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Plenary

Catalysis-enabled biomass economy

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Keywords: biomass valorization, catalyst design, catalyst supports, deoxygenation, hydrogenation

Biomass is a valuable raw material for future sustainable chemical industry. Nonetheless, its upgrading to valuable products still poses a significant challenge due to the specific features of primary products obtained by biomass transformation. In particular, the reactivity and structure of biomass-derived molecules make them susceptible to low atom economy when their transformation through hydrogenation and/or hydrodeoxygenation is targeted.

This presentation will highlight the importance of catalyst design to maximize the yields of targeted value-added products. It will illustrate the complexity of the design even when developing „simple" metal-oxide-supported catalysts and demonstrate the crucial role of common supports.

Catalyzing the energy transition

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The need to transition from fossil fuels to low carbon energy sources is indisputable and hoped to reach completion during the second half of this century. However, for this transition to occur smoothly and economically, several enabling technologies need to be further developed, especially in terms of energy vectors and their associated challenges. On the other hand, the transition to cleaner energy sources will have a very important consequences for oil refining and the way chemicals are produced.

In this lecture, we will highlight important R&D challenges of the Energy Transition and its consequences for other industrial sectors, with special emphasis on the role of catalysis and ongoing work at our labs on CO_2 neutral fuels, the use of ammonia as a hydrogen carrier and our vision on the refinery of the future.

Challenges and opportunities of the machine learning-based kinetic modelling of catalystic reactions

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Introduction

In industrial practice, it is common to design new reactors based on industrially available catalysts, often supplied by specialized companies. Often, due to the confidential nature of the catalyst recipes, the details on the composition and structure of the catalysts cannot be provided to the companies utilizing the catalyst in the final reactor. This fact often hinders the development of detailed kinetic models, due to the lack of information on the precise mechanism occurring during the target catalytic reaction. This lack of information is an important disadvantage for engineering companies, as a reliable kinetic model is the essential cornerstone for an effective reactor design. To overcome this challenge, in this paper we analyze the option to use AI-based regression models to obtain a reliable description of reaction kinetics, without the need to derive a detailed reaction mechanism, which would be impossible on several industrial catalysts due to the reasons mentioned above. We analyzed a wide array of available AI-based regression models and compare them with standard surrogate models. Additionally, we compared the most promising AI-based regression with Langmuir-Hinshelwood (LHHW) models obtained by regression of an arbitrarily assumed reaction mechanism. The work was performed over an industrial catalyst for the CO_2 methanation, which selectively produce CH4 as sole product.

Materials and methods

An industrial Ni-based catalyst was supplied to our laboratories and was tested in kinetic experiments. The actual composition of the catalyst was not known, and no characterization analyses were performed. The catalyst was loaded in an isothermal reactor, where the reaction kinetics were measured. The experimental space investigated ranges from 1 to 3 bar, 220 °C to 300 °C and space velocities between 70’000 and 200’000 h-1. The complete dataset consists of approximately 240 data points. The regressions included Power Law, LHHW model, Random Forests, neural networks.

Results and discussion

The parity plot of power law and ANN are reported in figure 1a. The data refer to the complete kinetic dataset. One can observe that the power law shows an inaccurate fitting. This is due to the scarce capability of power law to describe the complex interplay of adsorption sites on a catalyst for the CO_2 methanation. The most advanced AI-based models show a good fit, with the bilayer neural network showing an excellent fit of the experimental results. The LHHW model selected (not shown here) is also showing a good performance in describing the experimental results. However, the result shown was achieved only after an extensive research work on the determination of the best mechanistic model to describe the industrial catalyst. To further assess the differences between the models, we measured the sensitivity of the fit appropriateness by modifying the size of the regression data set. In this case, we observed that the LHHW model has high sensitivity to the amount and type of data used for the regression. The ANN-based models are instead more robust against the reduction of the dataset. The best kinetic models derived were used in a reactor design phase, to assess if these have an influence on the simulation of a full-scale reactor. We will show that, with the dataset obtained in this work, both approaches are suitable to describe the performance of a CO_2 methanation reactor.

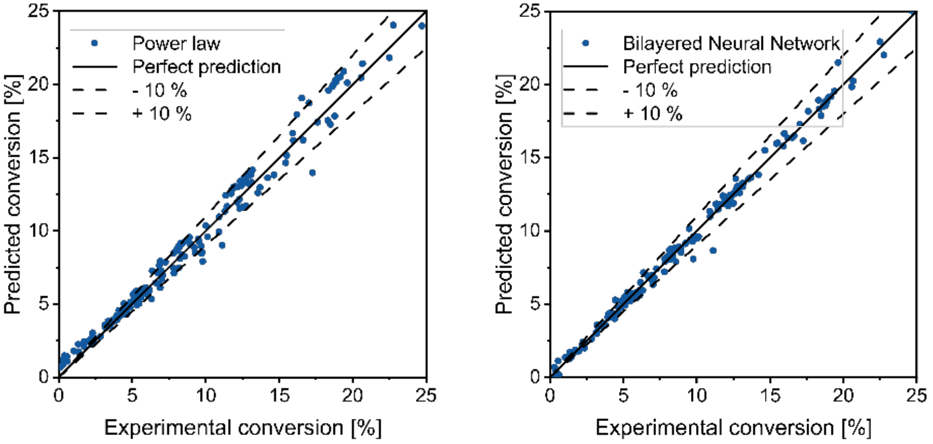

Figure 1. Parity plots for a) power law and b) Bilayered Neural Network-based kinetic models

Design of catalysts/photocatalysts using advanced oxidation processes for water and air cleaning

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Keywords: catalysts, advanced oxidation processes, organic pollutants, water cleaning, volatile organic compounds, air cleaning

Water and air pollution caused by organic pollutants has become a significant problem. Among the various treatment technologies developed to address this issue, advanced oxidation processes (AOPs) have attracted considerable attention. AOPs are based on the generation of highly reactive oxygen species that non-selectively and totally oxidise organic pollutants, ultimately converting them into harmless end products such as H_2O, CO_2, and inorganic salts.

The Fenton AOP, a homogeneous catalytic process, is the most industrially applicable AOP for removing organic pollutants from water. It uses iron salts as catalysts and hydrogen peroxide as the oxidant. However, it has disadvantages, such as the requirement for acidic pH, the formation of iron sludge, and excess iron ions. To address these issues, Fenton-like AOPs have been investigated as heterogeneous catalytic processes at neutral pH. The lecture will provide an overview of the design and development of Fenton AOP catalysts, as well as photo-Fenton AOP photocatalysts using sunlight, and will highlight the importance of understanding the complexity of these systems.

Photocatalytic AOPs, as heterogeneous catalytic processes, are the most promising AOPs for the removal of so-called volatile organic compounds (VOCs) from air. Titania (TiO_2) is the most commonly used material for these applications due to its advantageous properties: low cost, high stability, high photocatalytic activity, and the ability to promote the oxidation of major organic pollutants at room temperature. The lecture will provide an overview of the design and development of efficient and mechanically stable titanium-based composite coatings for the photocatalytic AOP removal of VOCs from air.

Acknowledgments

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Rethinking catalysis: A personal journey toward truly sustainable processes

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Keywords: sustainable catalysis, nanoparticles, single atom, metal free

Heterogeneous photocatalysis based on readily available, well-defined single-atom or metal-free catalysts is attracting growing interest, driven by the increasing pressure on industry to adopt more sustainable chemical production schemes. In the energy sector, nanostructured materials have demonstrated remarkable potential for the efficient conversion of biomass [1–2] as well as for the production of hydrogen and liquid hydrogen carriers [3–4].

With sustainability now at the core of photocatalyst design, graphitic carbon nitride (g-CN) has emerged as a highly versatile semiconductor nanomaterial, already recognized for a wide range of applications. We have recently highlighted the pivotal role that g-CN can play in photocatalytic organic synthesis [5]. In addition, we contribute to the ongoing debate on the respective roles of single-site catalysts versus clusters and nanoparticle-based systems, with particular emphasis on the identification of cooperative effects [6–9].

These emerging catalytic systems are expected to move beyond fundamental research and stimulate industrial interest in the development of green organic synthesis, renewable energy conversion, and pollution prevention and control - key challenges of the 21st century and the central focus of this presentation.

Acknowledgments

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References

1. N. Luo, T. Montini, J. Zhang, P. Fornasiero, E. Fonda, T. Hou, W. Nie, J. Lu, J. Liu, M. Heggen, L. Lin, C. Ma, M. Wang, F. Fan, S. Jin, F. Wang, Nature Energy, 4 (2019) 575.
2. M. Kaur, S. Rej, J. Navrátil, E. Yazmin Santiago, M. Otyepka, S. Livraghi, L. Mino, Š. Kment, Z. Xu, H. Zhu, P. Fornasiero, A. O. Govorov, P. Błoński, A. Naldoni, Nature Catalysis, 8 (2025) 1370–1381.
3. K.C. Christoforidis, Z. Syrgiannis, V. La Parola, T. Montini, C. Petit, E. Stathatos, R. Godin, J.R. Durrant, M. Prato, P. Fornasiero,, Nano Energy., 50 (2018) 468-478
4. P. Ren, Z. Gao, T. Montini, N. Ta, N. Luo, E. Fonda, P. Fornasiero, F. Wang, Joule, 7 (2023) 333.
5. G. Filippini, F. Longobardo, L. Forster, A. Criado, G. Di Carmine, C. D'Agostino, M. Melchionna, P. Fornasiero, M. Prato, Science Adv., 46 (2020) n° eabc9923.
6. H. Hong, Z. Xu, B. Mei, W. Hu, P. Fornasiero, C. Wang, T. Wang, Y. Yue, T. Li, C. Yang, Q. Cui, H. Zhu, X. Bao, Science, 388 (2025) 497
7. Z. Gao, T. Montini, J. Mu, N. Luo, E. Fonda, P. Fornasiero, F. Wang, J.Am.Chem.Soc., 146 (2024) 24440
8. Z. Xu, M. Gao, Y. Wei, Y. Yue, Z. Bai, P. Yuan, P. Fornasiero, J.M. Basset, B. Mei, Z. Liu, H. Zhu, Mao Ye, X. Bao, Nature 643 (2025) 691
9. P. Jin, P. Guo, N. Luo, H. Zhang, C. Ni, R. Chen, W. Liu, R. Li, J. Xiao, G. Wang, F. Zhang, P. Fornasiero, F. Wang, Science, 389 (2025) 1037

Redox catalysis on platonic oxide nanocrystals

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Keywords: spinels, hydrothermal synthesis, doping, redox, Fermi level, orbital overlap, O_2 and N_2O activation, CH_4 combustion

Redox catalysis on oxide materials is an intensively explored research field of key importance for developing new technologies for the fabrication of high-value-added chemicals and environmental protection. In this context, spinel oxides (Co_3O_4 and its derivatives) have received a great deal of theoretical and experimental interest owing to the spectacular activity in many redox processes that are vital for photo/electro/catalysis as a promising substitute for PGM in the CH_4, VOC or NH_3 oxidation, N_2O decomposition, and CO-PROX processes, for instance. The key redox properties of nanostructured cobalt spinel materials depend on the dimensionality, size, and shape of the crystallites. In particular, euhedral Co_3O_4 nanocrystals of Platonic shape expose single well-defined facets, allowing for advanced investigations into structure-reactivity relationships at real catalytic conditions, providing a direct, clear-cut connection between the experiment and theoretical modeling.

In this presentation, the mechanism of hydrothermal synthesis of euherdal spinel oxides, and the crystallite shape retrieval methods based on calibrated STEM pictures will be discussed. The next part will be devoted to periodic spin-unrestricted gradient (DFT-PW91+U) and hybrid (HSE06) modeling of morphology and electronic properties relevant for redox behavior of bare and doped cobalt spinel nanocrystals. The benefit of ab initio thermodynamics for elucidation of the stability of different terminations of cobalt and mixed spinels under various redox conditions (p_{O2} and T), and the structure of the generated defects (anionic and cationic vacancies) will also be explored. Three types of surfaces, containing under-stoichiometric, stoichiometric, and over-stoichiometric amounts of cobalt ions, will be analyzed in detail. For the most stable stoichiometric facet, formation of cationic and anionic vacancies will be examined, and a surface redox state diagram of the possible terminations in the wide stoichiometry range will be discussed. Intrinsic charge transfer processes involving electron (n-conductivity) and hole (p-conductivity) transfer between the octahedral and tetrahedral cobalt cations modeled using a small polaron approximation (Marcus-Dupuis model) will be compared with the results of contactless electronic conductivity, work function, and XAS measurements. For Li-doped Co_3O_4 the effect of the lithium locus on the valence pinning of the cobalt cations is resolved by HSE06/occupational matrix calculations. It will be shown how extrinsic redox processes, triggered by interfacial electron transfer (reductive activation of O_2 and N_2O) and back electron transfer (oxidative evolution of dioxygen) can be factorized and molecularly resolved. The key role here is played by the Fermi level energy and orbital line-up between MO of the reactants and DOS features of the active site for redox behavior of the catalyst. The competition between the Mars van Krevelen vs Langmuir-Hinshelwood mechanisms in the course of CH_4 oxidation will be rationalized, using the surface redox state diagrams constructed using the first principles thermodynamic modelling.

Acknowledgments
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Benchtop XRD and EPR spectrometers by Linev Systems: From structure to radicals reaction mechanism

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Keywords: EPR, ESR, XRD, diffraction patterns, oxidation reactions, photocatalysis, catalyst degradation, metal-organic systems, radical reactions

Understanding catalytic mechanisms requires correlation between the structural properties of catalytic materials and the evolution of reactive intermediates during chemical transformations. While advanced analytical techniques are often limited to centralized facilities, benchtop instrumentation is becoming increasingly attractive for rapid and routine mechanistic studies for every scientific group.

Moreover, a growing trend in analytical instrumentation is the increasing expectation that benchtop systems provide functionality traditionally associated with full-scale laboratory instruments. This demand motivates the development of new accessories, experimental configurations, and complementary analytical workflows that expand the range of accessible applications.

In this contribution, two compact analytical platforms developed by our company will be presented: a benchtop X-ray diffraction (XRD) TELLUS for structural and phase analysis and a benchtop electron paramagnetic resonance (EPR) spectrometer SPINSCAN X for detection of paramagnetic species and reaction intermediates.

Both XRD and EPR systems can be equipped with temperature-controlled accessories enabling measurements from room temperature to above 600 °C under vacuum (for XRD) or controlled gas atmosphere conditions. In addition, the SPINSCAN X EPR spectrometer supports measurements at cryogenic temperatures down to –180 °C. These capabilities support in situ/ an operando studies of catalytic processes, allowing correlation of structural changes, active phases, and thermal stability with catalytic performance.

In addition, the uncoupled goniometer design of the TELLUS diffractometer enables grazing-incidence XRD (GI-XRD) measurements, providing enhanced surface sensitivity for the investigation of thin surface layers, supported catalysts, and poorly crystalline phases.

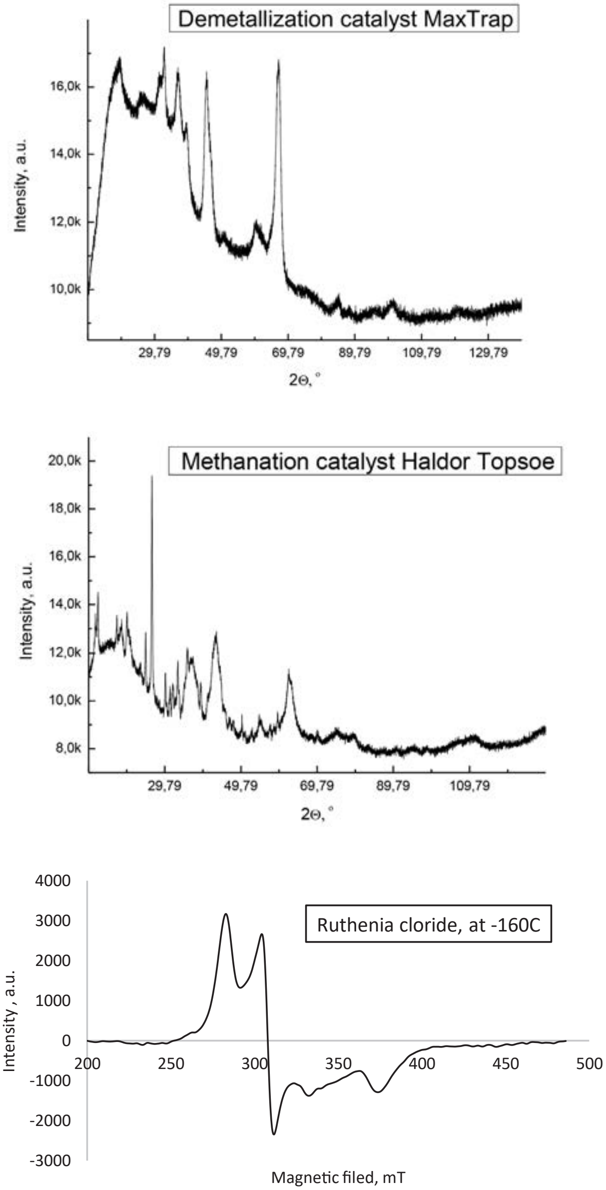

Fig. 1 Examples of XRD diffraction patterns measured with TELLUS and EPR spectra acquired with SPINSCAN for catalytic materials.

Oral Presentations

AI and computational research in catalysis

Unveiling the mechanistic shift in Wacker-type oxidations: A combined DFT and kinetic study on ligand-induced anti-Markovnikov selectivity

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Keywords: wacker-type oxidation, palladium catalysis, anti-markovnikov selectivity, density functional theory, sustainable chemistry

The regioselective oxidation of terminal alkenes to aldehydes (Anti-Markovnikov, AM) represents a key challenge in sustainable catalysis, as the classical Tsuji-Wacker process inherently favors methyl ketones (Markovnikov, M). [1,2] In this work, we present a comprehensive mechanistic investigation into the transition from M to AM selectivity, comparing the performance of the nitrile-ligated catalyst $PdCl_2(MeCN)_2$ with the traditional $[PdCl_4]^{2-}$ system in tert-butanol at 343 K. By integrating a systematic Design of Experiments (DoE) approach, we quantified the effects of catalyst concentration, $CuCl_2$ loading, temperature, and water content on selectivity. Statistical evaluation revealed strong parameter interactions: while high chloride concentrations promote the formation of $[PdCl_4]^{2-}$ and shift the system toward the ketone, low-chloride conditions under mild aerobic conditions favor the production of n-decanal from 1-decene. [3] Previous theoretical studies have highlighted the complex competition between internal syn- and external anti-nucleopalladation, noting that the preferred trajectory is highly sensitive to the ligand environment and solvent conditions. [4] Our DFT calculations support these trends and conclusively identify an external anti-nucleophilic attack as the operative mechanism for both catalysts. In the $[PdCl_4]^{2-}$ system, an energetic barrier of approximately 22 $kcal \cdot mol^{-1}$ almost entirely precludes aldehyde formation. Conversely, the $PdCl_2(MeCN)_2$ catalyst dramatically stabilizes the AM transition state, reducing the energetic gap to the M-pathway to a kinetically accessible 3.1 $kcal \cdot mol^{-1}$. These theoretical values correlate excellently with experimentally determined free activation energies (ΔEa=4.1 kcal/mol in favor of AM). A critical finding of this study is the elucidation of the transient nature of AM selectivity ("catalyst fatigue"). Kinetic profiles show a decline in the aldehyde rate after approximately 0.8 h. Ground-state studies confirm that this is due to a thermodynamically driven ligand exchange: the $[PdCl_4]^{2-}$ complex is 7.7 $kcal \cdot mol^{-1}$ more stable than the nitrile precursor. As the reaction progresses, chloride released by $CuCl_2$ leads to the irreversible formation of this "chloride sink," causing the system to return to M-selectivity.

Acknowledgments

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References

1. J. A. Keith, P. M. Henry, *Angewandte Chemie (International ed. in English)* **2009**, *48*, 9038, DOI 10.1002/anie.200902194.
2. P. Teo, Z. K. Wickens, G. Dong, R. H. Grubbs, *Organic letters* **2012**, *14*, 3237, DOI 10.1021/ol301240g.
3. T. Bouveyron, P. Bratenberg, P. Bell, M. Eisenacher, *Catalysts* **2024**, *14*, 360, DOI 10.3390/catal14060360.
4. P. Kočovský, J.-E. Bäckvall, *Chemistry (Weinheim an der Bergstrasse, Germany)* **2015**, *21*, 36, DOI 10.1002/chem.201404070.

Pd single sites in Au-rich nanoparticles on CeO_2 enable selective methane-to-methanol conversion with water

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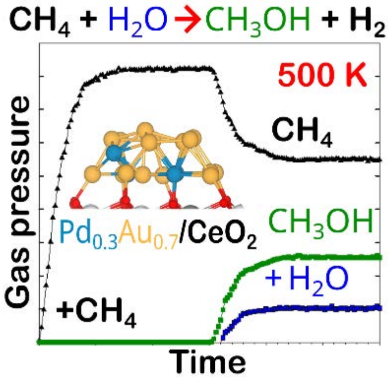
Keywords: Pd–Au/CeO_2, methane-to-methanol, water as oxidant, DFT+U, structure search, ML-assisted global optimization, isolated active sites, metal–support interface

Selective conversion of methane to methanol requires activating the first C–H bond while preventing fast degradation of oxygenated intermediates. Recent **theory–experiment** results demonstrate that **low-loaded Pd–Au/CeO_2** catalysts can produce methanol at mild temperature using **water as the only oxidant**, supported by ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) together with catalytic testing and complementary surface-sensitive characterization such as LEISS, CO-IRAS, TPD and STM.[1]

In this contribution, **emphasis will be put on the theoretical understanding** underpinning these observations and on how it informs the rational design of improved ceria-supported catalysts. Atomistic Pd–Au/CeO_2(111) models are generated via **ML-assisted global optimisation for structure discovery** (GOFEE-type workflows) [2] and subsequently analysed with **DFT(+U)** to determine relative stabilities and elementary-step energetics relevant to methane activation and oxygenate formation.[1]

The resulting models reveal stable configurations in which Pd is largely embedded in an Au-rich environment while an **isolated Pd site** remains exposed. DFT(+U) mechanistic analysis supports a functional separation consistent with the experimental trends: the isolated Pd site provides the required activity for methane activation and for key O–H bond activation steps, whereas the surrounding Au environment moderates subsequent surface chemistry, suppressing pathways that would otherwise destabilise methoxy/methanol intermediates. This atomistic picture rationalises how Pd–Au/CeO_2 can combine methane activation with enhanced methanol selectivity under mild conditions, highlighting **site isolation and metal–support interfacial structure** as central determinants of performance.[1]



Time evolution of gas-phase signals during direct methane conversion over **$Pd_{0.3}Au_{0.7}/CeO_2$** at **500 K**. Upon introducing **CH_4** (black trace) and subsequently **H_2O** (blue trace), the formation of **CH_3OH** (green trace) is observed, consistent with the overall reaction **$CH_4 + H_2O \rightarrow CH_3OH + H_2$**; inset shows a representative Pd–Au/CeO_2 catalyst model.

Acknowledgments

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References

1. E. Fernández-Villanueva, P. J. Ramírez, P. G. Lustemberg, R. Pérez, M. V. Ganduglia-Pirovano, and J. A. Rodriguez, *Angew. Chem. Int. Ed.* 64, e202505716 (2025)
2. M. K. Bisbo, B. Hammer, *Phys. Rev. Lett.* 124, 86102 (2020)

Modeling catalytic supported nanoparticles using machine learning interatomic potentials

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Keywords: nanoparticles, modeling, machine learning

Small, supported nanoparticles (NPs) with 1-5 nm diameter play an important role in catalysis and tuning metal nanoparticle-support interactions is a fundamental method to control catalytic reactions. Experimental techniques provide limited insights into how interactions with the support change the structure of nanoparticles whereas density functional theory calculations suffer from system size constraints and rely on idealized constructions. I will show in this presentation that the simulation of supported nanoparticles is possible in quantitative agreement with benchmark microcalorimetric measurements for adhesion, chemical potential, and heat of adsorption. Analysis of coordination number, strain, and crystallinity in optimized Ag nanoparticles supported on graphene/Ni(111) revealed surface features inconsistent with previously assumed idealized models. Our results demonstrated that the widely used Wulff and Winterbottom constructions are not satisfactory structural models of supported Ag nanoparticles smaller than 8 and 5 nm, respectively. The approach developed here based on machine learning interatomic potentials opens up an avenue to achieve simulating industrially relevant supported nanoparticles directly under catalytic conditions.

References

1. T. Maxson and T. Szilvási, *Angewandte Chemie Novit,* 1, e70008 (2025).

DFT modelling of the oxygen activation on $Co_3O_4|CeO_2$ heterojunctions – mechanistic role of the interface

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Keywords: $Co_3O_4|CeO_2$ heterojunctions, periodic DFT modelling, oxygen activation

The cobalt oxide and ceria heterostructures ($Co_3O_4|CeO_2$) are intensively investigated owing to their numerous applications as sensors, photocatalysts, catalysts, and recently as electrocatalysts. Those hybrid materials exhibit synergistic effects leading to remarkable photo-, electro- or thermo-catalytic performance, which is superior to that of the corresponding sole components. The catalytic activity of such composite catalytic systems has been recently investigated in CO, CH_4, and C_3H_6 oxidation, CO-PROX reaction as well as in N_2O decomposition. In all those reactions, oxygen activation and its surface mobility phenomena play a crucial role, being invoked in many elementary steps of the surface reaction mechanisms, epitomized by interfacial Mars van Krevelen (MvK) and suprafacial Langmuir-Hinshelwood (LH) pathways. It is generally assumed that the presence of CeO_2 and the catalyst's morphology exert a significant influence on the activity of the spinel active phase, modifying oxygen activation and handling formation of oxygen vacancies.

In the synthesis of catalytic heterojunctions, instead of using the co-precipitation method—which has several drawbacks, such as poor control over morphology and particle size, heterogeneity of the resulting mixed oxides, and the formation of undesired phases—a better-defined $Co_3O_4|CeO_2$ junction can be achieved by assembling the component oxides. These oxides are prepared separately with well-defined shapes, then combined into junctions using sonication or electrodeposition, allowing precise control over the structure of the heterojunction.

For $Co_3O_4|CeO_2$ heterojunctions, modeling within the framework of density functional theory (DFT) is particularly valuable, as it allows for an atomistic description of the interface structure and its influence on the system's electronic properties. DFT enables quantitative analysis of charge transfer between the ceria and spinel phases, changes in oxidation states (Ce^{3+}/Ce^{4+}, Co^{2+}/Co^{3+}), and stabilization of oxygen vacancies, which play a key role in the mechanisms of O_2 activation. Moreover, DFT calculations allow for the determination of O_2 adsorption energies, identification of preferred active sites at the interface, and analysis of reaction pathways leading to the formation of superoxide or peroxide species. This makes it possible to link the local electronic structure of the interface with the observed catalytic activity, providing crucial support for interpreting experimental data and guiding the rational design of more efficient CeO_2/cobalt spinel catalysts.

A significant challenge in this case, however, is constructing a reliable heterojunction model that provides an accurate description of the active sites of the two-component catalyst without exceeding the computational limits of the method. In this work, we present an approach for building an appropriate periodic model of the junction based on well-defined nanograins of both oxides, along with an analysis of the electronic state and stability of the model system during interactions with oxygen molecules (O_2 adsorption and activation, lattice oxygen release, and vacancy generation). The computational results are correlated with catalytic tests performed on heterojunctions obtained via sonication.

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Catalyst design & nanocatalysis

Hydrodeoxygenation of anisole over Ni-Mo catalysts

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Keywords: anisole, hydrodeoxygenaton, methoxycyclohexane, cyclohexane

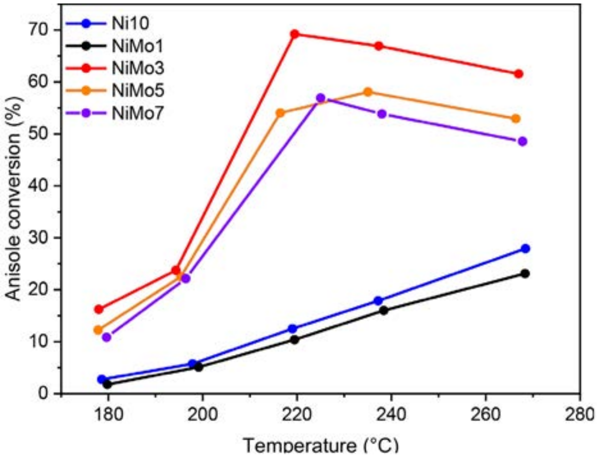
As the 2030 deadline for SDGs approaches, many countries still lag behind in decoupling economic growth from environmental degradation. Circular economy strategies provide a viable solution in which industrial by-products such as lignin that are currently burned for heat energy or discarded as waste are transformed into value-added products. In this regard, hydrodeoxygenation (HDO) has been widely studied as a promising technology for upgrading lignin derived oxygenates into components of sustainable fuels, however, developing active, selective, and stable catalysts remains a challenge.

In this study, we investigated the catalytic behavior of NiMoX/Al_2O_3 (where X = 1, 3, 5, and 7 wt % Mo), using 10 wt% Ni as the benchmark loading for each catalyst [1]. The catalytic activity was studied over a range of temperatures between 180 and 270 °C, using anisole as a model lignin-derived feedstock. HDO reactions were performed in a flow reactor at a constant pressure of 40 bar and variable weight hourly space velocities (30 - 480 h^{-1}) to elucidate the reaction pathways and the effect of Mo loading on HDO. This was compared with 10 wt % Ni/Al_2O_3 (Ni10) catalyst.

The product selectivities of anisole HDO were temperature dependent, yielding cyclohexane (CHN) and methoxycyclohexane (MCH) as major products. Signifcant differences in activity were observed from 220 °C. As shown in **Figure 1a**, Ni10 and NiMo1 showed similar anisole conversion, yielding CHN as the major product. However, NiMo3, NiMo5 and NiMo7 resulted in enhanced HDO activities, with more than 70% selectivity towards MCH (**Figure 1b**). This could be due to coke deposition or a decline in surface coverage resulting in the reactants desorbing from the active sites faster before the reaction can take place. The hydrogenation rate was found to be five times higher than demethoxylation rate for NiMo5 in comparison to NiMo1, suggesting that Mo interaction with Ni enhances H_2 activation, resulting in a spillover of H_2 that saturates the aromatic ring. Interestingly, at 270 °C, the selectivity of the higher Mo-loaded catalysts switched from MCH to more than 70% CHN as the final product.

Figures

a



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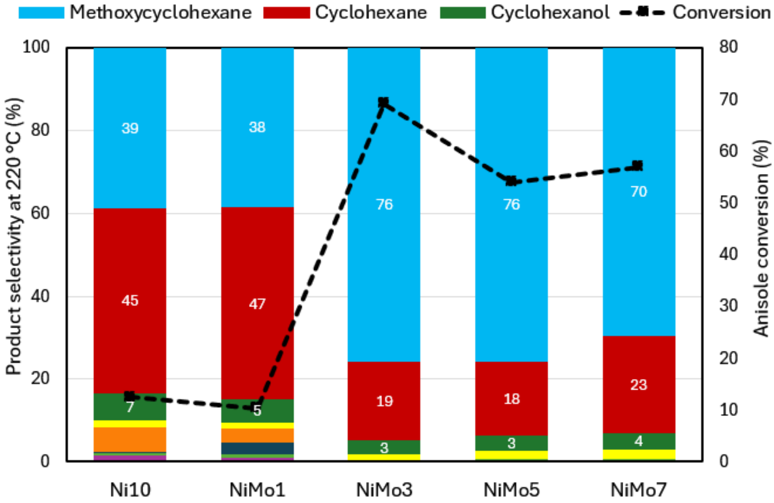

Figure 1 Dependece of anisole conversion on temperature (a) and product selectivity of the catalysts at 200 °C (b).

Acknowledgments

Funding from the Technology Agency of the Czech Republic project no. TS02030246 is acknowledged.

References

1. Dutta et al., J. Catal. 2024, 435, 115553.

Interface engineering of Pt–ZnO–CeO_2 by atomic layer deposition for advanced applications

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Keywords: ALD, particle growing, Pt/ZnO/CeO_2 interface, ethanol decomposition, in situ DRIFT spectra

The precise design of metal-oxide interfaces in heterogeneous catalysts is crucial for optimizing activity and selectivity in reactions such as ethanol decomposition. In this study, Pt_ZnO_CeO_2 composite catalysts were synthesized via atomic layer deposition (ALD) with systematically varied ZnO loadings to investigate the influence of support structure on platinum nucleation, interfacial properties, and catalytic performance (Fig.1). High-resolution TEM, XPS, ICP-MS reveal that ZnO strongly affects Pt growth, leading to non-monotonic trends in nanoparticle size, dispersion, and loading. These structural effects translate into distinct electronic interactions at Pt/CeO_2, ZnO/CeO_2 and Pt/ZnO interfaces, as reflected by XPS analysis. To probe the catalytic relevance of these interfaces, ethanol decomposition was employed as an interface-sensitive reaction. The results demonstrated that moderate ZnO loading (3–5 cycles) generated a Pt/ZnO/CeO_2 interface, that significantly increased ethanol conversion and promoted C1-product formation. At higher ZnO coverage (30 cycles), the catalyst surface was dominated by Pt/ZnO interactions, resulting in reduced C–C bond cleavage activity. These trends were supported by in situ DRIFTS by identifying the suppression of acetate formation and promotion of aldehyde intermediates at Pt-ZnO surfaces. These findings underscore the critical role of interfacial engineering via ALD in modulating catalyst structure, metal-support interactions, and reaction pathways.

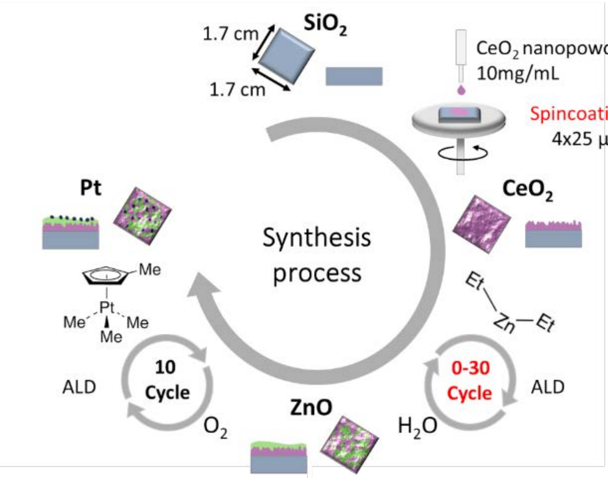

Figure 1. Synthesis procedure for the 10cPt_0-30cZnO_CeO_2 samples.

Acknowledgments

This paper was supported by the János Bolyai Research Scholarship Hungarian Academy of Sciences (I.S. BO/00369/25/7). 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.

Role of copper additive in catalysts based on Mg-Al oxides and FAU zeolites for Guerbet condensation of ethanol into higher alcohols

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Keywords: ethanol, 1-butanol, Guerbet condensation, Mg-Al oxides, FAU zeolites, copper

Guerbet condensation is important for producing higher alcohols from renewable bioethanol (EtOH). The process involves dehydrogenation, aldol condensation and reduction reactions. Conventional catalysts such as Mg-Al oxides and hydroxyapatites show low EtOH conversion due to limited dehydrogenation activity. Therefore, catalysts with adjacent Cu-based dehydrogenation sites were investigated to clarify how preparation method and copper loading affect the physicochemical properties of Mg-Al oxides and FAU zeolites and their performance in Guerbet condensation of EtOH into higher alcohols.

Hydrotalcite-derived Mg-Al(Y)-oxide catalysts were prepared by coprecipitation method and modified with Cu(Ni) via wet impregnation or coprecipitation during the synthesis. FAU zeolites were synthesised by hydrothermal method and modified with Cu using ion exchange. The samples were studied by XRD, TEM/SEM, EDX, N_2-ad(de)sorption, XPS, EPR, TPD-NH_3/CO_2, and TPD-H_2.

As expected, for 5%Cu/Mg-Al(2:1) oxide catalyst EtOH conversion rose significantly up to 75% compared with 31% for Mg-Al(2:1) at 275 °C. But the main product in this case was acetaldehyde, meaning the process stopped after dehydrogenation of EtOH. At lower copper concentration 0.5%Cu/Mg-Al(2:1) it was observed 1-butanol (BuOH) formation with selectivity around 10%, but still acetaldehyde was a predominant product. Thus, it was reasonable to change the method of catalyst modification to coprecipitation to avoid the coverage of aldol condensation sites by copper species. For Cu-Mg-Al-Y (0.1:1.9:0.9:0.1) oxide system addition of copper increased EtOH conversion up to 66% and resulted in a high selectivity to aldehydes (up to 44%) at 250 °C. Still, the selectivity to BuOH (10%) was much lower than that for the Mg-Al-Y oxide catalyst (54%). Halving copper concentration and addition of Ni to the Cu-Mg-Al-Y catalyst increased the selectivity to BuOH and higher alcohols. Moreover, EtOH conversion (around 10%) was carried out at 150 °C. The selectivity to BuOH together with higher alcohols (2-ethyl-1-hexanol, 1-hexanol, 2-ethyl 1-hexanol and 1-octanol) reached 60%.

Over Cu-modified FAU zeolites copper works similar in terms of reducing the temperature of the beginning of the process. At 150 °C acetaldehyde formation started and at 200 °C the fraction of BuOH and higher alcohols was observed (12%), while initial FAU zeolite almost had no catalytic activity at 200 °C and at higher temperatures resulted in formation of diethyl ether and ethylene. Increasing the pressure in the process from 1 to 20 bar leads to a rising in selectivity of BuOH and higher alcohols up to 29%.

Thus, copper additive in catalysts based on Mg-Al oxides and FAU zeolites leads to an enhancement of redox properties promoting the dehydrogenation step in the EtOH conversion. However, strict control on the method of introduction and concentration of copper additive, as well as selection of optimal working conditions for the Guerbet condensation should be applied to develop highly efficient catalyst for this process with further industrial implementation.

Acknowledgments

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Ceramics and porous materials in catalysis

Development of controlled-porosity alumina supports for high-surface area Ni catalysts in HVO synthesis

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Keywords: hydrotreated vegetable oil, alumina, nickel catalyst, hierarchical structures

The hydrotreating of biomass to produce hydrotreated vegetable oil (HVO) is a promising alternative for replacing fossil fuels with renewable energy sources. Given the urgency of mitigating climate change and reducing global temperature rise, developing efficient catalysts to remove heteroatoms and unsaturated bonds in biomass-derived oils is essential to HVO production [1,2]. In the present work, hierarchical porous alumina was prepared via a modified sol-gel to serve as a robust support for nickel as the active phases. A key feature of this synthesis was the control of porosity through spinodal decomposition during the solgel transition, induced by the addition of polyethylene glycol (PEG) with molecular weights ranging from 200 to 8000 g/mol. The active phase was incorporated through the wet impregnation method, at nickel concentrations of 10% and 20% (w/w). Structural characterization via X-ray diffraction (XRD) confirmed the formation of the γ-Al_2O_3 in all samples, while the nitrogen physisorption isotherms provided critical insights into the textural evolution of the material. The reference alumina (synthesized without PEG) exhibited a specific surface area of 239 m^2/g and a narrow pore size distribution centered at 6 nm. In contrast, samples with PEG-controlled porosity showed significantly enhanced properties, reaching a surface area of 325 m^2/g (using PEG 8000) and a larger pore size, centered at 28 nm. These samples displayed H2-type hysteresis, suggesting a complex "ink-bottle" pore morphology. Further analysis using Small-Angle X-ray Scattering (SAXS) revealed that the radius of gyration remains constant around 1.9 nm, suggesting the formation of organized particles. The Porod exponent remained near -4.0 for all samples, indicating non-fractal objects with smooth surfaces. The combination of XRD and scanning electron microscopy (SEM) analysis confirmed that the NiO_2 phase was well-distributed across the porous framework. These results indicate that the hierarchical alumina produced is a highly promising candidate for biomass hydroprocessing.

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References

1. R.V. Sreeharsha, N. Dubey, S.V. Mohan, Orienting biodiesel production towards sustainability and circularity by tailoring the feedstock and processes, J Clean Prod 414 (2023) 137526. https://doi.org/10.1016/J.JCLEPRO.2023.137526.
2. K. Malins, I. Malina, The effects of supported Pd, Pt, Re, Rh, Ru, Ir, Au, and Ni catalysts on renewable hydrocarbon production from alternative feedstock, Biomass Bioenergy 171 (2023) 106732. https://doi.org/10.1016/j.biombioe.2023.106732.

Characterization methods and surface science in catalysis

Operando soft and hard XAS investigation of a model Co/Silica Fischer-Tropsch catalyst under realistic reaction conditions

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Keywords: operando soft XAS, Fischer-Tropsch synthesis, Co/Silica catalyst, high pressure conditions

A new operando X-ray absorption spectroscopy (XAS) cell compatible wiht both soft and hard X-rays was used at the OÆSE endstation of BESSY II synchrotron facility (Berlin, Germany)[1] to investigate a model cobalt-based powder catalyst (10%wt. Co/Mn-Ti-SiO_2) under real Fischer-Tropsch reaction conditions (e.g., 10 bar and 250 ºC). The cell design features a thin SiN_x membrane of 200 nm thickness that separates the high-vacuum beamline/analysis chamber from the high-pressure reaction side where the powder catalyst sample was deposited by drop-casting on the membrane. By this arrangement the pathlength of the low energy (soft) X-rays in the high density/pressure media - and thus their attenuation – is minimized, enabling for the first time the compatibility of soft XAS with high-pressure reaction conditions.

A temperature-programmed in-situ reduction of the calcined catalyst was performed following the Co L_3 and O K-edges in fluoresence yield (FY) detection mode. Cobalt oxide reduction was found to be a two-step process, first reducing from spinnel Co_3O_4 to rocksalt CoO at around 215 ºC followed by almost complete reduction to metallic Co above 340 ºC. After reduction, the pressure was increased to 10 bar and different FTS conditions were applied varying the temperature and the H_2/CO ratio. The reaction products were followed by a GC-FID while at the same time operando FY-XAS measurements were possible. The activation energy of the reaction was found to be equal to 101.2 ± 5.1 kJ/mol, a typical value for kinetic control, implying that mass and heat transport phenomena are not limiting the observed reaction rate. An activity drop of 35% was observed during the first 13h on stream under typical FTS conditions (250 ºC, H_2:CO = 2, 10 bar) while Co remained mostly metallic and Mn promoter in +2 oxidation state. A shoulder in Co L_3 edge spectrum was observed upon exposing the catalyst to FTS conditions which was attributed to possible formation of Co_2C species. The intensity of this feature was enhanced with exposure time in radiation and by decreasing the H_2 to CO ratio.

These results are complementary to previous operando studies[2] adding soft XAS in the arsenal of operando techniques that can provide valuable insights of catalysts under working conditions.

References

1. R. Garcia-Diez et al., J. Synchrotron Radiat. **32**(Pt 3), 634–648 (2025).
2. N. Fischer, and M. Claeys, J. Phys. D. Appl. Phys. **53**(29), 293001 (2020).

Combustion kinetics and catalysis

Synthesis and study of catalytic properties of cobalt-based binary oxide catalysts

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Keywords: cobalt, sol-gel combustion method, catalyst, carbon monoxide

Despite the extensive study of low-temperature oxidation of carbon monoxide, this catalytic process is becoming increasingly important in the context of air purification due to the development of industry and the increase in the number of vehicles. Catalysts used to oxidize carbon monoxide to carbon dioxide can be divided into two main groups: noble metal and non-noble metal-based catalytic systems. Noble metal catalysts are characterized by high catalytic activity and stability, the ability to use them on various carriers, a wide temperature range, ease of preparation, resistance to chemical influences of the environment, and the possibility of reuse after the regeneration and activation process. That is why economically less expensive catalysts are used. Therefore, recently, transition metal catalysts have been widely used. From them, binary oxide catalysts based on copper, cobalt, nickel, copper, manganese, etc. are synthesized.

Recently, the sol-gel combustion method has been widely used for synthesis. This method has many advantages. Combustion occurs in one stage. The combustion process does not require a long time. Economically inexpensive reagents are used for synthesis [1-2].

$Co(NO_3)_2·6H_2O$, $Cu(NO_3)_2·3H_2O$, and $C_6H_8O_7·H_2O$ were used as starting materials. Initially, equal molar amounts of the metal nitrates and citric acid monohydrate were dissolved separately in distilled water, then mixed together under constant magnetic stirring to form a gel. After drying and calcining this gel, 1 g of the powder was combined with an alumogel binder and formed into granules. These granules were then heated in a muffle furnace at 500°C for three hours.

The final synthesized materials were analyzed using several physico-chemical methods: X-ray diffraction and Brunauer–Emmett–Teller (BET) surface area analysis.

When measured by the BET method, the specific surface area of the Co-Mn-containing binary oxide catalysts was 19, and the specific surface area of the Co-Cu-based binary oxide catalysts was 19.5 m^2/g. The pore volume was 0.034 cm^3/g for the Co-Mn compound and 0.029 cm^3/g for the Co-Cu.

The catalytic properties of the synthesized catalysts for the conversion of carbon monoxide to carbon dioxide were also studied. The results of the experiments show that the complete conversion of carbon monoxide in the Co-Mn catalyst was at 180^0C, and in the Co-Cu catalyst at 140^0C.

References

1. Amini, E., Rezaei, M., Sadeghinia, M. Low temperature CO oxidation over mesoporous $CuFe_2O_4$ nanopowders synthesized by a novel sol-gel method // Chinese Journal of Catalysis, 2013, 34 (9), p. 1762–1767.
2. Ambika, S, S.Gopinath, K.Saravanan [et al.]. Preparation and Characterization of Nanocopper Ferrite and Its Green Catalytic Activity in Alcohol Oxidation Reaction // Journal of Superconductivity and Novel Magnetism, 2018, v. 32, №9, p. 1–8.

Electrified & coupled catalysis

Development of a novel magnetic rotating disk electrode for advanced electrocatalytic studies

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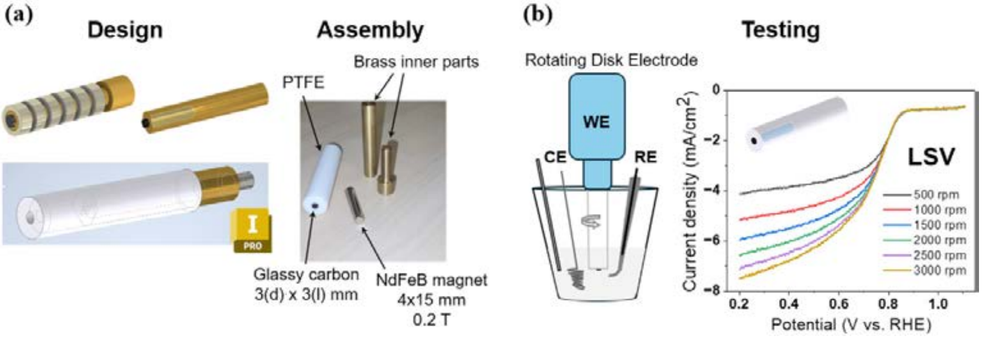
Keywords: electrocatalysis, oxygen reduction reaction (ORR), oxygen evolution reaction (OER), magnetic field effect, 3D CAD design

The rapid rise in atmospheric CO_2 levels underscores the urgent need for sustainable energy conversion and storage technologies to achieve global decarbonization. While hydrogen is a pivotal industrial feedstock and clean energy carrier, its current large-scale production relies heavily on steam methane reforming (SMR). The latter possesses a high carbon footprint, whereas electrochemical water splitting offers a carbon-neutral alternative. Its efficiency, however, is often limited by the sluggish kinetics of the anodic oxygen evolution reaction (OER), just as the oxygen reduction reaction (ORR) is the bottleneck in fuel cell performance. Recent studies indicate that applying an external magnetic field can enhance electrocatalytic activity by modulating mass transport and spin-selective charge transfer dynamics, thereby lowering the overpotential for oxygen electrochemical reactions. To systematically investigate theses phenomena, we designed and constructed a custom-built magnetic Rotating Disk Electrode (RDE) setup. Based on how the magnetic field is applied, two distinct configurations were attained: one integrating an axially positioned NdFeB bar magnet, and another featuring coaxially mounted NdFeB ring magnets within a rotating PTFE body. To ensure structural integrity and minimize magnetic interference, the internal conductive assembly was machined from diamagnetic brass, supporting a glassy carbon disk substrate. The setup was validated by evaluating the catalytic performance of benchmark Pt/C and magnetically responsive CoNi@NC heterostructures. Electrochemical measurements, including linear sweep voltammetry (LSV) and cyclic voltammetry (CV), were conducted in a standard three-electrode cell. Our results demonstrate that the external magnetic field effectively modifies the reaction kinetics for both OER and ORR and highlight the potential of magnetic-field-enhanced electrochemistry as a promising strategy for improving the overall energy efficiency of green hydrogen production and utilization.



(a) Schematic illustration of the magnetic Rotating Disk Electrode (RDE) design and the fabricated setup incorporating bar and ring magnets. (b) Typical LSV curves obtained for CoNi@NC in a three-electrode configuration using the magnetic RDE.

Exploring catalytic reaction mechanisms

Sustainable $CeO_2/CoFe_2O_4$ catalysts for the total oxidation of mixed VOC–CO emissions: From activity to mechanism

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Keywords: mixed-feed VOC oxidation, sustainable catalyst, *operando* FTIR, reaction mechanism

Catalytic oxidation research has largely focused on single VOCs or CO as isolated model pollutants. However, real emission sources including industrial stacks, indoor environments, biofuel combustion and chemical processing release mixtures of VOCs and CO simultaneously. These mixed feeds are more challenging because different molecules compete for the same surface sites and can inhibit one another's oxidation[1]. In this work, we evaluate the total oxidation of CO, ethanol and acetaldehyde (CEA) mixture over noble metal free sustainable catalysts, namely CeO_2, $CoFe_2O_4$ and their $CeO_2/CoFe_2O_4$ composite. The redox and acid-base properties of these catalysts were examined, and complementary studies were performed to gain mechanistic insight into competitive adsorption in mixed feeds, in order to enhance their performance.

Catalytic tests show that the temperature of complete conversion (T_{100}) is above 300 °C for CeO_2, 275 °C for $CoFe_2O_4$ and decreases to 225 °C for the $CeO_2/CoFe_2O_4$ composite, witnessing for a synergy between the material components. At 200 °C, the CO_2 productivity reaches 35, 10 and 60 $\mu mol \cdot g^{-1} \cdot min^{-1}$ for CeO_2, $CoFe_2O_4$ and the composite, respectively. Although CeO_2 displays a higher reaction rate than $CoFe_2O_4$ at this temperature, its higher T_{100} reflects its ability to oxidize ethanol and acetaldehyde but not CO in the mixed feed. Conversely, $CoFe_2O_4$ activates CO more readily but oxidizes oxygenates less efficiently. H_2-TPR and CO_2/pyridine adsorption confirm that $CoFe_2O_4$ is more reducible and contains more Lewis acid sites, while CeO_2 is more basic, accounting for the differences in their catalytic behaviours. Mechanistic insights were obtained through *operando* FTIR on the most active material (composite). Gas-phase analysis (Figure 1A) shows that ethanol is first converted into acetaldehyde, which accumulates before full oxidation, while CO conversion begins only after oxygenates disappear. Surface analysis (Figure 1B) reveals that CO initially forms hydrogen-carbonate species that are rapidly displaced by ethoxy and acetaldehyde species; upon heating, both convert into acetate, then formate, which no longer inhibit CO oxidation.

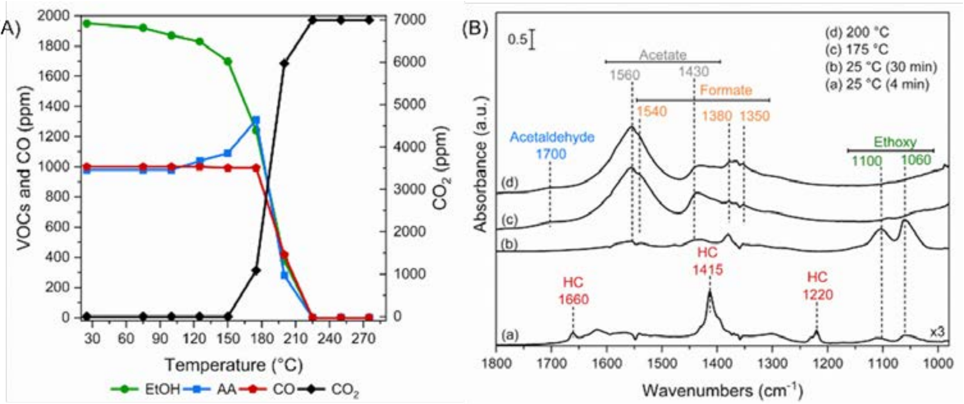

Figure 1: (A) Gas-phase FTIR during CEA oxidation over the $CeO_2/CoFe_2O_4$ composite, showing sequential ethanol and acetaldehyde consumption and delayed CO oxidation. (B) Operando FTIR spectra highlighting the evolution of surface species. Abbreviations: EtOH = ethanol; AA = acetaldehyde; HC = hydrogen carbonate.

References

1. Rochard, G. *et al.*, *Catalysts.* **2021***, 11*, 1218.

On the performance of FCC catalysts in polyolefin cracking

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Keywords: zeolite, FCC, polyolefins, chemical recycling of plastic, *operando* FTIR&GC-MS

Despite the convenience of plastics, their massive production poses serious waste management and environmental challenges, with only ~30% recycled and just 1% chemically. Catalytic cracking offers a promising solution, combining high activity and selectivity control while operating under milder conditions (e.g., lower temperatures). These advantages suggest strong economic potential, further supported by decades of industrial experience with Fluid Catalytic Cracking (FCC) a well-established, large-scale technology optimized over the past 70 years.

This study examines the performance of fresh (Cat-F) and equilibrium (Cat-E) variants of a commercial FCC catalyst (W.R. Grace), compared with an extrudate USY-31 (zeolite/γ-Al_2O_3 = 1). Catalysts were characterized using conventional structural, textural, and acidity analyses, and evaluated for cracking of polypropylene (PP) (Fig. 1A), low-density polyethylene (LDPE), and polystyrene (PS). Cat-F and Cat-E differ significantly in Brønsted acid sites (BAS) density, while their acid strengths remained comparable. Severe thermal treatment at 800 °C reduces BAS density but markedly increases acid strength. Among all catalysts, Cat-E treated at 800 °C possessed the strongest Brønsted acid sites and demonstrated the highest catalytic activity for LDPE and PP cracking. Thermogravimetric analysis show that for PP, the cracking performance - expressed as 50% and 25% ($T_{50\%}$ and $T_{25\%}$) correlates with BAS strength (Fig. 1B) and accessibility (Fig. 1C). In contrast, PP and LDPE selectivity depends primarily on BAS density, expressed per surface area ($BAS \cdot m^{-2}$) or micropore volume ($BAS \cdot cm^{-3}$). The fraction of C_3+C_4 hydrocarbons increases with BAS density, indicating their key role in recracking reactions, as reflected by an inverse correlation with the C_5+C_{6+} fraction. Coke formation and TPO-TGA regeneration studies reveal that Cat-E is 4–6 times more resistant to coking than Cat-F, regardless of polymer type.

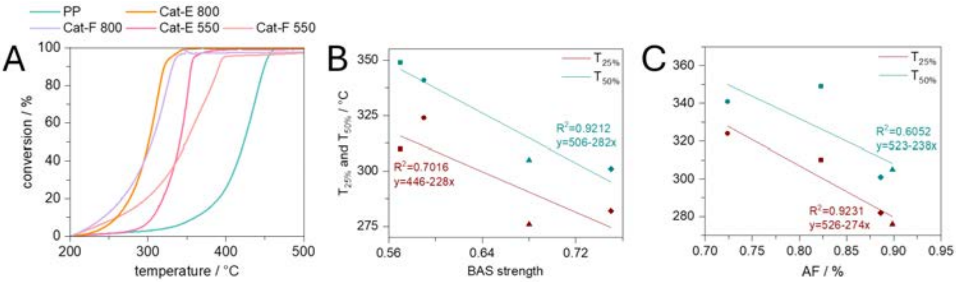

Figure 1. (A) Conversion curves for PP cracking, $T_{xx\%}$ versus BAS strength (B) or (C) accessibility factor.

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Acid-catalyzed permanganate oxidation of guaiacol: A kinetic and mechanistic insights

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Keywords: potassium permanganate, Guaiacol, oxidation kinetics, reaction mechanism, solvent effect

The kinetics and mechanism of the redox reaction between guaiacol and potassium permanganate have been investigated in acidic medium. The reaction exhibits first-order dependence with respect to both guaiacol and permanganate concentrations, while the observed rate constant increases linearly with acid concentration, following the relation $k_{obs} = a + b[H^+]$. Variation in ionic strength does not influence the reaction rate, indicating the involvement of neutral species in the rate-determining step. Activation and thermodynamic parameters were evaluated using Arrhenius and Eyring treatments. Spectroscopic analysis confirms 2-methoxyhydroquinone as the major oxidation product of guaiacol. Solvent effects were examined in different organic media and analyzed using Taft's and Swain's multiparametric correlations. The rate data show satisfactory correlation with Kamlet–Taft solvatochromic parameters (α, β, π^*), highlighting the role of solvent polarity and hydrogen-bonding interactions in the reaction kinetics. On the basis of kinetic, spectral, and solvent effect studies, a plausible reaction mechanism is proposed.

References

1. A. Agrawal, R. Sailani, P. Sharma, C.L.Khandelwal, P.D. Sharma, Oxidn. Commun., 2016, 39, 1273–1281.
2. A. Galano; J. R. Leon-Carmona; J. R. Alvarez-Idaboy, J. Phys. Chem. B. 2012, 116, 7129–7137.
3. M. J. Kamlet; J. L. M. Abboud; M. H. Abraham; R. W. Taft, J. Org. Chem., 1983, 48, 2877–2887.
4. S. Ehrenson; R. T. C. Brownlee; R. W. Taft, J. Am. Chem. Soc., 1972, 94, 9113–9122.
5. O. Exner, Collect. Czech. Chem. Commun., 1966, 31, 3222–3251.

Unraveling the role of reactant loading in methanol conversion over zeolite via operando spectroscopy and MCR-ALS analysis

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

Methanol-to-hydrocarbons (MTH) is an industrially important route for olefin production, with methanol obtainable from renewable resources. Catalysts with chabazite (CHA) topology, such as H-SAPO-34 zeotype and SSZ-13 zeolite, exhibit high activity and pronounced shape-selectivity in this reaction. Despite extensive study and reaction's commercial implementation, the detailed mechanism remains under debate. Current models are based on the hydrocarbon pool (HCP) mechanism, in which cyclic hydrocarbon intermediate species, including methylbenzene and cyclopentenyl/cyclopentadienyl cations, play a central role [1]. Operando mode investigations and advanced spectroscopic analysis approaches have gained increasing attention as tools for investigating the evolution of these species under reaction conditions.

In this study, the transformation of methanol over an H-SSZ-13 (CHA) catalyst was investigated under operando conditions, at high and low substrate loadings. Three consecutive 2-hour reaction cycles were performed. Catalytic performance was monitored by GC and MS, while operando UV-Vis and FTIR spectroscopy were employed to elucidate the mechanistic origins of the performance differences observed between the two loading conditions. In addition, MCR-ALS analysis of the UV-Vis spectra was applied to extract underlying spectral components and to identify spectroscopically distinct species contributing to the measured signals.

GC and MS measurements showed that high methanol loading led to rapid catalyst deactivation already in the second cycle with declining olefin yields and increasing DME selectivity, whereas lowering the methanol feed markedly extended catalyst lifetime and sustained C_2-C_4 olefin production. Operando UV-Vis spectroscopy supported by MCR-ALS analysis revealed that these differences arose from loading-dependent evolution of hydrocarbon pool species, with reduced feed delaying the formation of aromatic and polyaromatic coke precursors. MCR-ALS analysis of the initial 10 minutes of the first cycles uncovered the cyclization of protonated linear dienylic species into cyclopentenyl cations under both loading conditions, an effect not directly visible on the UV-Vis spectra, while indicating a prolonged induction period at low methanol loading. Extension of the analysis to subsequent reaction cycles showed that reduced loading suppressed the accumulation of polyaromatic species over multiple cycles, consistent with a distinct deactivation pathway, further supported by complementary GC-MS analysis of carbonaceous deposits.

Acknowledgments

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

References

1. Hernandez, E. D., & Jentoft, F. C. (2020). Spectroscopic signatures reveal cyclopentenyl cation contributions in methanol-to-olefins catalysis. ACS Catalysis, 10(10), 5764–5782.

Homogeneous & heterogeneous photocatalysis

Illuminating the path to vanillin: Tuning molybdenum complexes for selective oxidation

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Keywords: photocatalysis, alcohol oxidation, molybdenum complex, Schiff base

Selective oxidation of alcohols to aldehydes or ketones is a cornerstone of organic synthesis, enabling the production of high-value compounds for pharmaceuticals, flavours and the perfume industry. [1,2] A notable example is the conversion of vanillyl alcohol to vanillyl aldehyde, commonly known as vanillin, which serves as a key intermediate in the preparation of flavouring agents, fragrances and other bioactive molecules. [3,4] Its selective formation is therefore highly desirable, as it enables the production of high-value products with minimal byproducts. Photocatalysis has emerged as an efficient and sustainable approach for such selective oxidations, offering the advantages of mild reaction conditions, reduced energy consumption, and the ability to harness visible light for chemical transformations. [5,6] Using light-driven processes can also enhance reaction selectivity and reduce the formation of over-oxidation products.

In this study, a series of molybdenum complexes were synthesized using hydrazide-based ligands derived from oxalyldihydrazide, with variations in the aldehyde component: 2-hydroxy-, 2-hydroxy-3-methoxy- and 2-hydroxy-5-methoxy-benzaldehyde. This strategy generated a series of molybdenum catalysts featuring different functional groups on the benzene ring, allowing for systematic tuning of the ligand environment. The catalytic performance of these complexes was evaluated in the selective oxidation of vanillyl alcohol to vanillin under visible light irradiation using various co-solvents. Our investigations revealed that both the ligand structure and the choice of co-solvent significantly influence catalytic conversion and selectivity. Understanding these effects is crucial for optimizing catalytic systems, as it enables the rational design of catalysts tailored for high performance and selectivity, ultimately advancing sustainable approaches for the production of high-value chemicals like vanillyl aldehyde.

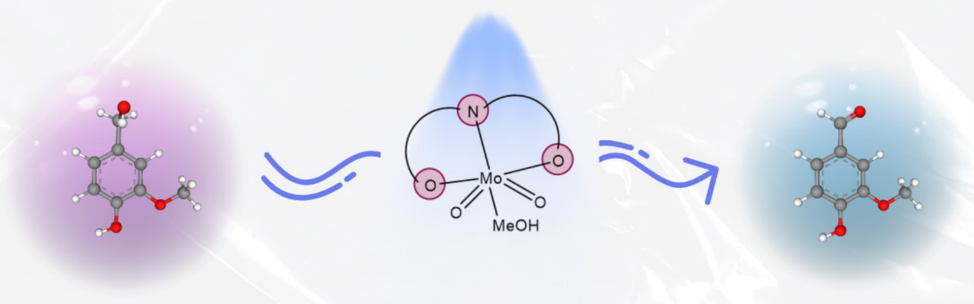

Figure 1. Graphical abstract

References

1. Y. Dong, Y. Feng, Z. Li, H. Zhou, H. Lv, G. Yang, *ACS Catal.*, 2023, **13**, 14346–14355.
2. D. Ribeaucourt, B. Bissaro, F. Lambert, M. Lafond, J. Berrin, *Biothenol. Adv.*, 2022, **56**, 107787.
3. N. C. Jana, S. Sethi, R. Saha, B. Bagh, *Green Chem.*, 2022, **24**, 2542.
4. A. Olatunde, A. Mohammed, M.A. Ibrahim, N. Tajuddeen, M.N. Shuaibu, *J. Med. Chem. Rep.*, 2022, **5**, 100055.
5. M.-Z. Jia, J.-W. Cui, C.-H. Rao, Y.-R. Chen, X.-R. Yao, J. Zhang, *ACS Sustainable Chem. Eng.*, 2022, **10**, 9591–9599.
6. L. Sun, B. Li, X. Chu, N. Sun, A. Qu, X. Zhang, I. Khan, L. Bai, L. Jing, *ACS Sustainable Chem. Eng.*, 2019, **7**, 9916–9927.

Industrial & environmental catalysis

Nitrogen-doped and g-C_3N_4-modified grass pellet biochar for enhanced PMS-mediated trimethoprim degradation under UV light

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Keywords: melamine modified biochar, trimethoprim, degradation, peroxymonosuflate

Advanced oxidation processes (AOPs) have become essential in modern wastewater treatment, particularly for degrading recalcitrant organic contaminants such as the antibiotic trimethoprim (TRIM). Among these, persulfate-based AOPs—using peroxymonosulfate (PMS) or peroxydisulfate (PDS)—have attracted significant attention in recent years due to their ability to generate highly reactive sulfate radicals ($SO_4^{-}•$) and other reactive oxygen species. Biochars are cost-effective and excellent adsorbents in water treatment; they can also be used as catalysts for radical generation. The combination of biochar with PMS is a promising, cost-effective AOP for removing organic pollutants from wastewater.

In this study, biochar was produced from waste grass pellets (GP) via pyrolysis at 700 °C, and nitrogen doping was employed to enhance its catalytic performance in PMS activation and radical generation. The catalytic efficiency was tested by removing the antibiotic drug trimethoprim (TRIM). Melamine, a nitrogen-rich precursor, was employed to modify the biochar. Two distinct approaches were investigated: in one-step co-pyrolysis, the raw grass pellet material was mixed with melamine and pyrolyzed at 700 °C, yielding nitrogen-doped biochar (N-doped biochar, N-BC). In the case of post-modification, pristine biochar (produced at 700 °C) was mixed with melamine and subsequently thermally treated at 550 °C, yielding a carbon nitride (C_3N_4)/biochar composite (CN/BC). In both synthesis methods, the mass ratios of melemine to grass pellet and melemine to biochar were systematically varied. The catalytic efficiency of the prepared materials was evaluated by measuring their ability to degrade TRIM under dark and UV irradiation, with and without PMS addition, to explore potential synergistic photocatalytic effects.

The most effective N-BC catalyst was prepared with a 2:1 melamine:grass pellet weight ratio. In dark conditions, the N-BC outperformed CN/BC, achieving complete TRIM removal in 20 min (80% degradation + 20% adsorption), whereas CN/BC reached only 44%. However, both composites exhibited >90% TRIM removal when PMS, UV light (398 nm), and a catalyst (N-BC or CN/BC) were combined, indicating strong synergy. Radical-scavenging assays confirmed that singlet oxygen (1O2), superoxide (O2•⁻), and direct electron transfer were the primary mechanisms of TRIM degradation in both cases. This work demonstrates that waste-based biomass is an effective precursor for biochar preparation and highlights its potential for PMS-based removal of persistent organic pollutants. These metal-free, waste-derived catalysts offer a sustainable, efficient, and environmentally benign approach for eliminating recalcitrant antibiotics from wastewater.

Composite Cu-based catalysts for H_2O_2 decomposition: Tuning ROS distribution by redox-electroprotic coupling for wastewater AOPs

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Keywords: reactive oxygen species, hydrogen peroxide, Fenton reaction, electroprotic mechanism, transition metal oxides, UV-Vis, EPR, advanced oxidation processes

Advanced oxidation processes (AOPs) based on H_2O_2 decomposition are an attractive route for the removal of persistent organic contaminants from industrial wastewaters. They generate highly reactive oxygen species (ROS) (primarily hydroxyl radicals (•OH) and singlet oxygen ($^1O_2$)) which can mineralize or transform recalcitrant molecules. Although classical, homogeneous Fenton chemistry (Fe^{2+}/H_2O_2) is effective, it suffers from narrow pH ranges, sludge formation and limited control over the type of ROS produced. Heterogeneous and modified Fenton-like systems, combining redox-active centres with stable, separable supports can overcome many of these limitations. Integrating redox-driven ROS generation with electroprotic pathways within a single composite material promises improved activity, controlled ROS selectivity and enhanced practical durability.

In this work, the synthesis and physicochemical/functional characterization of copper-based composite catalysts are presented, in which a redox-active crystalline phase (Cu-containing oxides) is combined with an electroprotic, hardly reducible support (e.g., Nb_2O_5). The study also examines the effect of different metal promotion on ROS activity and selectivity. Materials (single oxides, mixed Cu-Ce, Cu-Fe oxides and Cu hydroxo-nitrates) were prepared by solvothermal and precipitation methods. Comprehensive physicochemical characterization included powder X-ray diffraction (XRD) for phase identification, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) for morphology and local composition, and X-ray photoelectron spectroscopy (XPS) for surface elemental speciation and oxidation-state analysis. The generation and speciation of ROS were investigated by electron paramagnetic resonance (EPR) using DMPO and TEMP for radical and singlet oxygen detection, respectively. Catalytic performance was evaluated in degradation tests of Direct Blue 15 dye (DB15) which was utilized as a model pollutant in H_2O_2 driven AOPs reaction. The reaction kinetics were monitored by UV-Vis spectrophotometry.

The obtained results show that materials combining two redox-active metals, notably Cu and Ce or Fe, exhibited the highest DB15 degradation rates across the entire series. The presence of coexisting copper oxidation states (Cu^{2+}/Cu^{+}/) in the active phase correlated with enhanced Fenton-like activity, consistent with facile Cu(II)/Cu(I) cycling promoting efficient •OH generation. Ceria promotion altered not only activity but also the ROS distribution: Ce-containing composites showed a relatively higher contribution to $^1O_2$ formation compared to Cu-only materials, indicating that promoter selection is a practical handle to tune oxidative pathways.

Ongoing work focuses on detailed mechanistic quantification and kinetic analysis using ROS scavengers. The presented materials-design approach bridges surface-science insight and applied environmental catalysis, offering a promising direction for scalable, controllable AOP technologies.

Acknowledgments

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Proximity and productivity-based design principles of Fe-based tandem catalysts for CO_2 hydrogenation to C_5+ hydrocarbons

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Keywords: CO_2 hydrogenation, active site proximity, promoter, iron oxide, zeolite, spatial arrangement

Integrating Fe-based oxide catalysts and zeolites, offer a promising route for CO_2 hydrogenation to C_{5+} hydrocarbons. However, rational design has remained challenging due to complex interactions between catalyst components at different proximities.

As the distance between Fe-oxide and ZSM-5 rises, heavy hydrocarbons over Na-promoted Fe-oxide experience more hydrogenation reactions than aromatization results in the lower Aro/N-Aro ratio. However, with a K-promoted catalyst, hydro-isomerization reduces as distance rises and more aromatization take place, raising the Aro/N-Aro ratio.

Furthermore, in order to establish quantitative performance criteria, **Fig. 1** correlates CO_2 conversion, C_{5+} selectivity, and space–time yield (STY), highlighting the critical role of gas hourly space velocity (GHSV). As shown in **Fig. 1**, several catalysts exhibit similar C_{5+} yields (~21–22%); however, their STY differs significantly. For example, sample 56 (FeK1.5@HSG/ZSM5) achieves considerably higher C5+ STY (~57.5 mmolC_{5+} gcat^{-1} h^{-1}) due to its higher GHSV (26000 mL g-1 h-1).This shows that, catalysts with high conversion and selectivity do not necessarily achieve the highest productivity, as lower GHSV reduces throughput and limits STY despite favorable selectivity.

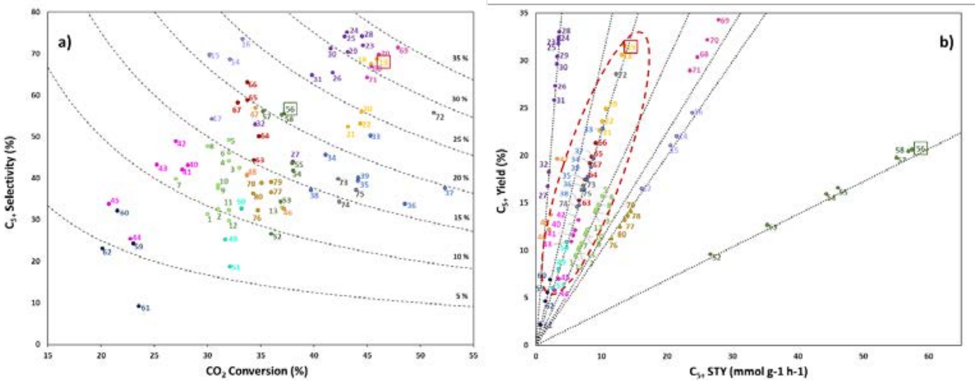

Fig. 1. CO_2 hydrogenation performance of the recently used catalysts: **a)** C_{5+} selectivity vs. CO_2 conversion and **b)** C_{5+} Yield vs. C_{5+} STY.

Acknowledgments

Dedicated to the memory of Prof. Gabor A. Somorjai. This work was supported by the National Laboratory for Renewable Energy (RRF-2.3.1-21-2022-00009), funded by the EU Recovery and Resilience Facility.

References

1. S. Najari, S. Saeidi, A. Sápi, Z. Kónya, G.A. Somorjai, Unveiling the Power of Proximity of Prevalent Fe-Based Tandem Catalysts in CO2 Hydrogenation via Modified Fischer–Tropsch: Crucial Relations toward Industrialization, Chemical Reviews 125(21) (2025) 10179–10247.

Prins reaction of indene with paraldehyde catalyzed by clay-based and zeolite-based materials

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Keywords: indene, paraldehyde, Prins reaction, montmorillonite, bentonite, zeolite, heterogenenous catalysis

The Prins reaction product formed from indene and paraldehyde, 4,4a,5,9b-tetrahydro-2,4-dimethylindeno[1,2-d]-1,3-dioxin (Magnolan®, Figure 1), is noteworthy for its use in the fragrance industry as well as for its documented biological activity, including its influence on the growth of certain bacterial species (e.g. *Malassezia*) and decrease of colagen degradation.

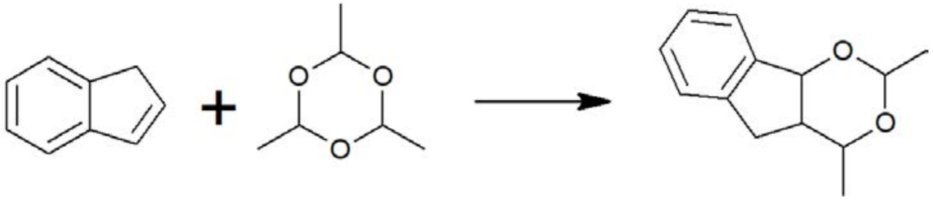

Figure 1. Prins reaction of indene with paraldehyde

In this study, a large number of clay-based materials (montmorillonite K10, montmorillonite K10 prepared in laboratory by acid treatment and ion-exchange with multivalent metal cations (Sn^{4+}, Zr^{4+}, Fe^{3+}), commercially available bentonite-clay based acid catalysts) and zeolites were used as heterogenenous catalyst for catalytic activity evaluation in Prins reaction of indene with paraldehyde. The physicochemical properties of the used materials were comprehensively characterized using X-ray fluorescence (XRF), nitrogen physisorption, and temperature-programmed desorption (TPD) techniques.

The influence of various reaction conditions (catalyst type and loading, solvent, reaction temperature, and reactant molar ratio, polymeration inhibitor) was systematically investigated. The findings confirm that used materials serve as efficient heterogeneous catalysts for this transformation and represent their first reported application in the Prins reaction of indene with paraldehyde. Montmorillonite treated with sulfuric acid provided almost total conversion of indene together with ca. 90% selectivity to desired product (toluene, 40 °C). Overall, these results highlight the significant potential of acid-treated montmorillonite and related clay-based materials as highly efficient heterogeneous catalysts for Prins-type transformations.

Synthesis of 1,4-diazabicyclo[2.2.2]octane (DABCO) and its derivates MDABCO using commercial and modified zeolites

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Keywords: zeolites, HZSM-5, PUR catalysts, DABCO, MDABCO

Polyurethane polymers (PUR) are well-known materials that are widely used as heat insulators, foams etc. Polyurethanes are manufactured by reaction (polycondensation) of diisocyanates and polyols or polyetherpolyols. These reactions are catalysed by wide group af tertiary amines, such as bis(dimethylaminoethylether) or 1,4-diazabicyclo[2.2.2]octane (DABCO) or methylderivates of DABCO – MDABCOs. DABCO can also be used as a catalyst for Baylis–Hillman reactions and electrophilic fluorination, or as a strong ligand and Lewis base.

DABCO is produced by catalysed reactions of compounds of the type $H_2NCH_2CH_2X$, where X can be -OH or $-NH_2$, so 2-aminoethan-1-ol (AE) or ethan-1,2-diamine (EDA), respectively. More complex molecules, e.g. *N*^{1}-(2-Aminoethyl)ethane-1,2-diamine (DETA) or piperazine (PIP) can also be used. Similarly, MDABCOs can be produced from, for example, $H_2NCH(CH_3)CH_2NH_2$ -1,2-diaminopropane (MEDA). In this study, EDA and MEDA were used (see figure).

Zeolites are commonly used as catalysts for the above reactions. Many types of zeolite have been studied in the past, but the published papers and patents are relatively old. Virtually nothing has been published on the synthesis of MDABCOs.

This work focuses on the use of commercial ZSM-5 zeolite and its modifications for the synthesis of DABCO and MDABCOs from EDA/MEDA in the gas phase at different temperatures and reactant ratios using ammonia as the carrier gas. The catalysts were characterised using techniques such as BET isotherms and temperature-programmed desorption (TPD). The results of kinetic studies were then correlated with zeolite properties, such as its specific surface area and acidity.

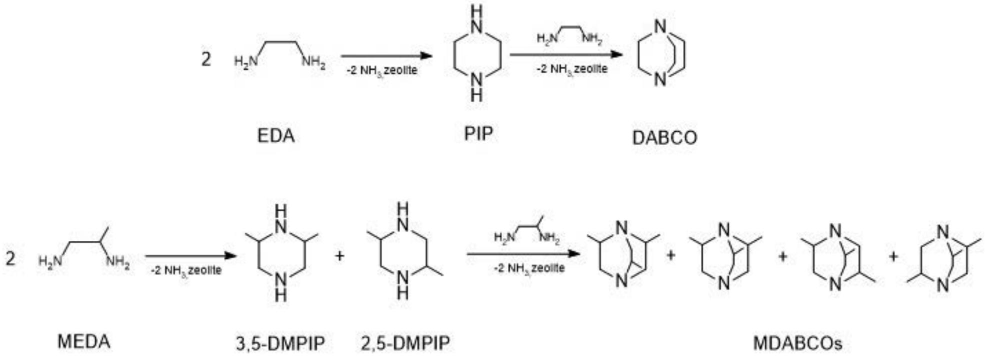

Fig: synthesis routes for DABCO and MDABCOs. EDA: ethan-1,2-diamine, PIP: piperazine, DABCO: 1,4-diazabicyclo[2.2.2]octane, MEDA: 1,2-diaminopropane, 3,5-DMPIP: 3,5-dimethylpiperazine, 2,5-DMPIP: 2,5-dimethylpiperazine, MDABCOs: isomers of methylDABCO

Mathematical reaction kinetics and reaction network theory

Differential coats–redfern framework for non-catalyzed and zeolite-catalyzed thermolysis of low-density polyethylene

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Keywords: differential coats–redfern, low-density polyethylene, zeolite catalysis, conversion-resolved kinetics, rate-parity, conversion-variant compensation

The classical Coats–Redfern (CR) method has been one of the standard tools for extracting Arrhenius parameters from non-isothermal experiments since 1964. In practice, however, $\ln[g(\alpha)/T^2]$ vs $1/T$ plots are often curved; the resulting "activation energy" obtained from linearization is then a window-averaged quantity that depends on the chosen integration bounds and no longer corresponds to the rigorous differential definition of activation energy, which can mislead subsequent kinetic analysis.

In this work, we reformulate CR in a differential framework (d-CR) that restores a rigorous, local definition of the activation energy. The d-CR formulation recovers conversion-resolved $E_a(\alpha)$ and $A(\alpha)$ directly from temperature-programmed data, including thermogravimetric analysis, and achieves pointwise rate parity with the experimental $d\alpha/dt$. We apply this framework to non-catalyzed and zeolite-catalyzed thermolysis of low-density polyethylene (LDPE). For these real, curved CR plots, the absolute deviations $|\Delta E_a| = |E_a,CR - \langle E_a,d\text{-}CR\rangle|$ span 0.23–197.16 kJ·mol^{-1} (0.29–36.63%), depending on the kinetic model and system, demonstrating how strongly window-averaged CR results can diverge from a rigorously local description.

For both non-catalyzed and zeolite-catalyzed LDPE thermolysis, d-CR yields $E_a(\alpha)$ profiles that exhibit physically meaningful plateaus or multi-step behavior and reveal conversion-variant kinetic compensation, whereas classical CR shows window-dependent biases that obscure these features. The method thus provides a practical, broadly applicable platform for analyzing non-ideal temperature-programmed kinetics data. A full derivation and extended validation datasets are available in our ChemRxiv preprint (DOI: 10.26434/chemrxiv-2025-2wfh3-v2).

Acknowledgments

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References

1. Vyazovkin, S.; Burnham, A. K.; Criado, J. M.; Pérez-Maqueda, L. A.; Popescu, C.; Sbirrazzuoli, N. ICTAC Kinetics Committee Recommendations for Performing Kinetic Computations on Thermal Analysis Data. *Thermochim. Acta* **2011**, *520* (1–2), 1–19.

Discrete state deterministic approach to chemical kinetics

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Keywords: deterministic kinetics, stochastic kinetics, discrete-state space, reaction extent

Two fundamentally different approaches are commonly used to describe chemical reaction networks: deterministic and stochastic modeling. The deterministic approach—where concentrations are treated as continuous variables—is primarily applicable to systems with large particle numbers, when statistical fluctuations can be neglected. In contrast, stochastic modeling describes the system as a continuous-time Markov chain, making it particularly reliable in the case of low molecule numbers. However, there exists an intermediate regime between these two descriptions that cannot be adequately handled by either traditional method. Kurtz's theorem states that the stochastic model converges to the deterministic approximation as the system volume increases, yet no model is currently known that operates on a discrete state space while providing a deterministic description of reaction kinetics.

To bridge this gap, the present work introduces a new approach: the continuous-time, discrete-state deterministic (CDD) model. The method is based on a newly introduced generalized concept of reaction extent, which quantitatively characterizes the progress of reactions[1]. This definition allows each reaction to occur in a discrete manner: a given reaction takes place when its associated reaction extent reaches an integer value. Consequently, the approximation ensures that the state vector of molecule numbers remains integer-valued at all times, while time evolves continuously and state changes occur in a stepwise fashion.

The operation of the CDD model is demonstrated through numerical calculations of models such as the Michaelis–Menten or a clock reaction, where the stepwise changes in molecule numbers and the dynamics of the reaction extents clearly illustrate the distinctive features of the approach. The results indicate that the CDD model also offers possibilities for extension to other reaction mechanisms. Altogether, these findings suggest that the proposed CDD model holds significant potential for providing a more accurate and versatile mathematical description of chemical reaction systems.

Acknowledgments

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References

1. Gáspár, V. & Tóth, J. Reaction extent or advancement of reaction: A definition for complex chemical reactions. *Chaos: An Interdisciplinary Journal of Nonlinear Science* 33. ISSN: 1089-7682 (2023).

Sustainable catalysis & green energy

Inorganic oxide–carbon type composite supported CO-tolerant Pt catalysts for PEM fuel cells

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Keywords: PEM fuel cell, CO tolerance, composite support, graphene, anode catalyst, SMSI

Carbon monoxide impurities severely compromise the performance of PEM fuel cell anodes by strongly binding to Pt active sites and suppressing the hydrogen oxidation reaction. In our previous studies, we demonstrated that composite-type catalyst supports with the general formula $Ti_{(1-x)}Mo_xO_2$-C (x: 0–0.2; C: Black Pearls 2000, Vulcan XC-72) offer significantly higher stability and enhanced CO electrooxidation activity for Pt active sites compared with carbon-only supports [1]. In this design, each component serves a specific function: TiO_2 provides corrosion resistance, Mo incorporated into the rutile lattice of TiO_2 acts as a co-catalyst enhancing CO electrooxidation activity, and the carbon component supplies high specific surface area and electrical conductivity to the support. Pt nanoparticles are well dispersed on these supports with abundant metal-oxide-carbon junctions (Figure 1). In this work, we investigate the CO tolerance of Pt electrocatalysts supported by hybrid composites where the carbon component is either functionalized carbon or mixture of graphene nanoplatelets and graphite oxide. The former was exposed to a reductive H_2 pretreatment at 350 °C to induce SMSI, which was verified by XPS.

The composite supported Pt catalysts were evaluated as a CO-tolerant anode material for PEM fuel cells using both pure H_2 and 100 ppm CO containing H_2, and their performance was systematically compared with commercial Pt/C and Pt-Ru/C benchmarks. While comparable activity was observed under CO-free conditions, the composite-supported Pt catalysts show markedly reduced voltage and power density losses in the presence of CO. This superior tolerance is attributed to a synergistic effect arising from the Mo-containing oxide support: molybdenum promotes the formation of OH_{ads} species at low potentials, enabling a bifunctional CO oxidation pathway, while SMSI electronically modify Pt, weakening CO binding strength. Beyond CO tolerance, these catalysts have previously demonstrated exceptional electrochemical stability under potential cycling, indicating that the stabilized Pt–support interface contributes to both durability and performance in realistic fuel cell operation [2, 3]. These results highlight that the use of $TiMoO_x$–mixed oxide–carbon composites offer a promising strategy for the design of advanced PEMFC anode catalysts capable of efficient operation under impure hydrogen feeds.

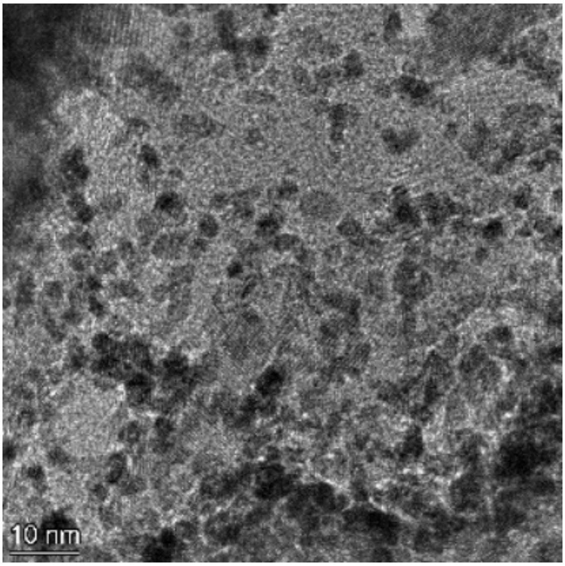

Figure 1. TEM image of Pt/$Ti_{0.8}Mo_{0.2}O_2$-GNP-GO

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References

1. Borbáth, I. et al. *Appl. Catal. A* 620 (2021) 118155.
2. Silva, C. et al. *Mater. Res. Bull.* 182 (2025) 113114.
3. Ayyubov, I. et al. *Nanomaterials* 15 (2025) 1753.

Base-catalyzed isomerization of glucose into fructose: A key step for a sustainable future

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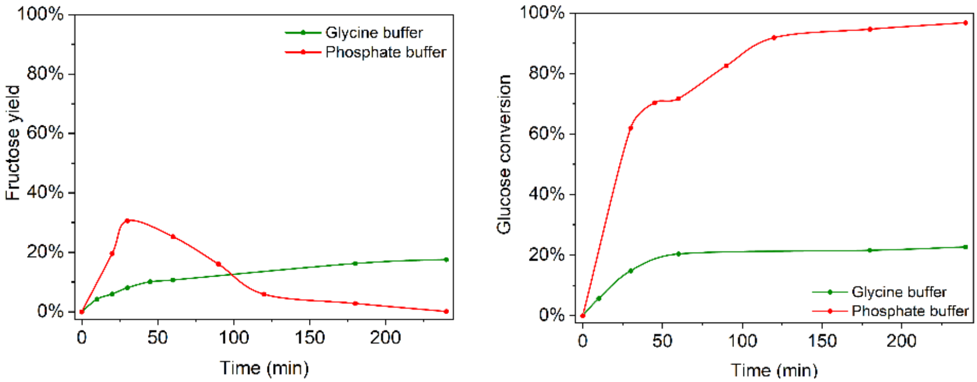
Keywords: base-catalysed reactions, reaction kinetics, glucose, fructose, isomerization

Isomerisation of D-glucose into D-fructose is a key reaction in biomass valorisation and a promising chemocatalytic alternative to enzyme-based processes [1, 2]. However, the factors controlling reactivity, selectivity, and side product formation under alkaline aqueous conditions remain poorly understood, particularly regarding the role of organic bases.

This work compares glucose isomerisation in sodium phosphate buffer and in glycine/NaOH systems under identical conditions (T = 40–70 °C, pH 11.0–11.5, 0.25–0.5 M). Preliminary results reveal different kinetic profiles: phosphate buffers significantly accelerate the reaction, achieving 100% glucose conversion within 4 hours. In contrast, glycine leads to a slower transformation but does not result in a significant degradation of the product. These contrasting outcomes indicate that the catalytic performance of a buffer is governed its chemical composition along with the pH value.

The goal of this study is to expore the reaction kinetics and understand the mechanistic origin of different catalytic performance of phosphate and glycine buffers, extending recent mechanistic insights [1]. In addition, we aim quantification of side products such as saccharinic acids obtained under various conditions. Understanding the correlations between base composition and its catalytic activity for the isomerization will support the future design of catalysts capable of directing glucose conversion toward specific high-value products.



Two graphs showing results at 0.5 M buffer, 60 °C, 300 rpm, 1% initial glucose, pH 11.

Acknowledgments

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References

1. M. Fischer, P. Drabo, I. Delidovich, Study of base-catalyzed isomerization of D-glucose with a focus on reaction kinetics, React. Kinet. Mech. Catal., 135 (2022) 2357–2377.
2. I. Delidovich, Toward understanding base-catalyzed isomerization of saccharides, ACS Catal., 13 (2023) 2250–2267.

Kinetic characterization of different catalysts: Comparison of conventional reaction, downstream distillation, and integrated membrane reactor

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Keywords: membrane reactor, reaction kinetics, catalyst screening, process intensification, hybrid processes

This study focuses on the kinetic characterization of acidic heterogeneous catalysts applied to the esterification of caproic acid with 2-propylheptanol. The investigation compares the catalytic performance of layered silicates against sulfonated cation-exchange resins (e.g., Amberlite IR-120). The primary objective is to evaluate the reaction kinetics and quantify the process intensification achieved by integrating a selective water removal step via a ceramic membrane reactor.

Experimental investigations were performed in three distinct configurations to benchmark the performance: (1) Equilibrium Study: Conventional batch experiments were conducted without water removal to determine the intrinsic kinetics and the thermodynamic chemical equilibrium. (2) Reference Process: A reaction setup coupled with distillation was analyzed to represent a conventional real-world process with active water separation. (3) Membrane Reactor: The reaction was transferred to a continuous packed-bed membrane reactor. In this configuration, the reactants pass through a catalyst bed surrounding a central ceramic membrane. A vacuum is applied to the membrane lumen to continuously remove the by-product water via vapor permeation.

The experimental kinetic data were fitted to a Langmuir-Hinshelwood model. The results indicate that the ion-exchange resin IR-120 exhibits superior activity. In the membrane reactor setup at 90 °C, a conversion of 75 % was achieved over a runtime of 24 hours, resulting in a product yield of 68 %. This confirms that the continuous removal of water effectively suppresses the reverse reaction compared to the equilibrium-limited batch process. The validated kinetic model demonstrates that the ceramic membrane reactor could enhances the space-time yield compared to the distillation-based reference process.

Acknowledgments

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References

1. Hoff, K. L., & Eisenacher, M. (2025). Process Intensification Strategies for Esterification: Kinetic Modeling, Reactor Design, and Sustainable Applications. *International Journal of Molecular Sciences*, *26*(15), 7214. https://doi.org/10.3390/ijms26157214
2. M.J.L. Leite, I.R. Marques, M.C. Proner, P.H. Araújo, A. Ambrosi, M. Di Luccio, Catalytically active membranes for esterification: A review,Chinese Journal of Chemical Engineering 53 (2023) 142–154. https://doi.org/10.1016/j.cjche.2022.03.009.
3. Xianshe Feng, Robert Y.M. Huang, Studies of a membrane reactor: Esterification facilitated by pervaporation, Chemical Engineering Science (1996) 4673–4679, https://doi.org/10.1016/0009-2509(96)00316-8.
4. Jyoti, Ghoshna & Keshav, Amit & J., Anandkumar. (2016). Experimental and Kinetic Study of Esterification of Acrylic Acid with Ethanol Using Homogeneous Catalyst. International Journal of Chemical Reactor Engineering. 14. 10.1515/ijcre-2015-0131.
5. Jyoti, Ghoshna & Keshav, Amit & J., Anandkumar & Bhoi, Stutee. (2018). Homogeneous and Heterogeneous Catalyzed Esterification of Acrylic Acid with Ethanol: Reaction Kinetics and Modeling: KINETICS AND MODELING OF ESTERIFICATION OF ACRYLIC ACID WITH ETHANOL. International Journal of Chemical Kinetics. 50. 10.1002/kin.21167.

Effect of pretreatment on the catalytic performance and stability of NiCeZrSmOx in methane dry reforming

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Keywords: methane dry reforming, CO_2 utilization, syngas production, Ni-based catalysts, ceria–zirconia supports, samarium doping, catalyst pretreatment

Dry reforming of methane (DRM) is an environmental friendly pathway for syngas production by converting CH_4 and CO_2 into a near-equimolar H_2/CO mixture suitable for Fischer–Tropsch and oxo synthesis. In this work, Ni-based catalysts supported on CeO_2–ZrO_2–Sm_2O_3 mixed oxides were synthesized via coprecipitation in reverse microemulsions to enhance metal dispersion and metal-support interactions.

The catalysts were subjected to four pretreatment protocols: reduction in 5% H_2/He, oxidation in 10% O_2/He, activation in 10% CO_2/He, and a sequential CO_2/H_2 treatment, all performed at 700 °C for 1 h. The initial catalysts were characterized by N_2 adsorption–desorption, XRD, TPR, CO_2-TPD, XPS, and TEM/EDX, while pretreated samples were further analyzed by XRD, TPR, XPS, FTIR and CO_2-TPD to determine their physicochemical state before the reaction, and which are used to establish structure/activity relationships.

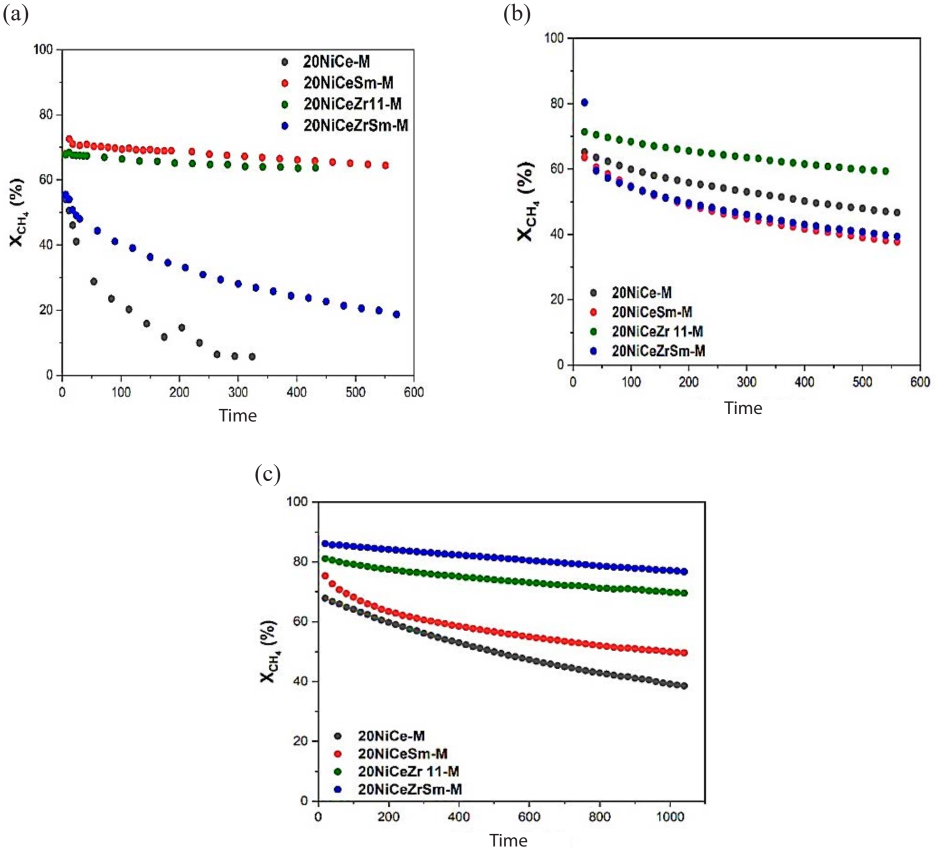

Figure 1. Methane conversion (XC_{H_4}) under DRM at 700 °C (a) after H_2 pretreatment; (b) after CO_2 pretreatment; (c) after sequential CO_2/H_2 pretreatment.

Catalytic performance in DRM (Fig. 1) was evaluated at 700 °C for up to 20 h, depending on catalyst stability. Subsequently, spent catalysts were regenerated under the same pretreatment conditions as the fresh samples and re-evaluated at 700 °C to assess activity recovery and catalyst stability.

Activity tests at 700 °C for 5,10 and 20 h showed 20NiCeZr11-M remained stable under all pretreatments, CO_2 enhanced activity/stability for 20NiCe-M, H_2 improved 20NiCeSm-M, and sequential CO_2/H_2 maximized 20NiCeZrSm-M performance. These experimental results were further complemented by theoretical DFT calculations, providing insight into the atomic-level interactions governing catalyst activity and stability. In conclusion, these results highlight the critical role of pretreatment atmosphere in improving structure, surface chemistry, and stability of Ni-based DRM catalysts.

References

1. Zhou, R., Mohamedali, M., Ren, Y., Lu, Q., & Mahinpey, N. A. Catalysis B: Environmental, 316(2022) 121696.

Valorizing industrial sludge into iron oxides integrated with g-C_3N_5 photocatalysts for CO_2 reduction and renewable energy generation

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Keywords: CO_2 reduction; renewable energy; g-C_3N_5; solar-light-responsive photocatalyst

In photocatalytic systems, semiconductor materials harvest solar energy to generate photogenerated electrons and holes, enabling the chemical reduction of CO_2 into value-added products such as CO, CH_4, CH_3OH, and COOH. This approach offers a promising strategy for advancing sustainable development and promoting renewable energy utilization. The design of efficient photocatalysts is crucial to this process, as they reduce activation energy barriers, enhance product selectivity, accelerate reaction kinetics, and improve overall conversion efficiency. Among various candidates, carbon nitride (CN)-based photocatalysts have drawn significant attention owing to their low cost, scalable synthesis, and favorable physicochemical properties, including visible-light responsiveness, high photostability, and notable photoactivity for both CO_2 reduction and water oxidation. However, despite these merits, CN-based photocatalysts still exhibit limited gas-production efficiency, mainly due to rapid recombination of photogenerated charge carriers and their relatively narrow visible-light absorption range.

Taiwan produces large quantities of industrial sludge enriched with metallic elements such as iron and zinc. Conventional disposal approaches are both economically burdensome and environmentally challenging, underscoring the urgent need for effective resource recovery strategies. To date, sludge valorization has predominantly focused on its conversion into construction materials or adsorbents. Although several studies have transformed heavy metal–containing sludge into catalytic iron oxides (e.g., Fe_2O_3) for organic pollutant degradation, the integration of sludge-derived iron oxides with photocatalysts for solar-driven hydrogen evolution and CO_2 reduction remains largely unexplored. This limitation restricts the development of integrated waste-to-energy systems.

In this work, we bridge waste valorization and green energy technologies by designing a nanocomposite photocatalyst for CO_2 reduction. Sludge-derived Fe_2O_3 was coupled with g-C_3N_5 to construct a heterostructured system aimed at enhancing charge separation and catalytic performance. The optimized composite containing 2.5 wt% sludge-derived Fe_2O_3 exhibited a 15.6% increase in CO generation efficiency compared with pristine g-C_3N_5. In addition, the g-C_3N_5/Fe_2O_3 nanocomposite demonstrated the capability to generate both methane and hydrogen under solar irradiation. These results suggest that sludge-derived iron oxides effectively promotes interfacial charge separation, providing a feasible dual solution for industrial sludge recycling and renewable energy production.

Poster Presentations

Catalyst design & nanocatalysis

Mixed metal oxide HfNbTaTiZr nanotube arrays as a catalyst for the degradation of antibiotic tetracycline

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Keywords: high-entropy alloy, mixed metal nanotube arrays, anodic oxidation, photo(electro)catalytic degradation, antibiotics

High-entropy materials have attracted considerable interest in catalysis due to their unique combination of properties, making them effective catalysts. The presence of five or more elements and their structural diversity can exploit synergistic effects, resulting in improved catalytic activity, selectivity, and stability, allowing them to break down hazardous substances efficiently [1]. In this work, we utilize anodic oxidation (AO) to synthesize mixed-metal oxide arrays with a unique nanotube morphology from the refractory HfNbTaTiZr high-entropy alloy (HEA). Thanks to their enhanced properties, the nanotubes are highly effective and reusable in the photo(electro)catalytic degradation of antibiotics in wastewater.

Pristine HfNbTaTiZr HEA disks were anodized in a two-electrode configuration with a glycerol-based electrolyte containing 25 vol. % of distilled water and 0.25 M NH_4F at constant potentials for two hours.

Increasing the anodization voltage from 10 to 60 V significantly increased the outer diameter of the nanotubes, suggesting that higher potentials favor wider nanotube diameters. The nanotube layers formed at 10 V were subsequently annealed at temperatures ranging from 250 to 1000 °C. Furthermore, temperature-dependent XRD and TEM analyses were conducted to monitor the stages of nanotube crystallization. Raman spectroscopy revealed a structural transition from amorphous to crystalline oxide at 1000 °C. The obtained nanotube arrays were then used for photo- (PC), electro- (EC), and photoelectrocatalytic (PEC) degradation of tetracycline (10 mg/L) in a custom-made photo(electro)reactor (Apria Systems). Despite their amorphous structure, films annealed at lower temperatures demonstrated higher PC performance. Moreover, neither the degree of amorphousness nor the band gap size showed a noticeable influence on the degradation efficiency. EC and PEC degradation experiments performed at applied voltages between 4 and 12 V showed enhanced catalytic activity with increasing voltage. Additionally, the degradation efficiency of the films improved with repeated reuse, with PEC at 4 V reaching up to 86 % after three reuse cycles over a three-hour period. The enhanced activity observed upon reuse is likely associated with the gradual removal of the upper oxide layer formed during the final stage of AO.

In this study, AO is demonstrated as a practical method for synthesizing self-ordered mixed metal oxide nanotube layers on refractory HEA. These structures exhibit great potential as catalysts for removing antibiotics from wastewater, underscoring their relevance in environmental remediation.

References

1. Y. Xin *et al.*, "High-Entropy Alloys as a Platform for Catalysis: Progress, Challenges, and Opportunities," *ACS Catal.*, vol. 10, no. 19, pp. 11280–11306, Oct. 2020, doi: 10.1021/acscatal.0c03617.

Formation mechanism of CP-derived Ag catalysts: Comparing freestanding and carbon fabric-supported systems via in situ techniques

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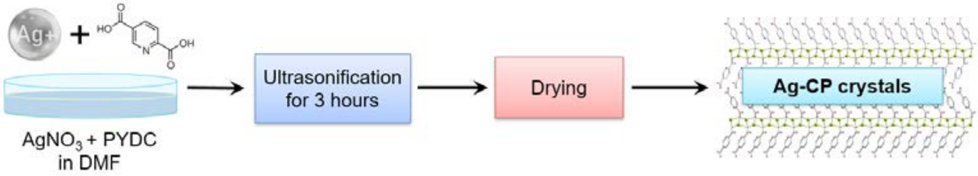
Keywords: coordination polymers, metal organic frameworks, silver nanoparticles, thermal decomposition, electrocatalysis

Coordination polymers (CPs) and metal-organic frameworks (MOFs) have garnered attention as catalyst precursors due to their structural tunability and their ability to yield highly dispersed metal nanoparticles upon reductive thermal, chemical, or electrochemical treatments. In earlier work, silver-based electrocatalysts were prepared by electrochemical decomposition of a silver coordination polymer (Ag-CP) deposited on a gas diffusion layer (GDL), which produced carbon supported silver nanoparticles with excellent performance in the electrochemical carbon dioxide reduction reaction (CO_2RR) [1]. Although the pristine Ag-CP material has been characterized in detail, the mechanism underlying its conversion to catalytically active silver nanoparticles has not been fully elucidated. Herein, Ag-CP was synthesized as freestanding crystals via the self-assembly of Ag(I) ions and the organic linker 2,5-pyridinedicarboxylic acid (PYDC), and its thermal decomposition was systematically examined under inert and reductive atmospheres by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Gaseous products released during thermal decomposition were identified by thermogravimetry coupled with mass spectrometry (TG-MS). Structural evolution throughout the process was monitored using in situ X-ray diffraction (XRD) and Raman spectroscopy. Morphological changes pre- and post-thermolysis were examined via scanning electron microscopy (SEM), while specific surface area and porosity were assessed by nitrogen adsorption. Furthermore, these results are compared with a benchmark silver coordination polymer, previously reported as a carbon fabric-supported gas diffusion electrode (GDE), to discern similarities and differences in their decomposition behavior and silver nanoparticle formation. By elucidating the thermal transformation mechanisms of Ag-CPs and related MOF-derived systems, this study facilitates the rational design of next-generation catalysts for both thermal and electrochemical applications.



Schematic illustration of the fabrication process for freestanding Ag-CP crystals.

References

1. R. Wang, H. Haspel et al.: ACS Energy Lett. 2019 4 2024–2031.

Insights into the effect of promoters on iron-based catalyst in direct CO_2 hydrogenation

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Keywords: CO_2 hydrogenation, Fe-based catalyst, promoter effect, C5+ selectivity

The rapid increase in carbon-based energy consumption alongside the development of the global economy is responsible for high carbon dioxide (CO_2) emissions, which lead to severe environmental issues. To mitigate the excessive emissions of CO_2 and also reduce reliance on fossil fuels, alternative routes for producing value-added chemicals and carbon-neutral fuels from captured CO_2 have received wide interest. The direct hydrogenation of CO_2 to value-added hydrocarbons may serve as a significant process contributing to a net-zero emission.

Fe-based catalysts are promising materials to convert CO_2. Fe and its oxides are widely known being active in both, reverse water gas shift (RWGS) reaction and Fischer-Tropsch synthesis (FTS). However, the harsh reaction conditions, including high temperature, reductive atmosphere, and the formation of water vapor, often induce a dramatic change in catalyst properties during the reaction. Thus, many research efforts have been devoted to employ chemical or structural promoters for better stability and catalytic performance.

In order to enhance the catalytic activity and stability of Fe systems, the addition of metal promoters is commonly employed, such as alkali (e.g., K, Na), alkaline earth (e.g., Ca, Mg), or transition metals (e.g., Mn, Cu, Zn), which can increase the conversion of CO_2, accelerate the carbonization of iron, slow the deactivation of the catalyst, hinder the deposition of carbon etc.

We synthesized M-Fe_3O_4 catalysts, promoted with the most widely used and promising metals (M = Na, K, Mg, Zn, Mn) with 1 w/w % loading and tested them in direct CO_2 hydrogenation.

In order to gain information about the surface and properties of the catalysts (adsorption-desorption behavior, reducibility, observation of surface species and phase changes etc.), several instrumental analyses such as temperature programmed desorption (CO_2-TPD) and reduction (H_2-TPR), X-ray diffraction (XRD), X-ray photoelectron sprectoscopy (XPS), in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) have been carried out.

K-Fe_3O_4 exhibited the highest CO_2 conversion (40%) and outstanding C_5^+ selectivity (36.6%), associated with enhanced Fe_5C_2 formation and strong electron donation. Na promotion increased surface basicity and favored C_2–C_4 olefin and C_5^+ formation while suppressing methane selectivity. In contrast, Zn promoted methane formation (61.8%) and altered Fe–Zn–O interfacial structures, whereas Mg induced strong metal–oxygen interactions, delayed reduction, and shifted selectivity toward paraffins. Mn provided balanced olefin/paraffin distribution due to moderated carburization and Fe–Mn redox interactions.

The results highlight that controlled promoter selection enables rational tuning of Fe-based catalysts toward enhanced C_5^+ formation under industrially relevant high-pressure conditions.

Acknowledgments

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Investigating the role of Zn, In, or Cu in Ni/γ-Al_2O_3 catalysts for methylcyclohexane dehydrogenation

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Keywords: LOHC, dehydrogenation, methyl cyclohexane, bimetallic catalyst, nickel/zinc/indium/copper

Methylcyclohexane-toluene (MCH-TOL) couple is a promising industrial candidate for an economical and safe liquid organic hydrogen carrier (LOHC) system. Platinum-based alumina catalysts are the most active and selective for the hydrogenation-dehydrogenation cycle, as they suppress hydrodemethylation side reactions that lead to benzene and methane. Substitution of noble metals with transition metals is a cost-effective solution, however, commonly used nickel catalysts are less selective due to their high hydrogenolysis activity and are also prone to thermodynamic sintering under high-temperature reaction conditions, leading to catalyst deactivation and aggravated carbon deposition.

To overcome these limitations, the introduction of a second metal has emerged as an effective strategy to enhance the catalytic performance of Ni-based catalysts. Bimetallic catalyst design offers a viable approach to simultaneously improve activity, selectivity, and stability, thereby mitigating undesired side reactions and catalyst deactivation. It has been well established that catalytic behavior can be systematically tailored by modulating the electronic and geometric structures of active metal sites, as well as their interactions with the support. The incorporation of a second metal enables precise regulation of surface-active sites through electronic and geometric effects, which can alter adsorption energies of reactants and intermediates, suppress C–C bond cleavage, and ultimately optimize catalytic activity and selectivity.

Mono- and bimetallic, Ni/(Zn/In/Cu)- γ-Al_2O_3 based catalysts were prepared and studied in the hydrogenation-dehydrogenation cycle of TOL-MCH. The support was loaded with a total metal content of 10 wt.% (sole Ni, or 6/7 wt. % Ni and 4/3 wt.% of Zn, In, Cu) by incipient wetness impregnation. The NiZn, NiCu and NiIn catalysts exhibited significantly higher activity and stability in the dehydrogenation reaction compared to the Ni/Al2O3 catalyst, achieving high selectivity (above 90%) and yield at a WHSV of 1 gMCH/(gcat·h). Hydrogenation of TOL proceeded with 100 % conversion and selectivity over all catalysts in the temperature range of 125-175 °C at 30 bar H_2 pressure. Textural characterization revealed that the bimodal alumina support has favorable surface properties, enabling the formation of finely dispersed metal particles. TPR measurements showed that the reducibility of nickel is hindered by addition of Zn, whereas presence of In and Cu shifts the reduction to lower temperatures. Modification of the nickel phase with Zn, In or Cu improved the selectivity by inhibiting the hydrodealkylation activity through changes in the electronic properties of the nickel phase.

Acknowledgments

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The activity of copper based catalysts in the decomposition of model organic pollutants via H_2O_2 activation towards ROS formation

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Keywords: Fenton reaction, advanced oxidation processes, transition metal oxides, composite catalyst

In response to the growing problem of water contamination by persistent organic pollutants such as dyes, pesticides, antibiotics, and phenolic compounds, advanced oxidation processes (AOPs) have attracted considerable attention. These technologies are based on the in situ generation of reactive oxygen species (ROS), including highly reactive hydroxyl radicals (•OH) and singlet oxygen ($^1O_2$), which are capable of non-selective oxidation and mineralization of complex organic molecules. Among various AOPs, hydrogen peroxide (H_2O_2)-based systems are particularly attractive, as H_2O_2 is relatively inexpensive, environmentally benign, and serves as an efficient precursor of ROS. Effective catalytic activation of hydrogen peroxide is therefore crucial for improving the degradation of recalcitrant pollutants, especially synthetic dyes that are resistant to conventional treatment methods.

The main objective of this study was to synthesize a composite material in which copper compounds constitute the active phase. From the perspective of Fenton-type reactions, the Cu(II)/Cu(I) redox cycle is thermodynamically more favorable than the conventional Fe(III)/Fe(II) system. This advantage may enhance the efficiency of hydrogen peroxide activation. Various materials with potential catalytic activity toward H_2O_2 decomposition and ROS generation were prepared and systematically examined. Their structural properties were analyzed using X-ray diffraction (XRD), which provided information on crystallinity and phase composition. Surface morphology and microstructural features were investigated by scanning electron microscopy (SEM), while energy-dispersive X-ray spectroscopy (EDS/EDX) was applied to determine elemental composition. In addition, X-ray photoelectron spectroscopy (XPS) enabled surface chemical analysis and identification of the oxidation states of copper species. Together, these characterization techniques allowed for a comprehensive evaluation of the crystalline structure, morphology, and chemical composition of the synthesized samples. The generation of ROS was confirmed by electron paramagnetic resonance (EPR) spectroscopy. The chemical activity of the synthesized composites and their suitability for application in advanced oxidation processes were further evaluated through the degradation of a model water pollutants, Direct Blue 15 (DB15) and methylene blue.

The results demonstrate that catalysts containing two distinct redox-active metal components exhibit the highest efficiency in dye degradation. The simultaneous presence of copper in multiple oxidation states significantly enhances the activity of the catalytic phase, facilitating continuous redox cycling and improved ROS generation. Furthermore, even a small amount of redox-active phase incorporated into the support material markedly increases overall catalytic performance. These findings confirm that rational design of copper-based composite catalysts combining redox and complementary functionalities can substantially improve hydrogen peroxide activation and pollutant degradation efficiency. Consequently, the developed materials show strong potential for application in advanced oxidation processes aimed at sustainable wastewater treatment and environmental protection.

Acknowledgments

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Compositional engineering of ZnO/Fe_3O_4 heterojunctions for alkaline oxygen evolution reaction

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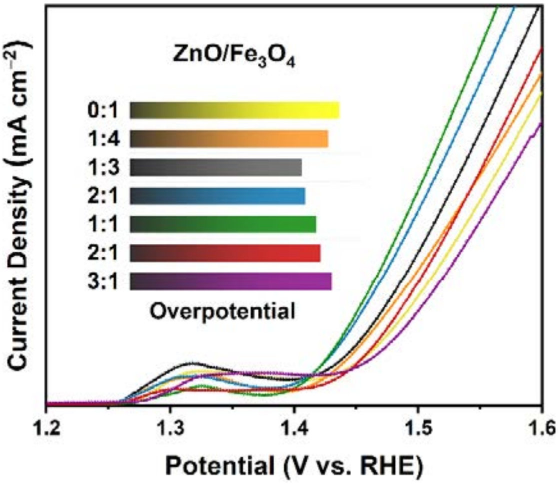
Keywords: ZnO/Fe_3O_4, oxygen evolution reaction, heterostructures, electrocatalysis

Driven by the global energy crisis and the urgent need to move beyond fossil fuels, research has increasingly focused on sustainable technologies such as water electrolysis for energy storage and conversion. The Oxygen Evolution Reaction (OER) remains the primary bottleneck in water splitting due to its sluggish four-electron transfer kinetics. In this work, ZnO/Fe_3O_4 heterostructures with various molar ratios were synthesized via a cyanometallate precursor route, followed by two steps of wet chemical and thermal annealing. The structural, optical, and electrocatalytic properties were systematically investigated, and X-ray diffraction confirmed the coexistence of hexagonal ZnO and cubic spinel Fe_3O_4 phases with high crystallinity and phase purity. SEM–EDS analysis revealed ultrafine, aggregated nanoparticles with homogeneous elemental distribution. Optical studies demonstrated dual UV–visible absorption features and a gradual band gap narrowing with the increase of Fe_3O_4 content, indicating strong electronic interactions within the heterostructure. Electrochemical evaluation in 1 M KOH demonstrated that the electrocatalytic performance strongly depended on the ZnO/Fe_3O_4 molar ratio. Among all compositions, the ZnO/Fe^3O^4 [1:3] electrode exhibited the highest OER activity, delivering a low overpotential of 214 mV at 20 mA cm^{-2} and a favorable Tafel slope of 97 mV dec^{-1}. Composites with intermediate Fe_3O_4 content (1:2 and 1:3) showed superior activity compared to ZnO and Fe_3O_4–rich samples, highlighting the importance of balanced heterointerface formation. Electrochemical impedance spectroscopy revealed reduced charge-transfer resistance for the optimal compositions, while electrochemically active surface area analysis confirmed a higher density of accessible catalytic sites. The optimized catalyst also displayed excellent operational stability over prolonged electrolysis. These findings demonstrate that precise compositional tuning of ZnO/Fe_3O_4 heterostructures plays a critical role in governing OER kinetics, providing a scalable and cost-effective pathway toward high-performance electrocatalysts for alkaline water splitting.

Figures



Linear sweep voltammograms (LSV) recorded for the oxygen evolution reaction (OER) in alkaline media over ZnO/magnetite heterostructures with various mass ratios.

Ceramics and porous materials in catalysis

From waste to value: Recycling industrial waste into functional nanocatalytic ceramic fibers

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Keywords: electrospinning, hydrometallurgical treatment, waste recycling, ceramic nanofibers, ceramic nanocatalysts

Significant amounts of zinc are present in secondary resources generated during primary and secondary zinc production, including slag, fly ash, dross/smears, and skimmings. These heterogeneous by-products are frequently classified as hazardous waste. Hydrometallurgical processing using acidic or alkaline aqueous media offers an effective route to leach target metals into solution, enabling both waste valorization and the preparation of precursor solutions for high-value-added materials such as electrospun ceramic nanofibers.

This work focuses on the synthesis and characterization of three types of ZnO-based ceramic fibers intended for photocatalytic applications. Sal ammoniac skimming residues from a wet-process hot-dip galvanizing plant were used as the starting material. The solid feedstock was characterized using XRD qualitative/quantitative analysis, elemental analysis by AAS, and SEM coupled with EDX. Zinc extraction was carried out using three leaching media (HCl, $(NH_4)_2CO_3$, and H_2SO_4). Subsequently, spinning solutions were formulated by adding poly(vinylpyrrolidone) and ethanol, processed by needleless electrospinning, and calcined in air at 600 °C.

The resulting fibers were characterized by SEM, EDX, XRD, DRS, and BET analysis. Morphological and chemical differences in the individual ZnO fibers were observed depending on the chemistry of the leachate, which in turn influenced the crystallite size, porosity, and specific surface area. Photocatalytic performance was evaluated by UV-vis spectroscopy using two model organic dyes — methylene blue (MB) and Reactive Black 5 (RB5). After photocatalytic experiments, the treated solutions were additionally analyzed by HPLC to assess intermediate composition and transformation/decomposition products, complementing the evaluation of dye degradation.

Acknowledgments

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Novel electrospun high-entropy ceramics for nanophotocatalysis

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Keywords: ceramic nanofibers, high-entropy ceramics, oxide ceramic nanofibers, photocatalysis, nanophotocatalyst

This research introduces a scalable synthesis route and comprehensive chemical-structural analysis of novel electrospun high-entropy ceramics for nanophotocatalysis. The study focuses on a multi-elemental transition metal system based on the elements of Group 4 and Group 5: Ti, Zr, Hf, Nb, and Ta. The equimolar composition was designed to achieve a high-entropy stabilization effect within a 1D nanofibrous morphology. Pre-ceramic composite PAN/MeO_x precursor fibers were fabricated via high-throughput reactive needleless electrospinning, followed by controlled thermal processing to remove the mandatory polymer carrier and initiate the crystallization of the ceramic component. Thermogravimetric analysis (TGA) was utilized to elucidate the polymer oxidation kinetics and optimize the calcination profile, establishing that 600 °C is the critical threshold for the synthesis of pure, carbon-free ceramic nanophotocatalysts.

The morphological evolution, specific surface area (S_{BET}), and elemental homogeneity of these novel high-entropy nanocatalysts were investigated using SEM/EDX and nitrogen adsorption. X-ray diffraction (XRD) confirmed the systematic phase evolution and the formation of dual-phase high-entropy ceramics with an overall composition of $TiZrHfNbTaO_{11}$ as a function of temperature and time.

Progressing toward the transformation into high-entropy nitride ceramics, the oxide fibers underwent controlled nitrogen modification by heat treatment in the nitrogen flow. The resulting nitrogen-modified high-entropy oxynitrides were characterized via SEM/EDX, XRD, and Diffuse Reflectance Spectroscopy (DRS), to monitor the integration of nitrogen, changes in the morphology and phase composition, and modulation of the optical band gap and electronic structure. The nanophotocatalytic performance of the prepared materials was evaluated through the degradation of organic pollutants, specifically Methylene Blue and Reactive Black 5. The mineralization process was monitored via UV-Vis spectrophotometry, while a detailed characterization of the reaction pathways and the identification of chemical intermediates were achieved through High-Performance Liquid Chromatography (HPLC). These results demonstrate that the combination of high-entropy lattice distortion and the high-aspect-ratio nanofibrous architecture creates an advanced platform for environmental remediation, distinguishing these materials from traditional photocatalytic systems.

Acknowledgments

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Iron active sites in FER for CO_2 and CH_4 conversion to oxygenates

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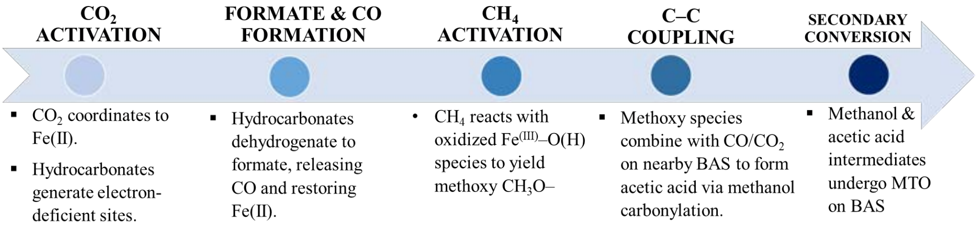
Keywords: ferrierite, carbon dioxide, methane, *in situ* FTIR&MS

The direct co-conversion of CO_2 and CH_4 into oxygenated products provides an atom-efficient route for simultaneously upgrading two major greenhouse gases. In this study, we combine spectroscopic, diffraction, and computational techniques to investigate Fe-substituted ferrierite (Fe-FER) as a bifunctional catalyst that selectively converts CO_2 and CH_4 to methanol and acetic acid, with methanol subsequently transformed into olefins. Our in situ FTIR–MS measurements reveal a sequential pathway in which methane is first oxidized to methanol on redox-active Fe sites under mild conditions. Subsequently, methanol undergoes carbonylation on Brønsted acid sites (BAS) to form acetic acid. At higher temperatures, methanol-to-olefins chemistry begins to compete. Mössbauer spectroscopy reveals that CO_2 adsorption reduces the electron density at the Fe centers, resulting in partial oxidation and shifts between tetrahedral and octahedral coordination environments.

The direct CO_2/CH_4 conversion over Fe-FER proceeds through a cooperative redox–acid mechanism given below:



CO_2 ACTIVATION
- CO_2 coordinates to Fe(II).
- Hydrocarbonates generate electron-deficient sites.

FORMATE & CO FORMATION
- Hydrocarbonates dehydrogenate to formate, releasing CO and restoring Fe(II).

CH_4 ACTIVATION
- CH_4 reacts with oxidized $Fe^{(III)}$–O(H) species to yield methoxy CH_3O–

C–C COUPLING
- Methoxy species combine with CO/CO_2 on nearby BAS to form acetic acid via methanol carbonylation.

SECONDARY CONVERSION
- Methanol & acetic acid intermediates undergo MTO on BAS

The interplay between redox-active Fe sites and Brønsted-acidic framework sites creates a cooperative microenvironment that couples CO_2 activation with CH_4 oxidation, enabling bifunctional catalysis for the production of methanol and acetic acid.

Acknowledgments
This research was funded by the National Science Centre, Poland [Grant No. 2022/47/I/ST4/00607] and the Czech Science Foundation [projects no. 24-14387L].

Characterization methods and surface science in catalysis

La-Ni -Cu perovskite-based catalysts for C_1-C_4 oxidation

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Keywords: C_1-C_4 oxidation, La-Ni-Cu perovskite-based catalysts

Volatile organic compounds (VOCs) are one of the major environmental pollutants. Monitoring and removal of VOCs play a key role in environmental protection efforts. Catalytic oxidation of these harmful emissions is considered one of the most promising approaches for their elimination. Despite extensive research, the development of highly efficient and stable catalysts for the removal of VOCs from industrial gases remains an ongoing challenge.

In this study, the catalysts La_2CuO_4, La_2NiO_4, and $La_2Ni_{0.5}Cu_{0.5}O_4$ were prepared via an auto-combustion method and characterized using N_2 physisorption, XRD, EPR, XPS, TPR, and O_2-TPD. X-ray diffraction analysis revealed that the catalysts predominantly consist of single–layer Ruddlesden–Popper (R–P) phase perovskites, along with small amounts of secondary phases such as La_2O_3 and CuO.

The catalytic performance of the prepared materials was evaluated for the complete oxidation of C_1–C_4 hydrocarbons. The experimental results obtained from the VOCs oxidation tests indicate that these hydrocarbons can be fully oxidized, although this occurs at relatively high temperatures. Among the catalysts tested, $La_2Ni_{0.5}Cu_{0.5}O_4$ exhibited the highest catalytic activity, while La_2CuO_4 showed the lowest performance under the same conditions.

Additionally, kinetic studies were carried out using ethane as a model compound, providing valuable insights into the underlying reaction mechanism and the factors influencing the catalytic oxidation process.

These studies not only highlight the structure-activity relationship of the prepared catalysts but also provide a basis for the rational design of more effective and stable materials for VOC reduction for practical applications.

Acknowledgments
This work was supported by the Bulgarian Science Fund (Contract No. КП-06-Н89/5).

Study of the activity and stability of $La_{0.5}Sr_{1.5}FeO_4$ perovskite-related catalyst for VOCs oxidation

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Keywords: VOCs oxidation, acid treatment, $La_{0.5}Sr_{1.5}FeO_4$ perovskite-related catalyst

A perovskite-related catalyst $La_{0.5}Sr_{1.5}FeO_4$ was synthesized and evaluated with respect to its catalytic activity and stability in the oxidation of volatile organic compounds (VOCs). The catalyst was prepared using a sol–gel auto-combustion method and subsequently treated with acetic acid. The obtained catalyst was characterized by N_2 physisorption, X-ray diffraction, Mössbauer spectroscopy, X-ray photoelectron spectroscopy, and Transmission electron microscopy. Additionally, the redox behavior and surface reactivity of the catalysts were evaluated through temperature-programmed reduction and temperature-programmed desorption studies. It was found that the acid-treated catalyst showed good thermal stability.

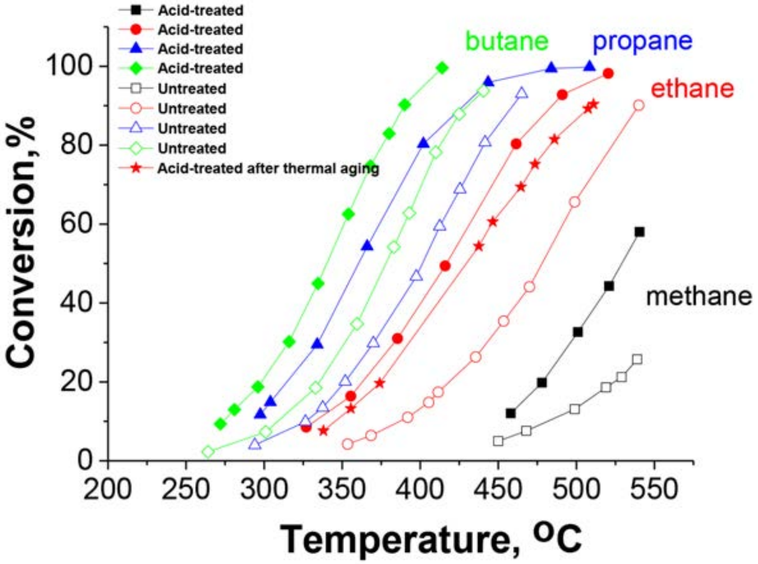

Figure 1. Dependencies of the conversion on the reaction temperature during the complete oxidation of different hydrocarbons on $La_{0.5}Sr_{1.5}FeO_4$ catalyst

The steady-state conversion of C_1-C_4 alkanes as a function of temperature was measured for the as-prepared and acid-treated $La_{0.5}Sr_{1.5}FeO_4$ catalyst (Figure 1). The VOCs test data show that the lowest T_{50} values are observed for n-butane. The catalytic activity increased in the case of the acid-treated sample, where the temperatures required for 50% conversion were about 40–60°C lower compared to the as-prepared catalyst. The reaction kinetics and the mechanism of the complete oxidation of ethane were investigated in detail. Given the activity exhibited by the prepared catalysts, it is reasonable to anticipate that these newly developed catalytic systems can be further optimized and ultimately implemented in practical environmental applications.

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Combustion kinetics and catalysis

Catalytic properties of high-entropy spinel obtained by different methods

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Keywords: high-entropy oxides, combustion synthesis, sonochemical synthesis, low-temperature hydrocarbon oxidation

High-entropy spinels have emerged as an attractive family of multicomponent oxide catalysts, where elevated configurational entropy promotes the formation of a stable, single-phase lattice characterized by significant cation disorder. By accommodating five or more transition-metal elements in approximately equimolar proportions, these materials exhibit a diverse array of local coordination geometries and oxidation states, leading to a large population of potential active sites. This intrinsic structural heterogeneity sets high-entropy spinels apart from traditional oxide catalysts and draws new pathways for tailoring catalytic performance and selectivity.

In the present study, a high-entropy spinel $(CoMnFeNiCr)_3O_4$ with a stoichiometric ratio of 1:1:1:1:1 was synthesized using two different approaches: solution combustion synthesis and sonochemical synthesis. The structural and morphological properties of the obtained samples were investigated by powder X-ray diffraction (XRD), low-temperature nitrogen adsorption, Mössbauer spectroscopy, and scanning electron microscopy (SEM). XRD results show the formation of single-phase materials for both samples. Nitrogen adsorption at low temperature shows a higher specific surface area of ≈112 m^2/g for the sample synthesized by sonochemical synthesis, and 58 m^2/g for the sample synthesized by the solution combustion synthesis method, respectively. The Mössbauer spectra at 6 K, show a difference in the distribution of iron in tetrahedral and octahedral positions: Fe^{3+}tetra/Fe^{3+}octa= 46/54 (sonochemical synthesis) and Fe^{3+}tetra/ Fe^{3+}octa= 33/67 (solution combustion synthesis). SEM analysis of both samples revealed that the material synthesized by solution combustion consists of similarly sized particles assembled into cauliflower-like aggregates, whereas the sonochemically prepared material predominantly forms micron-sized aggregates with smooth surfaces, along with a fraction of very small particles.

The catalytic properties of these spinels were investigated by the reactions of complete catalytic oxidation of methane, ethane, propane and CO. The lowest values for the temperature for 50% conversion in the oxidation of CO are achieved at 228°C for the sonochemically prepared material and at 181°C for the solution combustion material.

Based on the performed tests, the high-entropy spinels can be successfully applied in low-temperature oxidation reactions.

Acknowledgments

The authors are thankful to Project KP-06-M89/3 "Synthesis and characterization of High-entropy spinel oxides with applications in catalysis".

Characterization and catalytic activity of high-entropy spinel oxide $(CoMnFeNiCr)_3O_4$ prepared by the sonochemical method

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Keywords: low-temperature hydrocarbon oxidation, spinel, high-entropy oxides, sonochemical synthesis

High-entropy oxides (HEOs) with spinel-type structure have attracted significant research interest due to their promising magnetic, electrical, catalytic, and adsorption properties.

In the present study, a high-entropy spinel oxide with composition $(CoMnFeNiCr)_3O_4$, containing equimolar amounts of Co, Mn, Fe, Ni, and Cr (1:1:1:1:1), was synthesized by a sonochemical approach.

The as-prepared material was characterized by X-ray diffraction (XRD), N_2 physisorption, Mössbauer spectroscopy, and scanning electron microscopy (SEM). XRD analysis confirmed the formation of a single-phase spinel structure. N_2 physisorption measurements revealed a developed porous structure. Low-temperature Mössbauer spectra revealed a distribution of Fe^{3+} cations between tetrahedral and octahedral sites in the spinel lattice. SEM observations showed that the material forms predominantly micron-sized aggregates with irregular and rough surface morphology.

The catalytic performance of the $(CoMnFeNiCr)_3O_4$ spinel oxide was evaluated in the complete oxidation of methane, ethane, propane, butane and carbon monoxide (Figure 1). Among the tested reactions, the highest catalytic activity was observed for CO oxidation, with a temperature for 50% conversion (T_{50}) of 228°C.

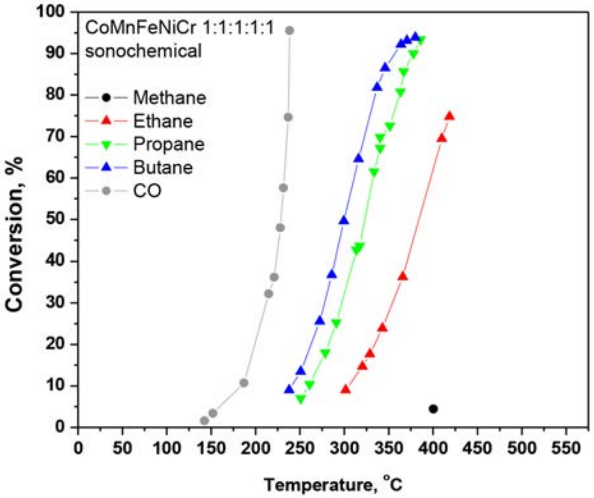

Figure 1: Catalytic activity of $(CoMnFeNiCr)_3O_4$ in CO and hydrocarbon oxidation reactions.

The observed catalytic efficiency in VOCs oxidation demonstrates the potential of high-entropy spinel oxides as promising candidates for environmental catalysis and low-temperature oxidation processes.

Acknowledgments

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Exploring catalytic reaction mechanisms

Harnessing stored molecular energy for intermolecular activation

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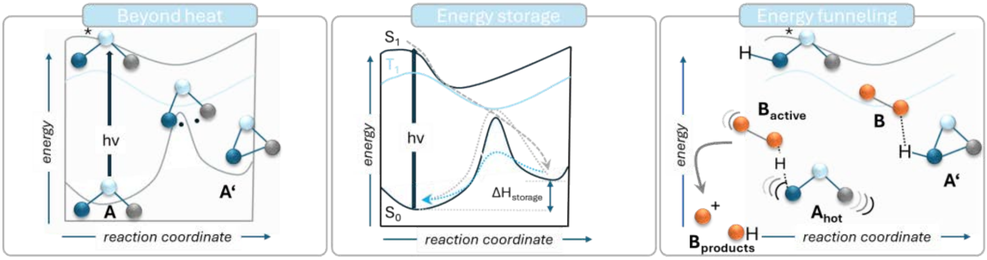
Keywords: solar energy storage, norbornadiene-quadricyclane, strain-release, H-bond-assisted vibrational energy transfer



Norbornadiene-quadricyclane (NBD/QC) photoisomers are promising candidates for solar energy storage owing to their high-energy double cyclopropane ring structure. In such systems, irradiation generates a metastable isomer from which the stored energy can be released on demand via thermal, catalytic, photochemical, or electrochemical activation.[1] Herein, we focus on the fundamental question of whether the **strain-release energy** associated with the QC-to-NBD back-conversion can be **directly harnessed to promote chemical transformations** rather than being dissipated thermally.

To address this challenge, we investigate the strain-release energy from QC to NBD (**A´**→**A**) that can be channelled through hydrogen-bond-mediated vibrational mode coupling into bound reactants (**B**), thereby enabling strain-driven chemical activation. We designed substituted NBD/QC systems bearing push-pull substituents (-COOH, -CN, and -Ph) to tune visible light absorption and introduce directional hydrogen- bonding sites. DFT calculations reveal that increasing push-pull character at the 2,3-positions enhances strain-release energy, while phenyl substitution with EWGs attenuates it. We monitored the photochemical NBD-to-QC interconversion and catalytic QC back-conversion by UV/Vis spectroscopy under thermal and photocatalytic conditions using Rh- and Ir-photocatalysts as well as PDI sensitizers[2]. Various catalyst materials were examined to investigate the type of catalytic reaction governing the back conversion via a singlet-triplet mechanism.[3] Ground-state Born-Oppenheimer molecular dynamics simulations indicate that QC ring-opening produces vibrationally hot NBDs. Excess of vibrational energy localizes along the breaking C-C bonds in these NBDs, enhancing the acidity at the carboxylic acid sites and facilitating proton shuttling and stronger hydrogen bonding. Together, these results establish a direct link between molecular strain release, vibrational energy redistribution[4], and acidic protonation, demonstrating that stored solar energy can be converted into chemically productive activation rather than being dissipated as heat.

References

1. Salthouse, J, R., Moth-Poulsen, K., *J. Mater. Chem. A,* **2024,** 12, 3180–3208.
2. Zika, W., Leng, A., Weiß, R., Pinter, S., Schüßlbauer, M, C., Clark, T., Hirsch, A., Guldi, M, Dirk., *Chem. Sci.,* **2023,** 14, 11096–11104.
3. Hemauer, F., Steinrück, H, P., Papp, C., *Chem. Phys. Chem.,* **2024,** 25 (9), e202300806.
4. Karmakar, S., Keshavamurthy, S., *Phys. Chem. Chem. Phys.,* **2020,** 22, 11139–11173.

Homogeneous & heterogeneous photocatalysis

Photochemical processes in aqueous quinone solutions: A combined UV-Vis and LC-MS analysis

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Keywords: quinone, photokinetics, PhotoCube™ photoreactor matrix rank analysis, LC-MS analysis

Quinone derivatives play an important role in biological systems. In addition, they are good model compounds in solar energy utilization experiments, in which the photosensitivity and redox properties of quinones are used. [1] These properties can be tuned by choosing the appropriate substituents.

Aqueous solutions of 1,4-benzoquinone and anthraquinone derivatives were examined in a PhotoCube™ photoreactor under illumination with UV (365 nm) and white light. Derivatives with different electron-withdrawing and electron-donating substituents were studied (namely: 2-chloro-1,4-benzoquinone, 2,5-dichloro-1,4-benzoquinone, 2,6-dichloro-1,4-benzoquinone, 2,6-dimethyl-1,4-benzoquinone and sodium anthraquinone-2-sulfonate). However, it was experimentally proven that different kinds of products were formed during storage in the dark than under illumination.

Using classical matrix rank analysis (MRA) and the M^3 method (which uses the steps of Gauss-Jordan elimination), the number of light absorbing species in each photochemical experiment were determined. [2, 3] In general, one of the colored particles is the quinone, and the other is a constant ratio mixture of hydroquinone and hydroxyquinone formed as photoproducts. [4] However, MRA showed the appearance of many other species during the course of the reaction. These species were studied by LC-MS as well.

For LC-MS measurements, aqueous solutions of the derivatives were irradiated with UV-light (365 nm) for varying time intervals up to a total of 2.5 hours, and subsequently kept in the dark. The products were identified based on their UV-Vis and MS spectra, as well as their retention times. Using this technique, the stepwise formation and disappearance of the intermediates (e.g. hydroquinone, hydroxyquinone and oxidized derivative of benzene-1,3,4-triol) were effectively detected.

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References

1. D. G. Kwabi, K. Lin, Y. Ji, E. F. Kerr, M.-A. Goulet, D. De Porcellinis, D. P. Tabor, D.A. Pollack, A. Aspuru-Guzik, R. G. Gordon, M. J. Aziz, Alkaline Quinone Flow Battery with Long Lifetime at pH 12, Joule, 2(9), 1894–1906 (2018).
2. G. Peintler, I. Nagypal, I. R. Epstein & K. Kustin, Extracting experimental information from large matrices. 2. Model-free resolution of absorbance matrices: M3, The Journal of Physical Chemistry A, 106(15), 3899–3904 (2002).
3. K. Csonka, P. Lukács & K. Ősz, Photochemical processes in aqueous benzoquinone and anthraquinone solutions studied by spectrophotometry, Reaction Kinetics, Mechanisms and Catalysis, 138(2), 625–646 (2025).
4. V. Kiss, G. Lehoczki & K. Ősz, Mathematical description of pH-stat kinetic traces measured during photochemical quinone decomposition, Photochemical and Photobiological Sciences, 16, 519–526 (2017).

Calibration of various light sources using actinometric methods

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Keywords: photochemistry, actinometry, ferrioxalate, Reinecke's salt

Actinometry allows the determination of the photon flux for a given system. The term actinometer usually refers to instruments used in the UV and visible spectral range. Chemical actinometers are photochemical systems with a known quantum yield that can be used to accurately determine the photon flux for specific photochemical reactions. This is necessary because the quantum yield of unknown photochemical reactions cannot be calculated without this information. [1] The actinometric calibration methods can, however, be improved to suit the specific design of photoreactors better.

In this work, we applied one of the most widely used chemical actinometric methods, the photochemical decomposition of the IUPAC standard ferrioxalate complex followed by complexation with ortho-phenanthroline [2,3], as well as ferrioxalate actinometry without complexation [4] to determine the light intensities of white, UV (365 nm), violet (395 nm), blue (457 nm) and cyan (500 nm) LED-s of the PhotoCube™ photoreactor.

In addition, our aim was to investigate the effect of different settings of the photoreactor on the light intensity (such as the number of panels used, relative light intensity and using low or high-mode illumination) by determining multiplication factors for the calibrated LED-s to calculate the emitted photon number and also to make it possible to determine it under measurement conditions where actual actinometric measurements could not be performed.

Furthermore, the Reinecke salt was synthesized, which is also suitable for determining the light intensity of LED-s operating at longer wavelengths such as green (523 nm), amber (595 nm) and red (623 nm). [5] The photochemical decomposition of this complex was studied in a diode array spectrophotometer in aqueous solutions with different pH values and in the 0.00375-0.015 mol/dm^3 concentration range. The change of pH before and after illumination was also measured.

Acknowledgments

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References

1. H. J. Kuhn, S.E. Braslavsky, R. Schmidt, *Pure and Applied Chemistry,* **76***,* 2105–2146 (2004).
2. C. A. Parker, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, **220 (1140)**, 104–116 (1953).
3. C. G. Hatchard, C. A. Parker, *Proceeding of the Royal Society London*, **A235**, 518-536 (1956).
4. T. Lehoczki, É. Jozsa, K. Ősz, *Journal of Photochemistry and Photobiology: A Chemistry*, **251**, 63–68 (2013).
5. R. Radjagobalou, J. F. Blanco, V. Dias da Silva Freitas, C. Supplis, F. Gros, O. Dechy-Cabaret, K. Loubière, *Journal of Photochemistry and Photobiology A: Chemistry,* **382**, (2019). List of references (with ordinal numbers), if applicable

Kinetic study of the photochemical reactions in aqueous cerium(III) and cerium(IV) solutions in perchloric and nitric acids

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Keywords: water oxidation, photocatalysis, quantum yield determination, dissolved oxygen

The light sensitivity of various aqueous cerium(III) and cerium(IV) complexes has been known since the 1950s. When an acidic aqueous cerium(III) solution is illuminated by UV light, water splitting occurs to form gaseous oxygen and hydrogen [1]. In the catalytic circle, excited cerium(III) ions first reduce water to liberate hydrogen, then cerium(IV) ions formed as a product oxidize water to oxygen in a separate process. This reaction is still considered to be one of the possibilities in storing solar energy in a chemical form [2].

In the present study, the spectral properties of cerium ions have been investigated in perchloric acid and nitric acid media. Calibration curves were plotted by varying the concentrations of cerium(III) and (IV) ions, and wavelength dependent molar absorption coefficient values were determined.

The photokinetic properties of cerium ions have been described under these acidic conditions quantitatively. For the illumination of the samples, as well as to follow the course of the reaction, a diode array spectrophotometer was used [3], after determining the number of emitted photons at each wavelength by ferrioxalate actinometry [4]. The shape of the photokinetic traces was fitted with the following mathematical equation:

$$\frac{\mathrm{d}c_{\mathrm{Ce(IV)}}}{\mathrm{d}t} = -\sum_{200\ \mathrm{nm}}^{420\ \mathrm{nm}} \frac{q_{p,\lambda}\Phi}{V}\left(1-10^{-A_\lambda}\right)\frac{A_{\mathrm{Ce(IV)},\lambda}}{A_\lambda}$$

where $A_\lambda = \left[\left(c_0 - c_{\mathrm{Ce(IV)}}\right)\cdot \varepsilon_{\mathrm{Ce(III)},\lambda} + \varepsilon'_{\mathrm{Ce(IV)},\lambda}\cdot c^2_{\mathrm{Ce(IV)}} + \varepsilon_{\mathrm{Ce(IV)},\lambda}\cdot c_{\mathrm{Ce(IV)}}\right]\cdot \ell$ and

$$A_{\mathrm{Ce(IV)},\lambda} = \left[\varepsilon'_{\mathrm{Ce(IV)},\lambda}\cdot c^2_{\mathrm{Ce(IV)}} + \varepsilon_{\mathrm{Ce(IV)},\lambda}\cdot c_{\mathrm{Ce(IV)}}\right]\cdot \ell = c_{\mathrm{Ce(IV)}}\left[\varepsilon_{\mathrm{Ce(IV)},\lambda} + \varepsilon'_{\mathrm{Ce(IV)},\lambda}\cdot c_{\mathrm{Ce(IV)}}\right]\cdot \ell.$$

Concentration- and pH-dependent quantum yield values have been determined under different experimental conditions (pH and acid concentration). While monitoring the spectral properties in the nitric acid media, the significant absorption of the acid in the UV range was also taken into account as an inner filter effect.

Concentration of dissolved oxygen produced in the water splitting reaction was also measured directly, using an amperometric sensor [5].

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References

1. L.J. Heidt, A.F. McMillan, Science 117 (1953) 75–76.
2. H.B. Gray, Eng. Sci. 60 (1997) 28–33.
3. I. Fábián, G. Lente, Pure and applied Chem. 82 (2010) 1957–1973.
4. T. Lehóczki, É. Józsa, K. Ősz., J. Photochem &Photobio. A:Chem, 251 (2013) 63–8.
5. A. F. Albantov, A. L. Levin, Biosensors & Bioelectronics, 9 (1994) 515–526.

Industrial & environmental catalysis

Catalysts based on ZSM-5 zeolites modified with Pd-Co_3O_4 for reducing greenhouse gas methane

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Keywords: methane combustion, Pd-MeOx/ZSM-5 catalysts

Catalytic combustion of methane is regarded as an attractive alternative to conventional thermal combustion for energy production, in order to decrease the emission levels of greenhouse effect gases in the atmosphere. Air pollution has been one of European Union's main environmental policy concerns since the late 1970s (http://ec.europa.eu/environment/index_en.htm). In 2013, the EU proposed a Clean Air Policy Package to further reduce emissions of air pollutants until 2030. CH_4. Methane is a major Greenhouse Gas (GHG) that accounts for 14% of the world's total amount of GHG emissions, originating mainly from agriculture, coal mines, land fields, wastewater and oil and gas facilities. The alumina-supported palladium catalyst is widely accepted as the most active catalysts for catalytic combustion of methane. The activity of Pd/Al_2O_3 decreases during time on stream, especially under water vapor. In recent years, the attention of scientists has focused on the use of zeolites as catalyst supports due to their thermal and acid stability, and moisture resistance. They have high specific surface area, which is a prerequisite for the creation of active catalytic systems. Metals and metal oxides can be deposited on them as highly dispersed nanoparticles and thus create active catalytic systems in which a large number of active centres are accessible to the reagents in the catalytic processes. After decades of little progress, zeolite-supported catalysts have recently attracted increased attention. The monometallic and bimetallic samples were prepared by impregnation of ZSM-5 (Si/Al=50 and 33) with aqueous solution of $Co(NO_3)_2.6H_2O$ and $Pd(NO_3)_2 2H_2O$. Two types of samples were prepared: in the first type, cobalt was deposited first and then calcined (Pd+Co/ZSM-5), while in the second type, the active components were deposited from a co-impregnation solution (PdCo)/ ZSM-The palladium and the cobalt loading on the surface of all prepared samples are about 0.5 wt % and 5wt% respectively. All samples were characterized by XRD (X-ray diffraction), TPR (temperature-programmed and XPS (X-ray photoelectron spectroscopy).

No palladium and cobalt phases were detected by XRD, revealing finely divided particles. Several TPR peaks are visible in the reduction profile of of Pd-Co catalysts. XPS analysis shou the present ff both Pd^{2+} and Pd^{4+} on the surface of the freshcatalysts modified with Co. The hydrogen consumption at lowest. temperature (70 °C) in the TPR spectra of all Pd-Co catalysts is attributed to the reduction of PdO [1]. The reduction of highly dispersed PdO can take place even below room temperature. Because of this Wu et al [1] assign the positive peak in the TPR profile of Pd catalysts modified with different oxides to the reduction of the stable PdO species. The row of activity in as follows: Pd+Co> (PdCo) > Pd, which means that the addition of Co improves significantly the catalytic activity and this depends on the sequence of cobalt and Pd introduction.

Acknowledgments

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References

1. Y. Wu, G. Li, W. Hu, F. Huang, J. Chena, L. Zhong, Y. Chena, Journal of the Taiwan Institute of Chemical Engineers, vol. 85, pp 176–185, 2018

Process intensification of CO_2-to-liquid fuels via tandem reverse water gas shift and fischer-tropsch reaction: Synergistic coupling of Cu/Al_2O_3 and Na-Promoted Fe_3O_4 catalysts

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Keywords: CO_2 hydrogenation, liquid fuels, tandem catalysis, process intensification

The reverse water gas shift (RWGS) reaction ($CO_2 + H_2 \rightleftharpoons CO + H_2O$) is a pivotal step for CO_2 valorization into syngas for Fischer-Tropsch (FT) synthesis. Traditional RWGS requires high temperatures (>700°C), causing energy inefficiency and catalyst deactivation. This work demonstrates that a conventional Cu/Al_2O_3 catalyst (10%Cu on γ-Al_2O_3 balls) achieves high performance at low temperatures (<350°C) and elevated pressures (up to 30 bar). High pressure significantly enhances reaction rate and CO_2 conversion while suppressing side reactions (methanol, methane), yielding high CO selectivity, water tolerance, and bridging temperature gaps to downstream units. This avoids interstage compression/decompression, reduces reactor size and costs, and improves process efficiency.

Coupling this intensified RWGS with a Na-promoted Fe_3O_4 ($NaFe_3O_4$) FT catalyst creates a synergetic tandem system. The low-temperature/high-pressure RWGS produces $CO+CO_2$ syngas under conditions compatible with FT operation. Na promotion in Fe_3O_4 enhances chain growth, olefin selectivity, and C_{5+} hydrocarbon formation in modified FT from CO_2-derived feeds, minimizing light products and over-hydrogenation. The integration leverages the $CO+CO_2$ from Cu/Al_2O_3 to boost overall CO_2-to-liquids efficiency, increasing liquid fuel yield through optimized syngas quality and reduced energy penalties.

This economical approach, using commercial-relevant catalysts, advances sustainable fuel production from CO_2 via process intensification.

References

1. M. D. Porosoff, et al., "Catalytic Reduction of CO_2 to CO via Reverse Water-Gas Shift Reaction: Recent Advances in the Design of Active Catalysts," Journal of Materials Chemistry A, 2014.
2. J. G. Chen, et al., "The Role of Pressure in the Design of Catalytic Processes for CO_2 Conversion," Chemical Engineering Science, 2021.
3. Najari, Sara, et al., "Synergistic enhancement of CO_2 hydrogenation to C_5+ hydrocarbons using mixed Fe_5C_2 and Na-Fe_3O_4 catalysts: effects of oxide/carbide ratio, proximity, and reduction." Chemical Engineering Journal 2024.

Scale-up of hydrogenation catalyst production to pilot scale and investigation of catalyst properties

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Keywords: hydrogenation catalyst, nitrobenzene, catalyst metal, catalyst support, pilot scale-up

The research and development project “Complex, integrated technological development of aromatic isocyanate feedstock production”, funded by the NKFI Fund and launched in October 2021 in cooperation with BorsodChem Zrt. and the University of Miskolc, aims to develop an industrially applicable hydrogenation catalyst system that meets current market expectations and environmental regulations, while improving process efficiency.

Within the framework of the applied research project “ARIZO”, BorsodChem Zrt. and the University of Miskolc are jointly working on the development of catalysts for the hydrogenation of aromatic nitro compounds, including nitrobenzene and 2,4-dinitrotoluene. Following the successful laboratory-scale development and evaluation of catalyst compositions, the current stage of the project focuses on the scale-up of catalyst production to pilot size and the investigation of the technological feasibility of the manufacturing process.

The poster presents the pilot-scale catalyst production process, highlighting the main technological steps and operational parameters applied in the larger-scale setup. In addition, the physicochemical properties of the catalysts produced under pilot-scale conditions were investigated and compared to laboratory-scale reference samples. Measurements included the evaluation of catalyst composition, structural properties, and metal distribution with the aim of comparing pilot production with laboratory methods.

The results obtained confirm that pilot-scale catalyst production can be successfully implemented while maintaining the catalytic properties required for industrial hydrogenation processes, thereby supporting further steps toward industrial application.

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References

1. A. Mihalkó, A. Jakab-Nácsa, B. B. Tamás, L. Vanyorek, B. Viskolcz, L. Farkas, Development of catalysts for the catalytic hydrogenation of aromatic nitro compounds for industry, Poster presentation, 3rd International Conference on Reaction Kinetics, Mechanisms and Catalysis, Budapest, Hungary, 22–25 May 2024.
2. B. Tamás, A. Mihalkó, F. Kristály, L. Farkas, Gas adsorption testing of carbon-based noble metal catalysts, in Symposium on Polymer(s) Innovation & Soil Innovation for Regenerative Agriculture (SPI-SIRA) Booklet, 2025, pp. 22–22.

Catalytic performance of Pd-Ni-Co/Al_2O_3 catalysts in methane combustion

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Keywords: methane combustion, Pd-Ni/Al_2O_3, Pd-Co/Al_2O_3 catalysts

Catalytic combustion of methane has been extensively investigated for emission control and power generation during the last decades. The alumina-supported palladium catalyst is widely accepted as the most active catalysts for catalytic combustion of methane. The activity of Pd/Al_2O_3 decreases during time on stream, especially under water vapor. The problem could be tackled by using promotors and application of supports According to the literature data the most promising promoters are oxides of Ni, Mn, Co[1].

In the present work, we investigate the activity of Pd/ Al_2O_3 catalysts promoted with metal oxides (MOx; M= Ni and/or Co). The Pd-based catalysts modified by metal oxide were prepared by sequential impregnation of Al_2O_3 with aqueous solutions of $Me(NO_3)_2.6H_2O$ and $Pd(NO_3)_2.6H_2O$ and next calcination. In the case where two oxides were used, they were deposited from co-impregnation solutions of the respective nitrates. The sample was then calcined, followed by the deposition of Pd. All samples were characterized by XRD (X-ray diffraction), TPR (temperature-programmed reduction), EPR (electron paramagnetic resonance) and XPS (X-ray photoelectron spectroscopy), HRTEM.

According to the XRD data finely dispersed palladium particles were formed on the surface of all samples. XPS analysis shou the present ff both Pd^{2+} and Pd^{4+} on the surface of the fresh catalysts modified with Co and Ni only. The EPR data also suggest the existence of Pd^{+} or Pd^{3+} forms on the surface of the monocomponent Pd/ Al_2O_3 and the exchange interactions between paramagnetic palladium species and nickel ions in Ni-Pd/Al_2O_3. Concerning Ni, EPR suggests the presence of Ni^{2+} ions located in partly dehydrated $Al(OH)_3$, orthorhombic Ni^{+} species and a Ni^{+} species in axial symmetry. The reduction behavior of the synthesized catalysts was investigated by means of TPR. Several reduction maxima were observed. The hydrogen consumption in the interval 70-103 °C is attributed to the reduction of PdO [2]. The peak at 350 °C in Ni modified catalyst is ascribe to the reduction of finely divided NiO particles [2]. The reduction peaks at 387 and 500 °C in Pd/Co/Al_2O_3 catalysts are ascribed to the two-step reduction of Co_3O_4. The hydrogen consumption above 500 °C in all samples is attributed to the reduction of Ni-Al or Co-Al oxide phases [2]. An improvement of activity was observed after modification with cobalt and oxides. We suggest that occurrence of Co-Al and Ni spinel phases plays a significant role for the stabilization of the palladium as PdO, leading to high activity and stability in methane combustion.The Pd+CoOx/ Al_2O_3 sample demonstrates remarkable stability after ageing thus the Pd/Al_2O_3 catalysts modified with Co exhibit the most promising catalytic activity for methane oxidation.

Acknowledgments

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References

1. J.G. McCarthy, Y.-F. Chang, V.L. Wong, M.E. Johansson, Div. Petrol.Chem. 1997, 42 158.
2. M. V. Gabrovska, R. M. Edreva-Kardjieva, D. D. Crişan, K. K. Tenchev, D. A. Nikolova, M. Crişan, Bulg. Chem. Comm. 2013, 45 617

Mathematical reaction kinetics and reaction network theory

Stochastic modeling and simulation of a repressilator model

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Keywords: stochastic kinetics, gene regulation networks, compartmental models, simulation

The repressilator model is a synthetic genetic regulatory network that demonstrates how a simple circuit of three genes can produce sustained oscillations. Introduced in [1], it was one of the first synthetic biology constructions to showcase the feasibility of designing and controlling gene expression dynamically. The repressilator serves as a foundational model for studying the principles of network topology and temporal regulation in genetic circuits. It is known that the stochastic modeling of gene expression is generally necessary to capture the random phenomena in transcription and translation which results in significant variations in mRNA and protein levels between cells. A possible way to describe this kind of behaviour is to use partial integro differential equation (PIDE) models where the variable is the time dependent protein distribution [2]. However, the theoretical analysis and even the numerical simulation of such PIDE models is difficult. Therefore, a special discretization in the space of molecule numbers was proposed in [3] which resulted in a linear time-varying conservative compartmental model. In this contribution, we use the discretization scheme of [3] to analyze and simulate the time evolution of the molecular distribution in a 3-dimensional repressilator model which includes time-varying manipulable external inputs in the form of inducers. Using classical and recent results from the theory of nonautonomous master equations [4], we show that the solutions are asymptotically stable. Moreover, for slowly varying inducer inputs, the stationary distribution is unique and globally asymptotically stable. The computational model-building and simulation is challenging from a computational point of view, since the dimension of the state variable (i.e., the number of compartments) can be in the order of hundred thousands or even millions for an appropriate resolution in the space of molecule numbers. Therefore, we utilize the structural regularities of the large coefficient matrix to speed up model construction. Moreover, we apply sparse matrix representation and efficient GPU-based solvers to determine the transient and stationary distribution functions of the model.

References

1. Elowitz, M. B., & Leibler, S. (2000). A synthetic oscillatory network of transcriptional regulators. Nature, 403(6767), 335–338.
2. Pájaro, M., Alonso, A. A., Otero-Muras, I., & Vázquez, C. (2017). Stochastic modeling and numerical simulation of gene regulatory networks with protein bursting. *Journal of Theoretical Biology*, 421, 51–70.
3. Vághy, M. A., Otero-Muras, I., Pájaro, M., & Szederkényi, G. (2024). A Kinetic Finite Volume Discretization of the Multidimensional PIDE Model for Gene Regulatory Networks. *Bulletin of Mathematical Biology*, 86(2), 1–26.
4. Pituk, M. (2023). Global asymptotic stability of nonautonomous master equations: A proof of the Earnshaw–Keener conjecture. *Journal of Differential Equations*, 364, 456–470.

Sustainable catalysis & green energy

Effect of pillaring loading and calcination temperature on product distribution on waste plastic pyrolysis along with characterization

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Keywords: waste plastic pyrolysis, carbon distribution, pillaring loading, characterization, pyrolysis oil analysis

Introduction: Recent reports have shown presence of waste plastics found almost everywhere. From oceans to landfills, plastic waste is piling up. In 2025 global plastic waste reached 460 million tons and in 2024 only 10% recycled and 22% have been mismanaged. Plastic waste management can be a way out of this challenge, to sustain the environment by improving the circularity of already present plastics in the environment. This study underlines in-house prepared novel clay-based catalyst. The experiments were performed both in small lab scale batch reactor setup and the results are validated on small pilot scale continuous feeding reactors. The pyrolyzing reactor was at 550°C, and fixed bed reactor was at 550°C at 1 bar pressure. *Results and discussion:* Two different sets of catalyst prepared with different pillaring oxide (mmol to gm of clay) ratio and different calcination temperatures of novel clay-based catalyst. The oil obtained from LDPE and waste plastics are comparable in carbon distribution having around 70% or more in C_1-C_{15}. Gases obtained from LDPE experiments have negligible CO and CO_2 as compared to waste plastics which contains environmental contaminants. Solids are considerably high with waste plastics as well in comparison to LDPE. The pyrolysis oil contains more olefins than paraffins and aromatics showing more unsaturated products identified. XRD spectra showed change in basal spacing from untreated clay to pillared clay catalyst. XRF analysis showed change in composition of the catalysts. NH3-TPD were performed to check the number of acid sites on the catalyst. Pyridine FTIR will give number of Brønsted or Lewis acid sites. TGA give thermal stability of catalyst at high temperature and to observe the mass changer at process temperature. BET also performed to check the specific surface area, pore volume and pore size distribution.

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References

1. Anuar, S. Z. K., Nordin, A. H., Husna, S. M. N., Yusoff, A. H., Paiman, S. H., Noor, S. F. M., Nordin, M. L., Ali, S. N., & Ismail, Y. M. N. S. (2025). Recent advances in recycling and upcycling of hazardous plastic waste: A review. Journal of Environmental Management, 380, 124867.

Multifunctional single-atom catalysts based on boron carbon nitride for efficient thermocatalytic biomass valorization

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Keywords: boron carbon nitride (BCN), single-atom catalysts (SACs), platform molecules, glucose conversion, biorefinery

Because of global warming, one of the most urgent challenges facing humanity is to find a low-cost, readily industrializable and sustainable carbon source that can replace fossil resources. To this end, lignocellulosic biomass and oleaginous feedstocks are so far considered the only two resources from which organic molecules can be produced without petroleum. The production of transportation fuels could be realized based on these raw materials if a sufficiently effective biorefinery system is established.[1] Proposed methods for transforming platform molecules into chemicals have been intensively reviewed last decade.[2] However, many approaches use conventional homogeneous reagents which generate waste or attempt to use commercial catalysts which are not fitted enough to the required multicomponent reactions. As they have both charge valuable metallic centres and Lewis base and acid sites, boron carbon nitride-based single-atom catalysts (SACs) seems to be good candidates for being the key elements of a catalytic biorefinery system even in the absence of UV-light irradiation found essential as yet.[3] To prove our hypothesise, both boron carbon nitride (BCN) and boron-doped carbon nitride systems were modified by transition metal specimens (Cu, Ni, Fe) via well-established post synthetic treatments or co-polymerisation route. The given structures are tested in the most decisive reactions of the biomass valorisation to get platform molecules (furfural or HMF) from available biomass derivatives such as glucose and hemicellulose. The as-prepared systems were able to promote the studied transformations with good (70%) to unique (100%) selectivity achieving plausible yields (55–69%) in all cases. Moreover, the alteration of these markers could be associated with the Lewis acid/base properties of the supporting materials by using spectroscopic (Raman, XPS, FT-IR) and microscopic (TEM) techniques. Furthermore, all structures were readily recyclable when using test mixtures that contains only the reactants and the actual solvent.

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References

1. B.C. Klein et al. Energy Environ. Sci., 2024, 17, 1202–1215.
2. I. Levin et al., Nat. Commun 2022, 13, 7747.
3. T. He et al., Small 2023, 19, 2302429.
4. Y. Shi et al., ACS Catal. 2025, 15, 2950–2958.

Photokinetic study of 2,3-dimethoxy-5-methyl-p-benzoquinone

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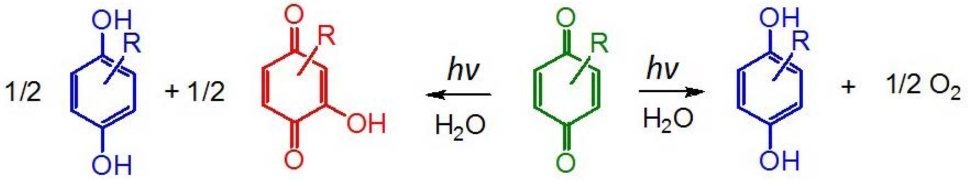
Keywords: quinone, photokinetics, Photocube, matrix rank analysis, HPLC

Quinone derivatives are used by nature in energy transfer or storage processes. The reactions of 1,4-benzoquinones are well-known in an aqueous environment, where they are exposed to polychromatic light to form hydroquinone, hydroxyquinone and oxygen. A new research area has emerged based on the quinone/hydroquinone conversion flow battery, [1] where in addition to storing electrical energy, illumination may increase the energy content because of the photochemical reactions.

The solution of 2,3-dimethoxy-5-methyl-p-benzoquinone in water was exposed to UV or polychromatic light via PhotoCube. As light passes through the sample, a photosensitive substance (the quinone in this case) is transformed by light and a photochemical reaction is induced. At the same time, the changes in the mixture are detected through absorbance measurements. [2] The PhotoCube gives us multiple possibilities to choose the wavelength of the light which will determine the reaction rate. By changing the concentration of the solution, we can measure the initial reaction rate. [3] The resulting quinone derivatives are readily detected by high performance liquid chromatography (HPLC) [4] or other analytical techniques as well.

Matrix rank analysis was used to determine the number of coloured particles in a spectrum series of the kinetic measurements. [5]



Reaction scheme of the photochemical decomposition of 1,4-benzoquinones

References

1. E.J. Son, J.H. Kim, K. Kim, C.B. Park: Quinone and its derivatives for energy harvesting and storage materials, Journal of Materials Chemistry A, 2016, 29, 11179–11202.
2. G. Lente, J.H. Espenson: Photoreduction of 2,6-dichloroquinone in aqueous solution: Use of a diode array spectrophotometer concurrently to drive and detect a photochemical reaction, Journal of Photochemistry and Photobiology A: Chemistry, 2004, 163, 249–258.
3. Kerezsi I.: Fotokémiai jelenségek a szulfition redoxireakcióiban, PhD értekezés (DE, 2006).
4. V. Kiss, G. Lehoczki, K. Ősz: Mathematical description of pH-stat kinetic traces measured during photochemical quinone decomposition, Photochemical and Photobiological Sciences, 2017, 16, 519–526
5. G. Peintler, I. Nagypál, I.R. Epstein, K. Kustin, Extracting experimental information from large matrices. 2. Model-free resolution of absorbance matrices

Efficient glucose isomerization by a base solid catalysts in a fixed-bed reactor

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Keywords: glucose isomerization, fixed-bed reactor, solid catalyst, MgO, MOF, kinetic modelling

Conversion of glucose to fructose plays an important role in biomass valorization. Recent research activity has been focused on a chemocatalytic isomerization as a potentially more economically attractive way of glucose production than the currently used enzymatic systems [1,2]. Solid supports, such as modified biochar and MOFs as a soluid catalytic offer a promising route to constructing robust and tunable active sites suitable for continuous fixed-bed reactors [3,4]. Recent studies have shown that while the fructose yield with pure MgO remains around 30%, incorporating MOF into the catalyst matrix can increase the fructose yield to approximately 45%, highlighting the potential of MgO/MOF composites. In addition, incorporating solid support into the catalyst enhances its reusability significantly. Four cycles of the isomerization catalyzed by MgO/MOF were conducted in a batch reactor, and fructose yield only decreased by 1.6% after the fourth cycle [5]. Nevertheless, challenges including competing side reactions, hydrothermal stability, and the evolution of MgO under continuous flow remain insufficiently understood [5]. This work addresses these gaps by developing and evaluating MgO-supported solid catalysts in a fixed-bed reactor to enable a stable, scalable, and industrially relevant glucose isomerization process.

This study aims to develop and optimize solid-supported MgO catalysts for efficient glucose isomerization in a fixed-bed reactor. MgO was loaded onto various support materials and comprehensively characterized using different methods to determine structural features, morphology, surface composition, and thermal stability. Catalytic performance was then assessed in a batch reactor and a fixed-bed reactor, where operational parameters such as temperature, pressure, and residence time were optimized to maximize fructose yield. Hydrothermal stability and side-product formation were assessed. The results of catalytic tests were used for kinetic modelling and compared to the data collected for homogeneous base catalysts.

Acknowledgments
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References

1. Yang F, Xia Q, Lin G, Su Y, Lin W, Zhang H, et al. Isomerization of glucose to fructose catalyzed by $MgCl_2$ in water. Fuel 2025;379. https://doi.org/10.1016/j.fuel.2024.132985.
2. Fischer M, Drabo P, Delidovich I. Study of base-catalyzed isomerization of d-glucose with a focus on reaction kinetics. Reaction Kinetics, Mechanisms and Catalysis 2022;135:2357–77. https://doi.org/10.1007/s11144-022-02277-9.
3. Lara-Serrano M, Morales-DelaRosa S, Campos-Martin JM, Abdelkader-Fernández VK, Cunha-Silva L, Balula SS. Isomerization of glucose to fructose catalyzed by metal-organic frameworks. Sustain Energy Fuels 2021;5:3847–57. https://doi.org/10.1039/d1se00771h.
4. Souzanchi S, Nazari L, Rao KTV, Yuan Z, Tan Z, Xu C (Charles). Catalytic isomerization of glucose to fructose using heterogeneous solid Base catalysts in a continuous-flow tubular reactor: Catalyst screening study. Catal Today 2019;319:76–83. https://doi.org/10.1016/j.cattod.2018.03.056.
5. Hou Q, Rehman MLU, Bai X, Xie C, Lai R, Qian H, et al. Incorporation of MgO into nitrogen-doped carbon to regulate adsorption for near-equilibrium isomerization of glucose into fructose in water. Appl Catal B 2024;342. https://doi.org/10.1016/j.apcatb.2023.123443.