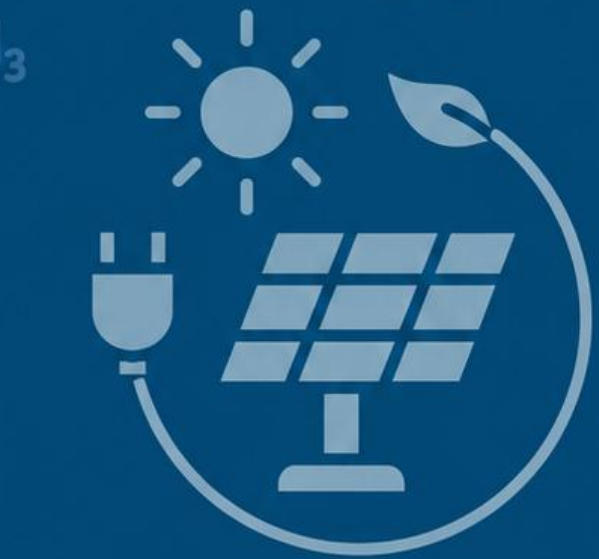
8th ANATOLIAN SCHOOL OF CATALYSIS

ASC-8

April 23-26

2026



ABSTRACT BOOK

Kataliz Derneği

GEBZE TECHNICAL UNIVERSITY

Book of Abstracts of the 8th Anatolian School of Catalysis (ASC-8)

23–26 April 2026 | Gümüldür, İzmir

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Editor

Assoc. Prof. Mustafa Karatok

Assoc. Prof. Oluş Özbek

Publication Date: 23.09.2026

ISBN: xxxxxxxxxxxxxxx

Preface

On behalf of the Turkish Catalysis Society and the Organizing Committee, we are pleased to present the Book of Abstracts of the **8th Anatolian School of Catalysis (ASC-8)**, held at Angora Beach Resort, Gümüldür, İzmir, Türkiye, between 23–26 April 2026.

Since its establishment in 2006, the Anatolian School of Catalysis has become a cornerstone educational and scientific activity of the Turkish catalysis community, providing a long-standing platform for advanced training, knowledge exchange, and interaction among researchers from academia and industry. Over the years, the school has continued to bring together graduate students, early-career researchers, and established scientists to promote a deeper understanding of catalytic science and its applications.

The eighth edition of the school continued this tradition by bringing together 98 participants, including 57 graduate students, 27 academic researchers, and 14 representatives from industry, creating a dynamic environment for scientific discussion, learning, and networking. The scientific program featured 21 invited lecturers and consisted of five thematic sessions covering **Concepts in Catalysis and Kinetics**, **Catalyst Preparation and Advanced Characterization**, **Reaction Engineering**, **Beyond Thermal Catalysis**, and **Computational Catalysis: The New Era**. In addition, two panel discussions addressed important topics extending beyond scientific knowledge: *Ethics, Integrity, and Responsibility in Scientific Publishing* and *Bridging Academic Research and Industrial Practice*. These sessions provided participants with a comprehensive perspective on modern catalysis, from fundamental concepts and emerging research directions to industrial applications and responsible scientific practices.

This abstract book contains 36 poster contributions presented during ASC-8. These contributions highlight the diversity and quality of research activities conducted by the participating young researchers and provide a snapshot of current developments across different areas of catalysis. We hope that this collection will serve as a valuable record of the scientific exchange during the school and inspire future collaborations and innovations.

We gratefully acknowledge the support of the **European Federation of Catalysis Societies (EFCATS)**, which contributed to the success of ASC-8. We sincerely thank our sponsors and partners: **Redoks** (Gold Sponsor), **Terralab** (Silver Sponsor), **Specson**, **ATS**, and **Anton Paar** (Exhibitors), **KUHyTech** and **Logos** (Bag Sponsors), and **Springer Nature** (Award Sponsor).

We also express our sincere appreciation to the Turkish Catalysis Society, the Organizing Committee, the Advisory Board, and the Scientific Committee for their dedication and efforts in making ASC-8 a successful educational and scientific event. Our special thanks go to all invited lecturers and participants for their valuable contributions and enthusiasm.

We hope that the interactions and ideas generated during the 8th Anatolian School of Catalysis will continue to foster scientific collaborations, strengthen the catalysis community, and contribute to future advances in catalysis research.

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Valorization of Red Mud and Fly Ash into Zeolites with High Methylene Blue Adsorption Capacity

Batuhan Orhan [1], M. Enes Lale [1,*], Sinem Ilgın Metin [3], Şule Naz Ezber [4] & Samira Fatma Kurtoğlu Öztulum [2]

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Abstract

The valorization of industrial solid wastes into high value functional materials represents a sustainable pathway for environmental remediation. Fly ash (FA), a byproduct of coal combustion generated in large quantities worldwide [1], and red mud (RM), an alkaline residue from alumina production[2], are both rich in aluminosilicate and iron oxide phases. However, their direct application as adsorbents is limited due to their inherently low surface area and modest dye removal capacities [3]. In this study, FA and RM were co-utilized to synthesize zeolite-based materials via alkali treatment, aiming to enhance structural properties and maximize methylene blue (MB) adsorption from aqueous solutions. Three different FA:RM ratios (9:1, 8:2, and 7:3) were systematically investigated to evaluate the influence of RM content on zeolite crystallinity, surface characteristics, and adsorption performance. XRD analysis confirmed the successful formation of zeolite X and zeolite A phases, replacing the quartz, mullite, and hematite phases originally present in FA and RM [4]. SEM images revealed the characteristic morphology of zeolite X crystals, particularly pronounced in the ZX-RM20 and ZX-RM30 samples [5]. BET analysis demonstrated a substantial increase in surface area from 1.05 m2/g (FA) and 17.07 m2/g (RM) to 133.61 m2/g for ZX-RM20, confirming the structural transformation into highly porous zeolitic frameworks. Adsorption experiments conducted with 10 ppm MB solution (50 mL) and 25 mg adsorbent showed that raw FA and RM achieved removal efficiencies of only ~5% and 19%, respectively, whereas synthesized zeolites exhibited dramatically enhanced performance. ZX-RM30 reached 92% removal efficiency, followed by ZX-RM20 (89%) and ZX-RM10 (77%), at identical conditions. Kinetic modeling indicated that MB adsorption follows pseudo-second-order kinetics, suggesting a chemisorption-controlled mechanism. Isotherm analysis revealed that the Langmuir model best described the equilibrium data, with a maximum adsorption capacity (qmax) of 54.11 mg/g for ZX-RM30, highlighting monolayer adsorption behavior. The adsorption performance was strongly pH-dependent, with significantly improved capacities under alkaline conditions due to enhanced electrostatic interactions between negatively charged zeolite surfaces and cationic MB molecules [6]. Regeneration tests further demonstrated that ZX-RM30 maintained approximately 96% removal efficiency even after three calcination cycles, indicating excellent reusability. Overall, this study demonstrates that co-synthesizing zeolite X and A from FA and RM significantly enhances surface area, crystallinity, and methylene blue adsorption capacity. The synergistic utilization of these two abundant industrial wastes provides a cost-effective and sustainable strategy for wastewater treatment applications while contributing to circular economy principles.

Keywords: Adsorption, Fly Ash, Industrial Waste Valorization, Methylene Blue, Red Mud, Sustainability, Zeolite

References

Atun, G., et al., A comparison of sorptive removal of anthraquinone and azo dyes using fly ash from single and binary solutions. J Hazard Mater, 2019. 371: p. 94–107.

Kumar, S., et al., Innovative methodologies for the utilisation of wastes from metallurgical and allied industries. Resources, Conservation and Recycling, 2006. 48(4): p. 301–314.

Sekizkardeş, B. and S.F. Kurtoğlu-Öztulum, Modified Fly Ash: An Eco-Friendly, Cost-Free, and Efficient Iron-Based Catalyst for Ammonia Decomposition to COx-Free Hydrogen. ChemCatChem, 2025. 17(5): p. e202401666.

Belviso, C., et al., Effects of ultrasonic treatment on zeolite synthesized from coal fly ash. Ultrasonics Sonochemistry, 2011. 18(2): p. 661–668.

Liao, H., et al., Efficiency and mechanism of amidoxime-modified X-type zeolite (AO-XZ) for Cs+ adsorption. Chemical Physics Letters, 2020. 741.

Ahmed, H.M., et al., Adsorptive removal of methylene blue dye by a ternary magnetic rGO/AK/Fe3O4 nanocomposite: Studying adsorption isotherms, kinetics, and thermodynamics. Chemical Physics Impact, 2025. 10: p. 100800.

Effect of Pt Content on the Activity and Selectivity of Au–Pt Dilute Alloy Catalysts for Propane Dehydrogenation

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Abstract

Propylene is a fundamental building block of the petrochemical industry, and the growing global demand has intensified the need for more efficient and selective propane dehydrogenation (PDH) Technologies [1,2]. Although Pt-based catalysts are widely used in commercial PDH processes, they typically suffer from rapid deactivation and overactivation of propylene, leading to coke formation and undesired cracking reactions [3]. Therefore, controlling the geometric and electronic structure of Pt active sites is essential to enhance selectivity and long-term stability [3]. Despite extensive efforts in catalyst development, a fundamental challenge in PDH remains the trade-off between activity and selectivity, where increasing Pt surface sites enhances propane conversion but also promotes over-dehydrogenation, C–C bond cleavage, and coke formation. Therefore, understanding how Pt content influences this balance is essential for improving Pt-based catalysts.

Au nanoparticles with an average size of approximately 16 nm were synthesized, followed by controlled incorporation of Pt at different relative amounts. The resulting Au–Pt nanoparticles were subsequently supported on Al_2O_3 and evaluated in a plug-flow reactor under non-oxidative propane dehydrogenation conditions following appropriate pretreatment procedures. The catalytic results revealed a clear dependence of performance on Pt content. Catalysts with lower Pt fractions exhibited higher propylene selectivity, whereas increasing Pt content enhanced propane conversion, accompanied by a moderate decrease in selectivity. Despite this expected activity–selectivity trade-off, all Au–Pt catalysts maintained significantly higher propylene selectivity than a commercial Pt reference under comparable conditions. These findings indicate that Pt content plays a critical role in governing the balance between propane activation and undesired secondary reactions.

Based on dilute alloy concepts reported in the literature, such composition-dependent behavior may be associated with changes in Pt site distribution within the Au matrix [4]. At lower Pt contents, a higher degree of Pt dilution may favor smaller Pt ensembles or more isolated Pt species, which are generally associated with suppressed deep dehydrogenation and C–C bond cleavage pathways [5]. Conversely, increasing Pt content may increase the probability of contiguous Pt sites, potentially enhancing overactivation reactions [5]. Additionally, electronic interactions between Au and Pt have been reported to influence adsorption strength of reaction intermediates, which could contribute to the observed selectivity trends [6]. Ongoing characterization studies are currently focused on elucidating the surface Pt ensemble configuration and electronic structure. A detailed understanding of these structural and electronic effects is expected to provide insight into the atomic-scale interaction between Pt and Au and its role in governing the PDH reaction mechanism.

Keywords: Propane Dehydrogenation, Dilute Alloys, Pt-Au Alloy Catalysts

References

Chen, S., Chang, X., Sun, G., Zhang, T., Xu, Y., Wang, Y., ... & Gong, J. (2021). Chem Soc. reviews, 50(5), 3315-3354.

Dai, Y., Gao, X., Wang, Q., Wan, X., Zhou, C., & Yang, Y. (2021). Chemical Society Reviews, 50(9), 5590-5630.

He, Z., Yang, J., & Liu, L. (2024). . JACS Au, 4(11), 4084-4109.

Zhang, T., Walsh, A. G., Yu, J., & Zhang, P. (2021). Chemical Society Reviews, 50(1), 569-588.

Deng, Y., Guo, Y., Jia, Z., Liu, J. C., Guo, J., Cai, X., ... & Ma, D. (2022). Journal of the American Chemical Society, 144(8), 3535-3542.

Hammer, B., & Nørskov, J. K. (2000). In Advances in catalysis (Vol. 45, pp. 71-129). Academic Press.

Influence of Synthesis Parameters on the Aggregation Behavior of Copper Nanoparticles Prepared via Chemical Reduction at Room Temperature

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Abstract

Copper is recognized as a key catalyst due to its high abundance, cost-effectiveness, and low toxicity. Copper nanoparticles are highly effective in organic synthesis, driving reactions ranging from oxidative coupling to azide–alkyne cycloaddition.1 Moreover, Cu-based materials are essential for environmental and energy applications, demonstrating high efficiency in NO_x reduction, CO oxidation, and the water-gas shift reaction.1 Despite the broad interest in copper-based catalysis, tailoring the size and shape of copper nanoparticles with the same precision as noble metals presents a significant challenge.2

One of the primary challenges in copper nanoparticle synthesis is the effective management of particle aggregation. Controlling this phenomenon is crucial as it directly regulates the active surface area and the density of catalytic sites. Even though uncontrolled aggregation limits the surface area, controlled aggregation could be a key factor in defining crystal shape during synthesis. The literature reports that aggregated particles can serve as intermediate transition forms in the synthesis of larger shape defined structures, such as cubic or octahedral particles. 3

Herein, we systematically examine the aggregation behavior of copper nanoparticles prepared by chemical reduction at room temperature. Through independent variation of synthesis parameters, our electron microscopy-based statistical analysis highlights distinct mechanisms on particle size and their aggregation. We observe that while copper precursor concentration strongly promotes aggregation, it has minimal impact on primary particle size. In contrast, the reducing agent plays a decisive role in both growth and aggregation; notably, increasing the injection rate serves as an effective strategy to suppress aggregate formation. The influence of the capping agent (PVP) was found to be comparatively limited. In conclusion, by establishing aggregation as an independently tunable parameter, this work provides essential guidelines for the scalable synthesis and rational design of optimized nanostructured copper catalysts.

Keywords: Copper nanoparticles, aggregation, size distribution, catalysis

References

Gawande, M. B., Goswami, A., Felpin, F. X., Asefa, T., Huang, X., Silva, R., ... & Varma, R. S. (2016). Cu and Cu-based nanoparticles: synthesis and applications in catalysis. Chemical reviews, 116(6), 3722-3811.

Xiao Y, Wiesner MR (2016) Nanoparticle aggregation and deposition in porous media. In: Xing B, Vecitis CD, Senesi N (eds) Engineered Nanoparticles and the Environment: Biophysicochemical Processes and Toxicity. 1st edn. Wiley, pp 224-244

Kuo C-H, Huang MH (2008) Facile Synthesis of Cu2O Nanocrystals with Systematic Shape Evolution from Cubic to Octahedral Structures. J Phys Chem C 112:18355–18360.

Controlling ROS formation in CuPt/TiO2 photocatalysts: Role of metal synergy and preparation medium

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Abstract

Photocatalytic removal of persistent organic pollutants from water largely depends on the generation of reactive oxygen species (ROS) and the efficiency of charge-carrier separation in semiconductor photocatalysts. Among various photocatalytic materials, nanocrystalline titanium dioxide (TiO2) remains one of the most widely studied systems due to its chemical stability, low cost, and favourable electronic properties. However, its practical photocatalytic efficiency is often limited by rapid recombination of photogenerated charge carriers and insufficient utilisation of visible light. Surface modification with metallic cocatalysts is an effective strategy to address these limitations. Metal nanoparticles deposited on TiO2 can form Schottky junctions that promote charge separation and suppress electron-hole recombination. In addition, plasmonic metals such as Au may enhance light absorption through localised surface plasmon resonance (LSPR), while bimetallic systems may exhibit synergistic effects arising from complementary electronic and catalytic properties. In this study, we systematically investigated the influence of mono- and bimetallic nanoparticle deposition (Cu, Au, and Pt) on TiO2 photocatalysts prepared by wet impregnation using two different solvents, ethanol (A-series) and water (B-series). The physicochemical properties of the resulting materials were characterised using X-ray diffraction (XRD), nitrogen physisorption (BET), diffuse reflectance spectroscopy (DRS), solid-state photoluminescence (PL), and electron paramagnetic resonance (EPR). Photocatalytic performance was evaluated through the degradation of bisphenol A (BPA) under visible-light irradiation in aqueous suspension and through the generation of reactive oxygen species. In particular, the formation of hydroxyl radicals (•OH) was quantified using the coumarin probe method based on the formation of fluorescent 7-hydroxycoumarin.

Structural analysis confirmed that the crystalline structure of TiO2 remained unchanged after metal nanoparticle deposition. Spectroscopic characterisation revealed enhanced generation of photogenerated electrons and suppressed charge-carrier recombination in metal-modified photocatalysts compared with bare TiO2. Photocatalytic experiments demonstrated that all metal-TiO2 systems exhibited improved BPA degradation efficiency relative to the unmodified semiconductor, with CuPt/TiO2 showing the highest activity. A combined analysis of scavenger experiments and coumarin probe measurements revealed distinct ROS fingerprints across the catalyst series. Although significant hydroxyl radical generation was detected for several catalysts, the coumarin signal does not directly correlate with BPA degradation efficiency. For example, the CuAu-B catalyst (prepared in water) exhibits a strong •OH signal but very limited photocatalytic activity. In contrast, scavenger experiments showed that the addition of p-benzoquinone strongly suppresses BPA degradation for most catalysts, indicating that superoxide radicals ($\bullet O_2^-$) are the primary oxidising species. The CuPt/TiO2 catalyst displays the most complex ROS network, where $\bullet O_2^-$ and $^1O_2$ dominate, while hydroxyl radicals also contribute to the oxidation pathway.

Overall, these findings demonstrate that the synergy between Cu and Pt cocatalysts, together with the preparation medium, provides an effective strategy to tune ROS generation and enhance the photocatalytic performance of TiO2-based systems.

Keywords: Heterogeneous photocatalysis; TiO2 photocatalysts; bimetallic cocatalysts; reactive oxygen species; coumarin probe; bisphenol A degradation

References

G. Žerjav, J. Zavašnik, J. Kovač, A. Pintar, "The influence of Schottky barrier height onto visible-light triggered photocatalytic activity of TiO2 + Au composites," Appl. Surf. Sci., vol. 543, 2021, p. 148799.

Š. Slapničar, G. Žerjav, M. Németh, J. Zavašnik, A. Pintar, "Design and evaluation of plasmonic metal-TiO2 nanostructures for photocatalytic degradation of BPA as a model pollutant," J. Colloid Interface Sci., vol. 700, 2025, p. 138361.

M. Lazar, S. Varghese, and S. Nair, "Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates," Catalysts, vol. 2, no. 4, p. 572, Dec. 2012.

Y. Huang, X. Xu, G. Fan, X. Zhu, L. Zhu, "Effect of TiO2 crystal phase on the construction of TiO2/g-C3N4 heterojunction photocatalyst for efficient sunlight photodegradation of naphthalene," Colloids Surf. Physicochem. Eng. Asp., vol. 694, 2024, p. 134170.

A. Meng, L. Zhang, B. Cheng, J. Yu, "Dual Cocatalysts in TiO2 Photocatalysis," Adv. Mater., vol. 31, 2019, p. 1807660.

Optimizing alumina-supported bimetallic Fe-Cu catalysts for total catalytic oxidation of volatile organic compounds

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Abstract

Volatile organic compounds (VOCs) are a major class of pollutants that can have significant adverse effects on human health as well as the environment. Thermal and catalytic oxidation are amongst the most widely used methods for VOC abatement [1]. Although effective, thermal oxidation requires high energy consumption (500-1000°C), which limits its use. Catalytic oxidation is a more energy-efficient alternative with noble metal catalysts reducing the operating temperatures down to 250°C. However, due to their drawbacks such as high cost, low availability, and tendency to deactivate due to coking and poisoning, the focus of recent research has been on finding a more cost-efficient and stable alternative. Supported transition metal catalysts have emerged as promising candidates exhibiting high stability, resistance to deactivation, and far lower production cost. However, due to a higher operating range than noble metal catalysts (280-450°C) the goal is to increase their activity and bring the operating range closer to their noble metal counterparts. In this work, we synthesized and evaluated the catalytic performance of bimetallic FeCu/γ-Al2O3 catalysts for total oxidation of toluene as a model VOC. Different Fe and Cu loadings were used to determine the best performing catalyst. Through optimization, it was found that the catalytic activity increased with the increase of Cu loading up to a molar ratio of Cu/Al = 0.08, and that the most efficient catalyst contained only a small amount of Fe (Fe/Al = 0.005). The best performing catalyst (Fe/Al = 0.005 and Cu/Al = 0.08) showed a T90 near 340°C, which is an improvement in comparison with the state-of-the-art catalysts of similar composition [2]. The catalysts were characterized by the following methods: X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Nitrogen physisorption, Transmission Electron Microscopy (TEM), and UV-VIS spectroscopy (UV-VIS). The measurements showed good compositional control during synthesis, relatively high surface area, and the compositional range in which good dispersion of the dopant metals can be achieved. This work highlights FeCu/γ-Al2O3 bimetallic catalysts as promising alternatives to noble metals in catalytic oxidation of VOCs. The obtained insights can be implemented for design and improvement of similar bimetallic transition metal systems.

Keywords: Cu-Fe, gamma alumina, synergy, catalytic oxidation, toluene, optimization

References

Ismail, A., Zahid, M., Ahmad, B., Raziq, F., Bakhtiar, S. U. H., Ali, S., Ali, S., Khan, A., Ali, N., Wu, X., Ali, S., Ali, S., He, W., Yi, J., & Qiao, L. Catalytic oxidation of volatile organic compounds: A review of recent advances in supported and non-supported catalysts. Coordination Chemistry Reviews, 535 (2025) 216617.

Žumbar, T., Arčon, I., Djinović, P., Aquilanti, G., Žerjav, G., Pintar, A., Ristić, A., Dražić, G., Volavšek, J., Mali, G., Popova, M., Logar, N. Z., & Tušar, N. N. Winning Combination of Cu and Fe Oxide Clusters with an Alumina Support for Low-Temperature Catalytic Oxidation of Volatile Organic Compounds. ACS Applied Materials & Interfaces, 15(2023) 28747–28762.

Impact of Deposition Strategy on the Stability and Photocatalytic Activity of TiO2 and ZnO Nanoparticles on Polypropylene

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Abstract

Photocatalytic nanomaterials deposited onto solid supports have attracted significant interest due to their potential applications in environmental remediation, including air and water purification as well as the inhibition of bacterial growth under light irradiation [1]. Among commercial substrates, polypropylene (PP) is particularly appealing due to its low cost, mechanical robustness, and chemical inertness. However, these properties that make PP attractive for large-scale use simultaneously hinder the immobilization of nanoparticles, necessitating tailored surface-engineering strategies. Therefore, activating PP surface is necessary, which can be done by introducing oxygen-containing functional groups with the use oxygen plasma treatment. Such procedure enables more effective deposition of photocatalytically active metal oxide nanoparticles [2].

A variety of deposition strategies can be employed to immobilize nanoparticles onto polymer surfaces, differing fundamentally in their dominant binding mechanisms - chemical interactions versus mechanical anchoring. In this work, two contrasting approaches were examined: pH-controlled electrostatic deposition and ultrasound-assisted deposition. Nanoparticles of TiO2, ZnO, and mixtures of both were deposited onto plasma-modified PP, and the resulting composites were evaluated with respect to nanoparticle loading (XPS, FAAS), surface morphology (SEM, AFM) and stability (photocatalytic tests). Both deposition methods yielded well-dispersed nanoparticles across the PP surface, demonstrating their suitability for producing homogeneous photocatalytic coatings.

Photocatalytic performance was assessed via terephthalic acid hydroxylation and dye-degradation assays. When normalized to nanoparticle loading, both deposition routes showed comparable photocatalytic activity in initial cycles. However, a distinct difference emerged in long-term stability: electrostatic deposition resulted in a progressive loss of activity due to insufficient adhesion and gradual nanoparticle detachment, whereas ultrasound-assisted deposition produced coatings with stable performance over multiple photocatalytic cycles.

The obtained results underline the importance of developing suitable deposition strategy to fabricate robust photocatalytic systems with optimized interfacial nanoparticles-polymer interactions. The study highlights that material stability - often overlooked in favor of initial activity - is critical for real-world implementation, where the lifetime of the photocatalyst is often more important than its intrinsic photocatalytic efficiency.

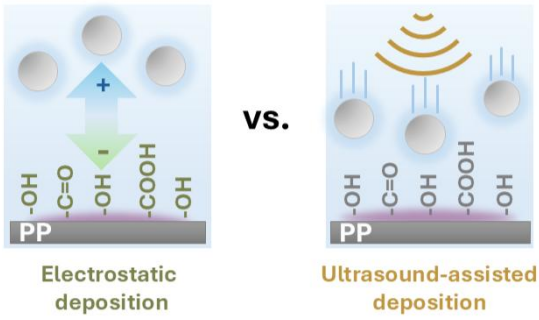

Fig. 1. Schematic comparison of electrostatic and ultrasound-assisted deposition approaches used for the preparation of composite photocatalysts.

Keywords: Polypropylene modification, Nanoparticle deposition, Interface stability, Ultrasound-assisted deposition, Composite photocatalyst

References

Wang, H.; Li, X.; Zhao, X.; Li, C.; Song, X.; Zhang, P.; Huo, P.; Li, X. A review on heterogeneous photocatalysis for environmental remediation: From semiconductors to modification strategies; Chinese Journal of Catalysis 2022, 43, 178–214, https://doi.org/10.1016/S1872-2067(21)63910-4

Zajac, K.; Macyk, J.; Szajna, K.; Krok, F.; Macyk, W.; Kotarba, A. Functionalization of Polypropylene by TiO2 Photocatalytic Nanoparticles: On the Importance of the Surface Oxygen Plasma Treatment; Nanomaterials 2024, 14, 1372, https://doi.org/10.3390/nano14161372

Effect of Calcination Temperature on the Catalytic Activity of Mo and Co–Mo/SiO_2 Catalysts under Ammonia Synthesis Conditions

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Abstract

Ammonia is one of the most important industrial chemicals and plays a critical role in global food production, with approximately 180 million tons produced and traded annually worldwide [1]. Despite its importance, conventional ammonia synthesis via the Haber–Bosch process remains highly energy- and carbon-intensive, contributing significantly to global greenhouse gas emissions [2]. These challenges highlight the need for improved catalytic systems and a deeper understanding of the parameters governing catalytic performance.

In this study, the influence of particle size and metal composition on the catalytic activity of supported mono- and bimetallic Mo-based catalysts was investigated. A series of catalysts supported on SiO_2 were synthesized, including monometallic 2 wt% Mo/SiO_2 and bimetallic 2 wt% Co–Mo/SiO_2 systems. The catalysts were prepared using the incipient wetness co- impregnation method followed by calcination at different temperatures with the aim to control particle size and metal dispersion. Catalytic activity tests were performed under N_2/H_2 reaction environments at 500 °C.

Preliminary test results indicated that measurable activity was observed at 500 °C. Among the tested samples, catalytic activity was detected in 2 wt% Mo/SiO_2 calcined at 600 °C and in 2 wt% Co–Mo/SiO_2 catalysts calcined at 500 °C, 600 °C, and 700 °C. Early observations suggest that increasing calcination temperature promotes catalytic performance. It can be seen in Fig. 1 that the 2 wt% Co–Mo/SiO_2 catalyst calcined at 500 °C has a rate of 5,5 µmol/(gcat*h) , 600 °C a rate of 12,3 µmol/(gcat*h), and at 700 °C calcination the rate was found to be 35,5 µmol/(gcat*h). Ongoing characterization and activity research aim to establish a clearer reason for varying catalytic activity in these Mo-based catalytic systems.

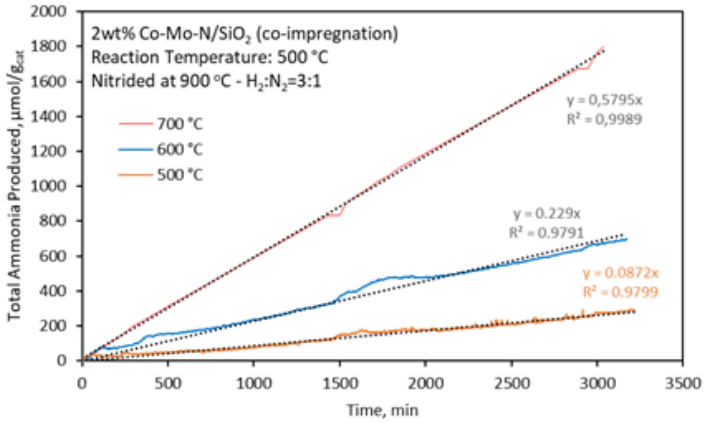

Fig. 1: Comparison of total ammonia produced over time at different calcination temperatures

Keywords: Ammonia synthesis; molybdenum catalysts; bimetallic catalysts; Co–Mo/SiO_2 catalysts; calcination temperature; catalytic performance; supported catalysts

References

Agustin V-M., Syed M., Daniel P., and Phil B. Ammonia. In: O'Connor J, Noble B, Lieuwen T, eds. Renewable Fuels: Sources, Conversion, and Utilization. Cambridge University Press (2022), 245-274.

Ribeiro, C.; Santos, D.M.F. Transitioning Ammonia Production: Green Hydrogen-Based Haber–Bosch and Emerging Nitrogen Reduction Technologies. Clean Technol. (2025), 7, 49. https://doi.org/10.3390/cleantechnol7020049.

Determining the State of a Pd/γ-Al2O3 Catalyst Using Pulsed Flow and Transient Spectroscopy

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Abstract

A precise understanding of heterogeneous catalyst structure and activity is required to design more efficient, greener, industrial chemical processes. While it is possible to resolve both the structure and activity of a catalyst, their innate complexity means it is nontrivial to unambiguously assign one to the other. Herein, we demonstrate how transient measurements, coupled with kinetic modeling, can be used to resolve kinetics with sufficient precision such that it is possible to resolve the identity of an "active site" over technical catalysts. We find that under CO rich conditions the transient activity and coverage dependencies measured over a Pd/γ-Al2O3 catalyst during pulsed flow and transient spectroscopy CO oxidation experiments can be quantitatively predicted using a kinetic model derived from ultrahigh vacuum surface science experiments over Pd(111) single crystals. Thus, we conclude that the state (i.e., structure and composition of the active site) of the Pd/γ-Al2O3 catalyst under reaction conditions is equivalent to that of a Pd(111) surface. Instead of determining a catalyst's structure and assigning it to activity, we instead propose a new approach: using precise kinetic measurements to infer the catalyst's state. This approach enables the identification of active sites that have been challenging to resolve using traditional spectroscopic or microscopic methods, offering a powerful and complementary tool for designing new catalysts.

Keywords: Surface Science, Transient Kinetics

Sulfur Poisoning and Regeneration Characteristics of Rh Single Atoms vs Rh Nanoparticles on Ceria

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Abstract

Platinum group metals (PGM) used in the formulation of three-way catalysts (TWC) which are utilized in automotive emission control systems often suffer from deactivation due to sulfur oxides which originate from impurities in fuels. An efficient way for reactivating TWC is thermal reactivation under high temperature (>600 °C) in the presence of a reducing agent (hydrocarbons, H2 etc.). High temperature treatments limit active site design, driving active sites to agglomeration and decrease active surface area and selectivity. In the current study, we investigate the sulfur poisoning and regeneration characteristics at low temperature (200 °C). The model rhodium ceria hydroxyapatite (0.5Rh/CeOx/HAP) exhibiting exclusively Rh single atom catalyst (SAC) vs. a conventional Rh/Ceria catalyst (0.5Rh/CeO2) containing predominantly Rh nanoparticles as well as minority Rh SAC sites is studied using in-situ FTIR, XPS, TPD, and XRD. Our findings indicate that on the 0.5Rh/Ce/HAP catalyst, Rh single atom sites can readily activate H2 and regenerate the SOx-poisoned Rh sites. On the other hand, on the 0.5Rh/CeO2 catalyst, most of the poisoned high coordination Rh sites fail to activate H2 and thus reveal poor regeneration behavior, while the minority Rh single atom sites on 0.5Rh/CeO2 can be effectively regenerated via H2. This dichotomy suggests that while H2 can reach the surface of Rh single atoms, the larger Rh domains are covered by a dense SOx layer blocking incoming H2.

Keywords: Single Atom Catalysis, Sulfur Poisoning, Hydrogen Activation, in-situ FTIR Spectroscopy

Engineering the Nature of Rh Catalyst for Integrated CO2 Capture and Utilization via Dry Reforming of Methane: Effect of CeOx and FeOx Promoters on HAP

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Abstract

Integrated CO2 capture and utilization (ICCU) through catalytic processes is a key strategy toward reducing anthropogenic greenhouse gas emissions and achieving carbon neutrality. Among these catalytic reactions, the dry reforming of methane (DRM) stands out as a sustainable and thermodynamically favorable pathway that mitigates CO2 and CH4 emissions by converting these major greenhouse gases into synthesis gas with an H2/CO ratio of 1, which is essential for downstream processes like Fischer-Tropsch synthesis. However, catalyst deactivation due to coke deposition and sintering remains a critical challenge, particularly for Ni-based systems. In this study, first, a series of catalysts were designed to investigate the effect of active metal (Rh) and promoter (CeO_x, FeO_x) on DRM activity, stability, and carbon resistance. Hydroxyapatite (HAP) was used as the support material due to its high thermal stability, basic character, and oxygen vacancy-rich structure, which are known to enhance coke resistance and CO2 activation. The catalysts were synthesized via wet impregnation and extensively characterized to establish structure-activity relationships. DRM performance tests were conducted on Rh- and Ni-based catalysts supported on HAP, and the effects of promoter addition were systematically evaluated to understand their role in improving redox properties and suppressing carbon deposition. Catalyst stability was assessed through time-on-stream (TOS) experiments. Post-reaction characterization of spent catalysts using TGA, Raman spectroscopy, and XPS revealed insights into the deactivation pathways and nature of possible coke species. Additionally, in-situ FTIR spectroscopy was performed on fresh catalysts under reaction conditions to identify surface intermediates and gain a deeper mechanistic understanding of the process. Following performance tests, selected catalysts were physically mixed with CaO, a high-temperature CO2 adsorbent, to produce dual-functional materials (DFMs) for an integrated CO2 capture and dry reforming of methane (ICC-DRM) process. After initial screening of CO2 adsorption and CH4 conversion under ICC-DRM conditions, selected DFMs were subjected to cyclic testing to assess their long-term performance and resistance to deactivation over multiple cycles. The results demonstrate that rational tuning of metal type and promoter selection can yield highly effective multifunctional materials for integrated carbon capture and utilization. This study provides insights for designing durable, coke-resistant DFMs for ICCU applications and contributes to the advancement of net-zero carbon technologies.

Keywords: Dry reforming of methane, dual-functional materials, hydroxyapatite (HAP), ICCU, carbon dioxide, methane, coke, ICC-DRM.

References

Kim, S.M., Abdala, P.M., Broda, M., et al. ACS catalysis 8.4 (2018)

Agún, B. and Abánades, A., International Journal of Hydrogen Energy 103 (2025)

Boukha, Z., Kacimi, M., Pereira, M.F.R, et al. Applied Catalysis A: General 317.2 (2007)

Akri, M., Zhao, S., Li, X., et al. Nature communications, 10.1 (2019)

Alkali Metal Cation Effect on Electrochemical Pulsed CO2 Reduction on Cu2O Nanocubes

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Abstract

Electrochemical CO2 conversion into fuels (CO2RR) has been promising approach to prevent global emission challenges. Electrocatalyst improvements have been done for decades, focusing less on the electrolyte effects despite being a huge impact on CO2RR. The electrocatalyst most commonly used are Cu2O in various nanostructural forms, which are known for their high CO2 conversion rate to C2+ and C1 products due to the presence of Cu+ and high surface area. For understanding the selectivity trends in the presence of different alkali metal cations, the roles of Cs+, K+ and Li+ in carbonate electrolytes were investigated at constant potential. Li+ was found to provide the highest methane efficiency (25 %) while Cs+ and K+ gave high ethylene efficiencies (33 %) where high H2 efficiency (40 % - 50 %) was observed for all due to the change of state of the surface and local pH. For the purpose of increasing C2+ and suppressing H2 efficiencies, which can be achieved with the presence of Cu+, pulsed electrochemical conversion under pulsed potential conditions were tested with the same set of alkali metal cations using different time ranges at constant anodic and cathodic potentials. As a result, H2 suppression (20 - 30 %) and C2+ formation were successfully observed (35 – 37 %), having the issue of the catalyst losing its activity with time for pulses of extended duration (ta/c = 60 s), significantly more in the presence of Li+. Further investigations by rotating ring disc electrode (RRDE) technique in combination with SEM, Raman, XPS, and XAS characterizations revealed that the state of the surface was more metallic in the presence Li+ due to higher dissolution of Cu(OH)2 and its reabsorption as metallic Cu on the surface while having more Cu+/Cu2+ in the presence of K+ and Cs+ due to the stabilization of the surface.

Keywords: cation, CO2RR, Cu2O

References

Li, C., Guo, Z., Mao, X. et al. Hydrophobically modified Cu_2O nanocube for selective CO_2 electroreduction to C2+ products. AIChE J. **71**, e70049 (2025). https://doi.org/10.1002/aic.70049

Tafazoli, S., Şekercioğlu, A., Zarenezhad, H., Ataş, B., Mohammadpour, A., Balkan, T. & Kaya, S. Cations responsible for varied CO_2RR product selectivity at high overpotentials over Cu_2O nanocubes. ACS Appl. Mater. Interfaces **17**, 50676–50685 (2025). https://doi.org/10.1021/acsami.5c09803

Wang, H., Wu, Q., Du, R. & Chen, G. Tuning *CO adsorption via Cu^+/Cu^0 interface engineering for enhanced ethylene selectivity in electrochemical CO_2 reduction. ACS Appl. Mater. Interfaces **17**, 55003–55012 (2025). https://doi.org/10.1021/acsami.5c15459

Synergistic Effects of Ultrasound, pH, and Cs^+ Ions on CO Electroreduction: A Comparative Study of Cu and Sn–Pb Alloy Electrodes

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Abstract

This study explores the electrochemical reduction of carbon monoxide (CO) as a pathway to generate high-energy fuels and chemicals, addressing critical barriers to industrial adoption: excessive energy losses from high overpotentials and restricted mass transport near the electrode surface. To overcome these limitations, the study employs 40 kHz ultrasonic irradiation as a process intensification tool, while systematically evaluating polycrystalline copper (Cu) and a tin-lead (Sn-Pb) alloy electrodes in 0.5 M KHCO3 buffer electrolyte whose pH was adjusted to 6.2 and 8 using 2 M HCl. Additionally, the research introduces cesium ions (Cs^+) at different concentrations to probe how large alkali cations modify the electrical double layer, potentially stabilizing reaction intermediates and lowering activation barriers.

The selection of Cu and Sn-Pb alloys stems from their contrasting catalytic identities. Copper possesses an optimal binding affinity for *CO intermediates, positioning it as a unique platform for C-C coupling necessary for multi-carbon products like ethylene and ethanol. In contrast, tin and lead interact weakly with CO, typically steering selectivity toward formate via oxygenated pathways, making the Sn-Pb alloy an ideal counterpoint for mechanistic comparison.

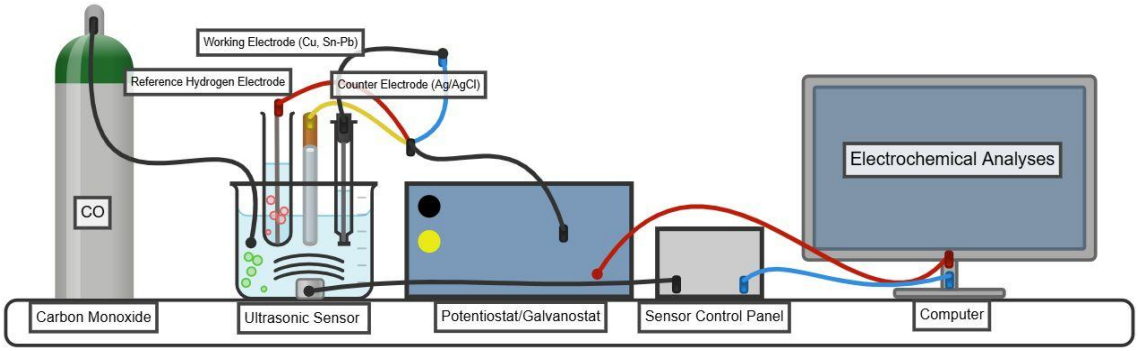
Cyclic voltammetry (CV) and Chronoamperometry (CA) analyses were performed to define the operative potential windows for both electrodes across these pH conditions. For the copper electrode, CV scans were conducted from -1.4V to 0V, based on which CA step potentials were applied at -1.3V and -0.2V at pH 6.2, shifting slightly to -1.4V and -0.2V at pH 8. The Sn-Pb alloy electrode exhibited a dramatic pH dependence: CV analysis was performed between -1.6V and 0V, with CA requiring -1.6V and 0V at pH 8, whereas at pH 6.2, the potentials shifted markedly to -0.6V and -0.2V. This contrast suggests that surface oxide/hydroxide speciation on Sn-Pb, and its responsiveness to local proton activity profoundly influences the energy required to initiate CO reduction.

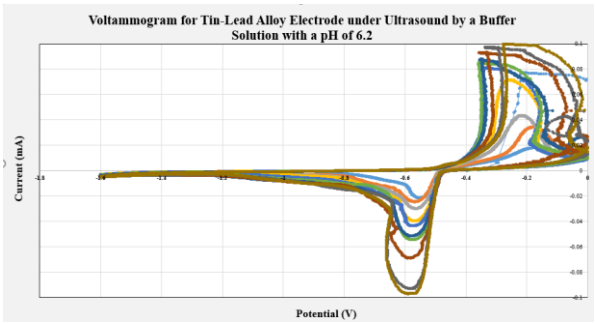
The introduction of 40 kHz ultrasound fundamentally altered reaction dynamics. Acoustic cavitation generates microjets and shockwaves disrupting the Nernst diffusion boundary layer, enhancing CO transport while sweeping away gaseous products and surface-poisoning intermediates. Visually, sonicated electrodes appeared shinier, confirming sustained surface renewal.

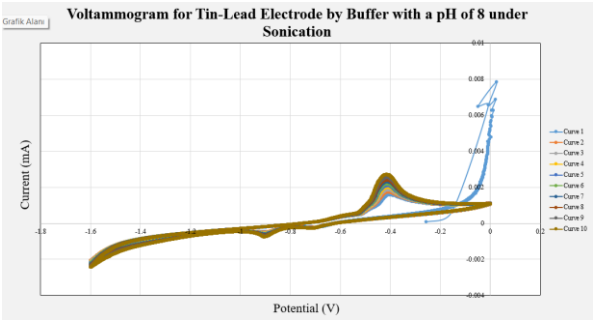
However, the interplay between pH and ultrasonic agitation revealed a nuanced outcome. Under silent conditions, the Sn-Pb alloy performed optimally at pH 6.2. Upon sonication, this trend completely reversed: pH 8 yielded significantly higher current densities. Copper, conversely, maintained superior activity at pH 6.2 even under ultrasound. This divergence underscores a critical insight: while sonication amplifies CO availability, it simultaneously accelerates proton flux to the electrode surface. At lower pH, this intensified proton transport exacerbates the competing hydrogen evolution reaction (HER) on Sn-Pb surfaces, overwhelming CO reduction pathways. Under alkaline conditions, however, the diminished proton concentration allows the mass transport benefits of ultrasound to prevail, while stabilizing oxygenated intermediates such as *OCHO that favor formate production on Sn-Pb.

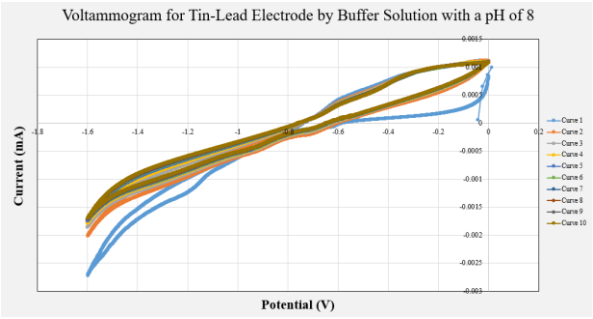
FT-IR analysis of liquid-phase products confirmed that Sn-Pb predominantly generates formate-related species, while copper retains its capacity for C-C coupling, evidenced by characteristic hydroxyl, carbonyl, and C(sp^3)-H vibrations.

Looking ahead, this study will incorporate UV-VIS spectroscopy to complement FT-IR findings and provide a more comprehensive product profile. Central to future efforts is the systematic introduction of Cs^+ at concentrations of 20 and 160 mM. Due to its large ionic radius and weak hydration shell, Cs^+ is anticipated to approach the electrode surface closely, altering the electrical double layer structure and electrostatically stabilizing negatively charged intermediates such as $*CO^-$. This modification could further lower the kinetic barrier for CO activation, potentially enhancing both energy efficiency and selectivity. When combined with optimized pH and the mass transport advantages of ultrasound, this approach offers a promising route toward viable CO electroreduction technologies.


Working Electrode (Cu, Sn-Pb)
Reference Hydrogen Electrode
Counter Electrode (Ag/AgCl)
CO
Electrochemical Analyses
Carbon Monoxide
Ultrasonic Sensor
Potentiostat/Galvanostat
Sensor Control Panel
Computer


Voltammogram for Tin-Lead Alloy Electrode under Ultrasound by a Buffer Solution with a pH of 6.2
Current (mA)
Potential (V)


Voltammogram for Tin-Lead Electrode by Buffer with a pH of 8 under Sonication
Current (mA)
Potential (V)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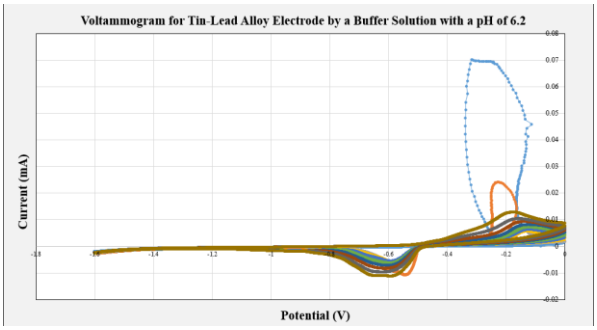
Current (mA)
Potential (V)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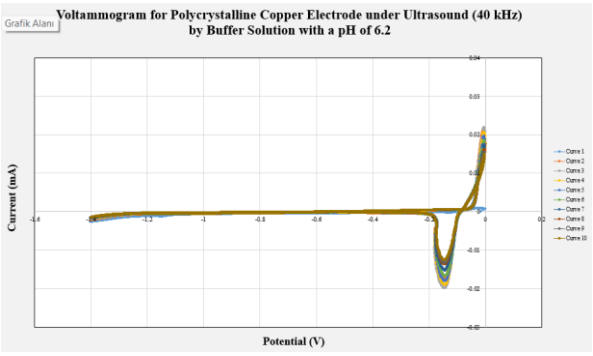
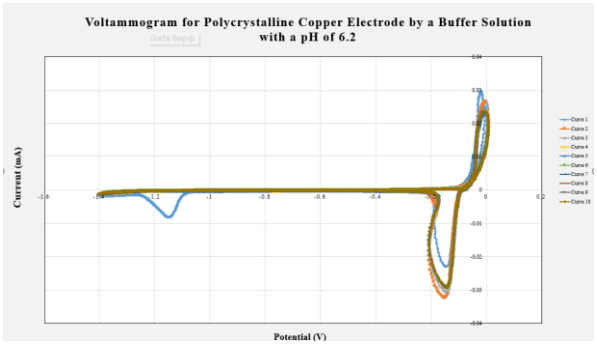
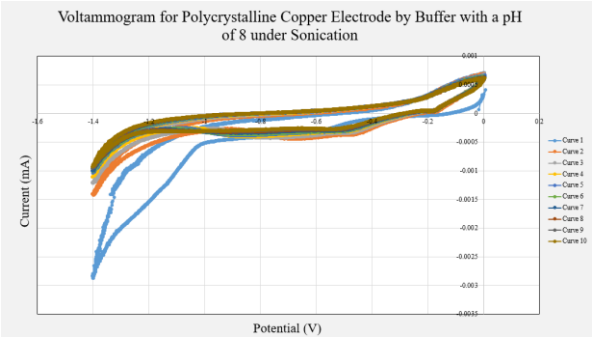
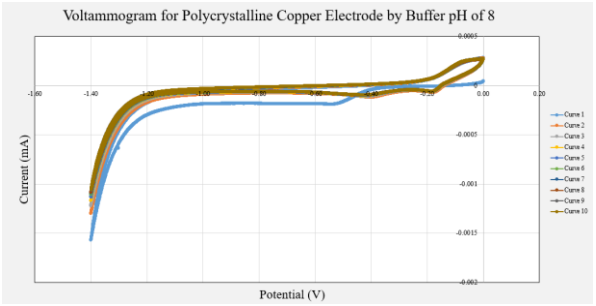
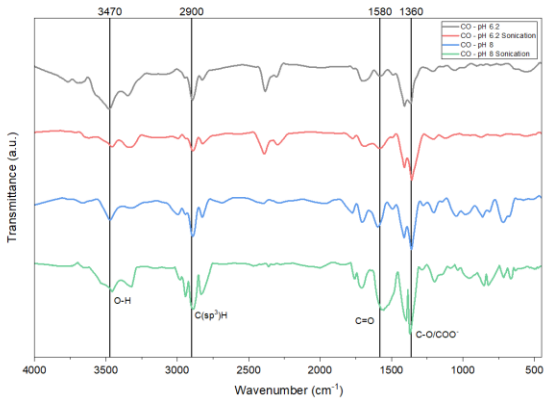
Current (mA)
Potential (V)


Voltammogram for Polycrystalline Copper Electrode under Ultrasound (40 kHz) by Buffer Solution with a pH of 6.2
Current (mA)
Potential (V)


Voltammogram for Polycrystalline Copper Electrode by a Buffer Solution with a pH of 6.2
Current (mA)
Potential (V)


Voltammogram for Polycrystalline Copper Electrode by Buffer with a pH of 8 under Sonication
Current (mA)
Potential (V)


Voltammogram for Polycrystalline Copper Electrode by Buffer pH of 8
Current (mA)
Potential (V)



Keywords: sono-electrochemistry, ultrasound, carbon monoxide, electro-reduction, caesium

References

Girichandran, N., Saedy, S., & Kortlever, R. (2024). Electrochemical CO_2 reduction on a copper-foam electrode at elevated pressures. Chemical Engineering Journal, **487**, 150478.

Yang, Y., et al. (2021). Ultrasound-boosted selectivity of CO in CO_2 electrochemical reduction. Ultrasonics Sonochemistry, **76**, 105623.

Rabiee, H., Heffernan, J. K., Ge, L., Zhang, X., Yan, P., Marcellin, E., Hu, S., Zhu, Z., Wang, H., & Yuan, Z. (2023). Tuning flow-through cu-based hollow fiber gas-diffusion electrode for high-efficiency carbon monoxide (CO) electroreduction to C_{2+} products. Applied Catalysis B: Environmental, **300**(2), 120-130.

Falling, L. J., Jaugstetter, M., Zhao, X., Girotto, G. Z., Altoe, V., Spronsen, M. A., Nemsak, S., & Salmeron, M. B. (2025). The anomalous behavior of cesium in the electrical double layer: An in-situ X-ray spectroscopy study on graphene. ChemRxiv.

Wang, Y., Niu, C., & Wang, D. (2018). Metallic nanocatalysts for electrochemical CO_2 reduction in aqueous solutions. Journal of Colloid and Interface Science, 527, 95–106.

Understanding the Charge Utilization Behavior of WO3 Photoanodes

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Abstract

Environmental effects and the scarcity of fossil fuels resulted in a shift toward clean energy applications, and green hydrogen technologies represent a promising solution due to their low waste and high energy density [1]. Among different production techniques, photoelectrochemical (PEC) conversion strategies offer a sustainable pathway for hydrogen production. These PEC cells work by coupling hydrogen evolution reaction at the cathode and oxygen evolution reaction at the anode in the presence of semiconductor photoelectrodes. For efficient hydrogen production, the kinetic limitations regarding the oxygen evolution reaction in the anode must be overcome.

The aim of this study is to reveal reaction and kinetic mechanisms of tungsten trioxide (WO3) photoanodes for efficient photoelectrochemical water splitting. WO3 is generally preferred due to its stability, efficient charge carrier transport, suitable band gap, long hole diffusion and ability to offer various surface morphology [1]. Charge carrier dynamics of WO3 under illumination are studied through chronoamperometric LED measurements and linear sweep voltammetry experiments. The behavior and charge utilization properties of WO3 varies when it is exposed to different light sources or surface modifications including sulfur doping, nickel layer catalyst coating or nitrogen doping. Potential dependent changes of photocurrent not only reflect effective charge transfer, but it also shows changes in charge transfer and reaction order. Near 1.0 V vs. RHE, trapping of charge carriers at the interface dramatically impacts water oxidation kinetics. The data obtained from the potential dependent LED experiments are utilized to construct a kinetic model.

This study provides an extensive understanding of charge carrier dynamics of WO3 photoanodes under different parameters. It ultimately aims to overcome the limitations imposed by oxygen evolution reaction, the bottleneck of water splitting process.

Keywords: Photoelectrochemical water splitting, Photoanodes,

References

Zheng, G.; Jiang, S.; Zhang, F.; Yu, H.; Zhang, Y. L. Synthesis and Characterization of WO3 Photoanodes for Efficient Photoelectrochemical Water Splitting. Applied Physics A 2025, 131 (1). https://doi.org/10.1007/s00339-024-08197-w.

Metal–Organic Gel Modified g-C3N4 Photocatalysts for Enhanced Photocatalytic Degradation of Doxycycline

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Abstract

The extensive use of antibiotics in human medicine, animal husbandry, and aquaculture has led to their increasing presence in aquatic environments, raising serious environmental concerns due to their persistence and potential ecological risks. Among these contaminants, doxycycline (DC), a widely used antibiotic, is frequently detected in surface waters because of its broad-spectrum antibacterial activity and widespread application in both human and veterinary medicine (1). However, the uncontrolled release and accumulation of antibiotics in water bodies not only promotes the development of antibiotic-resistant microorganisms but also poses significant threats to aquatic ecosystems (2). Therefore, the development of efficient photocatalytic systems for the removal of such contaminants has attracted considerable attention in recent years. Metal–organic gel (MOG) structures have emerged as promising materials for catalytic applications due to the presence of accessible metal centers and their tunable chemical properties. In this study, Fe- and Ni-based MOG modified graphitic carbon nitride (CN) photocatalysts were developed for the photocatalytic degradation of doxycycline under visible light irradiation. The hybrid photocatalysts were prepared via a thermal impregnation method by incorporating Fe-MOG and Ni-MOG into CN with different loadings in order to evaluate the influence of MOG content on photocatalytic activity. Photocatalytic degradation experiments demonstrated that the incorporation of MOG structures significantly improves the removal efficiency of DC compared with pristine CN. Degradation efficiencies of CN/Fe-MOG and CN/Ni-MOG photocatalysts for doxycycline were calculated as 98% and 96% under visible light irradiation, respectively, which are 1.51 and 1.48 times higher than that of pristine CN under the same conditions. To further investigate the photocatalytic degradation behavior of the prepared catalysts, additional experiments including pH-dependent studies, radical scavenger tests, and anion effect investigations were carried out to evaluate the influence of reaction conditions and reactive species on the degradation process. Furthermore, structural and optical characterization studies were performed to examine the properties of the synthesized photocatalysts. These findings suggest that MOG-modified CN photocatalysts show promising potential for the photocatalytic removal of antibiotic contaminants from wastewater.

Keywords: metal-organic gel, doxycycline, photocatalysis, graphitic carbon nitride

References

Ji Y, Cui M, Wei J, Shi Y, Bao L, Tian Z, et al. Interfacial oxygen vacancy engineering and built-in electric field mediated Z-scheme In2O3/Ag3PO4 heterojunction for boosted photocatalytic doxycycline degradation. Chemical Engineering Journal. 2024 Jun 1;489. doi:10.1016/j.cej.2024.151216

Mou Z, Tu S, Li H, Yu P, Wu S, Wang Z, et al. Nanostructured NiCo2S4 immobilized on nickel foam as recyclable catalyst for activating peroxymonosulfate toward doxycycline degradation: Performance and mechanism. Sep Purif Technol. 2025 May 1;357. doi:10.1016/j.seppur.2024.129990

Elucidating Site-Specific Kinetics of Ammonia Decomposition over Ru/MgO Catalysts: An Ongoing Study on Ru Dispersion and Activity

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Abstract

Ammonia decomposition is increasingly recognized as a viable strategy for the on-site generation of COx-free hydrogen (Morlanés et al., 2021). Among the various catalytic systems investigated, ruthenium supported on magnesium oxide demonstrates exceptional efficacy, largely attributed to robust metal-support interactions and the inherent basicity of the support (Hu et al., 2019). Nevertheless, optimizing this catalytic system requires a comprehensive understanding of how the local coordination of Ru atoms influences overall performance. This ongoing study seeks to elucidate the complex relationship between Ru dispersion and catalytic activity by modeling the reaction rate as a composite of distinct active sites.

To systematically probe this structure-activity relationship and deliberately change Ru nanoparticle size, a series of Ru/MgO catalysts were prepared using the incipient wetness impregnation method. To achieve different degrees of Ru dispersion, the calcination temperatures of the prepared catalysts were systematically varied in the range between 300°C and 700°C, with one sample utilized without calcination. Crucially, to determine the most ideal pre-treatment parameters prior to kinetic evaluations, Temperature-Programmed Oxidation (TPO) and Reduction (TPR) analyses were systematically conducted on all samples. Following these optimized pre-treatments, performance measurements were carried out in the kinetically limited region using a custom-designed mass spectrometer specifically engineered for ammonia decomposition.

Currently, ongoing characterizations, including CO pulse chemisorption and SEM, alongside atomic modeling, are being employed to quantify the different active sites present on the catalyst surfaces. Demonstrating the viability of this approach, preliminary CO chemisorption analysis of the sample calcined at 500°C revealed a Ru dispersion of 14.88%. In the subsequent phases of this work, this comprehensive methodology will be systematically applied to all synthesized catalysts to determine the intrinsic TOF values associated with each distinct active site. Ultimately, by implementing a site-specific kinetic model, the global TOF of the catalyst will be mathematically partitioned and reconstructed as the sum of these individual TOF values, providing a deeper understanding of the catalytic surface.

Keywords: Ammonia decomposition, Ruthenium catalysts, Hydrogen Production

References

Hu, X. C., Wang, W. W., Si, R., Ma, C., & Jia, C. J. (2019). Hydrogen production via catalytic decomposition of NH3 using promoted MgO-supported ruthenium catalysts. *Science China Chemistry*, *62*(12), 1625–1633. https://doi.org/10.1007/s11426-019-9578-8

Morlanés, N., Katikaneni, S. P., Paglieri, S. N., Harale, A., Solami, B., Sarathy, S. M., & Gascon, J. (2021). A technological roadmap to the ammonia energy economy: Current state and missing technologies. *Chemical Engineering Journal*, *408*. https://doi.org/10.1016/j.cej.2020.127310

Magnetically susceptible catalyst development for inductively heated syngas production by reverse-water gas shift reaction

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Abstract

Syngas (CO+CO2+H2) is a platform chemical, which can be produced by the reaction of captured CO2 with green H2 via the reverse water-gas shift reaction (RWGS: CO2+H2=CO+H2O). Providing the required energy by inductive heating allows electrification through renewable power, and combined with the availability of green H2, significantly reduces the carbon footprint of making syngas. Compared to conventional heating methods, inductive heating significantly reduces the mass heated, and in this reaction system, only the catalytic bed is heated. Inductive heating requires a susceptor, which is essentially a ferromagnetic material. In this work, Fe3O4 is selected as the catalyst support to act as a susceptor. RWGS is thermodynamically limited at low temperatures, where methanation can compete with CO formation depending on the catalyst type. Cu-based catalysts prevent undesired CH4 formation, but should be used at <~350 °C to avoid Cu sintering. We aim to synthesize CH4-free CO on a Cu/Fe3O4 catalyst heated by inductive heating at 250-300 °C. Along these lines, we elucidate the effect of Cu loading on Fe3O4 on CO2 conversion and CO yield. Cu is impregnated on in-house synthesized Fe3O4 support using incipient-to-wetness impregnation method. The support is prepared by precipitating 2:1 molar ratio Fe+3 to Fe+2 containing solution with NaOH solution. The activity tests are conducted by packing 1 g Cu/Fe3O4 in a downflow quartz reactor at 250-350 °C, 1 bar, total inlet flow and composition of 100 Nml/min and H2/CO2/N2=5/1/2, respectively. The catalyst is pretreated under 10 Nml/min pure H2 flow at 270 °C for 2 h. Feed and product analyses are carried out on-line by a gas chromatograph (GC) customized for reproducible quantitative analysis of CO, CO2, CH4, H2 and N2. Sample collection and analysis are done with 10 min interval. Stability experiments are conducted for 72 h. In all of the results reported herein, the atomic carbon mole balance is closed with <2% deviation. Performance of the ferromagnetic catalyst is evaluated in terms of CO2 conversion and CO yield. CO2 conversion and CO yield values are the same since no side product such as methane or coke formation are observed on Cu/Fe3O4 catalyst. The positive impact of increasing Cu loading is evident by leap in CO2 conversion between Cu loadings of 7.5 wt.% and 10 wt.%. On the contrary to increase in CO2 conversion between Cu loadings of 7.5 wt.% and 10 wt.%, increasing Cu loading to 15 wt.% showed no significant increase and 7.5 wt.% Cu loading is more stable in terms of CO2 conversion compared to other loadings. Current findings are very promising and show the possibility of making syngas from CO2 and H2 via electrification and renewable power. Studies for pre- and post-characterization of the ferromagnetic support material and the catalyst are ongoing to understand the root causes of the patterns of the activity/stability experiments and refine the susceptor/catalyst design.

Keywords: CO2 utilization, synthesis gas, reverse-water gas shift reaction, induction, ferromagnetic catalyst, magnetite

Tailoring Ti3CN MXene Photocatalysts through Etching Agent and Time Control for Enhanced Hydrogen Evolution

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Abstract

MXenes are considered promising materials for photocatalytic hydrogen production due to their high electrical conductivity, layered structures, and tunable surface properties. However, rapid charge carrier recombination and structural variations arising from synthesis conditions can influence their photocatalytic performance [1]. In this study, Ti3CN MXene photocatalysts were tailored by systematically controlling the etching agent and etching duration in order to optimize their structural and surface characteristics. Different etching conditions were applied to investigate their influence on the morphology, crystallinity, and surface functional groups of the resulting MXene structures. The photocatalytic hydrogen evolution performance of the prepared materials was evaluated using triethanolamine (TEOA) as a sacrificial agent. Structural and optical properties were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–vis diffuse reflectance spectroscopy (DRS), photoluminescence spectroscopy (PL), and Fourier-transform infrared spectroscopy (FTIR). In addition, Mott–Schottky analysis, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were conducted to examine charge carrier dynamics and interfacial charge transfer properties. The results demonstrate that controlling the etching parameters significantly influences the structural characteristics and charge separation efficiency of Ti3CN MXene, resulting in enhanced photocatalytic hydrogen evolution performance. This work highlights the critical role of synthesis parameter engineering in optimizing MXene-based photocatalysts for sustainable hydrogen production.

Keywords: Green hydrogen, Ti3CN, MXene, POM, Hydrogen Evolution

References

Pugazhendhi A, Kamarudin SK, Brindhadevi K. MXenes as catalyst for sustainable hydrogen production. Renewable and Sustainable Energy Reviews 2026;226. https://doi.org/10.1016/j.rser.2025.116376.

Optimization of Catalyst Bed Configuration for Sorption-Enhanced DME Synthesis from CO2

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Abstract

Introduction: Direct hydrogenation of CO2 to dimethyl ether (DME) offers a promising route for CO2 valorization; however, the presence of H2O produced during the reverse water-gas shift (RWGS) and methanol (MeOH) dehydration reactions thermodynamically limits CO2 conversion and kinetically inhibits the acidic function [1]. Sorption-enhanced DME synthesis (SEDMES) utilizes in-situ H2O removal to overcome these limits. A critical challenge in SEDMES is the kinetic mismatch between the rapid RWGS reaction and the slower dehydration step. This study investigates spatially optimized reactor bed configurations to manage this kinetic mismatch and enhance DME productivity.

Experimental: The reaction was carried out in a high-pressure fixed-bed reactor system at 3.0 MPa and 225–265 °C. The bifunctional catalyst system consisted of a synthesized CuO-ZnO-Al2O3 (CZA) metallic function for methanol synthesis and 30 wt.% phosphotungstic acid supported on γ-Al2O3 (PTA/γ-Al2O3) for dehydration [2]. Zeolite 3A (Z3A) was employed as the H2O-selective adsorbent. Products were analyzed by two GC's in series (Shimazdzu GC-2014, GC1: TCD, He carrier gas, Porapak T column. GC2: TCD, Ar carrier gas, Carboxen 1000 column.).

Results/Discussion: Three distinct bed configurations were evaluated against a baseline Mixed-Bed: SB-1 (catalyst and adsorbent distributed equally in two beds), SB-2 (CZA in Bed 1; PTA/γ-Al2O3 + Z3A in Bed 2), and SB-3 (increased acid density in Bed 2).

The baseline Mixed-Bed configuration exhibited significant performance penalties at high gas hourly space velocities (GHSV). Increasing GHSV from 3500 to 7000 h-1 reduced CO2 conversion from 35.5% to 25.9% and DME/MeOH selectivity (SDME/MeOH) from 32.9% to 24.8% due to insufficient contact time and competitive adsorption on acid sites. The SB-1 configuration offered marginal selectivity improvements but failed to decouple the reaction steps effectively.

The Adsorbent-Shifted Split-Bed strategy (SB-2) demonstrated superior performance by isolating the H2O-sensitive dehydration step. By creating a drier environment in the second bed, SB-2 achieved an SDME/MeOH of 62.2% at 7000 h-1, more than double that of the Mixed-Bed. Although separating the CZA from the adsorbent in Bed 1 reduced CO2 conversion (18.7%), the drastic improvement in selectivity resulted in the highest DME productivity observed (Table 1). Increasing the acid site density (SB-3) provided diminishing returns, reducing productivity due to inefficient catalyst utilization.

Table 1. Comparative performance of reactor configurations (Experiment conditions: 245 °C, 3 MPa, 7000 h-1, H2/CO2/N2 = 3/1/1, regeneration time = 30 min)

Bed Configuration	Bed Diagram	X_{CO_2} (%)	Y_{DME} (%)	$S_{DME/MeOH}$ (%)	Productivity x 10^2 ($kg_{DME}\ h^{-1}\ kg_{cat}^{-1}$)
Mixed-bed		25.9	4.4	24.8	2.0
SB-1		25.8	5.6	35.3	1.9
SB-2		18.7	6.6	62.2	**2.5**
SB-3		20.2	6.8	61.6	**1.3**

Keywords: DME Synthesis, Reaction Engineering, CO2 Utilization

References

Ozden, M., Altinsoy, N. S., Avci A. K. International Journal of Hydrogen Energy **2025**, 172(151320).

Ozden, M., Altinsoy, N. S., Jalal A., Erdali A. D., Ozcan O., Akin A. N., Ozensoy E., Avci A. K. ACS Sustainable Chemistry & Engineering **2026**, in press.

CO_2 Valorization to Syngas Via Separation Aided Reverse Water Gas Shift Reaction

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Abstract

Introduction: The mitigation of anthropogenic CO2 emissions remains a critical global challenge, driving the need for efficient carbon capture and utilization technologies. Converting CO2 into synthesis gas (syngas) via the reverse water-gas shift (RWGS) reaction (CO2 + H2 ⇔ CO + H2O) offers a highly promising valorization pathway, generating a versatile feedstock for the downstream production of synthetic fuels and value-added chemicals. However, the RWGS reaction is moderately endothermic and equilibrium-limited [1]. Achieving high CO2 conversion conventionally requires elevated temperatures, which introduces severe energy penalties, accelerates catalyst deactivation, and complicates reactor design. Sorption-enhanced RWGS (SE-RWGS) presents a strategic process intensification approach to overcome these thermodynamic bottlenecks at lower, more favorable operating temperatures [2]. By integrating a water-selective adsorbent to continuously remove H2O in situ, the chemical equilibrium is shifted toward the products according to Le Chatelier's principle, thereby unlocking higher CO yields. A key engineering challenge in scaling this technology lies in effectively coupling the catalytic reaction with continuous water removal and adsorbent regeneration via pressure swing adsorption (PSA) [3]. This study maps the baseline thermodynamic boundaries of the standard RWGS reaction to establish a robust comparative foundation for integrating a separation-aided PSA process.

Experimental: Steady-state baseline reactions were carried out in a high-pressure reactor system operating at pressures of 5, 10, and 15 bar, and temperatures of 275 °C and 300 °C. A commercial CuZn/Al2O3 catalyst was employed for the initial steady-state RWGS reaction. For the SE-RWGS phase, Zeolite 3A is utilized as the H2O-selective adsorbent under PSA conditions. Reaction products were continuously analyzed using a Shimadzu gas chromatograph to quantify effluent composition and calculate conversion and yield metrics.

Results/Discussion: Initial steady-state experiments established the performance limits of the unenhanced CuZn/Al2O3 catalytic system. At 275 °C, experimental CO2 conversion was restricted to approximately 20–21% across all tested pressures. While CO yield reached a maximum of 16.56% at 1 bar, increasing the pressure to 15 bar reduced the CO yield to 15.69% and promoted unwanted methanol byproduct formation (3.31% yield). A similarly constrained trend was observed at 300 °C, where CO2 conversion capped at 19.55% at 15 bar, illustrating the complex interplay of competing reactions and inherent thermodynamic limitations. These steady-state baseline metrics emphasize the necessity for reaction intensification. Ongoing experiments are currently integrating the Zeolite 3A adsorbent into the system to perform dynamic SE-RWGS. By continuously extracting H2O from the reaction zone, this configuration is designed to break the thermodynamic barriers quantified in the baseline trials. The finalized experimental results, which are anticipated to demonstrate a significant enhancement in CO2 conversion and syngas productivity, will be presented and discussed in full.

Keywords: Sorption-Enhanced RWGS , CO2 Valorization, Process Intensification, Pressure Swing Adsorption

References

Y. A. Daza and J. N. Kuhn, “CO2 conversion by reverse water gas shift catalysis: comparison of catalysts, mechanisms and their consequences for CO2 conversion to liquid fuels,” *RSC Advances*, vol. 6, no. 55, pp. 49675–49691, May 2016, doi: https://doi.org/10.1039/C6RA05414E.

A. Desgagnés, Ion Iliuta, and M. C. Iliuta, “Sorption-enhanced intensified CO2 hydrogenation via reverse water–gas shift reaction: Kinetics and modelling,” *Chemical Engineering Journal*, vol. 494, pp. 152052–152052, May 2024, doi: https://doi.org/10.1016/j.cej.2024.152052.

M. Simo, S. Sivashanmugam, C. J. Brown, and V. Hlavacek, “Adsorption/Desorption of Water and Ethanol on 3A Zeolite in Near-Adiabatic Fixed Bed,” *Industrial & Engineering Chemistry Research*, vol. 48, no. 20, pp. 9247–9260, Sep. 2009, doi: https://doi.org/10.1021/ie900446v.

Evolution of alkali surface state during the reduction of iron-based Fischer-Tropsch catalysts

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Abstract

Fischer-Tropsch synthesis (FTS) allows for the conversion of syngas (H2 + CO) into liquid hydrocarbons and has recently gained renewed interest as a sustainable method for synthetic fuel production. Especially promising seems the variant of this process using atmosphere-captured CO2, which, after conversion to CO, may be transformed to olefins. Among FTS catalysts, iron-based materials have been extensively investigated due to their low cost, abundant natural sources, and favourable selectivity to desired products.

Important additives to FT catalysts are alkali elements, especially potassium. It enhances the stability of the catalysts[2] and increases selectivity to desired products[3]. Its impact largely depends on concentration, with both too low and too high loading leading to non-optimum catalyst performance. Thus, optimising potassium concentration is of key importance in designing FT catalysts.

In our research, we used a unique technique, developed at the Jagiellonian University – species-resolved thermal alkali desorption (SR-TAD)[4]. It allowed us to get an insight into potassium surface state (migration, desorption, segregation) at elevated temperatures. As starting materials for the investigation of iron-based catalysts, we used a series of iron oxides (Fe2O3, Fe3O4, FeO), doped each of them with potassium via incipient wetness impregnation, and conducted alkali desorption measurements. We investigated both pristine and *in situ* reduced (5% H2/Ar, 500°C, 1 h) samples, intended to represent the state of the catalysts during FTS. SR-TAD results were supported by other characterization techniques, allowing us to investigate elemental composition (bulk – X-ray fluorescence spectroscopy, and surface – X-ray photoelectron spectroscopy), short-range arrangement (Raman spectroscopy), and phase composition (powder X-ray diffraction). Additionally, X-ray absorption spectra (XAS) for potassium and iron K-edges were measured at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, providing insight into the coordination environments and oxidation states of the elements. The overall results indicate that the state of potassium depends significantly on both the promoter concentration and the iron phase composition.

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

Keywords: Fischer-Tropsch synthesis, XANES, species-resolved thermal alkali desorption (SR-TAD), NAP-XPS, iron-based catalysts

References

O. P. Ketlogetswe, M. Khasu, W. Marquart, C. Drivas, E. B. McShane, S. A. Kondrat, G. Grzybek, P. Stelmachowski, A. Kotarba, M. Claeys, N. Fischer, *ChemCatChem* **2026**, 18, e01430.

L. Krausser, V. A. Kondratenko, H. Lund, S. Bartling, E. A. Fedorova, Q. Yang, E. V. Kondratenko, *ACS Catal.* **2025**, 15, 10627–10638.

O.U. Osazuwa, K.H. Ng, *Alexandria Engineering Journal* **2025**, 127, 309–335.

A. Kotarba, G. Adamski, Z. Sojka, G. Djega-Mariadassou, *Appl. Surf. Sci.* **2000**, 161, 105-108.

Investigation of the Restructuring of the Interfacial Environment of Cu2O Photocathodes During CO2 Reduction Reaction via Potential and Optical Pulsing Strategies

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Abstract

The conversion of CO2 to fuels and chemicals using renewable energy sources via electrochemical (EC) and photoelectrochemical (PEC) CO2 reduction reaction (CO2RR) is a critical pathway toward carbon-neutral energy cycles. Cu2O photocathodes offer suitable binding energies for multicarbon product formation, and band alignment and visible light absorption properties for PEC CO2RR. However, under cathodic bias in bicarbonate electrolytes, copper oxides undergo rapid surface reconstruction, deactivation, and concurrent photocurrent decay.

Previous studies have shown that pulsed illumination can enhance PEC stability and selectivity by refreshing the surfaces during dark periods by modulating the light induced deactivation. Also, electrochemical pulsing can regulate reaction selectivity, catalyst activity, and stability by controlling surface valence states and catalyst morphology, while also modulating the adsorption–desorption dynamics of surface intermediates thereby altering the interfacial chemical environment through the regulation of mass transport processes.

In our study, the transient photocorrosion behavior of Cu2O photocathodes was systematically evaluated in various reaction conditions and environments such as the fed gas atmosphere (CO_2, N_2, and O_2 saturated electrolytes), varying external bias, electrolyte pH (adjusted via N2- CO2 gas balance), photon flux intensity, and electrolyte composition (hole and electron scavengers, NO3-). Time resolved photocurrent measurements reveal a characteristic time dependent photocurrent behavior, varying in time but in a constant structure for all conditions. Slow and fast decaying anodic transients, the change in the pulse profile, then rapid loss of photocurrent were observed sequentially. The onset of these signature changes showed dependence on the reaction conditions. Photocurrent loss of Cu2O photocathodes during CO2 RR was strongly dependent on the reaction rates of charge extraction on the interface and the self-redox mechanisms of Cu2O itself. The conditions affected the shift between these competing pathways but did not completely prevent the photocurrent loss.A particularly significant observation from the TPC measurements was that periodically switching the potential to 1.0 V vs. RHE after each illumination pulse at 0.1 V maintained stable photocurrent for up to 2000 pulses, whereas under constant bias at 0.1 V the photocurrent completely decayed after approximately 300 pulses. This observation highlights the critical role of potential modulation in stabilizing the photocurrent. Rotating Ring Disc Electrode (RRDE) measurements were performed to detect the species transported from the disc surface during the pulsed photoelectrochemical CO2 reduction. Detectable ring currents in 0.0 V- 0.4 V vs. RHE were obtained when the anodic potential pulses were applied on the disc. These signals indicate the formation of transportable species on the

disc surface in anodic pulses, suggesting the generation of reaction intermediates during CO2 reduction, and/ or dissolved copper species.

This study provides an understanding of potential and light pulsing effects in PEC systems, focusing on the temporal aspects of the PEC CO2RR processes on Cu2O photocathodes. Via modulation of the frequency time domain of light illumination and potential, we introduce to control the PEC reaction interface dynamics, the metal oxide semiconductor stability and the restructuring of the interfacial environment.

Keywords: photoelectrocatalysis, Cu2O, Cu2O stability, pulsing, potential pulsing, optical pulsing, CO2 reduction

References

Kim, C.; Weng, L.-C.; Bell, A. T. Impact of Pulsed Electrochemical Reduction of CO 2 on the Formation of C 2+ Products over Cu. ACS Catal. **2020**, 10 (21), 12403–12413. https://doi.org/10.1021/acscatal.0c02915.

Arán-Ais, R. M.; Scholten, F.; Kunze, S.; Rizo, R.; Roldan Cuenya, B. The Role of in Situ Generated Morphological Motifs and Cu(i) Species in C2+ Product Selectivity during CO2 Pulsed Electroreduction. Nat. Energy **2020**, 5 (4), 317–325. https://doi.org/10.1038/s41560-020-0594-9.

Tafazoli, S.; Şekercioğlu, A.; Zarenezhad, H.; Ataş, B.; Mohammadpour, A.; Balkan, T.; Kaya, S. Cations Responsible for Varied CO2 RR Product Selectivity at High Overpotentials over Cu2 O Nanocubes. ACS Appl. Mater. Interfaces **2025**, 17 (36), 50676–50685. https://doi.org/10.1021/acsami.5c09803.

Jännsch, Y.; Leung, J. J.; Hämmerle, M.; Magori, E.; Wiesner-Fleischer, K.; Simon, E.; Fleischer, M.; Moos, R. Pulsed Potential Electrochemical CO2 Reduction for Enhanced Stability and Catalyst Reactivation of Copper Electrodes. Electrochem. Commun. **2020**, 121, 106861. https://doi.org/10.1016/j.elecom.2020.106861.

Density Functional Theory and Experimental Analysis of Promoted Copper Catalysts for Hydrogen Production

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Abstract

The shift toward a low-carbon economy requires efficient, high-purity hydrogen sources for proton exchange membrane fuel cells (PEMFCs). Methanol steam reforming (MSR) is a highly promising method for on-site hydrogen generation due to methanol's high hydrogen capacity and relatively low reforming temperatures [1]. However, conventional copper-based catalysts are often limited by thermal sintering and the generation of trace carbon monoxide (CO), which severely poisons platinum-based fuel cell anodes [2,3]. This study investigates the reactivity and density functional theory (DFT) analysis of promoted CuO/ZrO2/Al2O3 ternary catalysts with high hydrogen productivity and suppressed CO formation. Promoted and unpromoted catalysts were synthesized using an ultrasound-assisted, one-pot sonochemical co-precipitation method. The structural properties of these materials were characterized, and their catalytic performance was evaluated under MSR conditions at 200 ℃ and 246 ℃. Furthermore, periodic density functional theory (DFT) calculations were conducted to demonstrate the reaction energetics of methanol dehydrogenation on copper facets modified by zirconium species. Experimental characterization revealed that ultrasonic irradiation during synthesis drastically reduced the CuO crystallite size from 13.4 nm to 0.8 nm, enhancing copper dispersion compared to conventional, unsonicated preparation methods. Among the tested formulations, the La-promoted catalyst with the highest lanthanum-to-aluminum ratio exhibited the highest hydrogen productivity (0.22 s-1) and demonstrated catalytic stability over 144 hours of continuous operation. DFT calculations corroborated these experimental findings, demonstrating that ZrO2 modifications on copper surfaces stabilize key carbon-containing intermediates while simultaneously weakening CO adsorption. This kinetically and thermodynamically suppresses CO evolution without compromising overall catalytic activity, providing an active and selective system for high-purity, fuel-cell-grade hydrogen production.

Keywords: Methanol steam reforming, Hydrogen production, Copper-based catalysts, Density functional theory

References

Frei MS, Mondelli C, Short MIM, Pérez-Ramírez J. Methanol as a Hydrogen Carrier: Kinetic and Thermodynamic Drivers for its CO2-Based Synthesis and Reforming over Heterogeneous Catalysts. ChemSusChem 2020;13:6330–7.

Ploner K, Watschinger M, Kheyrollahi Nezhad PD, Götsch T, Schlicker L, Köck E-M, et al. Mechanistic insights into the catalytic methanol steam reforming performance of Cu/ZrO2 catalysts by in situ and operando studies. Journal of Catalysis 2020;391:497–512.

Tang X, Wu Y, Fang Z, Dong X, Du Z, Deng B, et al. Syntheses, catalytic performances and DFT investigations: A recent review of copper-based catalysts of methanol steam reforming for hydrogen production. Energy 2024;295:131091.

Investigating Cation, Concentration, and Pulsed Potential Effects on Nitrate Reduction Using Cu2O Catalysts

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Abstract

Electrochemical nitrate reduction is a crucial process that addresses two significant global sustainability challenges: the environmental remediation of nitrate-polluted wastewater and the sustainable, decentralised synthesis of ammonia. However, a significant challenge in the advancement of sustainable energy is the complex multi-electron, multi-proton transfer process, which frequently exhibits poor selectivity and faces severe competition from the hydrogen evolution reaction (HER), resulting in low overall efficiency. To address these limitations, the electrochemical nitrate reduction reaction (NO3RR) is investigated by utilising Cu2O nanocube catalysts. The present study focuses on the influence of cation type, electrolyte concentration, and pulsed potential applications. The evaluation of the cation effect, through a comparison of 0.1M KNO3+ 0.1M KOH and 0.1M LiNO3 + 0.1M LiOH environments, revealed that potassium ions significantly enhance ammonia production in comparison to lithium ions. Specifically, the Faradaic efficiency (FE) for NH3 reached a maximum of approximately 35% at -1.0V in the presence of K+, while Li+ trials exhibited lower maximum efficiencies, generally remaining within the 20-25% range across similar potentials. The concentration effect was analysed further by varying the molarity of KOH from 0 to 0.3 M. The findings indicated a robust positive correlation between hydroxide concentration and NH3 yield; for instance, the maximum yield rate escalated from approximately 5000 μg/hμgcat at 0.1 M KOH to nearly 7000 μg/hμgcat at 0.2 M KOH. Conversely, this increase in concentration led to a suppression of the intermediate nitrite, with its FE dropping from above 0.06% to below 0.03%. In addition to investigating the continuous potential applications, the study examined the impact of pulsed potentials to optimise the reduction process. Pulsed experiments were conducted at varying durations ranging from 1 to 30 seconds, alternating between reduction and resting potentials. Samples extracted from these pulsed trials were continuously analysed utilizing the Indophenol blue method for ammonia and the Griess test for nitrite to precisely quantify the generated products. In general, the manipulation of alkali metal cations, their relative concentrations, and the systematic application of pulsed potentials have been shown to have a significant influence on the efficiency of the Cu2O catalysed nitrate reduction process.

Keywords: NO3RR, Cu2O nanocubes , ammonia production , Faradaic efficiency , alkali metal cations , pulsed potential , hydroxide concentration

References

P. H. van Langevelde, I. Katsounaros, and M. T. M. Koper, Electrocatalytic Nitrate Reduction for Sustainable Ammonia Production, Joule 5, 290 (2021).

Y. Wang, C. Wang, M. Li, Y. Yu, and B. Zhang, Nitrate electroreduction: mechanism insight, in situ characterization, performance evaluation, and challenges, Chem. Soc. Rev. 50, 6720 (2021).

Y. Wang, W. Zhou, R. Jia, Y. Yu, and B. Zhang, Unveiling the Activity Origin of a Copper-based Electrocatalyst for Selective Nitrate Reduction to Ammonia, Angewandte Chemie International Edition 59, 5350 (2020).

K. Fan, W. Xie, J. Li, Y. Sun, P. Xu, Y. Tang, Z. Li, and M. Shao, Active hydrogen boosts electrochemical nitrate reduction to ammonia, Nat Commun 13, 7958 (2022).

DFT Investigation of CO and CO_2 Hydrogenation on Defective CuO(100) for Methanol Synthesis

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Abstract

Methanol synthesis has gained increasing attention due to its growing global demand, its expanding role as an energy carrier, and its importance in carbon capture and utilization strategies [1]. Despite significant research on methanol production catalysts and techniques, it remains uncertain regarding the selectivity of the carbon source (CO or CO_2), the active catalyst phase and the methanol production mechanism on industrially used Cu/ZnO catalysts [2], [3]. In this study, the mechanisms of CO and CO_2 hydrogenation on the CuO(100) surface were investigated using density functional theory (DFT). All calculations were carried out using the VASP package [4], employing PAW potentials [5], the RPBE exchange–correlation functional [6], and the Grimme-D3 dispersion correction [6]. A Hubbard U value of 8 eV was applied to the Cu d orbitals. The reactions were assumed to proceed via a Langmuir–Hinshelwood mechanism, where all species interact in their adsorbed states. The geometries of all intermediates were first optimized, and transition states were located using the CI-NEB method and subsequently refined with the dimer approach. The reliability of the obtained structures was confirmed through vibrational frequency analyses, and zero-point energy (ZPE) corrections were included in the reported energies. For CO hydrogenation, the results indicate that the pathway involving the formate (CHO*) intermediate is likely more favorable than the formyl (COH*) route. In particular, the relatively high activation energy associated with the CO* + H* → COH* step suggests that this pathway may be kinetically less accessible. In addition, the formation of an HCO* intermediate on the CuO(100) surface, followed by a possible hydrogen transfer step (HCO* → COH*), appears to provide an alternative description of the reaction sequence. It is also noted that no distinct transition state could be identified for the CH_3O^* + H* → CH_3OH step. In the case of CO_2 hydrogenation, the mechanism was examined through the direct formation of the formate (OCHO*) intermediate. The findings suggest that CO_2 interacts relatively weakly with the surface and that the initial hydrogenation step may proceed via an Eley–Rideal-like mechanism. Among the investigated steps, the OCHO* + H → OCH_2O^* transformation exhibits a comparatively high energy barrier, indicating that it may play a key role in determining the overall reaction rate. In summary, this study contributes to a more detailed understanding of CO and CO_2 hydrogenation on CuO(100), particularly in terms of possible reaction pathways, intermediates, and kinetically relevant steps involved in methanol formation.

Keywords: Methanol Synthesis, CO and CO_2 Hydrogenation, CuO(100) Surface, Density Functional Theory (DFT)

References

A. Giuliano, C. Freda, and E. Catizzone, “Techno-economic assessment of bio-syngas production for methanol synthesis: A focus on the water–gas shift and carbon capture sections,” Bioengineering, vol. 7, no. 3, pp. 1–18, Jul. 2020.

K. C. Waugh, “Methanol Synthesis,” Catal. Today, vol. 15, no. 1, pp. 51–75, May 1992.

J. Szanyi and D. W. Goodman, “Methanol synthesis on a Cu(100) catalyst,” Catal. Letters, vol. 10, no. 5–6, pp. 383–390, Sep. 1991.

G. Kresse and J. Hafner, “Ab initio molecular dynamics for liquid metals,” Phys. Rev. B, vol. 47, no. 1, p. 558, Jan. 1993.

G. Kresse and D. Joubert, “From ultrasoft pseudopotentials to the projector augmented-wave method,” Phys. Rev. B, vol. 59, no. 3, p. 1758, Jan. 1999.

J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized Gradient Approximation Made Simple,” Phys. Rev. Lett., vol. 77, no. 18, p. 3865, Oct. 1996.

Valorization of Ladle Furnace Slag as a High-Performance and Cost-Effective Adsorbent for Methylene Blue Removal

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Abstract

Ladle Furnace Slag (LFS) is an abundant and highly alkaline byproduct generated during the secondary refining stage of steelmaking in ladle furnaces. It mainly consists of calcium-rich mineral phases such as CaO, SiO2, MgO, and Al2O3, together with minor amounts of Fe2O3, SO3, and other oxides [1]. Due to its high calcium content (up to 70 wt.% CaO) and alkaline nature (pH >12), LFS exhibits significant chemical reactivity but also poses disposal and environmental management challenges, especially considering its global production of approximately 30 million tons per year [2]. This study investigates the strategic transformation of LFS from a low-value industrial waste into a functional adsorbent for the remediation of dye-contaminated wastewater. To evaluate the impact of different modification routes, a series of LFS-based materials were synthesized using water washing (WLFS), thermal treatment (WLFS-C600), and an acid-digestion precipitation treatment (MLFS-C600). The characterization results revealed that raw and physically treated slags retain a dense, crystalline mineralogy dominated by calcium-rich phases such as calcio-olivine and grossular. These materials exhibited very low specific surface areas (1.2–2.6 m2/g) and negligible Methylene Blue (MB) removal efficiencies of less than 7% (at an initial MB concentration of 10 mg/L, using an adsorbent dosage of 0.05 g, and a solution volume of 100 mL). In contrast, the acid-modified sample, MLFS-C600, underwent significant structural changes. According to X-ray diffraction (XRD) analysis, the HCl-mediated digestion effectively leached Ca-containing crystalline mineral phases, leading to the formation of a predominantly amorphous structure with only Fe2O3 peaks remaining detectable. This chemical modification resulted in an approximately 90-fold increase in specific surface area, reaching 144.9 m2/g, which significantly enhanced the availability of surface adsorption sites. The MLFS-C600 adsorbent demonstrated a significant shift in performance, achieving a removal efficiency of 91.12% under the identical conditions of 10 mg/L initial MB concentration, 0.05 g adsorbent dosage, and a 100 mL solution volume, significantly higher than as-received waste. Kinetic modeling showed that the MB uptake follows the Pseudo-Second-Order model (R2>0.999), indicating a chemisorption-controlled mechanism. The equilibrium data were best described by the Langmuir isotherm, suggesting homogeneous monolayer coverage. MLFS-C600 achieved a maximum monolayer adsorption capacity (qmax) of 72.23 mg/g, significantly higher than other reported waste-derived adsorbents [3]. Furthermore, MLFS-C600 exhibited robust stability, retaining over 90% of its initial efficiency after six consecutive regeneration cycles. These findings highlight the potential of utilizing engineered metallurgical residues as sustainable, cost-effective catalysts and adsorbents for advanced water purification applications.

Keywords: Ladle Furnace Slag, Waste Valorization, Acid-Modified Adsorbent, Methylene Blue, Adsorption Kinetics.

References

A. Rađenović, J. Malina, and T. Sofilić, “Characterization of Ladle Furnace Slag from Carbon Steel Production as a Potential Adsorbent,” Adv. Mater. Sci. Eng., vol. 2013, no. 1, p. 198240, 2013, doi: 10.1155/2013/198240.

L. Jacob, “Ladle Furnace Slag: Synthesis, Properties, and Applications,” ChemBioEng Rev., vol. 11, no. 1, pp. 60–78, 2024, doi: 10.1002/cben.202300024.

Z. R. Çınar et al., “Adjusting the Structural Properties of Fly Ash through Systematic Modifications for Enhanced Methylene Blue Removal: An Experimental and Computational Investigation,” Langmuir, Dec. 2025, doi: 10.1021/acs.langmuir.5c05306

Understanding the Activity of NiFe Oxide Based OER Catalysts

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Abstract

Recent advancements in water electrolysis demand highly active, stable, and cost-effective electrocatalysts to minimize overpotentials in the oxygen evolution reaction (OER). Mixed transition metal-based oxides, particularly NiFe combinations, exhibit superior performance compared to their pure counterparts. This study investigates the synthesis, structural characterization, and electrocatalytic properties of mesoporous NiFe oxide thin films with varying stoichiometries, fabricated via a lyotropic liquid crystal (LLC) templating method.

The structural and morphological properties of the synthesized mesoporous films were analyzed. Raman spectroscopy revealed that at lower iron concentrations (up to a Ni/Fe ratio of 7:2), iron atoms successfully substitute into the rock-salt NiO lattice. As the iron content increases (e.g., Ni6.0/Fe3.0), the formation of spinel-structured NiFe2O4 becomes dominant, while pure iron samples present as nanocrystalline α-Fe2O3. These phase transitions were corroborated by TEM/STEM imaging and Selected Area Electron Diffraction (SAED), which confirmed a sponge-like mesoporous framework with particle sizes ranging from 5 to 10 nm across the mixed oxide samples.

Electrochemical evaluations were conducted to assess OER activity and stability. Cyclic voltammetry (CV) highlighted the compositional changes associated with the Ni(OH)2/NiOOH redox couple, demonstrating reversible oxidative and reductive peaks that indicate active structural participation during the reaction. Notably, the mesoporous electrodes exhibited dynamic OER activity across successive CV cycles. To accurately isolate the structure-activity relationship, all critical electrochemical measurements were strictly conducted in a 1.0 M Fe-free KOH electrolyte. This precaution is essential because trace amounts of iron impurities naturally present in standard electrolytes can inadvertently incorporate into the catalyst and artificially enhance the reaction, masking the true intrinsic activity. X-ray Photoelectron Spectroscopy (XPS) analysis performed before and after testing in this clean electrolyte showed stable Fe 2p and Ni 2p spectra, alongside a decrease and shift in Br 3d peak intensity post-reaction.

To obtain precise kinetic data, Rotating Disc Electrode (RDE) measurements were performed. Mesoporous NiFe oxide powders, obtained by calcining the LLC gels, were formulated into catalytic inks utilizing Vulcan XC72 to enhance electrical conductivity. These inks were drop-cast onto Glassy Carbon (GC) electrodes and capped with a diluted Sustanion ionomer to facilitate hydroxide exchange. Linear Sweep Voltammetry (LSV) scans conducted at 1600 rpm in the purified alkaline media revealed that the powder-based inks delivered superior OER activity compared to their directly coated thin-film counterparts, though they presented persistent stability challenges under continuous operation.

Furthermore, temperature-dependent RDE experiments were conducted to evaluate thermal effects on reaction kinetics. The results demonstrated a clear enhancement in OER performance, significantly reducing the overpotential required to drive the reaction by up to 0.75 V. Notably, a stable mesoporous NiFe oxide sample achieved a current density of up to 800 mA/cm² at 1.8 V vs. RHE at room

temperature. Under elevated temperatures, the catalytic activity was further amplified, surpassing a current density of 1 A/cm². In conclusion, the LLC templating strategy successfully produced tunable mesoporous NiFe oxide electrocatalysts, providing a platform to understand the fundamental mechanisms governing enhanced OER kinetics in mixed-metal systems.

Keywords: NiFe oxides, OER, water splitting, LDH

Effect of Calcination Temperature on the Structural Evolution and Adsorption Performance of Sepiolite for Methylene Blue Removal

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Abstract

Sepiolite is a naturally occurring fibrous magnesium silicate clay mineral characterized by high porosity and surface activity arising from its open channel-tunnel framework, making it a promising low-cost adsorbent for the removal of cationic dyes from aqueous solutions. Although sepiolite has been widely explored as an adsorbent upon various modifications and incorporation into composite materials, the influence of calcination temperature on its structural properties and adsorption performance has not been systematically addressed. In this study, sepiolite samples were thermally treated at temperatures between 100 and 1000 °C to systematically investigate the structural and adsorptive consequences of thermal treatment on methylene blue (MB) removal from aqueous solutions. XRF analysis revealed that the bulk composition of the raw material is dominated by SiO2 (41.50 wt%) and MgO (31.55 wt%), consistent with the sepiolite structure, while the elevated CaO content (23.68 wt%) reflects the presence of dolomite as a significant impurity phase, as confirmed by XRD. In its raw form, Sep exhibits a distinctive fibrous morphology and a high BET surface area of 195.7 m²/g. Thermal treatment up to 600 °C leads to a moderate reduction in surface area (175.1 m²/g) as channel-blocking water is progressively removed, accompanied by a slight increase in average pore width (from 88 to 112 Å), consistent with the opening of the channel system. Calcination above 600 °C, however, results in a sharp collapse of the fibrous structure. The BET surface area drops to 65.9 m²/g at 700 °C and further decreases to 22.9 m²/g at 1000 °C, while the average pore width increases sharply to ~256 Å at 700 °C, indicating the loss of the original small-mesopore channel structure and its replacement by larger voids formed through fiber sintering. TGA and FTIR analyses indicate that this collapse is associated with the dehydroxylation of hydroxyl groups occurring around 700 °C. SEM images corroborate these findings, showing progressive loss of the fibrous morphology above 700 °C. XRD reveals that the sepiolite and dolomite phases disappear above 600 °C, replaced by calcium magnesium silicate and periclase. Sep600 exhibited the highest removal efficiency among all samples, achieving approximately 91.9% MB removal (contact time: 8 days, C_0 = 10 mg L^{-1}, V = 50 mL), while as received sepiolite remained at 64% MB removal under identical conditions. Notably, Sep500 and Sep600 showed comparable performance, both surpassing the as-received material, suggesting that the adsorption improvement is primarily driven by dehydration of the channel system already achieved at 500 °C. Samples calcined at 800 °C and above exhibited a marked deterioration in adsorption performance. Kinetic analysis of Sep600 was consistent with the pseudo-second-order model. Regeneration experiments demonstrated that Sep600 retained more than 90% of its initial adsorption efficiency over the first two cycles. These findings demonstrate that controlled calcination significantly improves the adsorption performance of sepiolite and identify 600 °C as the optimal calcination temperature for effective MB removal from aqueous solutions.

Keywords: Sepiolite; Adsorption; Structural Characterization; Methylene Blue Removal; Heat Treatment

CeO_2-Modified Bimetallic Heterogeneous Catalysts for Hydrogen Generation from Formic Acid

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Abstract

Heterogeneous catalysts for hydrogen generation from formic acid (FA) play a significant role in promoting sustainable energy systems, thus the preparation of efficient and reusable catalysts is meaningful. In this study, carbon spheres with high surface area were modified with cerium dioxide (CeO_2) and subsequently decorated with Pd-Co bimetallic nanoparticles to achieve high catalytic activity and reusability in the formic acid dehydrogenation (FAD). First, high-surface-area carbon spheres were modified with cerium oxide (CeO_2) with a wet impregnation procedure and then the impregnated carbon spheres were calcined. Then CeO_2 modified carbon spheres were functionalized with amine groups via reaction with aminopropyltriethoxysilane (APTES). Finally, PdCo bimetallic nanoparticles were deposited on these modified supports via chemical reduction methods. The goal was to generate well-distributed nanoparticles with a size distribution of 1-15 nm to optimize metal–support interaction and hence the catalytic activity.

A comprehensive investigation into the catalytic behaviour of the synthesized catalysts with different percentages of CeO_2 was conducted. Among the synthesized catalysts, the catalyst containing 10 wt. % CeO_2 and 2.5 wt. % PdCo nanoparticles exhibited the highest catalytic activity, achieving almost twice the activity of CeO_2-free catalyst. Reusability tests also confirmed that this catalyst showed stable performance over several cycles with negligible activity loss. In addition, CeO_2 content has a non-linear effect on the catalytic activity of heterogeneous catalysts. The ongoing characterizations, including SEM, EDS mapping, XPS and DFT modeling, are being conducted to understand this non-linear behaviour on the catalytic activity of catalysts.

Overall, this work illustrates a novel and cost-effective approach by constructing cerium oxide and bimetallic nanoparticles on carbon supports for high-efficiency hydrogen generation from formic acid.

Keywords: Hydrogen production, formic acid, heterogeneous catalysts, metal oxides, bimetallic nanoparticles.

References

Bockris J. O. M. 1972 “A hydrogen economy”, Science, 176, 1323-1324

Cao, T., Peng, J., Pang, Y., Liu, Y., Ma, J., Deng, M., Yao, M., Liu, F. 2022 “The role of CeO2 morphology on dehydrogenation from formic acid over Pd/CeO2 catalysts”, Materials Letters, 322, 132480.

Hamaloğlu, K. Ö., Tosun, R. B., Ulu, S., Kayı, H., Kavaklı, C., Kavaklı, P. A., Kip, C., Tuncel, A. 2021 “Monodisperse-porous cerium oxide microspheres as a new support with appreciable catalytic activity for a composite catalyst in benzyl alcohol oxidation”, New Journal of Chemistry, 45, 2019-2029.

Kim, Y., Jang, G., Kim, D. H. 2023 “Hydrogen Production via Cerium-Promoted Dehydrogenation of Formic Acid Catalyzed by Carbon-Supported Palladium Nanoparticles“, ACS Applied Nano Materials, 6, 6929-6939.

Zheng, G., Nomiyama, R., Sano, H., Uchiyama, Y. 2011 “CeO2 nanoparticles deposited on carbon nanotubes“, Materials Science and Engineering ,18, 082012.

Cubic vs. Spherical Copper Nanoparticles on TiO_2: Impact on Visible-Light Photocatalysis

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Abstract

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Wastewater generated by large quantities in the dye and textile industries poses serious environmental, health, and economic challenges due to its high content of persistent organic pollutants. These pollutants are chemically stable, resist natural degradation, and therefore requires external treatment for effective removal [1]. Various physical, chemical, and biological methods have been developed to address this issue, with ongoing efforts focused on achieving efficient pollutant removal in a cost-effective manner. Among these approaches, photocatalysis has emerged as a promising solution, as it enables the degradation of harmful compounds using sunlight as the sole energy input. [2]

Photocatalysts are materials that initiate or accelerate chemical reactions under light irradiation, enabling the breakdown of organic pollutants such as dyes [3]. Titanium dioxide (TiO2) is one of the most widely used photocatalysts due to its non-toxicity, stability, and low cost. However, its activity is limited to ultraviolet (UV) light, which constitutes only around 5% of the solar spectrum [3]. To overcome this limitation, and enhance visible-light activity, various modification strategies have been explored, among which metal doping stands out as an effective approach. [4]

In this work, copper nanoparticles with controlled sizes and morphologies (spherical and cubic) were synthesized and deposited onto commercial TiO2. The photocatalytic performance of the resulting materials was systematically evaluated under visible light using the degradation of Rhodamine B (RhB) as a model reaction. In a typical experiment, a known concentration of RhB solution was mixed with an optimized amount of catalyst and irradiated in a custom-built photoreactor equipped with Hg lamps (18 W) under continuous stirring. Aliquots were collected at regular intervals, centrifuged to remove the catalyst, and analyzed using UV-Vis spectroscopy. The degradation efficiency was quantified by monitoring the decrease in the characteristic absorption peak of RhB at 554 nm.

The results demonstrate that the degradation rate strongly depends on the Cu:TiO2 ratio for all catalysts. Moreover, TiO2 modified with cubic copper nanoparticles exhibits superior photocatalytic activity compared to its spherical counterparts. Based on literature reports, cubic copper nanoparticles are typically associated with cuprous oxide (Cu2O), whereas spherical particles are more commonly linked to copper (II) oxide (CuO). Accordingly, the observed difference in photocatalytic performance may arise from variations in morphology and/or oxidation state. Ongoing detailed characterization studies aim to verify these assignments and elucidate the underlying structure-function relationships to guide further optimization of these materials.

Keywords: Photocatalysis, Wastewater treatment, Copper nanoparticle,

References

Kumari, H., Sonia, Suman et al. A Review on Photocatalysis Used For Wastewater Treatment: Dye Degradation. Water Air Soil Pollut 234, 349 (2023). https://doi.org/10.1007/s11270-023-06359-9

Khan, S., T. Noor, N. Iqbal and L. Yaqoob (2024). "Photocatalytic Dye Degradation from Textile Wastewater: A Review." ACS Omega 9(20): 21751-21767

Chen, J., X. Lv, Y. Ma, W. Xu, S. Yi and D. Fang (2025). "TiO2-Based PVDF Integrated Photocatalytic Membrane with Excellent MB Dye Degradation Performance." Langmuir 41(32): 21265-21275.

Shama Rehman, Ruh Ullah, A.M. Butt, N.D. Gohar,Strategies of making TiO2 and ZnO visible light active,Journal of Hazardous Materials,Volume 170, Issues 2–3,2009,Pages 560-569,ISSN 0304-3894, https://doi.org/10.1016/j.jhazmat.2009.05.064

Effect of Support Acid-Base Properties on Fe-Catalyzed Ammonia Decomposition to Hydrogen: A Comparative Study of Boehmite-Derived γ-Al_2O_3 and Silica-Alumina Supports

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Abstract

Ammonia is a highly promising carrier for carbon-free hydrogen, yet its catalytic decomposition requires the development of cost-effective and highly efficient catalysts. This study systematically investigates the influence of support electron-donating properties on earth-abundant, iron-based catalysts for ammonia decomposition. Three commercially available, boehmite-derived supports (PURALSB, SIRAL10, and SIRAL40) were calcined at 700 °C and impregnated with 15 wt% Fe. Comprehensive characterization of the catalysts in their fresh, reduced, and spent states revealed a definitive correlation between support basicity and catalytic activity. The optimal catalyst, Fe/PURALSB-C700-r, demonstrated superior performance, achieving 99.6% ammonia conversion at 700 °C at a high space velocity of, alongside excellent stability over at least 140 hours of continuous operation. This enhanced activity corresponded directly to the PURALSB support possessing the highest point of zero charge (7.8) and the lowest acid-to-base site ratio (1.15). Furthermore, post-reaction X-ray diffraction (XRD) analysis indicated significant structural reorganization during the reaction, with metallic iron completely transforming into Fe_2N, accompanied by a reduction in crystallite size under nitriding conditions. Ultimately, these findings establish support basicity as a critical descriptor for the efficacy of iron-based ammonia decomposition catalysts, effectively extending the structure–activity relationships previously established for precious-metal ruthenium systems to economically viable iron alternatives.

Keywords: Ammonia, Hydrogen, Heterogeneous Catalysis, Iron

References

K. Smart, Review of Recent Progress in Green Ammonia Synthesis, Johnson Matthey Technology Review 66(3) (2022) 230-244.

Y. Kojima, M. Yamaguchi, Ammonia as a hydrogen energy carrier, International Journal of Hydrogen Energy 47(54) (2022) 22832-22839.

T. Kocer, F.E.S. Oztuna, S.F. Kurtoğlu, U. Unal, A. Uzun, Graphene aerogel-supported ruthenium nanoparticles for COx-free hydrogen production from ammonia, Applied Catalysis A: General 610 (2021) 117969.

N. Zhu, F. Yang, Y. Hong, J. Liang, Hydrogen production from ammonia decomposition: Advances in Ru- and Ni-based catalysts, International Journal of Hydrogen Energy 98 (2025) 1243-1261.

Sub-bandgap Light Induced Memory Effects and Surface Reconstruction in SnO2

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Abstract

Metal oxide semiconductors have long been used to harness light for diverse applications ranging from photocatalysis, gas sensing, photovoltaics, and optoelectronics [1]. The chemical and electronic properties are altered by light and persist long after the excitation source is removed, resulting in "memory" effects. These post-light irradiation memory effects, such as persistent photoconductivity (PPC) and dark photocatalysis, have recently attracted significant attention for the development of next-generation technologies [2]. Such phenomena are strongly correlated with defects in metal oxide semiconductors. The optoelectronic and chemical properties of semiconductor metal oxides can be influenced by various surface and bulk defects, which can modify reactive surface sites, energy levels within the bandgap, and the density of charge carriers. It is important to gain insight into the dynamic control of these defect sites, particularly oxygen vacancies in metal oxides, to enhance both the catalytic and photocatalytic activity of the surface [3,4]. In this study, we investigate the role of surface defects in driving these post-light-irradiation effects in single rutile and mixed orthorhombic/rutile phase SnO2 materials excited by sub-bandgap light. Transient electrical resistance measurements, in situ XAS, ex situ XAS, Raman, and XPS measurements suggest that sub-bandgap light irradiation leads to photoionization of surface oxygen vacancies, facilitating a metastable reconstruction of the surface.

Keywords: tin oxide, sub-bandgap, defect photoionization, oxygen vacancy

References

Gao SL, Qiu LP, Zhang J, Han WP, Ramakrishna S, Long YZ. Persistent Photoconductivity of Metal Oxide Semiconductors. ACS Appl Electron Mater. 2024;6(3):1542-1561. doi:10.1021/acsaelm.3c01549

Loh JYY, Sharma G, Kherani NP, Ozin GA. Post-Illumination Photoconductivity Enables Extension of Photo-Catalysis after Sunset. Adv Energy Mater. 2021;11(41). doi:10.1002/aenm.202101566

Ren Q, He Y, Wang H, Sun Y, Dong F. Photo-Switchable Oxygen Vacancy as the Dynamic Active Site in the Photocatalytic NO Oxidation Reaction. ACS Catal. 2022;12(22):14015-14025. doi:10.1021/acscatal.2c03353

Glass D, Cortés E, Ben-Jaber S, et al. Dynamics of Photo-Induced Surface Oxygen Vacancies in Metal-Oxide Semiconductors Studied Under Ambient Conditions. Adv Sci. 2019;6(22). doi:10.1002/advs.201901841

Boron-doped Carbon Nitride as a Metal and Halide-free Catalyst for the Cycloaddition of CO2 with Epoxides under Ambient Conditions

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Abstract

The synthesis of cyclic carbonates via the coupling of CO2 and epoxides is a highly promising, atom-economical pathway that directly supports net-zero emission goals [1]. However, conducting this fixation process under ambient, solvent-free conditions demands highly efficient catalysts to replace traditional methods reliant on toxic reagents [2]. In this study, we present boron-doped polymeric carbon nitride (PCN-B) as a novel, metal- and halide-free catalyst. This engineered material features synergistic dual-active sites: doped boron atoms acting as Lewis acids and nitrogen groups within the PCN framework functioning as Lewis bases [3]. Following detailed advanced structural characterizations of the PCN and PCN-B, the catalysts were evaluated for the chemical coupling of epoxides with CO2. Among the tested variations, the catalyst with 2.5 wt% boron exhibited superior performance due to abundant oxygen vacancies and enhanced acidic site formation. Under mild conditions, it achieved an exceptional epichlorohydrin conversion of up to 97% with 99% selectivity.

Kinetic investigations revealed that the PCN-B system significantly lowers the energy barrier for the critical ring-opening step, further facilitating CO2 transformation. The cycloaddition reaction follows pseudo-first-order kinetics, demonstrating a rate constant of 0.914 h-1 at 100 °C. Furthermore, the synergistic dual-active site engineering provides remarkable catalyst stability. The PCN-B system maintained exceptional recyclability over five consecutive runs without any drop in catalytic activity, consistently delivering yields above 90% and selectivities exceeding 93%.

Keywords: Carbon nitride; Boron; Metal-free catalyst; CO2 fixation; Epoxides; Cyclic carbonate.

References

K. H. S. Eisenhardt, F. Fiorentini, W. Lindeboom and C. K. Williams, Quantifying CO2 Insertion Equilibria for Low-Pressure Propene Oxide and Carbon Dioxide Ring Opening Copolymerization Catalysts. J. Am. Chem. Soc. 146(15) (2024) 10451-10464. https://doi.org/10.1021/jacs.3c13959

B. Schäffner, F. Schäffner, S. P. Verevkin, A. Börner, Organic Carbonates as Solvents in Synthesis and Catalysis. Chem. Rev. 110(8) (2010) 4554-4581. https://doi.org/10.1021/cr900393d

H. Wang, G. Liu, X. Hao, M. Li, L. Yang, P. Sun, H. Zhang, Rich-NH2 mesoporous g-C3N4 nanosheets efficient for cycloaddition of CO2 to epoxides without solvent and co-catalyst, ChemistrySelect 6 (2021) 3712-3721. https://doi.org/10.1002/slct.202100308

Rational Synthesis of Black Phosphorus/PCN-222 Heterojunctions for Visible-Light-Driven Photoredox Catalysis

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Abstract

C-X (X≡C,N) bonds are very important in synthetic organic chemistry since they enable the construction of functional organic materials and pharmaceutically relevant molecules. Despite their importance, processes such as C-H arylation, C-C oxidative coupling and C-N reductive transformations remain challenging. In this regard, developing heterogeneous photocatalysts that combine structural stability, broad solar spectrum absorption and potent strong redox abilities is essential to advance these transformations.

Black Phosphorus (BP), the most stable allotrope of phosphorus, is a two-dimensional (2D) semiconducting material possessing broad solar-light absorption, a tunable bandgap, and high charge mobility, making it a promising photocatalyst for a variety of applications. However, its usage is limited by ambient instability and rapid electron-hole recombination, which can be improved by rational heterojunction design with another semiconducting material.

In this study, we report a rational design and synthesis of BP/PCN-222 heterojunction photocatalysts that combines the superior optical properties of BP with the structural robustness of PCN-222. To enable the in situ growth of PCN-222 on the BP surface, BP nanosheets were first functionalised with aromatic nitro molecules via n-butyllithium (n-BuLi) chemistry, wherein Li^+ ions intercalate into the layers, rendering the BP surface positively charged. Then, PCN-222 MOF frameworks were grown directly on the positively charged BP surface, ensuring tight interfacial contact. The successful growth of PCN-222 is macroscopically confirmed by the color change from green to purple. To further elucidate the structure of yielded BP/PCN-222 heterojunctions, we performed various advanced characterization techniques. By using UV-Vis diffuse reflectance spectroscopy (UV-DRS) and Tauc analysis, an optimized band gap of ~2.97 eV is calculated; meanwhile, photoluminescence (PL) spectra indicate suppressed recombination in our photocatalyst. In Raman spectroscopy, specific vibrational modes (Ag1, Ag2, B2g) of BP were observed within the MOF matrix, indicating that, even with a tiny amount of BP, we successfully constructed the desired heterojunction. In photocurrent response, stable on-off cycles are exhibited. Electrochemical Impedance Spectroscopy (EIS) showed the charge-transfer resistance, and Cyclic Voltammetry (CV) revealed the improved redox activity. SEM micrographs indicated a sponge-like, porous morphology with BP nanosheets that are uniformly distributed throughout the PCN-222 MOF. The construction of the BP-PCN-22 enables directional transfer of photogenerated carriers, facilitates precise band alignment at the interface, minimises recombination, and extends the lifetime. As a result, these features establish BP/PCN-222 as a multifunctional heterojunction catalyst that mitigates BP's instability and PCN-222's conductivity limitations. To show their photocatalytic performance, we studied the photoredox C–H arylation of benzene with p-chlorobenzenediazonium salt as a model reaction, where we will only show the preliminary results.

Keywords: Black Phosphorus, PCN-222, Heterojunction Catalyst, Visible-Light Photocatalysis

References

Altan, O., Eroğlu, Z., Küçükkeçeci, H., & Metin, Ö. (2024). Chapter 15: Black phosphorus-based photocatalysts for energy and environmental applications. Nanostructured Materials for Energy and Environmental Applications.

Das, A., Gouthaman, S., & Thomas, K. R. J. (2024). Photocatalysis as a green alternative toolkit for the construction of nitrogen-enriched heterocycles via the direct and indirect activation of alkynes/alkenes. Green Chemistry, 26, 1223–1280.

Feng, D., Gu, Z.-Y., Li, J.-R., Jiang, H.-L., Wei, Z., & Zhou, H.-C. (2012). Zirconium-Metalloporphyrin PCN-222: Mesoporous Metal-Organic Frameworks with Ultrahigh Stability as Biomimetic Catalysts. Angewandte Chemie International Edition, 51(38), 10307–10310.

Li, B., Lai, C., Zeng, G., Huang, D., Qin, L., Zhang, M., Cheng, M., Liu, X., Yi, H., Zhou, C., Huang, F., Liu, S., & Fu, Y. (2019). Black phosphorus, a rising star 2D nanomaterial in the post-graphene era: Synthesis, properties, modifications, and photocatalysis applications. Small, 15(8), 1804565.

Sulphur-Doped Graphene Quantum Dots (S-Gqds)/2-D Materıal Heterojunctıons For Selectıve Oxıdatıon of Toluene to Benzaldehyde

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Abstract

Selective oxidation of toluene to benzaldehyde is industrially important yet remains challenging due to poor conversion and over-oxidation limitations (1). It also requires precise control over reaction pathways, as partial and deep oxidation products can both possess significant value in chemical manufacturing (1,4). In this work, sulphur-doped graphene quantum dots (S-GQDs) were integrated with two-dimensional semiconducting materials to construct heterojunction photocatalysts enabling tunable oxidation behavior in toluene conversion. Graphitic carbon nitride (g-C_3N_4) and black phosphorus (BP) were employed as complementary 2D platforms due to their suitable band structures and photocatalytic properties (2,3), while S-GQDs were synthesized via a hydrothermal method and incorporated through sonication-assisted physical mixing. The yielded S-GQDs-based heterojunctions were used as photocatalysts in the oxidation of toluene under visible light irradiation. To the best of our knowledge, S-GQD-based heterojunctions have not previously been explored for photocatalytic toluene oxidation.

Photocatalytic reactions were carried out under visible-light irradiation using a 400 nm Kessil lamp in a 1:1 water/acetonitrile system with oxygen bubbling as a green oxidant for 48 hours. Comprehensive structural and optical characterizations confirmed successful heterojunction formation and enhanced interfacial interactions, consistent with improved charge separation typically observed in semiconductor heterostructures (4,5). The catalyst family exhibited composition-dependent selectivity, demonstrating controllable oxidation pathways within a single material platform. S-1-GQDs/g-C_3N_4 achieved outstanding performance with >99% toluene conversion and >99% benzaldehyde selectivity, indicating efficient partial oxidation. In contrast, BP-containing ternary heterojunctions promoted deeper oxidation, with S-2-GQDs/BP/g-C_3N_4 yielding >99% conversion and 97% benzoic acid selectivity, while S-3-GQDs/BP/g-C_3N_4 maintained high activity with 98% benzaldehyde selectivity.

These findings demonstrate that S-GQD/2D heterojunction engineering enables controllable product distribution in photocatalytic aromatic oxidation through modulation of charge transfer pathways and reactive oxygen species generation, providing a versatile strategy for directing reaction outcomes under mild and sustainable conditions.

This work was supported by TÜBİTAK (The Scientific and Technological Research Council of Türkiye) under Project No.123Z056. The authors gratefully acknowledge financial support from TÜBİTAK.

Keywords: Graphene quantum dots, Heterogeneous catalysis, photocatalysis, 2-D materials, toluene oxidation

References

Sheldon, R. A.; Arends, I.; Hanefeld, U. Green Chemistry and Catalysis. Wiley-VCH, 2007.

Wang, Y.; Wang, X.; Antonietti, M. Angew. Chem. Int. Ed. 2012, 51, 68–89. (g-C_3N_4 photocatalysis review)

Zhu, Z.; Li, L.; Wang, J. Adv. Mater. 2017, 29, 1605005. (Black phosphorus photocatalysis)

Schneider, J. et al. Chem. Rev. 2014, 114, 9919–9986. (Photocatalysis fundamentals & ROS)

Low, J.; Yu, J.; Jaroniec, M. Adv. Mater. 2017, 29, 1601694. (Heterojunction charge separation)

Discovering the Potential of Bimetallic Co–Mo MOF Hybrid Photocatalysts for Emerging Contaminant Removal

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Abstract

The increasing presence of persistent organic pollutants in aquatic environments has become a major environmental concern, requiring the development of effective and sustainable treatment technologies. In this study, a hybrid photocatalytic system based on molybdenum-doped cobalt metal–organic framework (Co–Mo–MOF) integrated with V_2C MXene was developed for the degradation of emerging contaminants. Atrazine and ciprofloxacin were selected as model pollutants to evaluate the photocatalytic performance of the synthesized materials in the presence of H_2O_2 and PMS under light irradiation. V_2C MXene was incorporated into the MOF structure to construct a hybrid material aimed at improving charge separation and catalytic performance. A series of Co–Mo–MOF/V_2C composites with different V_2C loadings were synthesized (denoted as CM-MOF/Vx, where x = 25–500 mg of V_2C). The structural, morphological, and chemical properties of the prepared materials were characterized using SEM-EDS, TEM, XRD, XPS, UV–vis DRS, and PL analyses. Photocatalytic experiments revealed that the CM-MOF/V_2C hybrid materials exhibited enhanced photocatalytic performance compared to pristine CM-MOF. Among the prepared samples, CM-MOF/V25 showed the highest photocatalytic activity, achieving a degradation efficiency of 79.1% within 120 min in the presence of H_2O_2, which was significantly higher than that of pristine CM-MOF (44.9%). These findings suggest that MOF/MXene-based hybrid materials have strong potential as efficient photocatalysts for the removal of persistent organic contaminants from water.

Keywords: Photocatalysis, Metal–organic framework, MXene, Emerging contaminants

References

Akdag Türkay, S., Görener Erdem, N., Bektaş, N., & Bilgin Simsek, E. (2025). Transition-metal-induced oxygen vacancies and redox centers in $Ce_2(WO_4)_3$: A strategy for boosted photocatalytic removal of water contaminants. Journal of Water Process Engineering, 79, 109838.

Electron Spin Resonance for Monitoring the Effect of Preparation Conditions On the Vacancies in g-C3N4 Photocatalysts

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Abstract

g-C3N4 is a material that shows semiconductor properties, and its structural properties can be easily altered. During the preparation of this material, with some interventions, structural defects can be added. Atomic gaps can affect the electron distribution of semiconductors, and the free electrons in the system change the Fermi energy level. Additionally, it is possible that it can create intermediate energy levels between the valence band and the conduction band (Ajin & Lenus, 2025; Li vd, 2023). With intermediate levels, the prohibited energy range narrows. This allows the material to absorb sunlight (especially the visible region) more efficiently. Electron Spin Resonance (ESR) is one of the most powerful techniques used to prove the existence and behavior of gaps in materials (Üner & Yarar, 2022; Xia vd, 2019).

In this study, g-C3N4 samples were synthesized using urea and melamine as starting materials at different temperatures. The effect of synthesis conditions on the free electrons and gap distribution in the samples was investigated using a Bruker Micro ESR spectrometer. Obtained distributions were correlated with the methylene blue decomposition reaction in visible light. The presentation will also include the results of ESR analyses conducted to identify radicals formed in solution during photocatalytic reactions on graphitic carbon nitride (g-C3N4) in ongoing studies. These studies aim to identify free radicals (superoxide, hydroxyl) produced, particularly in photocatalytic processes.

Keywords: ESR, g-C3N4, Vacancy

References

Ajin, V. C. A., & Lenus, A. J. (2025). Engineering the role of oxygen vacancies in photocatalysts for environmental remediation and energy conversion applications: A comprehensive review. Materials Science in Semiconductor Processing, 197, 109705. https://doi.org/10.1016/j.mssp.2025.109705

Li, X., Li, K., Ding, D., Yan, J., Wang, C., Carabineiro, S. A. C., Liu, Y., & Lv, K. (2023). Effect of oxygen vacancies on the photocatalytic activity of flower-like BiOBr microspheres towards NO oxidation and CO2 reduction. Separation and Purification Technology, 309, 123054. https://doi.org/10.1016/j.seppur.2022.123054

Üner, D., & Yarar, M. (2022). Oxygen vacancies on Pd/TiO2 are detected at low pressures by ESR spectroscopy at ambient temperatures. Turkish Journal of Chemistry, 46(4), 1081-1088. https://doi.org/10.55730/1300-0527.3416

Xia, P., Cheng, B., Jiang, J., & Tang, H. (2019). Localized π-conjugated structure and EPR investigation of g-C3N4 photocatalyst. Applied Surface Science, 487, 335-342. https://doi.org/10.1016/j.apsusc.2019.05.064