ENREGAT (projects No. LM2023056 and LM2018098), by the European Union through the REFRESH—Research Excellence For REgion Sustainability and High-tech Industries project (No. CZ.10.03.01/00/22_003/0000048) under the Operational Programme Just Transition, COST Action EU4MOFs (COST Action CA22147) and by the Czech Ministry of Education, Youth and Sports under the project Metal-organic framework (MOF) Profiling for Cutting-Edge Wastewater Treatment: Characterization and Performance Assessment (LUC25056). The authors are grateful to Kamil Maciej Górecki for SEM, XRF, and FTIR measurements, Jan Bednárek for ζ -potential measurements, and Rozálie Wdóvková for TGA-DSC measurements.

Platinum-modified TiO₂ for green hydrogen formation from water splitting as a side reaction of CO₂ photoreduction

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Keywords: photocatalysis, titanium dioxide, green hydrogen, water splitting, CO₂ photoreduction

Photocatalytic green hydrogen production via water splitting, as a viable renewable technology for substituting fossil fuels, demands substantial investigation. Overall process efficiency, scalability, and process durability are still underdeveloped. Therefore, the selection of a photocatalyst plays a significant role in making this process feasible in the future [1]. An excellent example of such a material is platinum-modified TiO₂, which, in addition to CO₂ photoreduction, is highly effective for H₂ formation (when the reaction occurs in humid conditions).

In this study, all platinum-modified TiO₂ samples were synthesized via a sol-gel method utilizing titanium isopropoxide and dihydrogen hexachloroplatinate(IV) hydrate as TiO₂ and Pt nanoparticles precursors, respectively. After mechanical mixing of both precursors, calcination of samples was conducted at 400 °C in an argon atmosphere (see Figure 1).

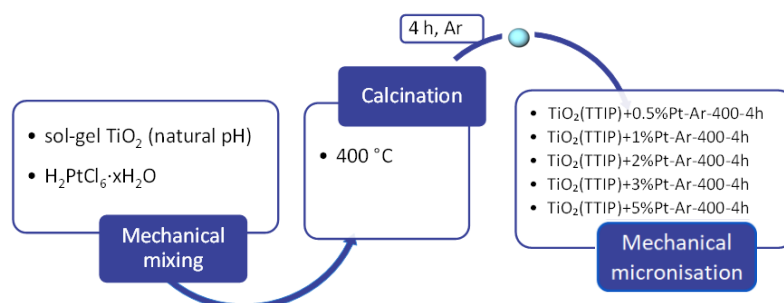


Figure 1: A scheme of Pt-modified TiO₂ photocatalysts synthesis

The obtained photocatalysts were characterized in detail by means of a low-temperature N₂ adsorption-desorption (S_{BET}, V_{total}, V_{micro}, V_{meso}), UV–Vis Diffuse Reflectance Spectroscopy (UV–Vis/DRS), Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT), Scanning Electron Microscopy (SEM), thermogravimetric analysis (TG/DTG), etc. The content of platinum was detected by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

The photocatalytic activity of Pt-modified TiO₂ photocatalysts was performed in a batch photoreactor (volume of 766 cm³) equipped with a gas circulation system and a UV light source (Figure 2a) [2]. Results of the tests are presented in Figure 2 b-d.

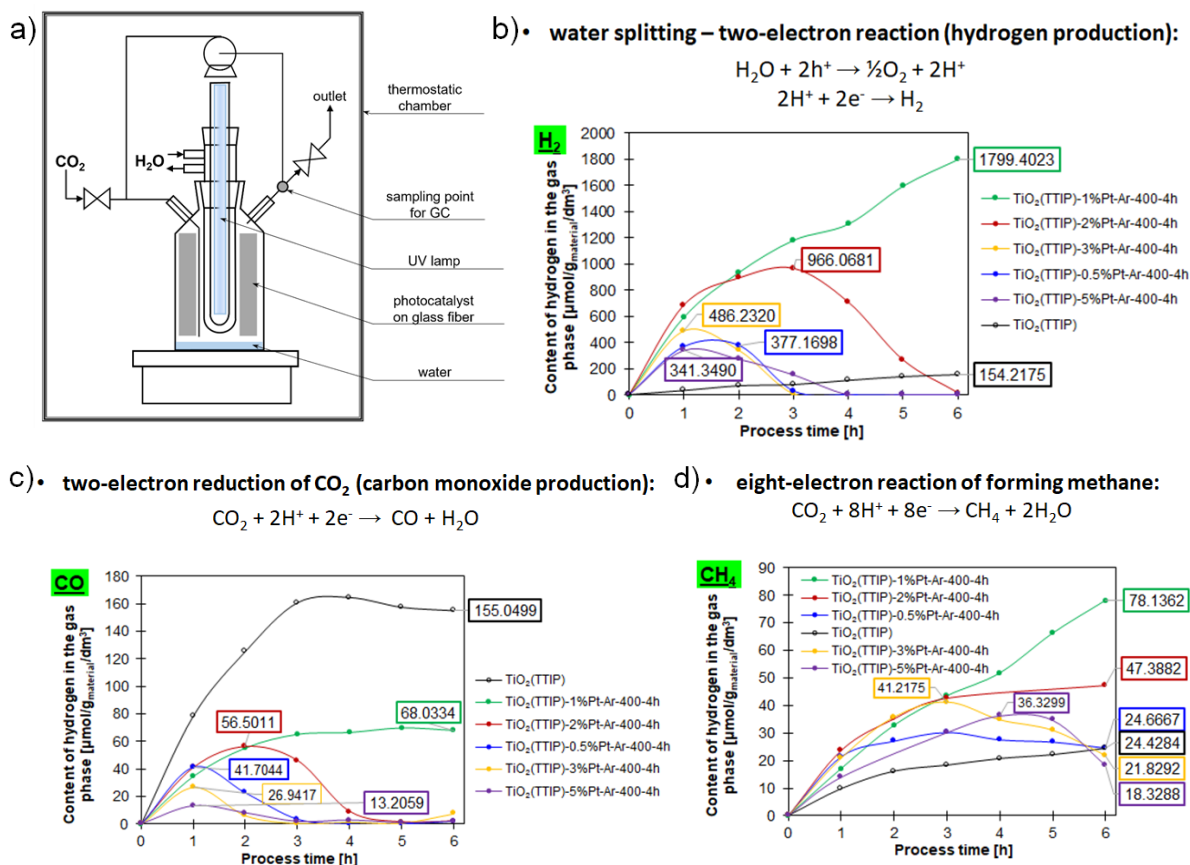


Figure 2: a) An experimental set-up; b) H₂ formation as a side reaction of CO₂ photoreduction; c) CO formation; d) CH₄ formation on Pt-modified TiO₂ in a humid environment

A platinum-modified TiO₂ with low CO₂ photoreduction efficiency (low amounts of CO and CH₄ were formed), was highly effective for the H₂ production under humid conditions (for TiO₂ modified with 1 wt.% of platinum, ca. 1.8 mmol/g_{cat}/dm³ was generated). It can generally be assumed that platinum-modified titania promotes green hydrogen formation, thereby limiting the rate of CO₂ photocatalytic reduction.

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Acknowledgement: Funded by the National Science Centre, Poland, under the OPUS-28 call in the Weave programme (Project no. 2024/55/I/ST8/01898). The authors also thank the Czech Science Foundation for project 26-19910L.

Defect-Engineered CeO₂ for CO₂ Photoreduction: Tuning Photoactivity and Selectivity via Ni₂P

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Keywords: Photocatalysis, CO₂ reduction, CeO₂, Ni₂P, defects

Carbon dioxide (CO₂) is one of the main drivers of global warming and climate change. Given these environmental issues, it is essential to continue the development of new technologies and improve the efficiency of existing ones for CO₂ utilization. Photocatalysis represents one of the most promising strategies, enabling the reduction and conversion of CO₂ molecules into valuable chemicals such as methane or carbon monoxide, which can be further utilized in other technologically important processes. However, despite its potential, its practical application remains limited, mainly due to low CO₂ conversion efficiency. Therefore, the design and synthesis of new advanced photocatalysts are essential to not only significantly enhance photocatalytic activity but also to control selectivity toward the formation of carbonaceous products [1-3].

In this study, CeO₂ and Ni₂P-modified CeO₂ photocatalysts were synthesized via chemical precipitation followed by calcination and hydrothermal treatment. The prepared photocatalysts were comprehensively characterized using XRD, XPS, and photocurrent measurements. Finally, the photocatalytic performance of the obtained samples was evaluated in a batch-stirred photoreactor under UV-C irradiation (8W Hg lamp, $\lambda_{\text{max}} = 254$ nm; Ultra-Violet Products Inc., Upland, USA; Fig. 1a). Photocatalytic tests were carried out in a reaction mixture consisting of an aqueous NaOH solution (0.2 M) and 20 mg of powder photocatalyst. During these experiments, samples of the gaseous phase were taken at predetermined time intervals (0, 2, 4, 6, and 7 hours) and analyzed using a gas chromatograph equipped with a BID (barrier discharge ionization detector). Hydrogen (H₂), carbon monoxide (CO), and methane (CH₄) were identified as the main reaction products.

Based on the results obtained, it is evident that among all tested photocatalyst samples, pure Ni₂P exhibited the highest photocatalytic efficiency for CO₂ photoreduction (Fig. 1b). Furthermore, the successful modification of CeO₂ with Ni₂P led to a significant increase in CO and CH₄ formation compared to pristine CeO₂. This improvement is likely related to the presence of oxygen vacancies and increased charge transport at the CeO₂-Ni₂P interface, possibly due to the formation of heterojunction, which promotes efficient charge carriers separation and enhances photocatalytic performance.

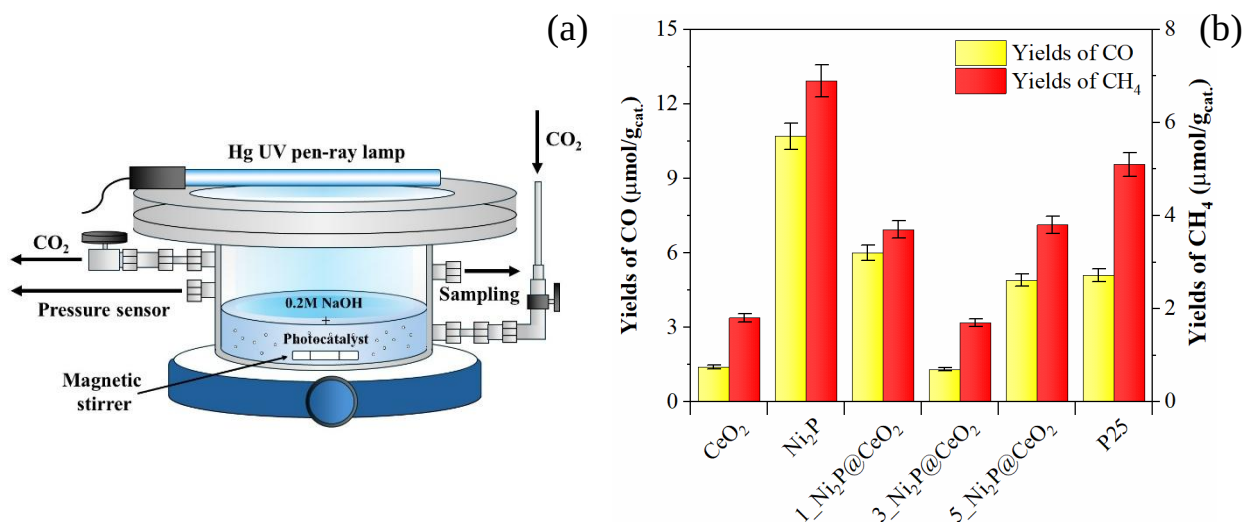


Fig. 1: Scheme of the batch-stirred photoreactor (a) and yields of carbonaceous products CO and CH₄ after 7 h of CO₂ photoreduction over the investigated photocatalysts (b).

In summary, the Ni₂P photocatalyst exhibited superior activity in CO₂ photoreduction and significantly enhanced the performance of Ni₂P@CeO₂ heterostructure photocatalysts. The improved performance can be attributed to the synergistic interplay between surface oxygen vacancies and increased interfacial charge transfer, possibly involving the formation of a heterojunction, which promotes efficient charge separation. These findings underscore the potential of Ni₂P-modified CeO₂ as a promising photocatalyst for CO₂ conversion.

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Acknowledgement

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Printed Oxygen Indicator for Smart Packaging

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Keywords: printed indicator, oxygen, photocatalysis

This work focuses on the study of the influence of dye selection on the performance of a photocatalytic oxygen indicator intended for potential application in smart packaging systems. Such indicators are designed to provide a simple visual signal of oxygen presence, which is critical for monitoring the integrity of oxygen-sensitive products, particularly in the food and pharmaceutical industries.

The investigated system is based on a TiO₂ photocatalytically activated mechanism. The indicator is initially activated by a short exposure to UV radiation under oxygen-free conditions. During this activation step, the dye undergoes photoreduction to its corresponding leuco form. This reduced form is typically colourless or weakly coloured. Upon subsequent exposure to trace amounts of oxygen, the leuco dye is oxidized back to its original coloured state, resulting in a visible colour change that serves as an indication of oxygen ingress.

The performance of this photocatalytic system depends on several interacting variables. Key parameters include the intensity of the activating radiation, the concentration and chemical nature of the electron donor, and the specific type of dye used. Among these, the choice of dye plays a particularly significant role, as it directly affects both the sensitivity of the indicator to oxygen and its optical properties.

In this study, different dyes were systematically evaluated with respect to their behaviour within the photocatalytic system. Special attention was paid to their reduction efficiency during UV activation and their responsiveness to low oxygen concentrations during reoxidation. Furthermore, the light stability (photostability) of the coloured form of each dye was assessed, as this parameter is crucial for practical applications where the indicator may be exposed to ambient light conditions over extended periods.

The results demonstrate that dye selection strongly influences not only the kinetics of the colour change but also the long-term stability of the indicator signal. Certain dyes exhibited rapid and reversible responses to oxygen but suffered from limited light stability, while others showed improved resistance to photodegradation at the expense of slower response times.

Overall, this work highlights the importance of careful optimization of dye properties within photocatalytic oxygen indicators. The findings contribute to the development of more reliable and robust smart packaging systems, where a balance between sensitivity, stability, and practical usability is essential.

Enhancing the Photo-response of ZnO through CdS/g-C₃N₄ Coupling for Efficient Dye Degradation and Solar Cells

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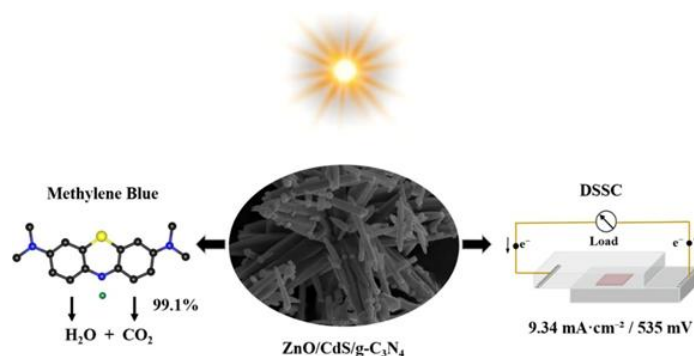
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Keywords: ZnO nanorods, CdS/g-C₃N₄, photocatalysis, Z-scheme, DSSC

Addressing the escalating worldwide need for renewable power and purified water requires the engineering of versatile materials designed for effective solar energy harvesting and environmental decontamination. While Zinc Oxide is a promising semiconductor, its practical efficiency is often limited by a wide optical band gap and rapid charge carrier recombination. In this study, we report the synthesis and characterization of hierarchical ternary ZnO/CdS/g-C₃N₄ heterostructure designed to overcome these limitations [1]. The ternary composite was fabricated via a three-step method involving the hydrothermal growth of ZnO nanorods, followed by the deposition of CdS nanospheres and the ultrasonication-assisted incorporation of graphitic carbon nitride. Comprehensive characterizations confirmed successful heterojunction formation along with a reduction in the optical band gap to 2.35 eV, extending light absorption deep into the visible region. The photocatalytic performance was evaluated through Methylene Blue degradation under UV-vis irradiation. The ZnO/CdS/g-C₃N₄ composite achieved a remarkable degradation efficiency of 99.1% within 75 min, with an apparent rate constant of 0.062 min⁻¹, approximately 2-3 times higher than those of the individual components. Radical scavenger experiments and band alignment analysis identified a double Z-scheme charge transfer mechanism, with superoxide radicals (•O₂⁻) acting as the primary reactive species. Furthermore, the material was integrated into dye-sensitized solar cells (DSSCs) using a novel layered photoanode configuration. The ternary composite delivered a power conversion efficiency (PCE) of 2.23%, with a short-circuit current density (J_{sc}) of 9.34 mA cm⁻² and an IPCE of 24.2% at 530 nm. These results demonstrate that the synergistic coupling of CdS and g-C₃N₄ with ZnO nanorods enhances visible-light harvesting and charge separation, offering a robust platform for both wastewater treatment and photovoltaic applications.

Fig. 1:



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Photoreforming of PET and PLA microplastics over TiO_2 and $\text{g-C}_3\text{N}_4$ photocatalysts

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Keywords: Microplastics, PET, PLA, photoreforming, hydrogen.

The photoreforming of polyethylene terephthalate (PET) and polylactic acid (PLA) microplastics has been investigated as a sustainable approach for the production of useful chemicals including hydrogen also known as “trash to treasure.” The photoreforming of both microplastics to obtain hydrogen was considered to be feasible based on the thermodynamic analysis of the degradation of PET and PLA as demonstrated in Table 1.

Tab. 1: Calculated thermodynamic parameters

Microplastics	ΔH^0_{298} (kJ mol ⁻¹)	ΔS^0_{298} (kJ mol ⁻¹)	ΔG^0_{298} (kJ mol ⁻¹)
PET	891	3.59	-181
PLA	277	1.13	-61.0

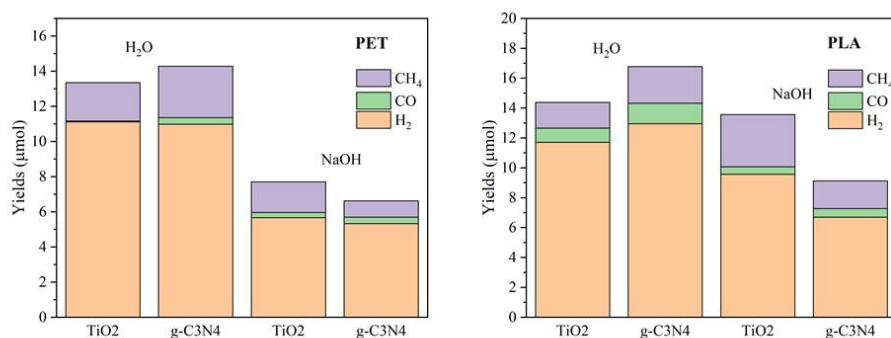


Fig. 1: Yields of three main gaseous products of PET (left) and PLA (right) degradation after 4 h under irradiation at 254 nm.

Photolysis experiments revealed that hydrogen was the main product, although methane and carbon monoxide were also produced. The introduction of NaOH reduced the hydrogen yield owing to the neutralisation of carboxylic groups and the scavenging of hydrogen radicals with hydroxide ions. The addition of TiO_2 and $\text{g-C}_3\text{N}_4$ photocatalysts (i.e., photocatalytic experiments) enhanced hydrogen evolution, with $\text{g-C}_3\text{N}_4$ outperforming TiO_2 in aqueous suspensions as shown in Figure 1. However, its structural stability was compromised under alkaline conditions leading to decreased photocatalytic efficiency.

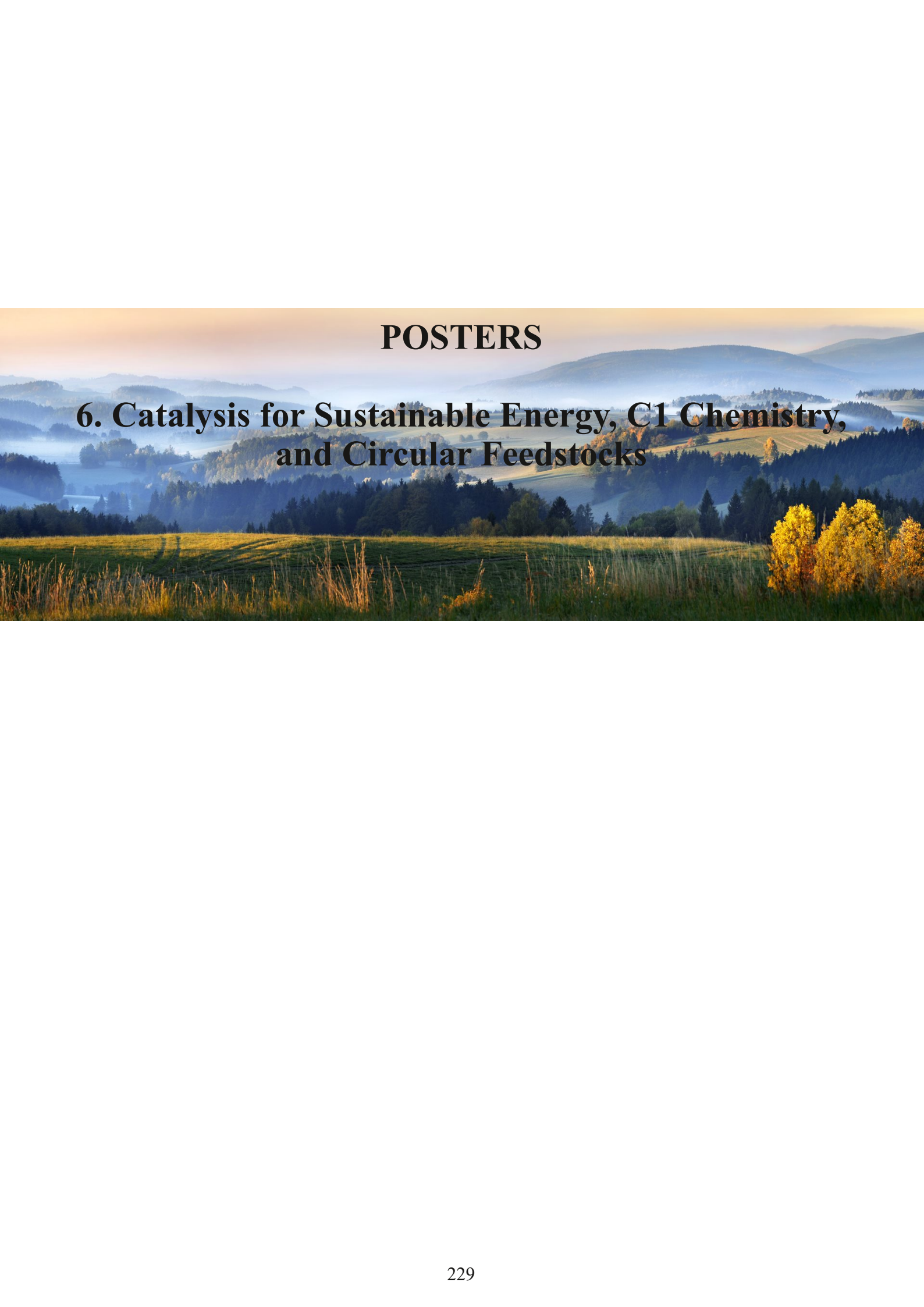
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Acknowledgement

This study was financially supported by the European Union under the REFRESH – Research Excellence For REgion Sustainability and High-tech Industries (Project No. CZ.10.03.01/ 00/22_003/0000048) via the Operational Programme Just Transition. The authors also thank the Large Research Infrastructure ENREGAT (Project No. LM2023056).

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POSTERS

6. Catalysis for Sustainable Energy, C1 Chemistry, and Circular Feedstocks

Molybdenum oxide as an efficient promoter for enhancing ethanol steam reforming over Ni/CeO₂ catalyst for hydrogen production

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Keywords: Ethanol steam reforming, Nickel catalyst, Mo doping, Hydrogen production

Ethanol steam reforming (ESR) is an endothermic process that can produce up to 6 mol of H₂ per mol of ethanol; however, its efficiency strongly depends on reaction conditions. High steam-to-ethanol ratios favour hydrogen production, whereas lower water content promotes side reactions that lead to CO formation and reduced H₂ yield. Due to its complex reaction network, ESR involves multiple pathways generating intermediates such as acetaldehyde, ethylene, and methane, which contribute to undesired reactions, including methanation and carbon formation, ultimately causing catalyst deactivation [1,2].

Ni-based catalysts are widely studied owing to their high activity and low cost, but their susceptibility to carbon deposition remains a major limitation [2]. Various approaches have been proposed to improve their performance, including support selection, promoter incorporation, and control of metal dispersion [2-4]. Among them, Mo addition has been reported to enhance catalyst stability by facilitating carbon removal [5]. Nevertheless, its role in ethanol steam reforming remains poorly understood. Therefore, this study aims to elucidate the role of Mo as a promoter in Ni/xMo–CeO₂ catalysts in ethanol steam reforming, with particular emphasis on activity, selectivity, and resistance to carbon deposition.

The catalysts were prepared by precipitation of the CeO₂ support, followed by sequential wet impregnation with Mo and Ni. Their physicochemical properties were characterised using XRF, XRD, H₂-TPR, N₂ adsorption–desorption, and TEM, enabling evaluation of metal dispersion, reducibility, and structural features. The catalytic performance was evaluated in ethanol steam reforming under controlled conditions at elevated temperature and a defined steam-to-ethanol ratio. The reaction was carried out in a continuous-flow system,

XRF analysis confirmed that the actual Ni loading is slightly lower than the nominal value, while the Mo content follows the intended trend. The textural properties of the catalysts remain largely unchanged after Mo addition, indicating that the support structure is preserved. However, Mo significantly influences the Ni dispersion, as evidenced by a decrease in Ni⁰ crystallite size from ~50 nm for Ni/CeO₂ to ~20 nm for Mo-containing samples.

XRD patterns after reduction reveal the presence of CeO₂ and metallic Ni, while no distinct Mo phases are detected, suggesting high dispersion of Mo species. This is supported by STEM–EDS mapping. H₂-TPR profiles indicate that NiO is reduced to metallic Ni at relatively low temperatures, whereas Mo species remain highly dispersed and are not clearly detectable.

Catalytic tests show complete ethanol conversion at the initial stage for all samples. The main products are H₂, CO₂, and CH₄, with H₂ selectivity increasing upon Mo addition. Mo-containing catalysts exhibit improved stability compared to Ni/CeO₂. This is accompanied by higher H₂ selectivity and reduced CH₄ formation, indicating suppression of methanation.

Post-mortem STEM–EDS characterisation confirmed the formation of carbonaceous deposits on the surface of all catalysts, which can be directly linked to catalyst deactivation during the reaction.

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Bimodal MOF-derived carbon as promoter of CZA catalysts for CO₂ hydrogenation to methanol

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Keywords: MOF-derived carbon, CO₂ hydrogenation, methanol

Introduction. Driven by the global imperative for carbon dioxide valorization, the catalytic hydrogenation of CO₂ to methanol (CO₂-to-MeOH) has emerged as a pivotal technology within the "power-to-liquid" (P2L) framework [1]. Beyond its role in mitigating greenhouse gas emissions, this pathway offers a robust strategy for chemical energy storage and serves as a sustainable alternative to traditional syngas-based production. However, the industrial viability of the CO₂-to-MeOH route is fundamentally constrained by the high thermodynamic stability of the CO₂ molecule, the exothermic nature of the reaction, and the competitive formation of side products. Furthermore, catalyst longevity remains a critical obstacle due to rapid deactivation and water-induced degradation. To address these challenges, recent research has shifted toward advanced material engineering to optimize catalytic efficiency.

In this work, we report the integration of metal-organic framework (MOF)-derived carbon architectures (C_{MOF}) featuring a bimodal pore population into conventional Cu/ZnO/Al₂O₃ (CZA) catalysts. This structural modification is designed to exploit the synergistic properties of carbon architectures, specifically to augment Cu dispersion and maximize the active surface area. Crucially, the introduction of C_{MOF} provides the catalyst with hydrophobic resilience, mitigating the water-induced deactivation and ultimately boosting the cumulative methanol yield.

Experimental. The bimodal pore population C_{MOF} was synthesized via the carbonization of MIL-53(Al), which was produced through a cost-effective hydrothermal method [2]. The heat treatment was performed at 600°C with a heating rate of 0.5°C/min for 5 hours under an inert atmosphere. To obtain the final carbon structure, the alumina template was removed using 10% hydrochloric acid at 80°C for 5 hours, a duration optimized based on TGA measurements; this resulted in a high-surface-area carbon (approximately 1500 m²/g) characterized by a channel-like bimodal pore-size distribution. The C_{MOF}-CZA catalysts were subsequently prepared by co-precipitating 1 M Cu-Zn-Al metal salt solutions (molar ratio of Cu:Zn:Al = 6:3:1) with 1 M NaHCO₃ at a constant pH of 7, incorporating varying weight percentages of C_{MOF} (0, 3, and 12 wt%). The synthesized materials were characterized using XRD, BET, SEM/TEM/EDX, TPR, and CO₂ & H₂-TPD techniques, while the active copper surface area was determined via the N₂O oxidation method. Furthermore, thermodynamic equilibrium was investigated under diverse temperature, pressure, and reactant molar ratio conditions through simulations in ChemCAD, using a Gibbs reactor model and the Soave-Redlich-Kwong (SRK) equation of state.

Results and discussion. X-ray diffraction analysis of the C_{MOF}-modified CZA materials reveals the presence of slightly smaller CuO crystallites compared to the CZA unmodified sample, with no distinct ZnO and Al₂O₃ diffraction lines, suggesting their presence in a highly dispersed and amorphous state within the samples. Additionally, specific surface area and total pore volume calculated from the N₂ sorption measurements (BET method) show increased values with increasing C_{MOF} loading, accompanied by a narrowing of the pore size distribution due to the bimodal porosity of the promoting MOF-derived carbon. The TEM/SEM/EDX analyses reveal a uniform distribution of catalyst components within the matrix for all samples. Interestingly, all C_{MOF}-modified CZA materials are more reducible compared to the unmodified sample, with maxima in the TPR profiles around 220 °C and 270 °C, respectively. The materials' interaction with hydrogen is highly dependent on the addition of promoting bimodal C_{MOF}; however, no clear relation between the amount of added bimodal carbon and the desorbed hydrogen during H₂-TPD runs was evidenced. Thus, the amount of desorbed hydrogen increases at least threefold for the C_{MOF}-modified CZA materials, reaching values of at least 50.5 μmol/g as compared to 15.8 μmol/g for the simple CZA sample.

Thermodynamic simulations revealed that the CO₂-to-MeOH process is mostly influenced by the reaction pressure (linear dependence), while the competing RWGS reaction narrows the operating temperature window. Additionally, catalytic activity tests evidenced that the steady state with respect to both CO₂ conversion and methanol selectivity is reached rapidly at each selected reaction temperature, while the enhanced hydrogen chemisorption capacity and different interaction of the C_{MOF}-modified CZA materials with CO₂ lead to improved performances in the CO₂-to-MeOH process.

Conclusions. The bimodally porous, versatile carbon architecture derived from the MIL-53(Al) framework endows these CZA composites with unique structural attributes, including an enhanced specific surface area and tailored reducibility. These properties, combined with augmented H₂ and CO₂ chemisorption capacities, position them as highly promising candidates for the catalytic hydrogenation of CO₂ to methanol.

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Spectroscopic and Computational Investigation of Structural Changes of Iron in Ferrierite

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Keywords: carbon dioxide, ferrierite, FTIR spectroscopy, DFT calculation, iron sites

1. Introduction

Zeolites have long been successfully employed as heterogeneous catalysts in a wide range of reactions, including fluid catalytic cracking (FCC), isomerization, alkylation, and NO_x abatement. Their catalytic versatility arises from the coexistence of Brønsted acidity and redox provided by transition metal ions such as Fe, Co, Zn, and Cu. Among these systems, iron-containing zeolites are of particular interest due to their ability to undergo a reversible Fe(II)/Fe(III) redox cycle, which is exploited in oxidation and carbonylation reactions of simple inorganic molecules.^{1, 2} In this context, ferrierite (FER) appears especially promising, as Fe cations can occupy two distinct crystallographic positions, denoted as α and β sites, which differ in their local coordination geometry. This structural diversity results in distinct redox properties of the iron centers, making ferrierite a highly attractive system for studying the selective activation of small molecules such as carbon dioxide and methane.

2. Methodology

A commercial ferrierite zeolite (Si/Al = 8) was impregnated using iron precursors FeCl₃-acetylacetonate solution in order to introduce iron (Fe/Al < 0.1) in exchangeable extraframework positions. A combination of spectroscopic techniques, including X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), and Mössbauer spectroscopy, supported by computational (DFT) and machine-learning methods (MLIPs), enabled a detailed description of the location and speciation of Fe sites in the zeolite structure. The material's ability to undergo a reversible Fe(II)/Fe(III) redox cycle was subsequently validated in the CO₂ and CH₄ co-conversion.

3. Results and discussion

CO and NO sorption quantitative FTIR studies revealed that the material contains mainly isolated Fe(II) cations with different local symmetries, including species susceptible (2196 and 2189 cm⁻¹) and resistant to oxidation (2193 cm⁻¹).³ Mössbauer spectroscopy confirmed that Fe(II) is located within six-membered rings, with β -site iron capable of undergoing a reversible Fe(II)/Fe(III) redox cycle.

The results demonstrate that Fe-FER activates CO₂ and CH₄ even at room temperature, as indicated by carbonyl-related bands (1800-1320 cm⁻¹). With increasing temperature, the formation of surface methyl groups suggests the presence of acetate-type intermediates, while water plays a key role in stabilizing hydrocarbonate and methoxy species via proton transfer. Mass spectrometry results reveal a sequential reaction pathway, where CO₂ activation precedes methane transformation, leading first to methanol

($m/z = 31$) and subsequently to acetic acid ($m/z = 60$). At higher temperatures, Brønsted acid sites promote the methanol-to-hydrocarbons (MTH) pathway, resulting in olefin formation ($m/z = 27$). Mössbauer results show that CO_2 exposure leads to a decrease of Fe(II) species at β -sites, while Fe(II) at α -sites remains unaffected, indicating their redox inactivity. DFT calculations further reveal that CO_2 activation via hydrocarbonate formation induces partial oxidation of Fe(II) and displacement of the cation within the 6MR by 0.4–0.5 Å.

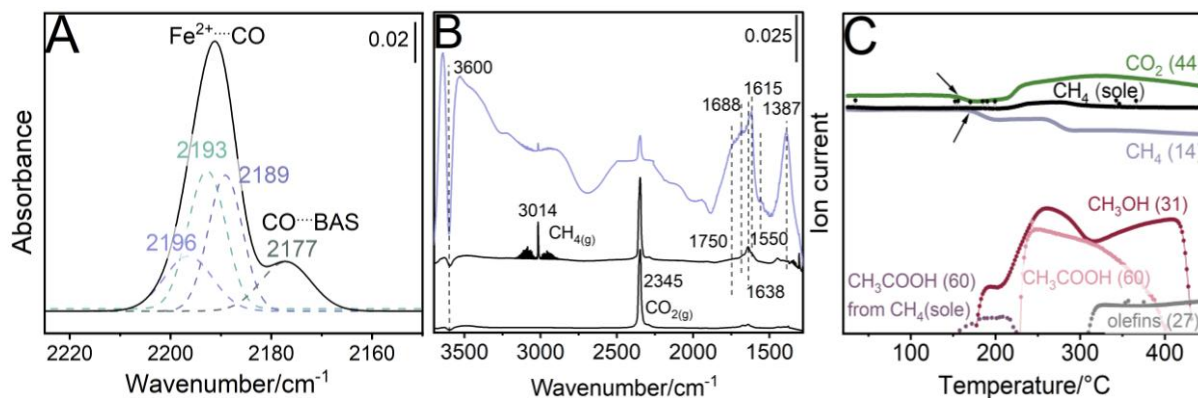


Fig. 1: FTIR spectra : A – from CO sorption on Fe-FER with its deconvolution, B – after CO_2 and CH_4 treatment (black lines), and heating system to 200 °C and colling down to RT (purple line), C – mass spectra of reactants during reaction: methane ($m/z = 14$), olefin ion ($m/z = 27$), methanol ($m/z = 31$), carbon dioxide ($m/z = 44$) and acetic acid ($m/z = 60$).

4. Conclusions

This study provides insight into the catalytic behavior and structural evolution of iron centers in FER zeolite during the co-conversion of CO_2 and CH_4 . A combination of in situ FTIR–MS, Mössbauer spectroscopy, and computational methods (DFT and MLIPs) enabled the identification of a bifunctional redox–acid mechanism. Carbon dioxide is initially activated on Fe(II) centers located at β -sites, forming hydrocarbonate species that undergo dehydrogenation to formates. Concurrently, methane is activated on oxidized Fe(III)–OH sites, leading to the formation of methoxy intermediates. These species subsequently react with CO/CO_2 in the presence of Brønsted acid sites to produce acetic acid. At higher temperatures, an alternative pathway emerges in which methanol-derived intermediates are further converted into olefins and hydrocarbons.

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Acknowledgement: The research was funded by the National Science Centre, Poland [2022/47/I/ST4/00607] and the Czech Science Foundation [24-14387L].

How additives affect the catalytic pyrolysis of polyolefins over HZSM-5.

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Keywords: pyrolysis, polyolefins, zeolite, additives

As living standards rise, plastic waste has become an increasingly pressing issue as its volume continues to grow. Consequently, the development of chemical recycling methods, such as catalytic pyrolysis, has gained attention. Most studies focus on virgin polymers often neglecting the presence of common additives in real plastic waste. Pyrolysis represents a promising strategy for transforming plastic waste into high-value fuels and chemical feedstocks. While additives (such as pigments, stabilizers, and fillers) are essential for enhancing the performance and durability of plastic products, they play a significant role in chemical recycling. At the end of the plastic life cycle, these additives can significantly influence both the yield and composition of pyrolysis products, either through beneficial interactions or detrimental effects. This study evaluates the impact of commonly occurring inorganic additives (Fe_2O_3 , MgO , TiO_2 , CaCO_3 and carbon black) and their combinations on the thermo-catalytic pyrolysis of polyolefins over HZSM-5 zeolites. A key challenge in processing real-world waste is catalyst deactivation, often caused by additives reducing acid-site activity. Our findings demonstrate that while individual additives may hinder the performance of the catalyst, carbon black was a notable exception, substantially promoting the yield of monoaromatic hydrocarbons.

Acknowledgement

Experimental results were achieved by using REFRESH – Research Excellence For Region Sustainability and High-tech Industries, CZ.10.03.01/00/22_003/0000048 and Large Research Infrastructure ENREGAT supported by MEYS, project no. LM2023056.

Biodiesel production from waste cooking oil with a focus on reducing the leaching of active ions from catalysts

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INTRODUCTION

Biodiesel is a renewable liquid fuel composed mainly of fatty acid methyl esters (FAME), which are obtained from vegetable oils or animal fats. Waste cooking oils (WCO) also represent an important feedstock, as they offer an environmentally and economically advantageous alternative to primary raw materials. The most common method of biodiesel production is the transesterification of triglycerides with an excess of alcohol, most often methanol, in the presence of a catalyst, producing fatty acid methyl esters and glycerol as a by-product [1].

In addition to traditionally used homogeneous catalysts, increasing attention is being paid to heterogeneous catalytic systems, mainly due to their easier separation from the reaction mixture and the possibility of reuse. Among promising catalysts are mixed oxides based on hydrotalcites, which, after calcination, exhibit suitable basic properties and good catalytic activity [2].

However, despite these advantages, their application may be limited by the leaching of metal species into the methyl ester phase, which can lead to contamination of the biodiesel, deterioration of its quality, as well as gradual catalyst deactivation and a decrease in reaction yield [3].

EXPERIMENTAL

As a feedstock, waste cooking oil from households was used. For comparison, the oil was applied in both its unrefined (contaminated) form and in a laboratory-refined form. The refining process was carried out in several steps: aqueous and acid degumming, oil neutralization, bleaching, and subsequent filtration through a silica gel column. The properties of the refined and unrefined oil samples were compared by determining the iodine value and acid value.

Four catalysts were prepared: Mg/Al, Mg/Al + NH₃ (Mg/Al = 3/1), Mg/Al/Zn, and Mg/Al/Zn + NH₃ (Mg/Al/Zn = 4/2.5/1). The synthesis of the catalysts was carried out by the co-precipitation method at room temperature for 1 hour. In the first step, three solutions were prepared: a metal nitrate solution, NaHCO₃ ((NH₄)₂CO₃), and NaOH (NH₃). The NaOH (NH₃) solution was added dropwise to the NaHCO₃ ((NH₄)₂CO₃) solution under constant stirring. After reaching pH 10, the metal nitrate solution was slowly added to the NaHCO₃ ((NH₄)₂CO₃) solution. The resulting precipitates were aged for 24 hours and then filtered using a Büchner funnel. After drying, the catalysts were calcined at 450 °C. The catalysts were subsequently characterized using methods such as XRD, TPD-CO₂, FTIR and nitrogen adsorption at -196 °C.

Heterogeneous transesterification was carried out on both oil samples using the prepared catalysts. Each reaction was performed in a batch reactor in two stages. Each reaction stage lasted 3 hours, and after its completion the product was processed by removing methanol and separating glycerol from the resulting fatty acid methyl esters (FAME).

RESULTS AND DISCUSSION

Catalysts with the addition of zinc were designed to increase the stability of the material and thereby reduce the leaching of active ions during the reaction. The Mg/Al + NH₃ and Mg/Al/Zn + NH₃ catalysts were prepared without the use of sodium compounds. The aim of this approach was to eliminate the leaching of Na⁺ ions into the reaction phase and thus achieve a higher-quality transesterification process.

The textural and basic properties of the prepared catalysts are summarized in Table 1.

Table 1: Properties of the prepared catalysts

Catalyst	S _{BET} (m ² /g)	V _a (cm ³ /g)	Basicity (mmol CO ₂ /g)
Mg/Al	240	0.86	0.84
Mg/Al + NH ₃	318	0.43	0.49
Mg/Al/Zn	196	0.57	0.70
Mg/Al/Zn + NH ₃	329	0.40	0.62

The Fig. 1 shows the percentage content of FAME after the first and second stages of heterogeneous transesterification of WCO (unrefined form) using the prepared catalysts.

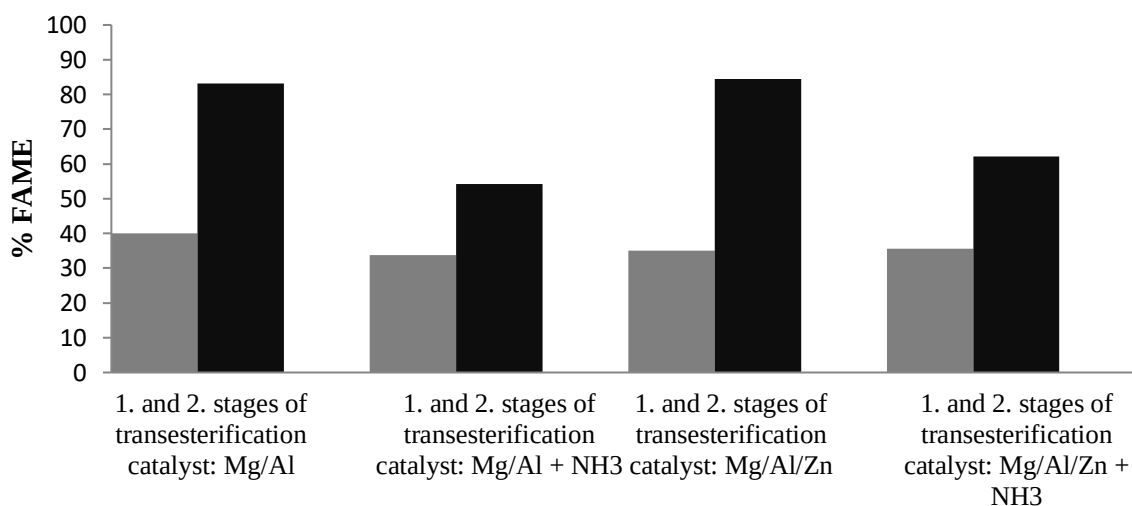


Fig.1: FAME content after the first and second stages of heterogeneous transesterification of waste (unrefined) oil using the prepared catalyst

The highest FAME content after the second reaction stage using unrefined form of WCO was achieved using the Mg/Al/Zn (84.4 %) catalyst. The results regarding the FAME content using refined WCO will be completed and presented in the poster section of the conference.

CONCLUSIONS

Based on the highest achieved FAME content using the Mg/Al/Zn catalyst, this material appears to be highly effective for processing more complex feedstocks such as WCO (unrefined). The higher structural stability of the catalyst may contribute to the reduced leaching of active species into the reaction medium, thereby promoting a more efficient reaction under heterogeneous conditions.

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High-efficiency synthesis of solketal over novel aluminum-modified mesoporous silicas for fuel applications

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Keywords: Glycerol acetalization, solketal, DMSN (Dendritic Mesoporous Silica Nanoparticles), MCF (Mesoporous Cellular Foams), SBA-3 (Santa Barbara Amorphous-3)

Introduction

Global energy demand continues to rise as a result of ongoing socio-economic development, including urban expansion and industrial growth. This trend increases reliance on fossil fuels, contributing to environmental degradation and elevated greenhouse gas emissions. Consequently, there is a growing need to develop sustainable and low-impact energy alternatives. Biodiesel has gained considerable attention as a renewable fuel due to its biodegradability, low toxicity, and carbon-neutral nature. However, its production generates a significant amount of crude glycerol (approximately 10 wt.%), leading to an oversupply that poses economic and environmental challenges. Efficient utilization of this byproduct is therefore crucial to enhance the sustainability of biodiesel production. Glycerol can be transformed into a variety of value-added chemicals through several catalytic pathways. Among these, acetalization with acetone stands out as an effective and economically attractive route, producing solketal as the main product. Solketal (2,2-dimethyl-1,3-dioxolane-4-methanol) is a valuable compound widely used as a fuel additive, as it improves fuel properties such as cold flow behavior and oxidation stability while reducing harmful emissions. Additionally, it finds applications as a green solvent and as an intermediate in the pharmaceutical and chemical industries. The acetalization of glycerol is an acid-catalyzed reaction, and its performance strongly depends on the nature and strength of the acidic centers of the catalysts [1]. While homogeneous acid catalysts provide high activity, their use is limited by issues related to separation, recyclability, and corrosion. For this reason, increasing attention has been given to heterogeneous catalysts, which offer advantages such as ease of recovery, lower environmental impact, and improved process sustainability. Building on previous findings that micro-mesoporous zeolites exhibit enhanced performance in solketal synthesis due to improved diffusion of reactants [1], the present work focuses on aluminum-containing mesoporous silicas with different pore architectures: two-dimensional (SBA-3) and three-dimensional systems (MCF and DMSN), synthesized via a one-pot. These materials represent novel catalytic systems in this reaction, as they have not previously been investigated for solketal synthesis.

Methodology

The aluminum-containing mesoporous silicas were synthesized via a one-pot hydrothermal-assisted sol-gel method, in which an appropriate amount of aluminum nitrate solution was introduced into the reaction gel prior to mesostructure formation. Due to the strongly acidic synthesis conditions hindering the incorporation of aluminum into the framework of MCF and SBA-3 materials [2], the pH of the synthesis gel was increased using an NH₄OH solution to facilitate effective Al incorporation. The influence of pore architecture and aluminum loading

on the structural and physicochemical properties of the obtained mesoporous silicas was investigated using XRD, nitrogen adsorption–desorption, TEM, SEM-EDS, NH_3 -TPD, and FT-IR spectroscopy with adsorbed pyridine. The catalytic performance was evaluated in the acetalization of glycerol with acetone under atmospheric pressure at 343 K for 4 h. Reaction products were analyzed by gas chromatography (GC) using a Varian CP-3800 equipped with a VF-5ms column and a flame ionization detector (FID).

Results and discussion

Aluminum incorporation did not disrupt the formation of mesoporous architectures, and all obtained materials (MCF, DMSN, and SBA-3) exhibited well-defined and properly developed structures. The presence of aluminum in the materials was verified by EDS analysis, which confirmed its effective introduction into the silica framework. Furthermore, the structural ordering and morphology of the synthesized materials were confirmed by SEM analysis, while XRD and TEM studies provided additional evidence of the preservation of the mesoporous architecture and the formation of properly ordered structures. All investigated catalysts exhibited high catalytic performance in the acetalization reaction, achieving glycerol conversion above 80%. Despite differences in pore architecture and acidity, only minor variations in the initial catalytic activity were observed, indicating that the reaction is not primarily governed by pore structure under the studied conditions. Instead, catalytic behavior, especially the catalysts stability appears to be more strongly influenced by the dispersion and accessibility of aluminum species within the silica framework. The observed differences in acidity suggest variations in the effective distribution and availability of acid sites, highlighting that not only their total number but also their accessibility within the porous network plays a crucial role in determining catalytic performance. The stability of the DMSN material under reaction conditions, confirmed over four consecutive reaction cycles, further demonstrates its application potential.

Conclusions

Catalytic performance in glycerol acetalization is governed primarily by the dispersion and accessibility of aluminum species rather than pore architecture, highlighting the importance of controlling active site availability in the design of efficient mesoporous catalysts.

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Acknowledgement

The authors acknowledge the financial support provided by the National Science Centre, Poland (Grant no. 2022/47/I/ST4/00607) and the Czech Science Foundation (project no. 24-14387L).

Formate Production from Bicarbonate via Catalytic Hydrogenation over Pd/C

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Keywords: hydrogenation, bicarbonate, formate, palladium

The catalytic hydrogenation of bicarbonate to formate represents an attractive route for carbon utilization and hydrogen storage, while also providing a practical alternative to the direct hydrogenation of gaseous CO₂. In contrast to molecular CO₂, bicarbonate is already present in a dissolved and activated carbon form, which helps to reduce gas-liquid mass-transfer limitations and improves reaction feasibility under relatively mild conditions [1]. This contribution focuses on the production of formate from bicarbonate over Pd/C catalysts, with particular attention to the interplay between catalyst properties and reaction environment. Pd/C is a promising system because palladium efficiently activates hydrogen, whereas the liquid-phase medium controls bicarbonate speciation, proton availability, and formate stability. Key reaction parameters include temperature, hydrogen pressure, catalyst loading, solvent composition, and pH, all of which strongly affect conversion and selectivity. Overall, bicarbonate hydrogenation to formate over Pd/C offers a scientifically relevant and potentially scalable pathway connecting carbon capture, catalytic conversion, and liquid hydrogen carrier concepts.

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This work is supported within the project „Waste as an alternative source of energy“, reg. nr. CZ.02.01.01/00/23_021/0008590 under the Programme Johannes Amos Comenius.

Development of scalable and sustainable carbon-based catalyst materials for methanol synthesis

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Keywords: Carbon carriers; nanoparticles; catalyst development; green methanol

CO₂ is one of the most prevalent greenhouse gases, and reducing global CO₂ emissions is essential to slowing down global warming. Particularly in industrial processes with hard-to-abate emissions (cement industry, waste treatment, chemical industry, ...), simply avoiding greenhouse gas emissions proves extremely difficult, making CCS/CCU technologies necessary. Furthermore, in the future it will be necessary to supply certain sectors (aviation, shipping, etc.) with fuels produced with low emissions, thereby utilizing the carbon dioxide emitted by industry. This supply of alternative fuels is still a major point of debate today; however, due to weight and economic considerations, powering these modes of transportation with battery solutions is technically difficult to implement.

Methanol (CH₃OH) is already emerging as an indispensable component for chemical energy storage and further processing into sustainable fuels and is also a key ingredient in the production of chemical products, although industrial production has so far relied on fossil-based methanol. Large-scale industrial production of methanol requires catalysts with long lifespans and high conversion rates; however, the commercial production method for these catalysts (catalytically active nanoparticles embedded in carrier materials such as Al₂O₃ or ZrO₂) is highly resource- and energy-intensive and therefore not very sustainable.

To make this process more sustainable while simultaneously advancing the development of green methanol, the ScaleCat project was launched in collaboration with Wood KPLUS and RHP. The project involves the development of porous, bio-based carbon support materials into which catalytically active particles are incorporated during the manufacturing process. The finished carbon supports with the embedded particles are further optimized through infiltration with metallic colloids. For the catalytically active particles, the focus is on Cu, Ni, Zn, Zr, and their alloys, which are obtained from recycled raw materials via laser ablation. At the end of their service life, the particles in the catalysts can be easily recovered through thermal decomposition, thereby closing a sustainable cycle.

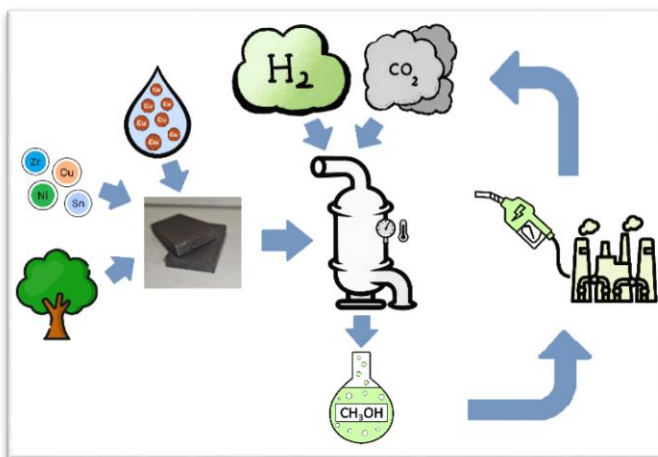
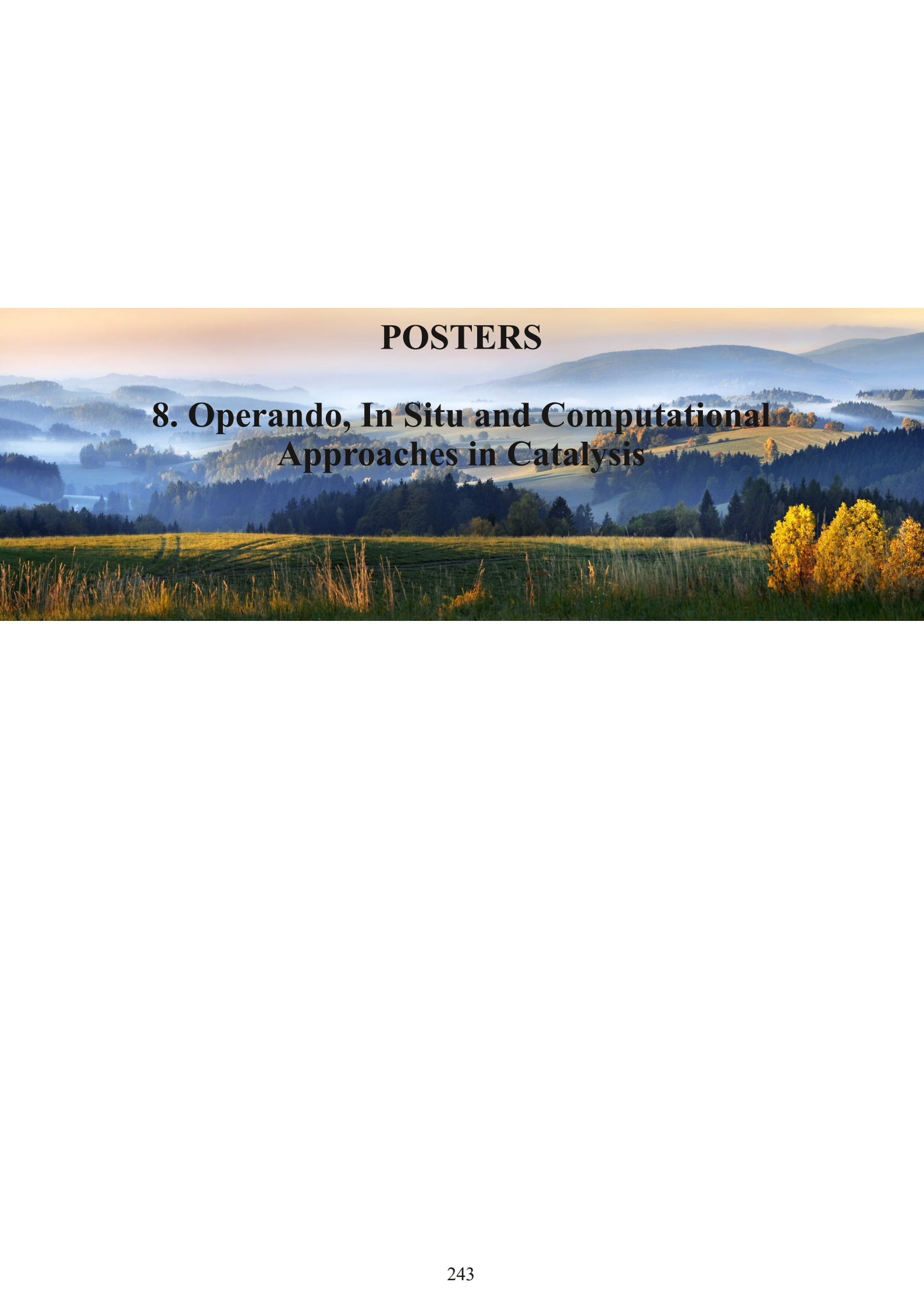


Figure 1: ScaleCat Catalysts for the Green Methanol Cycle

Acknowledgement:

We would like to extend a special thank you to our industry and research partners, our dear colleagues at Wood KPLUS and RHP



POSTERS

8. Operando, In Situ and Computational Approaches in Catalysis

Carbon dioxide methanation on nickel catalysts with natural aluminosilicates

Wojciech Gac, Karolina Karpińska-Wlizło, Witold Zawadzki, Paulina Krysa, Grzegorz Słowik
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Keywords: carbon dioxide methanation, natural aluminosilicates, nickel catalyst, in-situ DRIFTS

Reducing the level of atmospheric carbon dioxide is one of the most urgent environmental and scientific challenges. The concept of carbon capture and utilisation can be put into practice through hydrogenation reactions that lead to the production of methane, carbon monoxide or other valuable chemical compounds using green hydrogen, thereby stimulating the growth of the renewable energy sector. Despite significant progress in the development of catalysts for CO₂ methanation, there is a need for new catalysts that are more active, selective, durable and cost-effective. Furthermore, there is still a lack of in-depth understanding of the catalytic processes involved. Natural aluminosilicates constitute a broad group of inexpensive porous materials that possess favourable properties as supports for development of new nickel catalysts.

The aim of the studies was synthesis of new active and selective CO₂ methanation nickel catalysts with selected aluminosilicates as supports of layered or fibrous-like structure, determine their catalytic performance and the course of the elementary reaction stages.

The catalysts with 10 wt% Ni were prepared by the impregnation method in a similar way to that described earlier [1,2]. Selected aluminosilicate materials were used as supports, including natural attapulgite (supplied by Terra Eneo, Poland), sepiolite powder, montmorillonite K10 and halloysite nanoclay (Sigma Aldrich). Their properties were compared with those of a nickel catalyst using silica gel as a support and characterized using techniques such as low-temperature N₂ adsorption/desorption, X-ray fluorescence (XRF), X-ray diffraction (XRD), temperature-programmed reduction (TPR), hydrogen desorption (H₂-TPD), transmission electron microscopy (TEM) [1,2]. The activity of catalysts was assessed using a microreactor system coupled with custom-built GC equipment, in a manner similar to that described earlier [1,2]. The course of the key reaction stages was evaluated using in-situ DRIFTS-MS technique by investigating the nature of the surface species formed during the adsorption and desorption of CO, CO₂, and in the CO₂-H₂ reaction at various temperatures, using a Nicolet 6700 FTIR spectrometer equipped with a high-temperature DRIFTS reaction chamber (Harrick). At the same time, the products obtained were analysed using a quadrupole mass spectrometer (Hiden Analytical).

Studies have shown that the supports influenced the way of formation of nickel oxide species, their size and physicochemical properties. As a result of different metal-support interactions arising from the presence of exposed Si, Mg, Al or Fe structural units on the surface of supports and their specific porous properties, both easily and hardly reducible nickel oxide phases were formed. Such species were transformed into the nickel metallic nanoparticles of different size and surface properties. TPR studies of pure, natural attapulgite materials revealed complex transformations. The close proximity of the relevant forms of nickel and iron in this type of catalysts favoured the formation of dispersed phases of the NiFe₂O₄-type, or bimetallic nickel-iron nanoparticles. H₂-TPD studies have demonstrated a strong impact of the specific surface area and porous properties of supports on the size of nickel nanoparticles and nature of

adsorption centers. The large specific surface area of mesoporous silica gel led to the formation of catalysts with very large active surface area. In turn, the use of sepiolite and montmorillonite as supports enabled the development of catalysts with a smaller active surface area, but with a different nature of adsorption sites. In the case of attapulgite supported catalysts with lower active surface area, the respective changes were attributed to Ni-Fe interactions, resembling the behavior of other NiFe bimetallic catalysts [2].

Most of the catalysts obtained, in which aluminosilicates were used as supports, exhibited higher activity than the reference catalyst with a silica support. Given the smaller active surface area, these results were surprising. In-situ DRIFTS-MS studies indicated that the origins of such changes varied depending on the type of catalyst. Simultaneous analysis of the composition of the outlet stream from the DRIFTS reaction chamber (CO_2 , CO , H_2 and H_2O) using mass spectrometry allowed for the quantitative determination of the results and enabled a more reliable comparison of the processes occurring with different catalysts.

Two general types of CO_2 methanation reaction mechanisms have been considered in literature. The first assumes that all the key stages of the reaction take place exclusively on the surface of metallic nickel nanoparticles, i.e. the dissociative adsorption of H_2 and CO_2 , the formation of surface carbonyl groups, their direct decomposition into carbon and oxygen atoms, which are then hydrogenated to the corresponding compounds, or that the reaction proceeds via a specific hydrogen-assisted transformation, e.g. with the formation of surface formates as intermediate compounds. Consequently, the activity of catalysts can be significantly influenced by the nature of the metal sites and their number. The second concept, on the other hand, suggests that specific sites on the support or modifiers, such as acid-base or redox centers, play an essential and complementary role in the activation and subsequent conversion of CO_2 .

The results of in-situ DRIFTS studies showed that the first mechanism was predominant in catalysts based on a relatively inert silica support. The spectra recorded during adsorption of CO and CO_2 and their subsequent desorption evidenced formation of differently coordinated carbonyl groups to the metallic nanoparticles. Such species were transformed under hydrogenation reaction conditions to the intermediate formate species and then methane at elevated temperatures (above $200\text{ }^\circ\text{C}$). In turn attapulgite-containing catalysts, despite enhanced activity at low temperatures showed slightly worse activity at high temperatures ($300\text{--}400\text{ }^\circ\text{C}$) and lower selectivity to methane. We recently reported similar changes in activity for model NiFe bimetallic catalysts with a high iron content [2]. This may suggest the formation of NiFe bimetallic phases in such catalysts and the involvement of iron in redox processes that facilitate the reverse water-gas shift reaction (RWGS). The adsorption of CO_2 as well as CO on the surface of nickel catalysts with applied aluminosilicate supports was simultaneously followed by the formation of other complex surface species. Both differently coordinated carbonyl groups as well as versatile surface bicarbonate and carbonate species were indicated. The latter were particularly evident in the case of the sepiolite-supported catalyst, which exhibited exceptionally high activity.

The results confirmed the feasibility of using natural aluminosilicate materials as cost-effective supports for nickel catalysts in CO_2 methanation and indicated main directions of further modifications. The studies provided in part answers to key questions concerning the course of catalytic processes on obtained catalysts. However, further studies are required.

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Active Oxygen Species Mediated Direct Methane Conversion over Ce-LaO_x Catalysts: From Methanol to C₂ Products

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Keywords: methane to methanol, Ce-LaO_x mixed oxides, active oxygen species

Introduction

Methane (CH₄) is an abundant energy source but also a strong greenhouse gas. Its selective conversion into valuable products such as methanol (CH₃OH) and C₂ hydrocarbons is attractive but challenging due to the strong C–H bond and over-oxidation.¹ Ce–LaO_x mixed oxides are promising catalysts because of their tunable oxygen mobility and surface properties, although the role of surface oxygen species in product selectivity is still unclear.

Methodology

Ce–LaO_x catalysts with different Ce/La ratios were synthesized by a hydrothermal method and tested for direct methane conversion under continuous-flow conditions in a fixed bed reactor. In situ DRIFTS and AP-XPS were used to study surface intermediates and oxygen species during reaction. TPD–MS measurements were performed to investigate methanol adsorption and desorption behavior.

Results and Discussion

Ce–LaO_x catalysts show strong temperature-dependent selectivity. Methanol is the main product at 250–400 °C, while C₂ hydrocarbons become dominant above 450 °C. Water vapor also changes the product distribution, suggesting different reaction pathways at low and high temperatures. Among the catalysts, Ce₁La₄O_x shows the highest methanol production at low temperatures. La incorporation increases surface OH species and stabilizes CH₃O intermediates, promoting methane activation and methanol formation. AP-XPS results indicate that active oxygen species play an important role in controlling reaction pathways and suppressing deep oxidation.

TPD–MS results show that Ce₁La₄O_x weakens methanol adsorption and facilitates methanol desorption at lower temperatures, reducing further oxidation to CO_x and improving methanol selectivity. At higher temperatures, changes in surface oxygen species favor C₂ hydrocarbon formation.

Conclusions

Ce–LaO_x mixed oxides are promising catalysts for direct methane conversion with tunable selectivity toward CH₃OH and C₂ hydrocarbons. La incorporation modifies surface oxygen chemistry, increases OH species, stabilizes CH₃O intermediates, and weakens methanol adsorption, enhancing methanol selectivity at low temperatures. At higher temperatures, active oxygen species promote C₂ formation pathways.

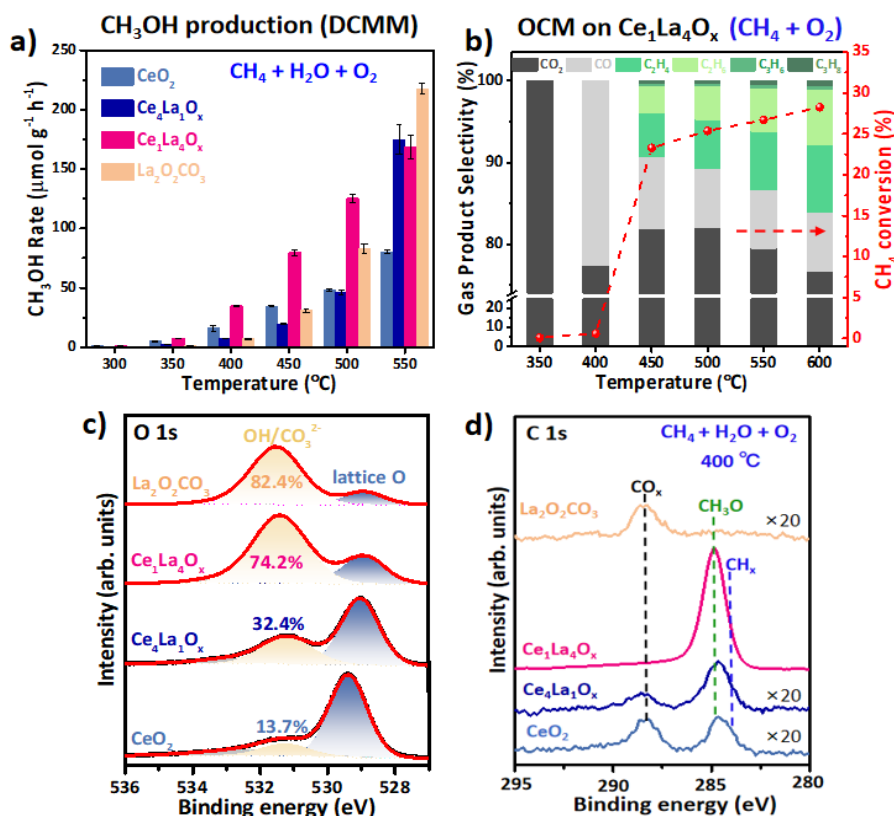


Fig. 1. a) CH₃OH yields over Ce-LaO_x; b) OCM selectivity and CH₄ conversion of Ce₁La₄O_x under CH₄ + O₂; c) O 1s spectra of Ce-LaO_x; d) AP-XPS C 1s spectra of Ce-LaO_x under CH₄ + O₂ + H₂O at 400 °C.

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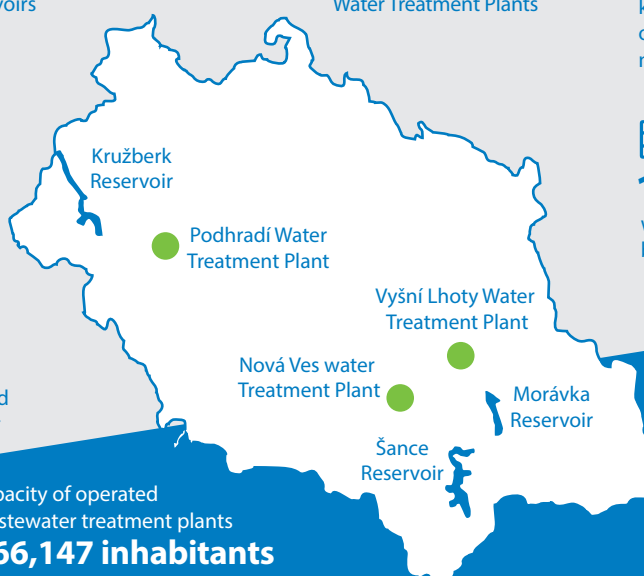
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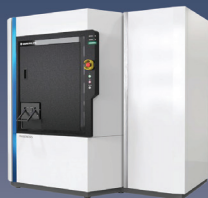


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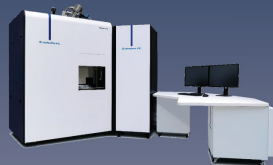
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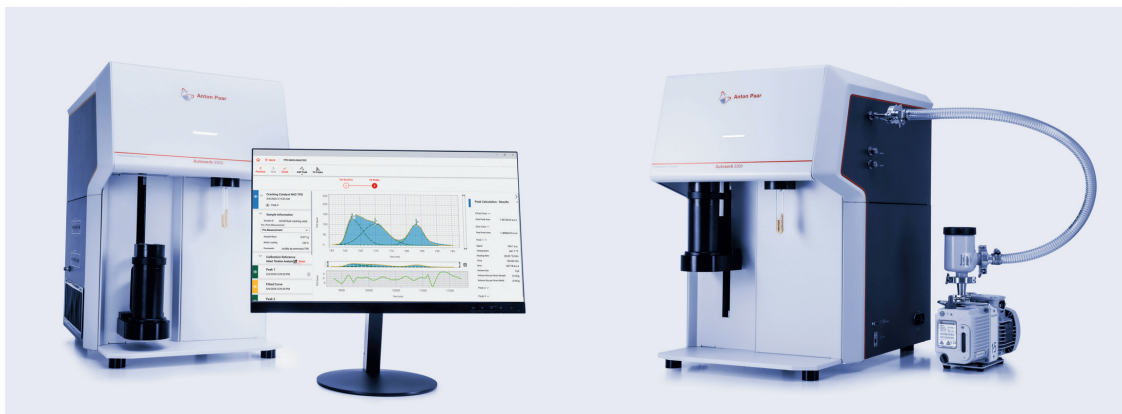


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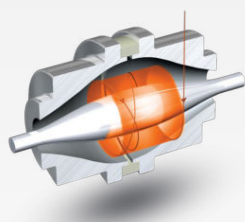
Autosorb 3300 dokáže detekovat aktivní povrchy menší než 0,03 m² a dosahuje opakovatelnosti kalibračních píků lepší než 0,5 %. Maximální teplota vzorku 1 200 °C, rychlost ohřevu až 100 °C/min a rychlé ochlazení z 800 °C na 50 °C za pouhých 28 minut zajišťují vysokou průchodnost měření.

Konstrukce Safe-Touch chrání obsluhu i při maximálních provozních teplotách. Ve spojení s intuitivním softwarem Kaomi React a pokročilými funkcemi automatizace – včetně míchání plynů, přepínání smyček a manipulace se vzorky – zaručuje Autosorb 3300 plynulé pracovní postupy pro výzkumné i kontrolní laboratoře.



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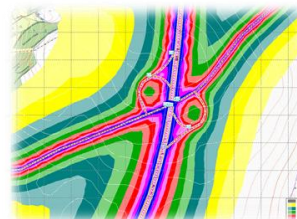
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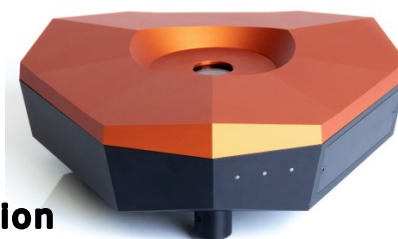
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