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ULUSAL KATALİZ KONFERANSI

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June 25-28, 2025 / Sivas

June 25, 2025
School of Chemical Reaction Engineering

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BOOK OF ABSTRACTS

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SCIENTIFIC PROGRAM

Time	25 June 2025	Place
16:30-17:30	Opening Ceremony	4 Eylül Kültür Merkezi
18:00-19:30	Opening cocktail	4 Eylül Kültür Merkezi
Time	26 June 2025	
08:00-08:30	Registration	
	Heterogeneous Catalysis (Chair: Prof. Dr. Deniz Üner)	Title
08:30-09:30	*Plenary Lecture-Prof. Dr. Dimitry Murzin*	Catalysis for making sustainable aviation fuel
09:30-09:50	*Berfin Güleryüz , Seda Karaboğa, Ayse Dilay Erdali, Yusuf Kocak, Rukiye Babacan Tosun, Miray Tamer, Kaan Karaca and Emrah Özensoy*	Structure Sensitivity in DeNOx Catalysis on Shape-Defined Cu_2O Nanocrystal Model Catalysts
09:50-10:10	*Asım Ahmet Dede, Ayse Dilay Erdali and Emrah Özensoy*	How Single Atoms Keep Your Catalysts Alive: Effect of Particle Size on Sulfur Poisoning and Regeneration of Rhodium Active Sites
10:10-10:30	*Musab Esmail Khalil Doutoum and Hüseyin Arbağ*	Investigation of Sulfur-resistant Nickel-based catalysts in the dry reforming reaction of biogas: Effect of lanthanum loading percentage on the activity
10:30-11:00	Coffee Break	
	Catalyst Design, Synthesis, Characterization and Theory (Chair:Prof. Dr. Ahmet Kerim Avcı)	
11:00-11:20	*Mustafa Karatok, Hio Tong Ngan, Xiwen Jia, Christopher R. O'Connor, Anibal J. Boscoboinik, Dario J. Stacchiola, Philippe Sautet and Robert J. Madix*	Atomic-Level Insights into Pd-Ag Alloy Surfaces for Selective Hydrogen Production from Formic Acid
11:30-13:15	Lunch- Restoran 346	Sponsor: Sivas Belediyesi
	Unconventional Catalytic Processes (Chair:Prof. Dr.Emrah Özensoy)	
13:20-14:20	*Plenary Lecture-Prof. Dr. Christopher Hardacre*	Plasma Catalysis for Net Zero Applications
14:20-15:30	Coffee Break	
	In Situ and Operando Characterization (Chair: Prof. Dr. Emrah Özensoy)	
15:30-16:20	*Plenary Lecture-Prof. Dr. Andreas-Neil Unterreiner*	Femtosecond absorption spectroscopy to elucidate elementary mechanisms of molecules in complex environments
16:20-16:40	*Prof. Dr. Deniz Üner and Bartu Kiray*	Operando 1H NMR monitoring of catalytic decomposition of methanol over Pt/TiO_2 in the presence of H_2O_2
16:40-18:00	*Poster Session 1*	
Time	27 June 2025	Title
08:00-08:30	Registration	
	Sustainable Catalytic Processes (Chair: Asst. Prof. Dr. Samira Kurtoğlu Öztulum)	
08:30-09:30	*Plenary Lecture- Prof. Dr. Marcus Rose*	Catalysis for the Transformation of Chemistry-Nexus of Catalyst and Process Design
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09:50-10:10	*Necdet Semih Altınsoy and Ahmet Kerim Avcı*	Synthesis gas production by intensified reverse-water gas shift reaction
10:10-10:30	Coffee Break	
	Homogenous Catalysis (Chair: Prof. Dr. Alper Tapan)	Title
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11:30-12:15	*Pleanary lecture Prof. Dr. Saim Özkar*	Metal-Ligand Interactions in Catalysis
	In Situ and Operando Characterization (Chair: Prof. Dr. Alper Tapan)	
12:15-12:35	*Kaan Karaca, Seda Karaboğa, Ayse Dilay Erdali, Miray Tamer , Yusuf Kocak, Berfin Güleryüz, Rukiye Babacan Tosun and Emrah Özensoy*	Unraveling Structure-Functionality Relationships of Shape-Defined Cu_2O Nanocrystal Model Catalysts for Methanol Decomposition
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09:10-09:50	***Pleanary lecture Assoc. Prof. Dr.Ali Can Kızılkaya***	**Structure-activity relationships for carbon dioxide utilization over bimetallic catalysts**
09:50-10:10	***Fatıma Büşra Aslan and Murat Oluş Özbek***	**CO Hydrogenation Mechanism on Oxygen-Deficient CuO (100) and CuO (111) Surfaces For Methanol Synthesis**
10:10-10:30	**Coffee Break**	
10:30-10:50	***Assoc. Prof. Dr. Yeliz Gürdal Durğun***	**Mechanistic Exploration of Cobalt Polypyridyl Catalysts for Hydrogen Evolution Using ab-initio Moelcular Dynamics and Metadynamics**
10:50-11:10	***Prof. Dr. Niyazi Alper Tapan and M. Erdem Günay***	**Exploration of operating , catalytic and material conditions towards CO in CO_2 electrolyzers: A machine learning study**
	Photocatalysis (Chair: Prof. Dr. Ayşe Bayrakçeken)	
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12:00-12:20	***Melike Kopa , Alattin Çakan and Elif Akbay***	**Upcycling Polymer Waste for Immobilized Tungstophosphoric acid-based Photocatalyst in Dye Degradation**
12:20-13:30	**Lunch**	
	Electrocatalysis (Chair: Assoc. Prof. Dr. Oluş Özbek)	**Sponsor: KUHyTech**
14:00-14:40	***Pleanary lecture Prof. Dr. Ayşe Bayrakçeken***	**Methods used to improve the activity of PEM fuel cell electrocatalysts**
14:40-15:20	*Assoc. Prof. Dr. Sarp Kaya*	**Probing the Active Phase of Electrocatalysts**
15:20-15:40	**Coffee Break**	
15:40-16:30	***Pleanary lecture Prof. Dr. Tuğrul Çetinkaya***	**Oxygen Redox Catalysis in Lithium–Air Batteries: Materials, Mechanisms, and Challenges**
16:30-16:50	***Asst. Prof. Dr. Büşra Dereli***	**Quantum Chemical Characterization of Selectivity Control in Sustainable Transformations**
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POSTER PROGRAM OF NCC10

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P2	**Rahime Aybike Koraş, Fatma Eda Özgüven, Mustafa Karatok** *Hacettepe University/* Nanotechnology and Nanomedicine	Controlled Size Distribution of Copper Nanoparticles via a One-Pot Synthesis Approach
P3	**Zeynep Ciğeroğlu, Justin S.J. Hargreaves, Mustafa Yasın Aslan** *Uşak University/Chemical Engineering*	Effect of Synthesis Method on the Catalytic Performance of Supported Cobalt–Molybdenum Nitrides in Ammonia Synthesis
P4	**Ceren Şahin, Yaren Ataseven, Mert Yekta Doğan, Sena Yaşyerli, Nail Yaşyerli Hüseyin Arbağ and H. Mehmet Taşdemir** *Gazi University/Chemical Engineering*	The Comparison of Activities of Mo, Fe and Activated Carbon Catalysts for H_2S Decomposition
P5	**Alyaa Wael Abdullah, Hasan Hayati Uçak, Yaren Ataseven, Hale Akansu and Sena Yaşyerli** *Gazi University/Chemical Engineering*	Catalytic Activities of Alumina Supported Co Catalysts in H_2S Decomposition
P6	**Hilal Dağaşar, Duygu Yılmaz, Ilknur Altın** *Karadeniz Technical University/Chemistry*	Synthesis and characterization of $ZnTiO_3$ photocatalyst for degradation of methylene blue
P7	**ParwanaKoshki, Ilknur Altın, Ilhan Altınok, Vittorio Boffa, Emin Bacaksız and Muzaffer Feyzioğlu** *Karadeniz Technical University/Chemistry*	Green synthesis of graphene sheets decorated by Fe_3O_4 magnetic nanoparticles and their photocatalytic properties toward bisphenol A

P8	**Tuna Gündoğan, Deniz Üner and Seyithan Deniz Ergül** *Middle East Technical University/ Chemical Engineering*	Surface composition determination through Monte Carlo simulations of bimetallic catalysts
P9	**Meryem Usta and Kadriye Özlem Hamaloğlu** *Hacettepe University/ Chemical Engineering*	Hydrogen generation from formic acid over carbon-supported bimetallic and reusable heterogeneous catalysts
P10	**Zafer Say** *TOBB University of Economics and Technology/ Materials Science and Nanotechnology*	Integrated Carbon Capture and Utilization Through Dry Reforming of Methane
P11	**Emine Şimal Mirza and Mustafa Karatok** *Hacettepe University/ Nanotechnology and Nanomedicine*	Selective Propane Dehydrogenation over Pt-Cu Dilute Alloy Catalysts
P12	**Aleyna Özliyen, Saliha Çetinyokuş and Meltem Doğan** *Gazi University/Chemical Engineering*	Development of Zr-Based Catalysts for Isobutene Production from Synthesis Gas
P13	**Ahmet Arda Turk, Rukiye Babacan Tosun, Berfin Güleryüz, Yusuf Kocak, Ali Dörtbudak, Ayse Dilay Erdali and Emrah Özensoy** *Bilkent University/Chemistry*	Ethanol-Mediated Tailoring of Photocatalytic NOx Oxidation and Storage on Reducible Metal Oxides: Probing Molecular Basis of Reactivity
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Silver-N-Heterocyclic Carbene Complex Catalyzed A^3-Coupling Reaction

Enes Evren[1], Belgin Önder[1], Mitat Akkoç[2], Nevin Gürbüz[1,*] & Ismail Özdemir[1]

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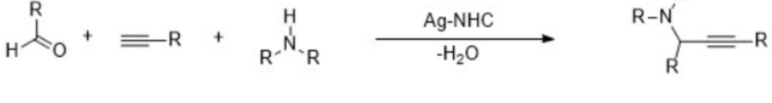
Abstract

The multicomponent reaction (MCR), also known as A^3-coupling (aldehyde–alkyne–amine coupling), is an efficient technique for producing propargyl amines [1,2]. From a sustainability perspective, the MCR is attractive because it facilitates the synthesis of complex molecules while reducing preparation time, minimizing solvent use, and limiting energy consumption [3]. The desired products are also obtained with H_2O as the only byproduct. Propargyl amines are versatile intermediates for the preparation of heterocyclic compounds such as pyrroles, pyridines, thiazoles, and oxazoles as well as other important chemical derivatives of biologically-active pharmaceutical and natural products, such as Selegiline and Rasagiline, which are used to treat symptoms in early Parkinson’s disease, as well as Ladostigil, which is used as a neuroprotective agent.

N-heterocyclic carbenes are excellent σ-donor ligands and their electronic and steric characteristics can be easily modified by changing their nitrogen-based substituents. In 2003, Li and colleagues described the first examples of Ag-catalyzed A^3-coupling [4]. Using 3 mol% of AgI, propargyl amine synthesis was achieved in H_2O at 100 ◦C under N2 atmosphere. Importantly, this salt was found to be particularly effective at transforming aliphatic aldehydes when compared to known Cu and Au catalysts. Recently some examples of NHC-Ag requiring the mildest reaction conditions for A^3-coupling are reported [5-6].

Therefore, in this study, new Ag-NHC complexes containing benzimidazole ligands that acetal and benzyl substitution were synthesized and their structures were elucidated by various spectroscopic methods. The catalytic activities of the prepared complexes in A^3-coupling reaction were investigated. (Scheme 1).



Scheme 1. Ag-NHC catalyzed A3-coupling reaction.

Acknowledgements: This work was financially supported by the Technological and Scientific Research Council of Türkiye (TÜBİTAK-124Z430).

Keywords: A^3-coupling reaction, Propargylamine, Catalyst, Ag(I)-NHC.

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Synthesis, Characterization of Nhc-Based Pd-PEPPSI Complexes and Investigation of Their Catalytic Activities in Suzuki Reaction

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Abstract

Carbenes are highly reactive intermediates and have short lifetimes. NHCs, where the carbene center is located on the N-heterocyclic ring, are organic species with a divalent carbon atom containing six electrons in its valence shell. In 1991, Arduengo synthesized the first stable and free carbene containing a bulky ligand such as adamantyl, which increased the interest in these ligands [1]. With this groundbreaking discovery, NHCs have found applications and have been used effectively in many fields, from organometallic chemistry to catalysis, from material science to biomedical applications. In addition, the versatile electronic and steric properties of NHCs, their strong bonds with metal, and their stability against air and moisture have increased the popularity of these ligands.

Palladium complexes containing bulky NHC ligands, two halides and a labile 3-chloro-pyridine were first introduced by Organ and named PEPPSI (Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation) [2]. Pd-PEPPSI complexes, which are stable to air and moisture, have been effectively used in many applications as catalysts of C-C and C-N cross-coupling reactions due to their easy preparation and ready activation under reaction conditions [3]. In addition, PEPPSI complexes are readily available and easy to handle, unlike other Pd NHC precursors [4-6].

Cross-coupling reactions are among the most important catalytic processes in fine organic synthesis, whether for industrial or academic applications. Many Pd-PEPPSI complexes have been reported in the literature to be good to excellent catalysts for various cross-coupling reactions. Therefore, in this study, new Pd-NHC-PEPPSI complexes were synthesized and their structures were elucidated by various spectroscopic methods. In addition, the catalytic activities of the prepared complexes in Suzuki reaction were investigated.

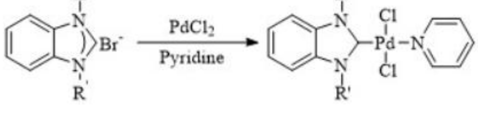

Figure 1. General synthesis of Pd-PEPPSI complexes.

Keywords: Benzimidazole, PEPPSI, N-heterosiklik carbene, Suzuki reaction

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Investigation of The Catalytic Activity of Thiazole-Derived Substrates

Enes Evren[1], Nevin Gürbüz[1,*] & Ismail Özdemir[1]

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Abstract

In recent years, the use of N-heterocyclic carbene (NHC) ligands in transition metal complexes has significantly advanced organometallic chemistry. Among these, bis-NHC-palladium(II) (bis-NHC-Pd) complexes—featuring two NHC ligands coordinated to a single Pd(II) center have drawn attention due to their strong σ-donating ability, structural tunability, and high chemical stability [1]. These properties make them superior to many classical ligand systems in terms of catalytic efficiency and durability. Bis-NHC-Pd complexes typically exhibit an NHC–PdX_2–NHC structure, which can be symmetric or asymmetric. The dual coordination of NHC ligands profoundly influences the electronic and steric properties of the metal center. Electronically, the NHC ligands enhance the electron density on palladium, facilitating key organometallic steps such as oxidative addition and reductive elimination [2]. This makes them highly effective in cross-coupling reactions. These complexes are widely applied in palladium-catalyzed C–C and C–N bond formation, especially in reactions like Suzuki–Miyaura, Heck, and Buchwald–Hartwig amination. Their electron-rich nature enables these transformations under milder conditions and with lower catalyst loadings while maintaining high efficiency [3]. Furthermore, they show excellent compatibility with sensitive substrates, including heteroaromatics, phenols, amines, and boronic acids. Compared to Pd-PEPPSI-type complexes, bis-NHC-Pd complexes often provide greater electron density at the palladium center, contributing to a more reactive and robust catalytic environment [4–6].

This study aims to evaluate the catalytic performance of newly synthesized bis-NHC-Pd complexes in C–C coupling reactions involving thiazole derivatives. By analyzing how variations in ligand structure affect reactivity, this research contributes to the development of efficient catalytic systems for the functionalization of heterocyclic compounds.

Keywords: Benzimidazole, Bis-NHC-Pd, Catalysis, Coupling, Organometallic

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Selective Propane Dehydrogenation over Pt-Cu Dilute Alloy Catalysts

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Abstract

Propylene is a key platform chemical in the petrochemical industry, serving as a primary feedstock for the large-scale production of polypropylene, propylene oxide, acrylonitrile, and isopropanol [1]. As of 2024, global demand for has reached approximately 140 million tons and is projected to rise steadily in the coming years [2]. Currently, the majority of propylene is produced via naphtha steam cracking and liquefied petroleum gas (LPG) cracking in petroleum refineries. However, these processes are associated with significant drawbacks, including high energy consumption, low propylene selectivity, and the generation of a wide range of by-products [3].

With the growing availability of natural gas and LPG, direct propane dehydrogenation (PDH) has emerged as a promising alternative route for propylene production [4]. This approach offers a more energy-efficient and selective conversion by minimizing by-product formation [5]. Commercial PDH processes such as Oleflex and Catofin, commonly rely on Pt- or Cr-based catalysts. Despite their industrial relevance, these catalysts suffer from key limitations including high operating temperatures, rapid deactivation (primarily due to coke formation), and restricted regeneration capability [6]. These challenges underscore the urgent need for the development of advanced catalytic systems that can achieve high selectivity and long-term stability at lower temperatures, thereby enhancing the overall efficiency and sustainability of propylene production [7].

Dilute bimetallic alloys offer a promising strategy to overcome the current limitations in propane dehydrogenation by leveraging the complementary roles of the metals. These systems exhibit dual-functionality, wherein the more active metal component (e.g., Pt) facilitates the initial activation of propane through C–H bond cleavage, generating reactive intermediates. These intermediates can then migrate to the less reactive metal component (e.g., Cu), where further transformation occurs with enhanced selectivity. The incorporation of a less active metal helps to moderate the binding strength of intermediates, such as propylene, reducing the likelihood of over-dehydrogenation. As a result, the desired product is more likely to desorb from the surface before undergoing complete dehydrogenation, thereby improving both selectivity and catalyst stability.

In this study, the influence of platinum dilution within copper host on catalytic performance in propane dehydrogenation was systematically examined. Pt–Cu alloys with varying Pt loadings were synthesized and dispersed onto Al_2O_3, then evaluated under non-oxidative PDH conditions. Their catalytic behavior was compared against a commercial Pt/Al_2O_3 catalyst tested under identical conditions. Among the synthesized materials, the Pt:Cu (1:10) alloy catalyst achieved propane conversion and product distribution (propylene, methane, ethylene, and ethane) closely matching that of the commercial benchmark at 450 °C. Remarkably, the catalyst with a Pt:Cu ratio of 1:40 delivered 100% propylene selectivity, completely suppressing the formation of undesired by-products. These findings demonstrate that diluting Pt atoms within a Cu matrix effectively limits over-activation of propylene and inhibits C–C bond cleavage reactions. Overall, the results underscore the potential of low Pt-content Cu-based alloys as a promising approach for achieving high selectivity in propane dehydrogenation.

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

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Controlled Size Distribution of Copper Nanoparticles via a One-Pot Synthesis Approach

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Abstract

Copper has attracted considerable attention in recent years as a catalyst due to its low cost, earth abundance and low toxicity. Cu nanoparticles are utilized in a broad spectrum of organic transformations, including azide–alkyne cycloaddition (“click chemistry”), redox reactions, cross-coupling, C–H functionalization, borylation, and oxidative coupling [1]. Beyond organic synthesis, Cu-based catalysts also find applications in environmentally and energetically critical processes, such as NO_x reduction, CO oxidation, and the water–gas shift reaction [1]. However, despite its versatility and promise, copper’s catalytic activity remains limited in many reactions due to its relatively low inherent reactivity toward organic substrates. To overcome this limitation, small amounts of more reactive metals such as Pt or Pd are often alloyed with copper. This strategy has demonstrated significant improvements in catalytic performance across a variety of reactions.

Copper nanoparticles often function as the host component in bimetallic systems to enhance the product selectivity, while the more reactive metal initiates the reaction cycle through bond cleavage. It plays a crucial role in modulating reaction pathways by weakening the adsorption strength of intermediate species, thereby suppressing undesired side reactions and improving selectivity toward target products [2]. For instance, PtCu nanoparticles have been shown to increase the selectivity toward formate by 74% in the electrochemical CO_2 reduction reaction [4].

Bimetallic alloys are inherently dynamic systems, and their surface composition can vary significantly depending on the reaction environment. Under certain conditions, active metal atoms may irreversibly diffuse into the bulk of the host metal, leading to a loss of surface-active sites and consequent catalyst deactivation. This surface-to-bulk redistribution is strongly influenced by both the alloy composition and the particle size of the host material. In particular, the stability and catalytic performance of Cu-based alloys are highly sensitive to the size of the copper nanoparticles. However, achieving controlled synthesis of copper nanoparticles remains a significant challenge due to copper’s high susceptibility to oxidation and the pronounced sensitivity of its nucleation and growth processes to subtle changes in reaction parameters. Precise control over particle size and alloy composition often requires intricate synthetic strategies involving careful adjustment of multiple variables, making the preparation of well-defined Cu-based nanostructures a technically demanding task [1], [2], [5].

In this study, we developed a straightforward, one-pot synthesis method for producing metallic Cu nanoparticles with controlled particle sizes. By systematically varying key synthetic parameters, including the choice of reducing agent, capping agent, precursor concentration, and injection rate, we achieved size tunability across a broad range, from 20 nm to 1 µm, as confirmed by SEM analysis. The use of strong reducing agents such as $NaBH_4$, faster reduction rates, or higher concentration of capping agents (e.g., PVP) led to the formation of smaller particles. In contrast, employing weaker reducing agents like ascorbic acid or slowing the reduction process, even with a strong reducing agent, resulted in the formation of larger particles. This simple approach provides a robust platform for systematically investigating the role of copper particle size in Cu-based alloy systems. The ability to synthesize various sizes of pure Cu nanoparticles using a consistent protocol allows for controlled doping of active metals, facilitating detailed studies on how Cu particle size influences catalytic performance across different reactions.

Keywords: Copper Catalysts, Nanoparticle Synthesis, One-Pot Synthesis

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Oxidative Coupling of Methane (OCM) at Low Temperature Using Nanowire-Structured La_2O_3 and $La_2O_2CO_3$ Catalysts: High Activity, Selectivity and Stability

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Abstract

The oxidative coupling of methane (OCM) is a promising route for the direct conversion of methane into high-value C_2 hydrocarbons such as ethylene. Compared to conventional multistep processes, OCM has the potential to operate in a single step with lower energy input and environmental impact. However, the industrial application of OCM remains limited due to high operating temperature requirements (>750 °C) and poor C_2 selectivity [1-3]. Therefore, the development of new catalysts that enable low-temperature activation of methane with high selectivity is of significant interest [4].

In this study, nanowire-structured La_2O_3 and $La_2O_2CO_3$ catalysts were synthesized via hydrothermal methods and systematically investigated for their performance in the low-temperature OCM reaction. The catalysts were prepared using aqueous ammonia as the precipitating agent under varying hydrothermal conditions (120–220 °C for 12–24 h), followed by calcination at 500 °C and 700 °C. The structural and morphological properties were characterized using X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, CO_2 temperature-programmed desorption (CO_2-TPD), and field-emission scanning electron microscopy (FE-SEM).

Catalytic activity was evaluated in a fixed-bed microreactor system coupled with gas chromatography (GC). As shown in Figure 1, the catalyst prepared at 200 °C for 16 h and calcined at 500 °C exhibited the highest performance, achieving 13,1 % C_2+ selectivity at 500 °C. In addition, the long-term performance and structural stability of nanowire-structured $La_2O_2CO_3$ catalysts were systematically investigated in a low-temperature OCM environment. The reaction conditions were $CH_4/O_2/N_2$ = 72/24/4, with a total 100 mL/min flow. The stability test was carried out at 500 °C over 50 hours of continuous operation and is given in Figure 2. The $La_2O_2CO_3$ nanowire catalyst demonstrated remarkable stability during the test, maintaining CH_4 conversion above 30% and C_2+ selectivity around 42% with minimal fluctuations. These findings suggest that $La_2O_2CO_3$ nanowires exhibit sufficient long-term stability and selectivity, making them strong candidates for low-temperature OCM applications.

This work is among the first to provide comprehensive insight into the long-term performance of $La_2O_2CO_3$-based nanowire catalysts in low-temperature OCM.

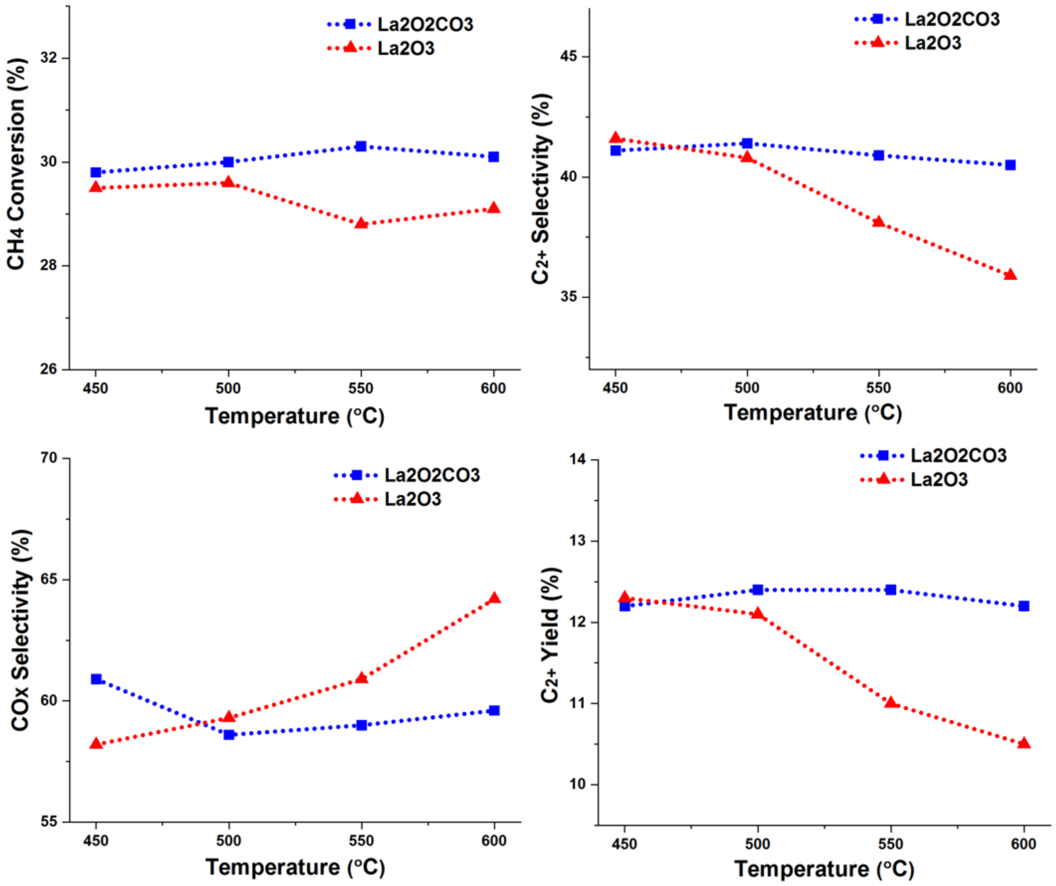

Figure 1. Catalytic activities of $La_2O_2CO_3$ and La_2O_3 nanowire catalysts.

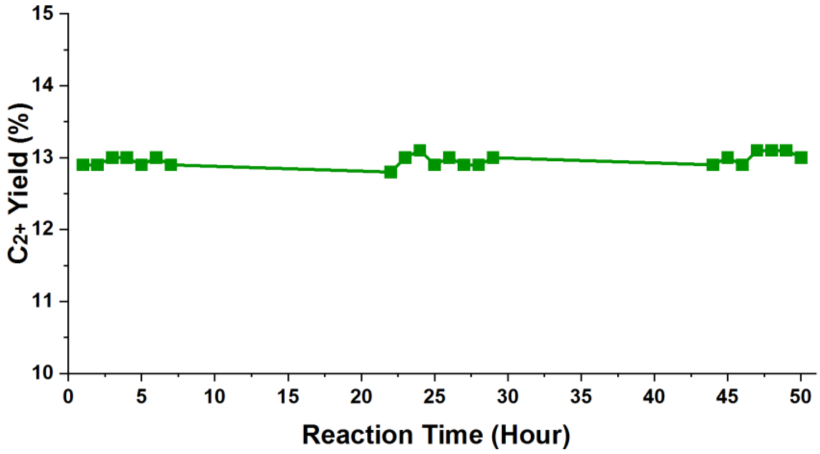

Figure 2. Stability test of $La_2O_2CO_3$ nanowire catalyst.

Keywords: Nanowire catalyst, long-term stability, low temperature OCM, hydrothermal synthesis

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Investigation of Sulfur-Resistant Nickel-Based Catalysts in the Dry Reforming Reaction of Biogas: Effect of Lanthanum Loading Percentage on the Activity

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Abstract

Dry reforming of biogas is an important process that converts biogas into syngas. This reaction helps combat climate change by using methane (CH_4) and carbon dioxide (CO_2)-two key greenhouse gases-as raw materials. The produced syngas has a near 1:1 H_2/CO ratio, making it ideal for producing valuable chemicals through Fischer-Tropsch synthesis [1]. As a strongly endothermic process, this reaction requires elevated temperatures to overcome its activation energy barrier. Consequently, a catalytic system is essential to enhance conversion and product selectivity while reducing reaction times and energy requirements. Nickel (Ni) is commonly used as an active metal due to its cost-effectiveness and efficiency in cleaving C–C, C–H, and C–O bonds [2–5]. However, Ni-based catalysts undergo deactivation due to coke deposition, which ultimately leads to reactor blockage and lower product yield. Coke deposition is attributed to two side reactions: methane cracking and the Boudouard reaction (CO disproportionation). This phenomenon occurs primarily due to the high C/H_2 ratio of the biogas [6]. To mitigate these limitations, Ni-based catalysts are enhanced through promotion with secondary metals, leveraging synergistic interactions between Ni and these promoters. The composition of biogas varies depending on its source and anaerobic digestion conditions but is predominantly composed of CO_2 and CH_4, with minor concentrations of H_2S, NH_3, and volatile organic compounds (VOCs) [7]. Even at trace (ppm) concentrations, H_2S significantly degrades catalytic activity through sulfur poisoning. Consequently, developing robust catalysts resistant to both coke deposition and sulfur-induced deactivation is imperative. While substantial research efforts have focused on improving catalyst stability against coke deposition, significantly less attention has been given to enhancing resistance to sulfur poisoning. In the present study, the influence of lanthanum (La) loading percentage on the activity and sulfur resistance of alumina-supported Ni catalysts was investigated. The alumina support material (SGA) was prepared via the sol-gel method. Ni was added at 8 wt.%, and La was incorporated into the 8Ni@SGA catalyst at 3 wt.% and 16 wt.%. The catalysts were prepared via the wet impregnation route, and catalytic activity tests were conducted in a tubular fixed-bed reactor at 750°C and 1 atm with a total flow rate of 60 mL/min and equivalent volumetric flow rates of CH_4, CO_2, and Ar under 50 ppm H_2S. When La was loaded at 3%, a reduction in the activity of the 8Ni@SGA catalyst from 77% to 62% was observed. However, TGA results showed that adding 3% La to the 8Ni@SGA catalyst reduced coke deposition from 9% to 1.2%. This reduction indicates that La has a positive effect on suppressing coke formation, likely due to its ability to increase surface basicity, as reported in previous studies [8]. CO_2 adsorption capacity increases on basic surfaces, thereby reducing coke formation via the reverse

Boudouard reaction ($C + CO_2 \rightarrow 2CO$) [9]. However, when the La loading was further increased to 16%, the activity dropped sharply to 4%. Incorporating La at a lower percentage appears to have a positive effect on reducing carbon formation, whereas higher percentages of La deactivate the catalyst.

Keywords: Dry reforming, Biogas, Syngas, Hydrogen sulfide, Sulfur poisoning, Lanthanum

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Hydrogen Generation from Formic Acid over Carbon-Supported Bimetallic and Reusable Heterogeneous Catalysts

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Abstract

It has been stated in the European Union Green Agreement that the carbon footprint should be reduced and the dependence of energy production systems on fossil fuels should be reduced and the transition to a carbon-free economy should be ensured by 2050. Therefore, clean and renewable energy sources and/or carriers are needed in order to reduce the damage to our environment. Hydrogen can be used in both internal combustion engines and fuel cells for electricity generation. The use of hydrogen in the industry is severely restricted due to limitations in the storage and transportation of hydrogen [1]. At this point, liquid organic hydrogen carriers (LOHC), which have the capacity to store and transport high amounts of molecular hydrogen, come to the fore. Formic acid (FA) is a preferred hydrogen carrier because it is liquid and stable at room temperature, and is not toxic and environmentally harmful. [2] When the literature is examined, it is seen that the performances of heterogeneous catalysts used in formic acid dehydrogenation (FAD) are still not satisfactory when compared with homogeneous catalysts. In order to use hydrogen as a fuel in today's technology, it is necessary to develop heterogeneous catalysts so that hydrogen can be obtained more economically with FAD. [1-8] In this proposed study, it was planned to design new composite heterogeneous catalysts consisting of bimetallic nanoparticles and carbon spheres for use in FAD. In the heterogeneous catalyst synthesis, carbon spheres having higher specific surface area were obtained by a two-step method. Firstly, carbon spheres were synthesized by a reaction of glucose solution in a hydrothermal reactor. Then carbon spheres were treated with KOH solution and reacted at higher temperatures under inert medium. Afterwards, the activated carbon spheres were treated with aminopropyltriethoxysilane (APTES) to functionalize with amine groups. Lastly, amine functionalized carbon spheres were decorated with bimetallic nanoparticles, i.e. Pd with non-noble metal nanoparticles (Co, Ni and Cu), by precipitation and reduction method with different percentages by weight. The bimetallic heterogeneous catalysts were characterized with Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy Mapping (EDS-mapping), Brunauer–Emmett–Teller (BET), X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) analyses. The dimensions of micron-sized carbon spheres are around 3.5 µm. The specific surface area of micron-sized activated carbon spheres is 966 m^2/g. From the XRD results, it was proved that the carbon spheres are amorphous. From the XPS results it was shown that the bimetallic heterogeneous catalysts (amine functionalization and bimetallic nanoparticle decoration) were formed successfully. After the characterizations of the bimetallic heterogeneous catalysts, their catalytic performances were examined by FAD reaction. Bimetallic heterogeneous catalyst synthesized with Pd and Co nanoparticles with a ratio of (5:1) a total metal loading of 2.5% by weight (2.5PdCo(5:1)@N@mACS) performed the highest catalytic activity when compared with other bimetallic heterogeneous catalysts. For the 2.5PdCo(5:1)@N@mACS catalyst, the TON and TOF values in the first 10 minutes were calculated as 53.7 and 322 h^{-1}, respectively. TON and TOF values were also calculated for the monometallic heterogeneous catalyst synthesized with Pd nanoparticles with a metal loading of 2.5% by weight (2.5Pd@N@mACS) and found as 40 and 240.1 h^{-1}, respectively. Reusability tests were also carried out with the catalyst showing the best activity. It was seen that after 5 uses the catalytic performance remained same for 2.5PdCo(5:1)@N@mACS, while the catalytic performance of 2.5Pd@N@mACS decreased 43,31%.

Keywords: Formic acid dehydrogenation, heterogeneous catalysis, carbon spheres, bimetallic nanoparticles

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Surface Composition Determination through Monte Carlo Simulations of Bimetallic Catalysts

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Abstract

Bimetallic catalysts have emerged as key materials in advanced energy conversion systems due to their improved catalytic performance and resistance to deactivation. Their growing use has prompted both academia and industry to focus on developing optimal catalyst compositions. Among them, Cu–Ni catalysts have shown great promise for methane steam reforming, offering a balanced combination of catalytic activity and reduced carbon deposition. In particular, copper's ability to suppress carbon buildup and nickel's high catalytic efficiency make their surface composition critical to overall performance. This study investigates the surface segregation behavior of Cu–Ni bimetallic nanoparticles using Monte Carlo simulations based on the Metropolis algorithm, implemented in MATLAB.

A cubo-octahedral nanoparticle model was constructed from crystallographic data and visualized using CrystalTool with Miller indices (100), (111). Surface energies specific to each facet were incorporated to build a Wulff construction of 110-atom system. Initially randomized atomic configurations were subjected to iterative Monte Carlo steps, allowing atomic redistribution based on changes in energy, coordination numbers, and broken bonds.

Results showed a preferential migration of copper atoms to the surface, attributed to their lower segregation energy compared to nickel. This trend aligns with classical thermodynamic predictions, validating the simulation's accuracy. The MATLAB-based simulation framework proved effective in forecasting the surface composition and provided insights into structural stability under segregation conditions.

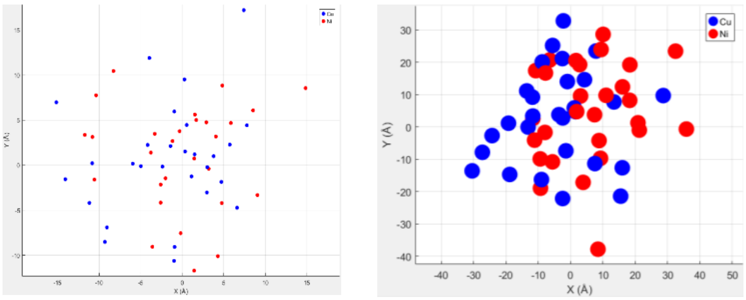

Figure 1. MATLAB Simulation Outputs (Red dots represent Nickel, Blue dots represent Copper)

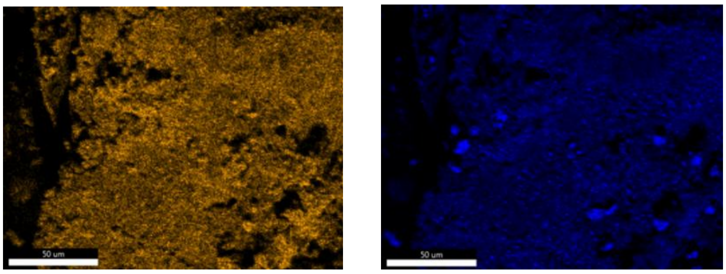

Figure 2. EDX Mapping Results to Compare with the Simulation Outputs (Yellow spots represent Nickel, Blues represent the Copper atoms)

Comparing the MATLAB outputs and mapping results given in Figures 1 and 2, respectively, it could be highlighted that the tendency of copper atoms to be located in the outer parts in a certain plane and to dominate the middle regions of the plane are validated both computationally and experimentally. In both distribution outputs, the nickel atoms seemed to be segregated homogeneously at inner surfaces most often. These findings underline the importance of predictive modeling in catalyst design. Understanding surface composition behavior in advance enables the development of more efficient and durable Cu–Ni catalysts, contributing to the optimization of hydrogen production technologies and enhancing long-term catalyst performance.

Keywords: Bimetallic catalysts, Surface Segragation, Monte Carlo Simulation, Metropolis Algorithm, Catalyst Surface Composition

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Green Synthesis of Graphene Sheets Decorated By Fe_3O_4 Magnetic Nanoparticles and Their Photocatalytic Properties Toward Bisphenol A

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Abstract

Recently, with the development of nanotechnology, the principles of green chemistry have been employed in the synthesis and application of nanomaterials [1]. In this framework, the topic of green chemistry is strongly emphasized as it could find a new way for chemical catalysts with process that reduce or eliminate the usage and production of hazardous substances. From this point of view, in the green production strategy of nanomaterials, besides the usage of non-toxic chemicals, the usage of bio-wastes as raw materials also attracts attention in reducing pollution-related problems [2]. Graphene, a one-atom thick layer composed of hexagonally arranged sp2 bonded carbon atoms, has recently attracted significant attention in the synthesis of nanocomposites due to its unique electronic properties [3-6].

In this study, graphene was prepared from harvested hazelnut wastes by mechanical exfoliation method. Glucose was used to form graphene nanosheets (WGS) from the final product graphene (WG). In the synthesis of Fe_3O_4 microspheres, a thermal-solvothermal method was used and magnetic spheres were synthesized by the reduction reaction between $FeCl_3$ and ethylene glycol (EG). Fe_3O_4 magnetic catalyst was loaded to the prepared WGS by hydrothermal method. The structure of the synthesized nanomaterials was confirmed by various characterization techniques. Photocatalytic removal of bisphenol a (BPA) pollutant in water was carried out under visible light using magnetic WGSs. The results showed that waste-derived magnetic WGSs were highly effective in degrading BPA and could be used as a promising material especially in large-scale studies.

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Keywords: Waste derived graphene; Photocatalysis; Fe_3O_4; Bisphenol a

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Synthesis and Characterization of $ZnTiO_3$ Photocatalyst for Degradation of Methylene Blue

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Abstract

In the past few decades, the application of heterogeneous photocatalysis has become one of the promising techniques for the removal of organic dye pollutants. The production and characterization of nanostructures has attracted great attention in recent years [1,2]. ZnO and TiO_2, which are wide bandgap semiconductors, are of great interest for the application of photodegradation in either bare or composite form [3]. Preparation of ZnO-TiO_2 system can result in the formation of $ZnTiO_3$ perovskite structure, Zn_2TiO_4 spinel structure and $Zn_2Ti_3O_3$ defect spinel [4]. In particular, $ZnTiO_3$ (ZTO) is one of the perovskite-type materials that can be practically used for photocatalytic degradation of pollutants with high performance [5,6].

In this study, $ZnTiO_3$ catalyst was synthesized from the mixture of tetrabutyl titanate and zinc acetate as precursors and ethanol as dissolvent. In addition, benzene-1,3,5-tricarboxylic acid (Trimesic acid) as a new chelator was used in the sol–gel approach. Thus, precalculated amount of zinc acetate and tetrabutyl titanat ($Ti(C_4H_9O)_4$) was mixed with Trimesic acid solution. Benzene -1,3,5-tricarboxylic acid initiates the polymerization reaction by its three functional groups, which permits the precalculated amount of Zn and Ti to be compatible with the eventual material (zinc titanate). The photocatalytic degradation of methylene blue (MB) under visible light irradiation was investigated in presence of $ZnTiO_3$ as an effective photocatalyst. The photocatalytic activity of MB was also evaluated in the presence of different radical sources such as potassium peroxymonosulfate and hydrogen peroxide under the same experimental conditions.

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Keywords: $ZnTiO_3$; Methylene blue; visible light driven photocatalysis

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Catalytic Activities of Alumina Supported Co Catalysts in H_2S Decomposition

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Abstract

Hydrogen is a sustainable energy carrier with a variety of applications from fuel cells to commercial industrial processes. Today, hydrogen production is mostly carried out using fossil fuels, resulting in large amounts of COx emissions. Hydrogen sulfide, on the other hand, is a promising feedstock for hydrogen production. Hydrogen production from hydrogen sulfide can be accomplished by a one-step thermal and catalytic decomposition reaction (R.1). By this reaction, both high purity carbon-free hydrogen and elemental sulfur production and disposal of toxic H_2S gas can be achieved simultaneously. However, the reaction is highly endothermic and thermodynamically limited. To achieve high conversion of H_2S at relatively lower temperatures, the improvement of low cost, active and stable catalyst is a challenge problem [1-5].

$$H_2S(g) \leftrightarrow H_2(g) + 1/2\ S_2(g) \quad (R.1)$$

In this study, 10 wt. % by Co-containing catalysts were prepared using alumina support materials synthesized by different routes and their catalytic activities in hydrogen production by H_2S decomposition reaction were investigated. For this purpose, alumina support materials were prepared by hydrothermal (H-Al_2O_3) and complexation (C-Al_2O_3) routes and Co metal was added to the support structure by wet impregnation method. Commercial alumina (T-Al_2O_3) was also used in comparison with the synthesized alumina in this study. Catalytic activity tests of Co-containing catalysts were carried out using 1% H_2S-containing (with N_2 balance) feed gas mixture with a total volumetric flow rate of 100 mL/min at 800°C and 1 atm. H_2S conversion values obtained with the catalysts were calculated using the H_2 concentration at the reactor outlet.

As a result, Co@C-Al_2O_3 and Co@H-Al_2O_3 catalysts exhibited higher catalytic activity than the commercial alumina supported catalyst (Co@T-Al_2O_3). The catalytic activity tests results showed 22%, 26% and 27% H_2S conversions over Co@T-Al_2O_3, Co@H-Al_2O_3 and Co@C-Al_2O_3 catalysts, respectively. All these catalysts exhibited stable activity for one hour of reaction period. Moreover, condensed elemental sulfur accumulation was observed at the reactor outlet during activity tests for all catalysts. Conversions obtained with Co@H-Al_2O_3 and Co@C-Al_2O_3 catalysts were close to the thermodynamic equilibrium H_2S conversion (800°C, 1% H_2S, 28%). Characterization studies on the fresh and spent materials are ongoing to explain the relationship between catalyst properties and catalytic performance.

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Keywords: Co, H_2S, COx-free H_2.

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The Comparison of Activities of Mo, Fe and Activated Carbon Catalysts for H_2S Decomposition

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Abstract

The growing global demand for sustainable and environmentally friendly energy solutions has significantly accelerated research into alternative hydrogen production methods [1]. In this context, the decomposition of hydrogen sulfide (H_2S) has emerged as a promising approach, enabling hydrogen generation and facilitating the detoxification of a highly hazardous byproduct. Abundantly present in natural gas and crude oil reserves, H_2S poses severe environmental and industrial risks due to its highly toxic and corrosive nature [2]. The decomposition of H_2S into hydrogen and elemental sulfur is an endothermic and non-spontaneous process, which becomes thermodynamically feasible only at elevated temperatures [3]. Therefore, achieving high conversion rates requires using thermally stable, selective, and catalytically active materials. This process is good as a pathway for COx-free hydrogen production and represents a viable alternative that aligns with the carbon-neutral energy vision. This study synthesized activated carbon (AC) from waste sawdust using a chemical activation method with phosphoric acid (H_3PO_4). In order to form more graphitization in activated carbon, the carbonization step was carried out at 900 °C for 120 minutes. Subsequently, monometallic catalysts were prepared by wet impregnating the AC with 10 wt% iron (10Fe@AC) and molybdenum (10Mo@AC). XRD analyses were performed to investigate the crystal structures of the synthesized catalysts. A catalytic activity test of the catalysts was conducted in a conventional continuous-flow packed-bed reactor system. A gas mixture containing 1% H_2S (balanced with high-purity N_2) with a 100 mL/min flow rate was used as the feed gas [4]. At the reaction temperature of 800 °C, average H_2S conversion rates of 27%, 26%, and 28% were obtained for AC, 10Fe@AC, and 10Mo@AC, respectively. Considering the theoretical thermodynamic equilibrium conversion at this temperature is approximately 28%, the catalysts demonstrated conversions very close to the equilibrium limit [4]. These results reveal that Fe and Mo catalysts supported on biomass-derived activated carbon offer a sustainable and cost-effective alternative for COx-free hydrogen production through H_2S decomposition. The near-equilibrium performance of the synthesized catalysts confirms their effectiveness at high temperatures and underscores their potential for clean hydrogen generation and the remediation of hazardous gases.
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Keywords: Activated Carbon, H_2S Decomposition, Hydrogen, Fe, Mo

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Effect of Synthesis Method on the Catalytic Performance of Supported Cobalt–Molybdenum Nitrides in Ammonia Synthesis

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Abstract

Ammonia is predominantly produced on an industrial scale via the Haber–Bosch process, which requires high temperatures (>400 °C) and high pressures (150–200 atm) [1,2]. These harsh operating conditions lead to significant energy consumption and increased production costs [3-6]. In recent years, ternary molybdenum nitrides have attracted considerable attention due to their promising catalytic activity for ammonia synthesis [7,8].

In this study, both bulk Co_3Mo_3N and SiO_2-supported CoMo catalysts were synthesized and evaluated for their catalytic performance in ammonia synthesis. The 5 wt% $CoMo/SiO_2$ catalysts were prepared using two different methods: wet impregnation and incipient wetness impregnation. The synthesized catalysts were preliminarily characterized using X-ray diffraction (XRD) and elemental analysis. The XRD pattern of the oxide phase of the $CoMo/SiO_2$ catalyst prepared via the wet impregnation method (Figure 1) revealed the presence of $CoMoO_4$ crystallites on the support surface, along with some impurities. In contrast, the catalyst synthesized via the incipient wetness impregnation method showed an amorphous structure in its XRD pattern. Ammonia synthesis tests were carried out at 400 °C and 1 atm, using a H_2:N_2 gas mixture with a 3:1 ratio. The initial results showed that the catalyst prepared by the wet impregnation method exhibited measurable activity, with an ammonia synthesis rate of 387 µmol NH_3 $g_a$ctive-site-1 h-1. In comparison, the catalyst prepared by incipient wetness impregnation was inactive under the same conditions. These findings suggest that the choice of synthesis method has a significant impact, in terms of formation of desired nanoparticles, on the catalytic performance of $CoMo/SiO_2$ catalysts in ammonia synthesis.

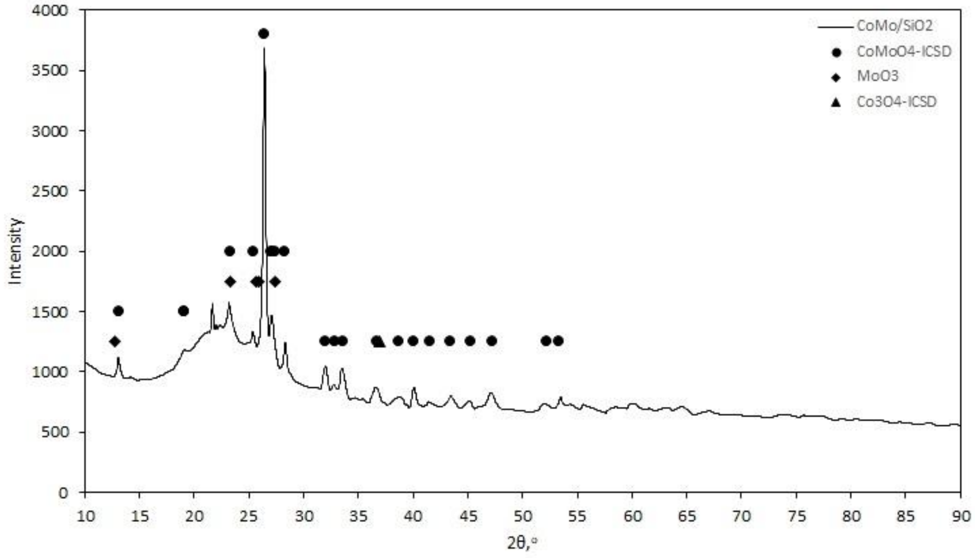

Figure 1. XRD diffractogram of oxide phase CoMo/SiO_2 catalyst

Keywords: Nitrides, Ammonia Synthesis, Catalyst Synthesis

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Integrated Carbon Capture and Utilization Through Dry Reforming of Methane

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Abstract

Integrated CO_2 capture and utilization (ICCU) provides a direct pathway to carbon-neutral fuels and chemicals by coupling CO_2 adsorption with catalytic conversion. Within this scheme, dry reforming of methane (DRM) offers a thermodynamically favorable route that converts CO_2 and CH_4 simultaneously into syngas ($H_2/CO \approx 1$), the ideal feedstock for downstream processes such as Fischer–Tropsch synthesis [1,2]. Yet even highly active rhodium (Rh) catalysts can deactivate under severe DRM conditions because of carbon deposition and particle sintering.

Here, a series of Rh catalysts were designed to investigate the effect of promoters (CeOx, FeOx) 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 CO_2 activation [3,4].

DRM performance tests were conducted on Rh-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 CO_2 adsorbent, to produce dual-functional materials (DFMs) for an integrated CO_2 capture and dry reforming of methane (ICC-DRM) process. The adsorption–desorption behavior of CaO was investigated by temperature-programmed desorption (CO_2-TPD), providing insight into its capture capacity and regeneration potential. After initial screening of CO_2 adsorption and CH_4 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. [1-12]

Keywords: ICC-DRM

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Transition Metal-Functionalized Boron Carbon Nitride Catalysts for Hydrogen Evolution through Borohydride Methanolysis

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Abstract

Fossil fuels, including coal, oil and natural gas, are non-renewable energy sources widely utilized in industrial production and daily life. However, excessive exploitation of these resources is depleting their reserves, making it crucial to identify environmentally friendly alternative energy materials. These alternatives are essential to address the energy crisis and mitigate environmental pollution. In this context, hydrogen emerges as a highly promising energy carrier, offering numerous advantages such as non-toxicity, exceptional energy density, safety, durability and ease of control. Therefore, in the quest to revolutionize clean energy solutions, the catalytic methanolysis of sodium borohydride ($NaBH_4$) has gained significant attention as a promising method for hydrogen production. This study takes a bold step forward by exploring the innovative fabrication and catalytic performance of transition metal-functionalized boron carbon nitride (BCN) composites, aiming to unlock their full potential in enhancing hydrogen generation from $NaBH_4$ methanolysis. By incorporating metals such as cobalt (Co), chromium (Cr), copper (Cu) and nickel (Ni) into the BCN framework, this research delves into the synergistic effects of these advanced materials to dramatically boost hydrogen production rates. With the Ni@BCN catalyst achieving an outstanding hydrogen generation rate (HGR) of 40557 $mL\cdot min^{-1}\cdot g^{-1}$, it outperformed pristine BCN by four times (9225 $mL\cdot min^{-1}\cdot g^{-1}$) and significantly surpassed Co@BCN (11476 $mL\cdot min^{-1}\cdot g^{-1}$) and Cr@BCN (16044 $mL\cdot min^{-1}\cdot g^{-1}$), highlighting its exceptional catalytic efficiency in enhancing hydrogen production. In the reaction mechanism, the B sites in the BCN framework act as Lewis acid centers, aiding $NaBH_4$ cleavage, while Ni sites function as electron sinks, stabilizing H- ions and enhancing hydrogen production. The Ni@BCN catalyst exhibited a low activation energy of 16.19 kJ/mol and consistently generated 390 mL of H_2 over five cycles, demonstrating excellent stability and reusability.

Keywords: Boron Carbon Nitride, Transition Metal Functionalization, Borohydride Hydrolysis, Hydrogen Generation, Hydrolysis Kinetics

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Ammonia Synthesis through a Pulse Feeding Strategy Reveals Ammonia Desorption as the Major Bottleneck in the Reaction

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Abstract

Sustainable ammonia production represents a significant challenge for the 21st century, primarily because the Haber-Bosch process consumes substantial amounts of energy and resources, contributing to global pollution [1,2]. One of the proposed solutions to this issue is the implementation of an unsteady-state feeding strategy for the reactants to overcome H_2 poisoning effect in the presence of Ru-based ammonia synthesis catalysts [3-5]. This approach can enhance the instantaneous ammonia synthesis rate on the catalyst surface, thereby improving the overall reaction efficiency. From a thermodynamic point of view, although offers the potential to achieve higher product yields per pass and to eliminate several cost factors, such as those associated with gas compression, the probability of condensation of ammonia on the pores/surface of the catalyst and inside/outlet of the reactor should not be ignored due to the thermophysical properties of ammonia.

In this study, ammonia synthesis reaction over 1 wt% Ru/SBA-15 catalyst was carried out by applying steady and unsteady state feeding strategies. 1 wt % Ru/SBA-15 catalyst was prepared via incipient wetness method. The characterization studies of the Ru/SBA-15 catalyst showed the presence of Ru nanoparticles both on the surface and within the pores of the SBA-15 support. The steady-state experiments demonstrated consistent ammonia production and stable NH_3 signal response. In contrast, transient-state experiments indicated that ammonia desorption from the catalyst surface and reactor can represent a significant bottleneck for ammonia synthesis under mild operating conditions due to the thermophysical properties of ammonia.

Keywords: Ammonia Synthesis, Ru, Unsteady State Feeding

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Quantum Chemical Characterization of Selectivity Control in Sustainable Transformations

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Abstract

Improving catalytic selectivity is a long-standing theme for chemical synthesis. The key to attaining the desired chemo-, site- and/or stereoselectivity lies in the use of the appropriate catalyst or ligand. In this context, designing and developing new catalyst platforms for selective reactions can lead to selective access to one of two isomers or one of several possible products that the reaction can produce. To showcase the concepts of the strategies for selective reactions, I will focus on two different reactions taking advantage of the structural and electronic modularity of molecular complexes involved in sustainable transformations. As catalysts, iron-based complexes are appealing as iron is earth-abundant and exhibit versatile chemical reactivity. Iron-based systems remain of special interest because they offer unique opportunities for tuning of the catalyst spin state, overall charge, and oxidation state either of the metal or the ligand over a broad range of accessible redox potentials. Along these lines, I will focus on the selective aqueous electro-reduction of CO_2 to CO by porphyrin and phthalocyanine complexes of iron and cobalt metals. The rational functionalization of metal-porphyrins made it possible to reduce CO_2 to the prescribed composition of CO-H_2 mixture in water, but the activity can be very low. Thus, anchoring functionalized Fe and Co porphyrin and phthalocyanine molecular catalysts on support with high surface area is promising in the field of electrochemical CO_2 conversion. To this end, I will present deeper mechanistic studies that can availably accelerate the rational design of the selective and stable metal-porphyrin and metal-phthalocyanine electrocatalysts with specific focus on Fe and Co metals.

Metallaphotoredox catalysis, i.e. metal catalysis merged with photoredox catalysis, is a new and rapidly growing research area. By using metallaphotoredox catalysis, it is possible to access nucleophilic organometallic reagents. Nickel photoredox allylation of aldehydes with allylacetates is a promising class of photocatalyst. In line with that, I will present an enantioselective photocatalytic reaction where steric factors govern the product selectivity with a summary for the recipe of selection of geometric and electronic descriptors for accurate enantioselectivity prediction in asymmetric catalysis.

Keywords: DFT, electrocatalysis, photocatalysis, transition-metal complexes, selectivity control

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Energy Production from Cheese Whey Using Boron-Doped Graphene Oxide Catalyst in Plant-Based Microbial Fuel Cells

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Abstract

The depletion of fossil fuel reserves and their increasingly detrimental environmental impacts have intensified the global search for sustainable and eco-friendly energy alternatives. Among these, plant-based microbial fuel cells (P-MFCs) have emerged as a promising and innovative technology for green energy production[1]. These systems harness the metabolic processes of microorganisms, utilizing plant root exudates and organic waste [2-4] such as wastewater as fuel to generate electricity [5,6]. The integration of plant-derived systems in microbial fuel cells not only contributes to energy recovery but also promotes simultaneous wastewater treatment, offering a dual-function platform for environmental remediation and clean energy.

In this study, we investigated the performance of P-MFC enhanced with graphene-based electrocatalysts, including pure graphene and boron-doped graphene materials synthesized through electrochemical exfoliation and ultrasonic-assisted techniques. The influence of cheese whey, a high-organic-load wastewater, on the efficiency of the system was also assessed in terms of both energy output and wastewater purification capabilities. Boron-doped graphene catalysts were synthesized at varying temperatures and characterized using Raman spectroscopy and inductively coupled plasma optical emission spectrometry (ICP-OES) to determine their structural and elemental properties. Furthermore, cyclic voltammetry was employed to evaluate the electrochemical activity of the catalysts.

To assess the overall system performance, polarization and power density curves were generated under whey supplementation for nine different P-MFC configurations, tracking changes from plant maturation stages to the end of the water treatment process. As can be seen in Fig. 1, cheese whey supplementation led to a significant enhancement in power output across all systems, indicating its strong effect in boosting microbial activity and electron transfer. In the 201 ppm boron-doped graphene (BGO-5) electrocatalyst loaded anode+cathode system, the maximum power density increased from 0.62 mW/m² to 1.47 mW/m² following substrate addition. In fact among the catalysts, BGO-5 demonstrated the highest overall performance, especially in the anode+cathode loaded configuration. On the other hand, 651 ppm boron-doped catalyst (BGO-55) showed lower power output compared to BGO-5, which is likely due to the negative effect of excessive boron content on oxygen reduction reaction at the cathode side [7].

In addition to the above findings, complementary analyses, including total dissolved solids (TDS) and pH measurements were also performed to monitor water quality and treatment effectiveness throughout

the polarization experiments. We believe that this work provides valuable insights into the effect of advanced electrocatalysts on bioelectrochemical systems.

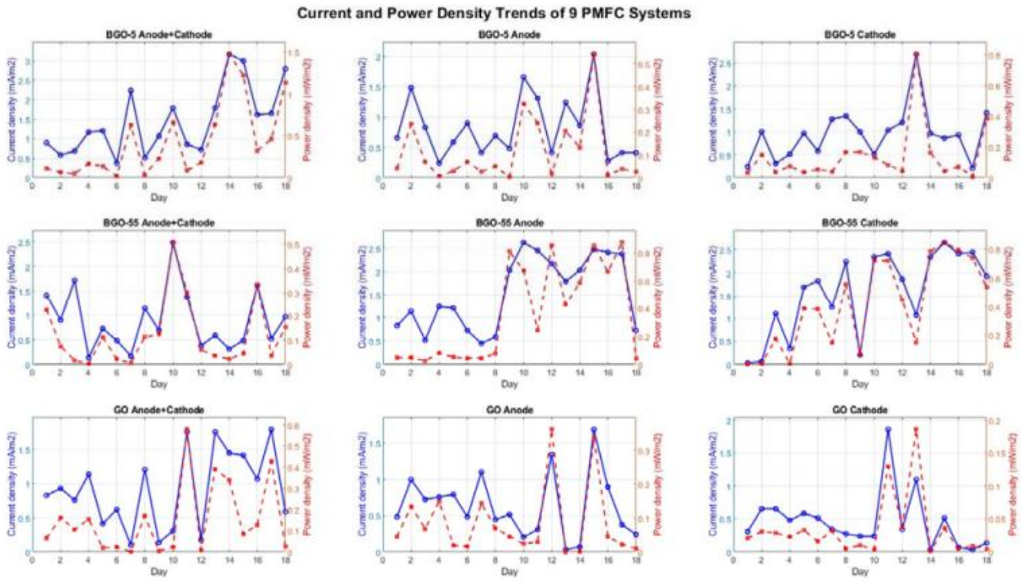

Fig. 1 Current and power density graphs of 9 PMFC systems.

Keywords: Boron, graphene, plant, fuel cell, cheese whey

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Methods Used to Improve the Activity of PEM Fuel Cell Electrocatalysts

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Abstract

Hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) occur at the anode and cathode electrodes of proton exchange membrane fuel cells (PEMFCs). Most of the studies are devoted to increase the activity of the electrocatalysts to improve sluggish kinetics of ORR by using mostly supported electrocatalysts [1]. Carbon is an important support material, for hosting Pt nanoparticles as PEMFC electrocatalyst, due to its outstanding properties including high surface area, high electrical conductivity, low cost and good metal-support interactions [2]. Different types of carbon materials including activated carbon, carbon nanotube, carbon aerogel, graphene, graphene aerogel are used which have different structural properties, surface functional groups and so different metal-support interactions [2]. Several routes are followed in order to increase the activity of these supported electrocatalysts such as different catalyst synthesis methods [3], different carbon supports, treatment of carbon supports or electrocatalysts via heteroatom doping [4] or thermal treatment [5]. The goal of this study is to give a brief summary of our studies about the routes followed to increase the activity of PEMFC electrocatalysts. Supercritical carbon dioxide deposition and microwave irradiation methods will be summarized for supported electrocatalyst synthesis. Heteroatom doping can be achieved by using different routes: a) nitrogen doping carried out during the synthesis of carbon-based material b) carbon-based material treatment with nitrogen-containing chemicals c) electrocatalyst treatment with nitrogen doping. Effect of heteroatom doping level and also doping type on the properties of the carbon supports and the electrocatalysts will be summarized. One of the alternatives to improve the activity of the electrocatalyst is thermal treatment [6]. A brief summary also will be given in order to highlight the effect of electrocatalyst thermal treatment.

Keywords: PEM fuel cell, carbon, heteroatom doping, thermal treatment

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Probing the Active Phase of Electrocatalysts

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Abstract

Probing the active phase of electrocatalysts is crucial for unraveling the structure–activity relationships that dictate their performance and for enabling the rational design of more efficient and robust electrocatalytic systems. Even noble metals such as those from the platinum group are susceptible to structural and chemical transformations under electrochemical operating conditions, particularly at moderate to high current densities. Among the suite of operando characterization techniques, electrochemical Raman spectroscopy (EC-RS) stands out as a powerful tool for monitoring both the chemical state of electrocatalysts and the evolution of surface-bound intermediates in real time.

In this talk, the application of EC-RS to the hydrogen evolution reaction (HER) and carbon dioxide reduction reaction (CO_2RR) will be presented. MoS_2 presents a promising electrocatalyst for the HER, but the understanding of its active sites has remained limited. The activity of the edge sites of MoS_2 flakes have been well demonstrated; however, the basal plane's activity depends on structural defects. First, a correlation between HER activity and the 1H-to-1T structural transformation in nitrogen-doped MoS_2 trilayers will be shown [1,2]. Second, the chemical transformation of NiS_2 and the emergence of the most active phase of nickel sulfides during HER will be demonstrated [3]. Various structural forms of nickel sulfides present HER activity, it is however rather challenging to compare their activities on the same basis [4]. HER is an integral part of CO_2RR in aqueous electrolytes since it provides protons required for the formation of value-added products. Although numerous electrocatalytic materials have been proposed for CO_2RR due to their high electrical conductivity and inherent catalytic activity, the formation of carbon-based products such as C1–C2–C3 alcohols and hydrocarbons remains exclusive to Cu-based electrocatalysts. In the final part, the potential-dependent selectivity changes of CO_2RR on Cu_2O films and nanocubes will be examined through the lens of EC-RS spectral features [5–8].

Keywords: Electrocatalysts, HER, CO_2RR, operando Raman spectroscopy

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Synthesis and Electrochemical Performance of NiMn-Decorated Activated Biochar Composites Derived from Tea Waste for Supercapacitor Applications

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Abstract

Biochar has emerged as a sustainable and cost-effective candidate for energy storage systems owing to its high surface area, porous structure, and environmental compatibility [1]. The physicochemical properties of biochar, especially porosity and surface functionality, are greatly influenced by the activation techniques employed, which directly impact electrochemical performance [2-4]. In this work, activated biochar was produced from raw tea waste (RTW), an abundant agricultural by-product in Turkey, through chemical activation with 3M KOH followed by pyrolysis at 700 °C under a nitrogen atmosphere. This activated biochar (RTW-KOH-P700) was further utilized as a conductive support for NiMn-based binary metal oxide composites synthesized via a one-step hydrothermal process [5]. Various compositions were prepared using different ratios of $NiCl_2·6H_2O$, $MnCl_2·4H_2O$, and hexamethylenetetramine (HMTA), resulting in five distinct hydrothermal composites (labeled HC1–HC5).

Electrodes were fabricated by modifying glassy carbon electrodes with the composite/Nafion suspension. Electrochemical characterization was conducted using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) in a three-electrode system with 6 M KOH electrolyte. Among the samples, HC2 exhibited the highest specific capacitance of 253.37 F/g, with other samples ranging from 200.5 to 253.37 F/g. X-ray fluorescence (XRF) analysis confirmed that this sample contained 5.72% Ni and 0.88% Mn, indicating a significant influence of metal composition on capacitive behavior.

Fourier-transform infrared (FTIR) spectroscopy revealed functional groups indicative of biochar-metal oxide interaction: –OH (~3430 cm^{-1}), C–H stretching (2920 and 2850 cm^{-1}), aromatic C=C or O–H bending (~1600 cm^{-1}), and C–O stretching (1000–1100 cm^{-1}). Crucially, strong and well-defined peaks in the 500–700 cm^{-1} range confirmed successful incorporation of Ni–O and Mn–O bonds, with HC2 showing the most pronounced features. This enhanced bonding is attributed to its superior electrochemical performance.

In conclusion, NiMn-loaded biochar derived from RTW demonstrates significant promise as a high-performance and environmentally sustainable electrode material for supercapacitor applications.

Keywords: Biochar, Tea Waste, NiMn Oxides, Hydrothermal Synthesis, Supercapacitor, Electrochemical Analysis, KOH Activation

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Functional Carbon-MOF Hybrids: Glucose Sensing Performance of Activated Biochar-ZIF-8 Composites

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Abstract

Biochar is a carbon-rich material produced from biomass waste through thermochemical processes such as pyrolysis, hydrothermal carbonization, and gasification [1]. Due to its large surface area and high porosity, biochar has attracted significant attention as an alternative material in electrochemical energy storage and sensing applications [2]. These properties can be tailored by adjusting the activation methods, which critically influence performance. Among various agricultural wastes, hazelnut shells stand out as a locally abundant and underutilized biomass source in regions with high hazelnut production, such as Türkiye. Instead of being incinerated or discarded, utilizing these shells for functional material synthesis offers both environmental and economic advantages.

Zeolitic imidazolate frameworks (ZIFs), such as ZIF-8, are porous crystalline structures composed of metal ions and organic linkers, known for their potential in sensors due to their high surface area and tunable pore structure [3-4]. However, ZIF-8 suffers from limited conductivity, restricting its standalone use in electrochemical applications. This limitation can be addressed by incorporating conductive carbon materials like biochar to form functional composites.

In this study, biochar was synthesized from hazelnut shells (HZN) via pyrolysis after activation using various methods (acidic, basic, and ultrasonically assisted) at 500°C. The resulting biochars were then composited with ZIF-8 as reported in [5], and the electrochemical behavior of these composites was systematically investigated. Electrochemical analyses were conducted using a Gamry potentiostat/galvanostat in a three-electrode setup, where the working electrodes were prepared by drop-casting a suspension of the composites with Nafion binder onto a glassy carbon electrode.

FTIR results indicated an increase in surface hydroxyl groups, particularly in acid-activated samples, while XRF analysis showed Zn content ranging from 0.76% to 37.27%, increasing with ZIF-8 loading. XRD data confirmed the preservation of ZIF-8's crystal structure within the composites, albeit with slight crystallinity reduction due to biochar incorporation. Among all samples, the ZIF-8/HZN-P500 (50:200) composite exhibited the highest current response, which increased proportionally with glucose concentration, indicating promising glucose sensing capabilities. The enhanced performance is attributed to the well-dispersed ZIF-8 on the biochar surface and the favorable microporous structure supporting electrochemical activity.

These findings demonstrate that biochar/ZIF-8 composites, particularly the ZIF-8/HZN-P500 formulation, are promising candidates for glucose sensor applications.

Keywords: Glucose sensor, Zeolitic imidazolate framework (ZIF-8), Biochar, Electrochemical sensor, Biomass waste

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Synergistic Enhancement of Glucose Sensing via Copper Nanowire–Biochar Nanocomposites

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Abstract

In this study, a non-enzymatic glucose sensor was developed by combining copper nanowires (Cu NWs) and iron-loaded biochar (Fe-BC) to form a hybrid electrode. Cu NWs, known for their excellent electrical conductivity, high aspect ratio, and electrocatalytic activity, were synthesized via a modified seed-mediated chemical reduction method. Meanwhile, Fe-BC was prepared from hazelnut shell-derived biochar through phosphoric acid-assisted pyrolysis at 500°C and subsequent $FeCl_2$ treatment to introduce Fe_3O_4 nanoparticles. Both components were drop-cast onto a glassy carbon electrode (GCE), forming a composite sensing layer without the use of enzymes. The synergistic combination of electroactive Fe_3O_4-loaded porous biochar and conductive Cu NWs resulted in enhanced glucose sensing performance. The hierarchical porous architecture of the biochar not only provided a high surface area but also enabled improved dispersion of the active components and facilitated efficient electron transfer. The embedded Fe species introduced abundant redox-active sites, thereby promoting electrocatalytic glucose oxidation. Together, the dual functionality of Fe-BC and Cu NWs established a stable and synergistically active electrocatalytic interface, significantly enhancing the reaction kinetics and overall analytical performance of the non-enzymatic glucose sensor [1,2].Cyclic voltammetry (CV) was used to evaluate the electrochemical response of the composite-modified electrode towards glucose, demonstrating significantly enhanced current response compared to electrodes modified with only Cu NWs or Fe-BC. Structural and morphological properties were characterized using X-Ray diffraction (XRD) and scanning electron microscopy (SEM), confirming the crystallinity and surface interaction between the components. This drop-cast Cu NW/Fe-BC hybrid material offers a promising and cost-effective route for non-enzymatic glucose sensing applications [3-6].

Keywords: biochar, copper nanowire, non enzymatic glucose sensor,

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Enhanced Supercapacitor Performance of Polypyrrole-Based Nanocomposites with Biochar and ZIF-8

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Abstract

Increasing population and the energy demand, along with the limited sources of fossil fuels and their environmental damage, have led to a growing interest in clean and sustainable energy sources in recent years [1]. The key limitations of renewable energy sources such as time and location dependency and voltage drop of solar and wind energy on the efficient storage of produced energy, have increased interest in energy storage Technologies [2]. Consequently, energy storage systems such as environmentally friendly electrochemical supercapacitors have become an important research topic [3]. Supercapacitors attract attention with their high power performance, good energy storage capacity, long cycle life, and fast charge/discharge characteristics [4]. Conductive polymers that store charge through the pseudocapacitance mechanism have significant potential for supercapacitor applications[2]. Among these conductive polymers, polypyrrole (PPy) stands out due to its good conductivity, flexibility, low cost, and environmentally friendly nature. However, PPy has important disadvantages such as low cycle life and mechanical stability during the cycling process[4]. To address these shortcomings, composite studies involving different materials with a large surface area and high conductivity, such as metal-organic frameworks (MOFs) and biochar, have gained importance for enhancing the electrochemical properties of PPy [5-6]. In this study, PPy/biochar and PPy/ZIF-8 nanocomposites were obtained via the in-situ polymerization of pyrrole monomer on the surface of biochar and ZIF-8. The electrochemical properties of the produced nanocomposites were investigated through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) analyses, applying a three-electrode configuration. The electrochemical characterization results indicate that the PPy/biochar and PPy/ZIF-8 nanocomposites possess superior electrochemical properties compared to pure PPy, highlighting the significant potential of PPy/biochar and PPy/ZIF-8 based electrode materials for supercapacitor applications.

Keywords: Polypyrrole, Nanocomposite, Biochar, Zif-8,Sensor

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Ethanol-Mediated Tailoring of Photocatalytic NOx Oxidation and Storage on Reducible Metal Oxides: Probing Molecular Basis of Reactivity

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Abstract

To enhance photocatalytic NOx oxidation and storage (PHONOS) of TiO_2 under UVA light, a simple monohydric alcohol impregnation protocol was developed to induce defects and incorporate oxygenates from ethanol (EtOH) onto commercial P25 (TiO_2) photocatalysts at mild temperatures. Thermal treatment and EtOH loading were varied to determine the optimal reduction conditions. The resulting samples were evaluated in 1-hour photocatalytic performance tests, which revealed that the color of the catalyst does not directly correlate with overall photocatalytic performance (i.e., the DeNOx Index). The colored-reduced TiO_2 obtained through calcination at 150 °C in the presence of 3 mL of ethanol (TiO_2-EtOH-150) exhibited the best NO conversion and NOx storage selectivity following the 1-hour PHONOS test.

Long-term activity assessments indicated that both P25 and TiO_2-EtOH-150 catalysts rapidly deactivate over time due to surface poisoning by NOx and a loss of NOx storage capacity. The addition of a basic metal oxide (i.e., CaO) successfully enhanced and sustained NOx storage selectivity even after 15 hours. Characterization via XRD, Raman spectroscopy, DR-UV-Vis, XPS, and VB-XPS revealed no significant bulk structural changes but highlighted the presence of defects and altered electronic properties in the EtOH-treated samples. Notably, the unique valence band structure and surface functionalities of TiO_2-EtOH-150 contributed to its superior photocatalytic performance.

In addition, in-situ FTIR spectroscopy confirmed the formation of surface species resulting from ethanol oxidation on TiO_2. It was observed that adsorbed EtOH is partially oxidized to acetaldehyde and acetate. The IR spectral signature of surface-bound acetaldehyde disappears at temperatures above 150 °C, whereas surface acetate species continue to accumulate. This suggests that surface acetaldehyde functionalities are closely associated with catalytic reactivity due to EtOH functionalization at 150 °C. Current results demonstrate that functionalization of titania surfaces with oxygenates can be a simple but very effective strategy to improve photocatalytic NOx oxidation and storage.

Keywords: Photocatalysis, Reduced TiO_2, Oxygenates, PHONOS, NOx Storage, DeNOx Index

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Upcycling Polymer Waste for Immobilized Tungstophosphoric acid-based Photocatalyst in Dye Degradation

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Abstract

The development of cost-effective, eco-friendly and widely applicable technologies for treating textile dyeing wastewater has become a focal point of global scientific research. Photocatalysis, a leading advanced oxidation process (AOP), stands out as an innovative and eco-friendly technology for advanced tertiary treatment. This method utilizes efficient photocatalysts activated by visible light, offering key benefits such as waste-free operation, recyclability, minimal by-product formation and compatibility with sunlight. Beyond removing toxic chemicals, its reliance on visible light establishes it as a sustainable and environmentally superior alternative to conventional methods. This study introduces an innovative and pioneering approach to enhancing the photocatalytic performance of Ag-TPA by appropriately immobilizing it onto polystyrene, a widely available and cost-effective polymer. Specifically, it introduces an innovative composite photocatalyst, Ag-TPA@Polystyrene composite films, addressing the challenge of highly soluble tungstophosphoric acid (TPA) by immobilizing it onto commercial polystrene (PS-C) and waste-derived polystyrene (PS-W). The immobilization not only overcomes the recovery difficulties associated with pure TPA but also enhances its operational feasibility. The composite material was evaluated for its photocatalytic efficiency in the degradation of methylene blue (MB) under both UV-A (32 W) and visible light (20 W) conditions. The Ag-TPA@PS-C composite film demonstrated a notable photocatalytic activity, achieving 100% photodegradation efficiency under UV-A and 90.57% under visible light within 120 min. The reusability and stability of the Ag-TPA@PS-C composite film was validated over seven consecutive cycles, retaining nearly 100% efficiency, with no significant leaching of active species, as confirmed by hot filtration tests. This study introduces a cost-effective and sustainable strategy for wastewater treatment by utilizing recycled waste polystyrene, showing the potential of Ag-TPA@Polystyrene as a highly efficient and scalable photocatalyst.

Keywords: Waste Polystyrene Upcycling; Tungstophosphoric Acid Immobilization; Ag-TPA@Polystyrene Composite Film; Advanced Oxidation Processes; Photocatalytic Dye Degradation

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Exploration of Operating, Catalytic and Material Conditions Towards CO in CO_2 Electrolyzers: A Machine Learning Study

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Abstract

The capture, conversion, and valorization of CO_2 play a pivotal role in combating global warming and mitigating the impacts of climate change. Varying CO2 feed stocks from heavy industries to atmospheric air can be converted by electrolyzers to CO which is a bridge towards higher hydrocarbons, alcohols and liquid fuels. Although there is an advantage of transforming CO_2 to syngas through electrolyzers with low energy requirements against thermochemical pathways [1] (dry reforming, reverse water gas shift, methanation and thermochemical splitting), commercial readiness still needs optimization of electrolyzer from the point of cell design, electrodes, membrane, electrocatalyst, electrolyte and operation conditions etc. and still needs exploration of complex interactions between these operating, material and catalytic conditions which can be handled by machine learning (ML) algorithms. Although CO as a key electrolyzer reduction product towards selectivity of multicarbon products by C-C coupling and is well known as critical surface intermediate by DFT studies on transition metals [2,3], the selectivity of CO in an electrolyzer involves many factors as emphasized by our previous classification ML models based on a global CO_2 reduction dataset. Our previous ML model discovered different routes with nodes of different transition metals, applied potential, cell designs, operating conditions, membrane type and electrolyte composition [4].

In this study, it was decided to develop our previous study further to search for hidden optimum conditions for maximum selectivity, search for the effect and importance of key factors on selectivity with new data mining tools (visualization tools, feature engineering, ML optimization algorithms) [5,6,7,8]. Visualizations and principal component analysis gave suggestions to experimenters about selection of certain cathode elements (Pd,Ag, Cu, Au), GDL types (Sigracet, TGP), membrane type (N212), certain anolyte concentrations (KCl) for high selectivity and warn about conditions toward low selectivity. Boruta analysis through highest accurate ML regressor indicate cathode elemental compositions, pH, potential, CO_2 flux dominate faradaic efficiency. GBR-PSO optimization algorithm extracted hidden maximum in the CO_2 reduction dataset at high pH (13), high potential (2,97V) and high CO_2 flux ($48 ml/min.cm^2$) with multielemental cathode electrode. Partial dependence plots from DNN architecture of 9 hidden layers after hyperoptimization with a 8.8% RMSE testing accuracy indicate optimal conditions for Cu at.%, pH and CO_2 flux, positive and negative correlations with other operating, material and catalytic conditions and indicate that cathode surface at. compositions, CO_2 flux and applied potential dominate on the CO selectivity.

Keywords: electrolyzer, carbon dioxide, carbon monoxide, machine learning, data mining

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DFT-Based Comparison of Cu-doped BN vs. Graphene as MFC Catalysts

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Abstract

The development of efficient and cheap catalysts is a widely studied topic in fuel cell research [1], [2], [3]. Conventional methanol fuel cell catalysts based on platinum group metals (PGMs) offer a decent performance despite common problems such as poisoning or sintering [4], but, these catalysts are highly costly and economically unsustainable [5], due to limited availability and high demand. In search of promising alternatives, copper-doped 2D materials have drawn increasing interest. In this study, copper-doped two dimensional, hexagonal boron nitride surfaces as methanol oxidation catalysts were explored theoretically via DFT methodology and the results were compared to those of copper-doped graphene (CuG) surface, based on prior DFT study of Akça et al. [6].

The reaction pathway that was proposed in CuG study as $CH_3OH \rightarrow CH_3O \rightarrow CH_2O \rightarrow CHO \rightarrow CO$ was reproduced on Cu/B and Cu/N surfaces, where copper replaces a boron and a nitrogen atom, respectively. Adsorption, activation and reaction energies were calculated for intermediate steps, including ground and transition states, to form a complete energy profile. To facilitate comparability, computational parameters were selected as close to the reference study, with a minor difference in adsorbed hydrogens. While the CuG study neglected hydrogen accumulation on the surface, this study accounted for hydrogen atoms on the surface until they formed molecular H2 and desorbed. Moreover, the reference study reported the energies for each reaction step but did not construct a complete energy profile; consequently, the results were compared on a step-by-step basis for each individual sub reaction.

Cu/N offered the strongest methanol adsorption energy (-99 kJ/mol), surpassing CuG (-83 kJ/mol) and Cu/B (-54 kJ/mol). CuG exhibited reasonable activation energies, with the highest energy observed during $CH_3O \rightarrow CH_2O$ step as 142 kJ/mol. In contrast, Cu/B and Cu/N surfaces had comparably higher activation energy requirements for different steps, with the highest barrier of each layout being 207 kJ/mol observed during $CH_3OH \rightarrow CH_3O$ and 257 kJ/mol observed during $CH_3O \rightarrow CH_2O$, respectively.

The CuG surface favored C-H bonds over C-O bonds which facilitates hydrogen adsorption and supports the desorption of final CO molecule. Similarly, both Cu/B and Cu/N surfaces promoted hydrogen adsorption on B or N atoms but showed negligible affinity toward other intermediates, including CH3OH and CO. This behavior not only favors methanol dehydrogenation but also prevents poisoning on the non-active sides of the catalyst surface, where the primary objective is to adsorb hydrogen leaving the methanol molecule.

Although Cu-BN and CuG surfaces are candidates as cost-effective, stable and poison resistant catalysts for methanol oxidation, theoretical results for Cu-BN surfaces suggest high kinetic barriers, limiting their applicability. Further modifications such as co-doping or surface engineering may result in a higher catalytic activity. Overall, Cu-BN surfaces exhibited favorable traits as an oxidizing catalyst but high energy barriers should be overcome for feasible and sustainable applications.

Keywords: DFT, Cu-BN, Cu-Graphene, Methanol Decomposition, Heterogeneous Catalysis

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Mechanistic Exploration of Cobalt Polypyridyl Catalysts for Hydrogen Evolution Using ab-initio Moelcular Dynamics and Metadynamics

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Abstract

Photocatalytic water splitting presents a sustainable pathway for hydrogen (H_2) production, utilizing solar energy to drive the hydrogen evolution reaction (HER). Transition metal-based molecular catalysts, particularly cobalt (Co) complexes, offer a cost-effective alternative to noble metals for HER [1]. In this work, we investigate the mechanistic pathways of hydrogen generation for two cobalt-based catalysts—$CoPy_5$ and $Co(bPy)_2CO$—using Ab-initio Molecular Dynamics (AIMD), Density Functional Theory (DFT), and Metadynamics simulations using CP2K simulation package [5].

For the $CoPy_5$ catalyst, characterized by a penta-pyridyl ligand in an octahedral arrangement, both ECEC (electron–proton–electron–proton) and EECC (electron–electron–proton–proton) mechanisms were explored. Simulations revealed that spin multiplicity and ligand geometry significantly influence electron transfer and protonation steps. Notably, distorted geometries facilitated more efficient H_2 release compared to ideal octahedral coordination, where steric hindrance prevented H_2 diffusion [2]. The proton transfer dynamics were found to be affected by the steric arrangement of pyridyl ligands, with solvent interactions, particularly the diffusion behavior of hydroxide (OH^-) ions, playing a crucial role in advancing proton transfer to the Co center [3].

For the $Co(bPy)_2CO$ complex, featuring a planar structure, exhibited a distinct preference for the EECC mechanism. Energy barriers associated with ligand-water coordination hindered proton transfer dynamics in the ECEC pathway . Metadynamics simulations provided insights into solvent-mediated hydrogen bonding and coordination fluctuations, identifying an energy barrier of approximately 0.3 eV for Co-H bond formation. Following the second electron injection in the EECC pathway, steady Co-H^+ coordination was established, leading to successful H_2 formation and diffusion into the solvent. This contrasts with the $CoPy_5$ catalyst, where compact ligand structures restricted H_2 diffusion [4].

Our computational insights elucidate how spin states, ligand environments, and solvent interactions collectively determine HER efficiency, offering guiding principles for the design of next-generation photocatalysts for solar hydrogen production.

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Keywords: Density Functional Theory, Free Energy Perturbation Theory, Hydrogen Evolution Reaction

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Mechanistic Insights into Methanol Formation and Decomposition via First-Principles Simulations

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Abstract

Methanol (CH_3OH) is an important molecule in the clean energy landscape, offering versatile utility as a liquid fuel, hydrogen carrier, and chemical feedstock [1]. Its formation through syngas ($CO/CO_2 + H_2$) [2] conversion supports renewable fuel production, while its decomposition provides a practical route to on-demand hydrogen generation-particularly important for high-temperature proton exchange membrane (PEM) fuel cells [3]. Advancing these applications requires a deep mechanistic understanding of surface reactivity and selectivity at the atomic scale.

Through a series of studies, we employ density functional theory (DFT) to investigate the formation and decomposition of methanol on copper and zinc surfaces. For methanol synthesis, we explored CO and CO_2 hydrogenation pathways on Cu(100), (110), (111), and stepped (211) surfaces, as well as Zn(0001), (1000), and (1100) surfaces. All plausible reaction routes—including C–O bond cleavage and intermediate hydrogenation steps—were analyzed. Our goal is to understand the selectivity shift in industrial Cu/ZnO catalysts from CO to CO_2 hydrogenation [4,5], given the known difficulty of C–O bond cleavage on bare Cu. In addition, single-atom doping effects (Cu in Zn, and vice versa) were investigated to assess local compositional impacts. These insights offer atomistic explanations for experimental trends observed in Cu/ZnO catalyst systems and represent one of the most comprehensive DFT-based evaluations of methanol-related mechanisms to date.

We also examined methanol decomposition on clean and Zr-modified Cu(100) and Cu(111) surfaces, motivated by experimental evidence showing enhanced catalytic performance with Zr and ZrO_2 additions [6]. Specifically, we modeled copper surfaces modified with single Zr atoms and small ZrO_2 clusters and compared them to the clean surfaces. Our simulations provide theoretical validation of the experimentally observed enhancement in methanol decomposition selectivity and reveal how metal–oxide interfaces affect dehydrogenation energetics, promote selective H_2 evolution while suppressing CO formation-crucial for fuel cell integration.

Altogether, this work bridges theoretical surface science with applied catalyst design, offering atomic-level insights to guide the development of selective and efficient methanol-based energy technologies.

Keywords: methanol, DFT, catalysis, mechanism

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DFT Investigation of CO_2 Hydrogenation Pathways on Cu(100) and Cu(111) Surfaces for Methanol Production

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Abstract

Methanol, often described as the simplest alcohol, is a fundamental chemical that can be produced from a wide variety of carbon-based feedstocks, including natural gas, coal, biomass, carbon monoxide (CO), and carbon dioxide (CO_2) [1]. Thanks to its versatility, it serves not only as a fuel and solvent but also as a hydrogen carrier and a key building block in chemical manufacturing. In recent years, the catalytic hydrogenation of CO_2 into methanol has drawn growing interest—particularly for its potential to support greenhouse gas reduction goals and contribute to the development of a circular carbon economy [2].

Industrial methanol production is typically carried out using synthesis gas (a mixture of CO, CO_2, and H_2) at 50–100 atm and 200–300 °C on Cu/ZnO-based catalysts [3]. Although metallic copper alone exhibits limited activity in cleaving the C=O bond in CO_2, its presence in industrial catalysts still leads to significant CO_2 conversion [4]. This contradiction raises a fundamental question: Why does CO_2 hydrogenation proceed efficiently on Cu/ZnO catalysts, even though pure copper surfaces are generally ineffective in breaking the C–O bond [5]. Exploring this puzzle through computational methods provides valuable insights that can guide the rational design of more efficient catalytic systems [6].

The presented work is part of the TÜBİTAK 1001 project titled “Computational Investigation of Factors Determining CO and CO_2 Selectivity in Methanol Production from Synthesis Gas.” The main goal of the project is to elucidate the mechanistic factors that govern the selectivity between CO and CO_2 hydrogenation pathways during methanol synthesis and to determine at which stage of the reaction mechanism this selectivity is established.

As part of this project, Density Functional Theory (DFT) calculations were performed to investigate CO_2-based hydrogenation pathways on Cu(100) and Cu(111) surfaces. The contribution of this study focuses on modeling adsorption geometries, reaction intermediates, transition states, and activation barriers along CO_2 conversion pathways. This theoretical study aims to provide fundamental insights into surface reactivity and catalytic function at the atomic scale and ultimately contribute to the design of more selective and efficient catalyst systems for methanol production via CO_2 hydrogenation.

Keywords: Methanol synthesis, CO_2 hydrogenation, DFT calculations, Copper surfaces, Reaction selectivity

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ZIF-90 Under External Electric Field: An Ab Initio Molecular Dynamics Perspective on Catalytic Potential

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Abstract

Metal–organic framework (MOF) structures have garnered attention in smart material design due to their structural flexibility in response to external stimuli such as electric fields. Pioneering studies in the literature have demonstrated that electric fields can induce controllable and reversible modifications in MOFs. For example, Namsani et al. [1] showed that halogenated ligands in IRMOF-7 rotate under an electric field, altering the pore size and influencing CH_4 diffusion pathways. Tam et al. [2] revealed that turnstile-like molecular motions in Mg-MOF-74 can be activated by an electric field. Ghoufi et al. [3] demonstrated the transition of MIL-53(Cr) to a narrow-pore configuration and its subsequent effect on CH_4 diffusion. Experimentally, Knebel et al. [4] reported that the application of a 500 V/mm electric field to ZIF-8 and HKUST-1 slows down the diffusion of H_2, CO_2, and CH_4, and that this effect is reversible. These studies underscore the potential for dynamically controlling MOF behavior via electric fields, thereby enhancing their applicability in functional devices.

Introduced to the literature by Yaghi et al. [5], ZIF-90 is a metal–organic framework (MOF) formed by the coordination of Zn^{2+} ions with 2-carboxaldehyde-imidazole ligands. With a surface area of 1270 m^2/g, well-defined porosity, and aldehyde-functionalized ligands, ZIF-90 holds significant potential for catalytic applications. These functional groups allow for easy chemical modification and controlled placement of active sites within the porous framework, making it highly suitable for conformation-controlled catalysis. ZIF-90 shares a similar topology with ZIF-8, which has been successfully employed in such catalysis using the multivariate approach. Yuan et al. [6] demonstrated that tuning hydrophilic linker ratios in ZIF-8 modulated enzyme–framework interactions and enhanced activity by stabilizing specific enzyme conformations. This ability of ZIF-8 suggests that ZIF-90, with its comparable structure and additional chemical tunability, also holds strong promise for advanced conformationally controlled catalysis.

In this study, the structural response of ZIF-90 to an external electric field is systematically investigated for the first time, with an emphasis on how these dynamics may influence its catalytic performance. Using the CP2K simulation package, electric fields ranging from 0 to 4 V/nm were applied in the x-direction at 100 K, 200 K, and 300 K. The dynamic behavior of the structure was analyzed via DFT-based ab initio molecular dynamics (AIMD), and ligand dihedral angle distributions and time-dependent rotations were examined through VMD analysis. The results reveal that ZIF-90 exhibits notable conformational flexibility under increasing electric field and temperature, as the ligands undergo

adaptive rotations, potentially enabling new interaction modes within the framework. This dynamic behavior suggests that ZIF-90 offers a tunable platform for fine adjustment of active site geometries.

The conformational adaptability of ZIF-90 under electric field conditions highlights its potential as a strong candidate for multifunctional MOF-based catalytic systems. This simulation-driven approach provides valuable insights into designing environmentally responsive active site architectures, thereby offering guidance for the development of next-generation MOF catalysts.

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Keywords: ZIF-90, Metal-Organic Frameworks (MOFs), Electric Field, Ab Initio Molecular Dynamics (AIMD)

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H_2S Adsorption Properties of Electric-Field-Responsive ZIF-71 for Catalyst Protection

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Abstract

Hydrogen sulfide (H_2S) is a critical contaminant in industrial gas streams, leading to catalyst poisoning and operational challenges[1]. This study explores the functionality of ZIF-71 [2] for H_2S capture, along with its structural response to external electric fields. ZIF-71 offer significant potential for various industrial applications requiring H_2S removal and catalyst protection. In petroleum refining, this material could be integrated into hydrodesulfurization units to safeguard Co-Mo/Al_2O_3 catalysts from H_2S poisoning, while enabling continuous operation through efficient electric field-assisted regeneration cycles[3]. For gas purification, ZIF-71 promises selective H_2S removal from dry air [4]. The framework also shows promise in syngas processing, where it could serve as a protective layer for Fischer-Tropsch catalysts (Fe-based) in synthetic fuel production by capturing H_2S upstream of the catalytic beds[5]. These industrial application scenarios are supported by ZIF-71's H_2S capture potential and its structural responsiveness to electric fields. Computational studies demonstrate that ZIF-71 not only exhibits significant adsorption rates also features a pore geometry that can be dynamically modulated via external electric fields. Grand Canonical Monte Carlo simulations reveal that ZIF-71 achieves significant adsorption capacities of 25.88 mg/g for H_2S at 193 K, demonstrating its potential for gas purification applications. Structural analyses through ab initio molecular dynamics simulations indicate that ZIF-71's ligand dihedral angle distributions exhibit field-dependent behavior. Under applied electric fields of 2–3 V/nm, a distinct narrowing of dihedral angles occurs, suggesting possible modulation of the framework's pore geometry. These observations imply that external fields could fine-tune ZIF-71's adsorption properties, potentially enhancing its selectivity for H_2S capture.

Keywords: Physisorption, H2S adsorption, electric field response

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CO Hydrogenation Mechanism on Oxygen-Deficient CuO (100) and CuO (111) Surfaces For Methanol Synthesis Using DFT

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Abstract

Methanol (CH_3OH) is an essential chemical compound extensively used in various critical sectors, including energy storage, liquid fuels, solvents, and the manufacture of numerous industrial products [1]. Despite substantial efforts in developing catalytic systems for methanol production, the carbon source (CO or CO2), the active catalyst phase and the selectivity of the methanol formation mechanism on the widely used Cu/ZnO catalyst remain subjects of ongoing debate [2], [3]. From this perspective, the CO hydrogenation mechanism leading to methanol formation on CuO (100) and CuO (111) surfaces is systematically investigated using periodic Density Functional Theory (DFT) simulations. Particular attention is given to surface modifications involving the introduction of oxygen vacancies, aiming to reduce the high adsorption energies induced by hydrogen atom binding. All computational analyses were conducted using the Vienna Ab Initio Simulation Package (VASP), utilizing norm-conserving Projector Augmented-Wave (PAW) basis set in conjunction with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [4], [5]. To enhance the accuracy of interaction energies and electronic structure predictions, Grimme-D3 dispersion corrections and Hubbard U (DFT+U) adjustments were applied. The results demonstrate that the combined use of van der Waals corrections and DFT+U methodology is crucial for a reliable description of CO adsorption and intermediate species formation. Moreover, the introduction of oxygen vacancies significantly alters the reaction energetics, lowering the energy barriers and stabilizing key intermediates. These findings contribute to a deeper understanding of alternative Cu-based catalyst surfaces and offer insight into the role of surface defects in promoting methanol synthesis via CO hydrogenation. These insights provide guidance for designing more efficient methanol synthesis catalysts.

Keywords: Methanol Synthesis, Density Functional Theory (DFT), Catalyst

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Structure-Activity Relationships for Carbon Dioxide Utilization Over Bimetallic Catalysts

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Abstract

Our world is undergoing a critical transition. How do we produce the ever increasing needs of the growing human population with sustainable methods [1]. How do we generate more energy and produce more chemicals with lower amounts of input. Catalysts are the key materials that can unlock a sustainable or even circular economy as they allow us to produce fuels and chemicals with less energy input and waste. Catalytic conversion of CO2 to valuable chemicals stands out as a promising process, as it has the potential to yield negative emissions. Furthermore, there is a possibility to build-up on the industrial Fischer-Tropsch Synthesis (FTS) experience on the use of highly active cobalt-based catalysts. However, cobalt has unfavorable selectivity when CO is replaced with CO_2 in synthesis gas.

Is there a way to optimize cobalt catalysts for CO_2 utilization via fundamental design principles. Combining the active cobalt surface sites with a secondary metal such as iron in the form of bimetallic catalysts and the use of alkali promoters proved to be effective methods to shift the selectivity from methane to desired products such as CO, longer chain paraffins, olefins and oxygenates [2-3]. However, bimetallic FeCo catalysts have very complex and dynamic structures incorporating metallic, oxidic and carbidic phases. Furthermore, the interaction of alkali promoters with these phases and how these influence the selectivity stand as unsolved challenges in the catalysis community. Experimentally, the dynamic nature and the complexity of active phases makes their direct characterization extremely challenging. Molecular modeling of catalysts[4], combined with surface-sensitive experimental techniques can provide us these valuable structure-activity relationships, which can help us design innovative catalysts with tunable selectivity to desired products.

In this talk, I will demonstrate how important design principles for novel catalysts can be obtained via carefully integrating the understanding from experimental findings and molecular modeling. First, I will talk about the production of olefins[5], a desired but not industrially obtained product, in Fischer-Tropsch Synthesis, by cobalt catalysts. I will further elaborate on the selectivity optimization of cobalt catalysts, via the descriptors we have obtained, for carbon dioxide utilization. In this second part, I will talk about the design principles[6] of iron-cobalt (FeCo) bimetallic catalysts. The insights we obtain show that the introduction of iron and alkali promoters have complimentary effects on key catalytic properties, which can be utilized to fine-tune the selectivity by changing their relative compositions. I will also demonstrate how the atomic scale insights obtained from Density Functional Theory can be integrated with Kinetic Monte Carlo methods to yield mesocale kinetic results that can be compared with experimental findings. Finally, I will discuss how a careful analysis of experimental data with the

computational results can guide the design of selective catalysts for CO_2 utilization. The findings that I present show that molecular modeling yields valuable insights for rational design and optimization of cobalt catalysts for carbon dioxide utilization.

Keywords: Catalysis, Density Functional Theory, Cobalt, Iron, Carbon dioxde

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Beyond Equilibrium CO_2 Hydrogenation to Dimethyl Ether

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Abstract

Introduction

Dimethyl Ether (DME) is a clean, high-efficiency fuel alternative producible directly from CO_2 hydrogenation where CO_2 is converted into CO and H_2O (RWGS), followed by methanol synthesis and dehydration to DME [1]. However, the H_2O co-produced via RWGS thermodynamically and kinetically hinders DME formation and can lead to catalyst deactivation [2]. One solution is to remove H2O in-situ as it is formed if a steam-selective adsorbent like Zeolite 3A (Z3A) is added to the catalyst mixture [3]. While sorption-enhanced DME synthesis from pure CO_2 has been less explored, this study provides a comprehensive parametric assessment of this CZA+PTA/γ-Al2O3+Z3A system, investigating the effects of acidic catalyst type, catalyst composition. Z3A loading, GHSV, and regeneration parameters on CO_2 conversion, DME selectivity, and productivity for intensified CO_2-to-DME synthesis.

Experimental

The methanol synthesis catalyst (CZA) was prepared via an ultrasound-assisted one-pot coprecipitation method. The acidic dehydration catalyst, 30 wt.% PTA/γ-Al_2O_3, was synthesized by the incipient-to-wetness impregnation technique, a choice informed by prior work [4]; γ-Al_2O_3 (Alfa Aesar) was used as a benchmark. Commercial Zeolite 3A (Sigma Aldrich), was crushed and sieved (250-350 μm) for use as the adsorbent.

Experiments were conducted in a ½” fixed-bed stainless-steel reactor. Initial sorbent-free tests evaluated catalyst acidity (PTA/γ-Al_2O_3 vs. γ-Al_2O_3) and CZA:acidic catalyst mass ratios (1:1, 1:3) across temperatures of 215-265 °C, at 3 MPa, H_2:CO_2:N_2 feed ratio of 3:1:1, and GHSV of 1750 h^{-1} (based on CZA volume). For sorption-enhanced studies, a 1:1 mass ratio of CZA:PTA/γ-Al_2O_3 (1 g total catalyst) was physically mixed with Z3A (2, 6, or 10 g). These tests were performed at 245 °C, 3 MPa, H_2:CO_2:N_2=3:1:1, with GHSV varying from 5250 to 10500 h^{-1}. Adsorbent regeneration was achieved by pressure swing (depressurization to 0.1 MPa) with a 50 N ml/min N_2 purge at 245 °C for durations ranging from 5 to 70 minutes. Feed and product streams were analyzed by two on-line gas chromatographs. Performance was evaluated by CO_2 conversion (xCO_2) and DME selectivity (SDME), defined as per [32, 33], and DME productivity ($kgDME\cdot kgCAT^{-1}\cdot h^{-1}$).

Results and Discussion

In sorbent-free experiments, PTA/γ-Al_2O_3 significantly outperformed γ-Al_2O_3 for DME synthesis. The specific DME production rate (per gram of acidic catalyst) was maximized at 245 °C with a CZA:PTA/γ-

Al_2O_3 mass ratio of 1:1, achieving 4.7x10^{-5} molDME·gacidic cat^{-1}·min^{-1}. Consequently, this temperature and the CZA:PTA/γ-Al_2O_3=1:1 catalyst system were selected as the default for subsequent sorption-enhanced experiments.

With integrated Z3A, sorption-enhanced experiments showed that both CO_2 conversion and DME selectivity increased with higher Z3A loading and lower GHSV. The highest CO_2 conversion (43.5%) and DME selectivity (53.5%) were observed at 5250 h^{-1} with 10 g Z3A, representing a 115% and 49% improvement, respectively. However, DME productivity, peaked at 2.1x10^{-2} kgDME·kgCAT^{-1}·h^{-1} under conditions of 7000 h^{-1} GHSV, 6 g Z3A, and a 30-minute regeneration period.

Varying the regeneration time for the Z3A adsorbent indicated that shorter periods could improve overall DME productivity despite lower instantaneous conversions during the reaction step, due to significantly reduced overall cycle times. For instance, with 10 g Z3A at 7000 h^{-1}, reducing regeneration from 70 min to 5 min increased productivity from 1.9x10^{-2} to 2.1x10^{-2} kgDME·kgCAT^{-1}.h^{-1}.

Long-term stability testing of the CZA+PTA/γ-Al_2O_3+Z3A system (at 7000 h^{-1}, 6g Z3A, 30 min regeneration) over ~50 hours with 18 reaction and 17 regeneration steps demonstrated robust performance. Despite an initial ~9% decrease in peak CO_2 conversion between the first (38.6%) and second (35.1%) reaction stages, attributed to fresh catalyst interaction with in-situ steam, the system subsequently maintained stable CO_2 conversion, DME yield, and DME selectivity. This contrasts with some hybrid Cu-based metallic and zeolite-based acidic catalyst systems prone to deactivation [5].

Keywords: Sorption-enhanced, CO_2 hydrogenation, Process Intensification

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Synthesis Gas Production by Intensified Reverse-Water Gas Shift Reaction

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Abstract

Synthesis gas ($CO+CO_2+H_2$) is a platform chemical, which can be synthesized by the reaction of captured CO_2 with green H_2 via the reverse water-gas shift reaction (RWGS: $CO_2+H_2=CO+H_2O$). RWGS is thermodynamically favored at high temperatures where methanation can compete with CO formation depending on the catalyst type unless temperature is increased >700 °C. Cu-based catalysts rule out undesired CH_4 formation, but their use is limited to <400 °C due to low thermal stability [1]. We hereby aim to synthesize CH_4-free CO on a $CuO/ZnO/Al_2O_3$ (CZA) catalyst by integrared H_2O adsorption to beat the low-temperature induced thermodynamic restrictions.

In-house synthesized CZA catalyst is mechanically mixed and packed with the Zeolite 3A adsorbent (Sigma Aldrich) in a tubular downflow quartz reactor. CZA catalyst with a theoretical composition of CuO (65 wt.%), ZnO (25 wt.%), and Al_2O_3 (10 wt.%) is prepared by an ultrasound-assisted one-pot co-precipitation method [2]. CZA and Z3A are packed at the amounts of 1 g and 10-25 g, respectively, and tested at 250-300 °C, 1 bar, total inlet flow and composition of 100 N ml/min and $H_2/CO_2/N_2=5/1/2$, respectively. The catalyst is pretreated under 10 N ml/min pure H_2 flow at 230 °C for 2 h. Feed and product analyses are carried out on-line by a gas chromatograph (GC) customized for reproducible quantitative analysis CO, CO_2, CH_4, H_2 and N_2. Upon its saturation, Z3A is regenerated at 350 °C for 1 h under inert (Ar) flow. Upon regeneration, the system is cooled down to the pertinent reaction temperature and the next cycle is onset by dosing the reaction mixture. Sample collection and analysis are done with 10 min intervals starting at 5th min after the onset of reaction. In all of the results reported herein, the atomic carbon mole balance is closed with <2% deviation. CO is detected as the only carbon-containing product; neither CH_4 nor coke formation is observed.

Performance of the intensified system is evaluated in terms of reactor productivity (kgCO/kgcat.h), CO_2 conversion and CO yield. CO productivity is investigated depending on adsorbent loading and reaction temperature. In the absence of Z3A, an expected increase in CO production with temperature is observed and CO production is subject to thermodynamic restrictions. The positive impact of intensification (in-situ H_2O capture) is evident by significant leap in CO productivity at all reaction temperatures. Increasing Z3A loading improves productivity, but the extent of change differs with temperature. At 250 °C, increasing Z3A loading from 10 to 25 g changes productivity by ~83% (i.e. from 5.8×10^{-2} to 10.6×10^{-2} kgCO/kgcat.h). However, the increase is ~72% at 325 °C. The results also point out that productivity is maximized to 11.1×10^{-2} kgCO/kgcat.h when RWGS is run at 275 °C with the assistance of 25 g Z3A adsorbent. 275 °C is found as the optimum reaction temperature under the current conditions.

Cyclic repeatibility/stability of the sorption enhanced system is also studied to understand the regenerability of Z3A and the possible impacts of these thermal conditions to CZA. The results show initial CO2 conversion and CO yield >90% which decrease to the pertinent thermodynamic limit as of ~30 min from the onset of the reaction where Z3A is saturated. Closeness of the three successive cycles shows the stability of CZA and Z3A. We currently carry out longer cycles which (not reported here) seem to confirm stability.

Beyond thermodynamic, CH_4-free, stable CO formation is demonstrated by sorption-assisted RWGS. Current findings are very promising and show the possibility of making syngas from CO_2 and H_2, without depending on energy intensive, natural-gas based reforming routes. Studies for investigating the effects of regeneration time and temperature on CO productivity are ongoing.

Keywords: Synthesis gas, Reverse water-gas shift, Sorption enhancement, In-situ steam removal

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Development of Zr-Based Catalysts for Isobutene Production from Synthesis Gas

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Abstract

Isobutene is a valuable chemical used as a raw material and intermediate product in the synthesis of organic compounds and can be converted into polymer and oligomer compounds in various fields. Isobutene, traditionally produced in oil refineries, requires alternative production methods due to high energy consumption and limited oil reserves [1, 2]. Syngas obtained from coal, natural gas and urban waste is an important alternative for isobutene production. The FTO (Fischer-Tropschs to olefins) process is effective in the production of isobutene from syngas. FTO mainly involves the reaction of CO and H_2 in the presence of an active catalyst. The active component Zr stands out in the production of isobutene from FTO [1, 3]. Zr has high activity as well as high thermal and corrosion resistance. In the literature, it has been shown that ZrO_2, when in small crystallite size and in monoclinic form, weakens the adsorption of formate species, which cause the formation of undesirable products when adsorbed on the catalyst surface.In this study, the synthesis of active and selective new Zr-based catalyst for the production of isobutene from syngas was aimed. ZrO_2 catalyst was synthesized hydrothermally via urea ($CO(NH_2)_2$) and zirconium oxynitrate salt ($N_2O_7Zr{\cdot}xH_2O$). The salt and urea mixture, which was stirred at room temperature for 30 minutes, was taken into a teflon-steel autoclave and subjected to heat treatment at 180°C for 20 h. The sample was then washed by centrifuging until the pH value of the filtrate became ~7. The washed sample was dried at 60 °C for 12 h and then subjected to heat treatment in a muffle furnace at 500 °C for 4 h. The synthesized ZrO_2 catalyst was characterized by XRD analysis (Rigaku Ultima IV X-Ray Diffractometer). It was observed that monoclinic and tetragonal forms coexisted in the structure of the ZrO2 catalyst.. The crystal sizes were calculated as 5.5 nm and 5.6 nm, respectively, from the Scherrer and Modified Scherrer equations. With the synthesis method used, the small crystallite sized (~6 nm) monoclinic phase, which is mentioned as the active form for the reaction in the literature, was successfully obtained [4]. It is predicted that the ZrO_2 catalyst obtained with small crystallite size and relevant crystal structure will exhibit high CO conversion and isobutene selectivity.

Keywords: Isobutene, Synthesis gas, Zr-based catalyst, catalyst synthesis, FTO.

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Atomic-Level Insights into Pd-Ag Alloy Surfaces for Selective Hydrogen Production from Formic Acid

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Abstract

Hydrogen is widely recognized as a promising green energy carrier; however, challenges related to its safe, cost-effective storage and long-distance transport continue to hinder its practical implementation [1]. To address the limitations of traditional hydrogen storage, including the high cost of pressurized gas cylinders, limited volumetric capacity, and safety hazards, liquid organic hydrogen carriers have emerged as viable alternatives for fuel cell technologies. Among them, formic acid stands out due to its advantageous properties: high volumetric hydrogen storage capacity, greater energy density compared to commercial hydrogen tanks, ambient liquid state, and low toxicity and flammability [2]. Additionally, formic acid can be obtained from renewable sources such as biomass or carbon dioxide, making it an environmentally favorable hydrogen storage option [3].

While palladium (Pd) is one of the most effective catalysts for the decomposition of formic acid, its tendency to produce carbon monoxide (CO) as a byproduct is a major drawback. CO binds irreversibly to active Pd sites, thereby deactivating the catalyst. Incorporating silver (Ag) into Pd has been shown to mitigate CO poisoning and enhance hydrogen selectivity. Nevertheless, further suppression of CO formation is essential, as even trace amounts can significantly impair fuel cell efficiency, particularly at lower operating temperatures [4]. Gaining atomic-scale insights into how Ag influences selectivity is therefore critical to optimizing catalyst performance.

Although understanding catalyst surface structures at the atomic scale is critically important, the inherent complexity of nanoparticle surfaces makes it challenging to isolate and examine the reactivity of each unique surface atom. To overcome this, planar single crystals with uniformly structured surface atoms are employed as model catalysts, enabling systematic investigation of structure–reactivity relationships. These studies are typically carried out under ultra-high vacuum (UHV) conditions to ensure precise molecular-level control and to facilitate the use of high-resolution spectroscopic techniques.

In this study, the decomposition of formic acid on PdxAg1-x surface alloys on Pd(111) single crystal was investigated under ultra-high vacuum (UHV) conditions. A combination of infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) was employed to probe the structural and electronic properties of the catalyst surfaces. The results revealed that Ag atoms in close proximity to Pd within the alloy undergo electronic modification relative to bulk Ag. While bulk Ag remains inert toward formic acid, these modified Ag sites become catalytically active, promoting an alternative reaction pathway that exclusively yields H_2 and CO_2 [5]. Additionally, temperature-programmed reaction spectroscopy (TPRS) showed that small Pd ensembles (even isolated Pd atoms) retained activity similar to Pd(111), albeit with limited CO formation [6]. Overall, these findings demonstrate that precise atomic-level control of surface morphology in Pd–Ag alloys enables highly selective hydrogen production from formic acid.

Keywords: Liquid Organic Hydrogen Carriers, Formic Acid Decomposition, Hydrogen Production, Pd-Ag Alloys, Model Surfaces

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Influence of Rh Single Atom Loading on Catalytic Ethanol and CO_2 Interactions: Ethanol Oxidation vs. Ethanol Decomposition

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Abstract

Co-adsorption of ethanol and CO_2 was investigated via in-situ FTIR, TPD, XANES/EXAFS, XPS, and TEM on Rh single-atom catalysts (SACs) with various loadings (0.2 wt% and 2 wt% Rh) adsorbed on ceria-promoted hydroxyapatite (Ce-HAP) support in relevance to dry reforming reactions. 0.2Rh/Ce-HAP exhibited relatively oxygen-rich CeOx domains revealing Ce+4 sites accommodating relatively reduced Rh(3-x)+ species leading to the formation of ethoxides, carbonates, and bicarbonates at 50 °C. Increasing the temperature to 350 °C resulted in oxidation of adsorbed ethoxide species to acetate. In contrast, 2Rh/Ce-HAP catalyst exhibiting $Rh^{3+,}$ oxygen vacancies, and reduced Ce^{+3} sites facilitated ethoxide decomposition to acetaldehyde, CO, and CH_4 via C–C/C–H bond activation. This behavior suggested that increasing Rh loading of single atom sites on Ce/HAP imposes an alteration in reactivity patterns where a catalytic route including ethoxide oxidation to acetate is replaced with an alternative route comprised of ethoxide dehydrogenation and C–C/C–H bond scission. Current results demonstrate that single atom Rh catalysts lacking large Rh nanoparticles can reveal significant variations in their surface electronic properties and their catalytic reactivity patterns as a function of the Rh single atom loading due to substantial alterations in metal-support interactions and oxygen vacancy formation.

Keywords: Single-atom catalysts, SAC, Rh, ceria, hydroxyapatite, Ethanol, CO_2 adsorption, in-situ FTIR spectroscopy.

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How Single Atoms Keep Your Catalysts Alive: Effect of Particle Size on Sulfur Poisoning and Regeneration of Rhodium Active Sites

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Abstract

SOx poisoning and regeneration behavior of a Rh single atom catalyst (SAC) was investigated via in-situ FTIR spectroscopy and temperature programmed desorption (TPD) in a comparative manner to that of a Rh nanoparticle catalyst on different ceria support materials. SOx poisoning of the Rh single atom catalyst (i.e., 0.5 wt.%Rh/5 wt.%Ce/HAP, HAP: hydroxyapetite) with SO_2(g) + O_2(g) at 400 °C (PSO_2+O_2 = 2 Torr, PSO_2 : PO_2 = 1:10, 10 min) resulted in the formation of sulfates and sulfites. Consecutive regeneration of Rh/CeHAP SAC with H_2 revealed that Rh single atom sites could be readily regenerated under the currently used SOx poisoning and regeneration (PH_2 =10 Torr, 200˚C, 2 h) conditions despite the fact that regeneration process inflicted a limited extent of Rh agglomeration to form small (presumably multi-atomic/oligomeric) Rh clusters. In contrast, on the 0.5 wt.% Rh/CeO_2 catalyst which was comprised of predominantly large Rh nanoparticles along with a relatively smaller number Rh single atom minority sites, sulfur-poisoned large Rh nanoparticles were found to be almost entirely incapable of being regenerated with H_2; while Rh single atom minority sites were observed to be readily regenerated with H_2 under identical conditions. SOx-TPD experiments indicated that sulfur-poisoned Rh/CeO_2 catalyst containing large Rh nanoparticles adsorbed significant amounts of sulfates and sulfites which desorbed mostly in the form of SO_2(g) within 500-750˚C. On the other hand, sulfur-poisoned Rh/CeHAP SAC adsorbed a considerably smaller amount of sulfates/sulfites where sulfates/sulfites were found to adsorb on the Rh/CeHAP surface in a substantially stronger manner than that of Rh/CeO_2, evident by SO_2 desorption from sulfur-poisoned Rh/CeHAP SAC within 650-900 ˚C. Poor regeneration capability of sulfur-poisoned large Rh nanoparticles are attributed to the presence of a dense sulfate/sulfite multilayer precluding the transport and diffusion of hydrogen to the underlying Rh sites due to steric hindrance, while high regeneration efficiency of Rh single atom sites can be associated to the favorable accessibility of SAC sites to the adsorbed hydrogen.

Keywords: Single atom catalysts, SAC, Rhodium, sulfur, SOx poisoning, H_2, regeneration, in-situ FTIR spectroscopy, TPD.

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Structure Sensitivity in DeNOx Catalysis on Shape-Defined Cu_2O Nanocrystal Model Catalysts

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Abstract

The complex structure of CuOx-based DeNOx catalysts can be efficiently unraveled using shape-defined Cu_2O nanocrystal model catalysts. In this context, the present study investigates the NO_x decomposition mechanism on well-defined Cu_2O nanocrystals. We successfully fabricated highly uniform cubic and octahedral Cu_2O nanocrystals (NCs) with well-defined facets ({100} and {111}, respectively), and employed them to investigate the facet-dependency on NO_x adsorption and reduction with H_2. The catalysts were systematically characterized via SEM, XRD, XPS, and probe molecule adsorption (NO_x, NO_x +H_2) experiments were performed using in-situ Fourier transform infrared spectroscopy (FTIR), allowing real-time monitoring of surface species. Additionally, temperature-programmed desorption (TPD) experiments were conducted to evaluate the thermal stability of the adsorbed species and quantify the relative NO_x storage capacities of cubic and octahedral Cu_2O nanocrystal model catalysts.

SEM imaging confirmed the uniform morphology and narrow particle size distribution of the synthesized Cu_2O nanocrystals, while XRD analysis verified their crystalline nature. In situ FTIR spectroscopy revealed facet-dependent NO_x adsorption behavior. Pressure-dependent NO_2 adsorption at low temperatures led to the formation of distinct surface NO_x species on Cu_2O NCs with exposed {100} and {111} facets. In cubic catalysts, bridging and bidentate nitrate/nitrite species were predominantly observed, while in octahedral catalysts, monodentate nitrate/nitrite species were dominant [1-3]. Since the cubic Cu_2O catalyst exposed {100} facets, its active sites were primarily terraces comprised of high-coordination surface sites; however, for the octahedral Cu_2O catalyst, kinks and edges (i.e., extended line defects) revealing coordinatively-unsaturated (cus) sites were dominant, which made the adsorption of nitrate/nitrite species as polydentate configurations less favorable on the octahedral Cu_2O catalyst [4-6].

Current temperature-dependent in-situ FTIR and TPD studies further indicated that NO_x adsorption intermediates exhibit greater thermal stability on the {111} facets compared to {100}, despite the shorter Cu–O bond length of the latter, which is typically associated with higher NO_x stability [4,7]. Complementary in situ FTIR and TPD experiments conducted over a temperature range of 50–700 °C demonstrated that thermal decomposition and reduction pathways are structure-sensitive. Cubic and octahedral Cu_2O nanocrystals displayed distinct NO_x desorption profiles, indicating differences in the

thermal stability of adsorbed species. Interestingly, despite their weaker IR signals, octahedral Cu_2O released more NO_x during TPD, which is attributed to the smaller IR absorption cross-section of adsorbed NO_x species on octahedral Cu_2O as compared to that of cubic Cu_2O nanocrystal model catalyst surface.

Keywords: Cu_2O, Shape-defined catalysts, NO_x decomposition, in situ FTIR spectroscopy

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Unraveling Structure-Functionality Relationships of Shape-Defined Cu_2O Nanocrystal Model Catalysts for Methanol Decomposition

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Abstract

Methanol is an important C1 feedstock and energy source, but mechanistic studies on its conversion using Cu-based catalysts are hindered by materials and pressure gaps. Shape-controlled Cu_2O nanocrystals offer a valuable model system to investigate structure–function relationships under realistic conditions, bridging fundamental research and industrial relevance. Cubic and octahedral Cu_2O nanostructures were synthesized and comprehensively characterized using techniques including SEM, XRD, XANES, EXAFS, ATR-IR, XPS, and H_2-TPR. Surface-active sites were probed through in-situ FTIR spectroscopy with CO as a probe molecule. The influence of crystal morphology on methanol decomposition was investigated using in-situ FTIR and temperature-programmed desorption (TPD) methods. Current study highlights a clear correlation between the crystal shape of Cu_2O and its catalytic behavior. Cubic Cu_2O (c-Cu_2O) exhibits highly reactive surface oxygen species that promote the complete oxidation of methanol and methoxy intermediates, predominantly yielding CO_2 and H_2O. Conversely, the octahedral form (o-Cu_2O), with its lower surface reducibility, favors partial dehydrogenation, producing CO and H_2 as the main products. Notably, o-Cu_2O generates three times more CO than c-Cu_2O, therefore, the CO_2 to CO ratio for c-Cu_2O is approximately four times higher than that of o-Cu_2O, reflecting its enhanced oxidative strength. The contrasting tendencies toward total and partial methanol oxidation on c-Cu_2O and o-Cu_2O can be attributed to differences in the nature and reactivity of their surface oxygen species, as evidenced by H_2-TPR results. On c-Cu_2O, the presence of weakly bound doubly coordinated $O_{2}C$ sites results in more labile and reactive oxygen species, enabling efficient methanol oxidation at lower temperatures and favoring complete oxidation. In contrast, o-Cu_2O contains strongly bound triply coordinated $O_{3}C$ sites that limit oxygen activation, thus promoting partial oxidation pathways. These results demonstrate the significant impact of morphology on catalytic function, providing a pathway for tuning methanol conversion through crystal shape control.

Keywords: Cu_2O, Methanol Decomposition, Model Catalysts, Structure-Functionality Relationships

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Operando 1H NMR Monitoring of Catalytic Decomposition of Methanol over Pt/TiO_2 in the Presence of H_2O_2

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Abstract

Photocatalytic hydrogen production through water splitting is an attractive route for solar based energy carriers. The major drawback of this technology is the thermodynamic limitation over direct water splitting reaction. Addition of sacrificial reagents such as methanol enhances hydrogen production; in the presence of methanol the reaction is thermodynamically more favorable due to altered reaction route and altered Gibbs Free energy landscape [1, 2] . As a preliminary study to monitor the reaction under operando conditions in an NMR spectrometer [3-5], H_2O_2 was added as a proxy source of OH radicals. A thorough monitoring of behavior of methanol water mixtures as well as H_2O_2 water mixtures in neat solutions revealed unique solution phase clustering behaviors of these compounds. Furthermore, a thermodynamic analysis of water splitting in the presence of methanol and methanol and H_2O_2 was performed. Catalytic H_2O_2 decomposition supplied the solution phase with abundant amounts of OH radicals, which are used to decompose methanol. The presence of OH radicals were orders of magnitude higher than that couuld be produced by the photocatalyst, expediating the reaction and enabling abundant amounts of intermediates in solution. In situ and operando monitoring of the reaction by single pulse 1HNMR experiments revealed at least four intermediate species in the aqueous phase during the reaction. When the OH radicals through the limiting reagent is completely consumed overnight and the reaction terminated, the intermediate species also disappeared from the reaction medium, suggesting the full oxidation of inermediates to CO_2. Another experiment to monitor the effluent gases through NDIR confirmed the presence of CO_2 in the reactor effluent. Solid catalyst in this aqueeous media was also monitored through 2D NMR experiments of relaxation time measurements. Distinct short spin lattice relaxation times indicated the accesibility of the solid surface by the present sytem designed for primarily liquid NMR spectroscopy. Very short T1 times imply a solid state NMR signal, attributed to the surface hydroxyls on Pt/TiO_2. The spectral investigation of spin lattice relaxation time measurements further revealed several distinct signals from solid domains of surface hydroxyls.

Keywords: methanol decomposition; catalytic reforming of methanol; H_2O_2 decomposition; operando NMR

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Catalysis for the Transformation of Chemistry – Nexus of Catalyst and Process Design

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Abstract

The defossilization and partial decarbonization of the energy sector towards renewable and more sustainable energy carriers and systems will have a tremendous influence and transform the chemical and related industries in the foreseeable future. To obtain actual sustainable value-added chains, all carbon feedstock has to be non-fossil and renewable, i.e., derived within a circular economy. This includes the utilization of chemicals and materials in advanced chemical recycling processes, the utilization of biobased platform chemicals as well as captured carbon dioxide and products derived thereof. Catalysis is a key enabling technology for this transformation and catalyst development has to go hand in hand with process design in order to be successful. This contribution summarizes and highlights selected recent developments regarding drop-in solutions for established as well as new value-added chains based on bio-renewable platform chemicals. Opportunities and challenges of their technical implementation are discussed.

Among the chosen examples are recent developments for the production of polyols and glycols by chemocatalytic hydrogenolysis of carbohydrate feedstock of the first and second generation as well as the catalytic amination thereof to derive biobased amines [1-3]. The focus is on supported bifunctional metal-catalysts that possess suitable hydrogenation and dehydrogenation activity as well as the opportunity for high performance and stability in aqueous reaction mixtures.

Furthermore, the opportunities of Fe-based catalysts are presented [4,5]. On the one hand, highly dispersed supported mono- and bimetallic iron catalysts exhibit enormous potential as alternative to industrially established Pd-Ag catalysts in the selective hydrogenation of acetylene. Also, Fe-containing zeolites exhibit promising performance in the selective oxidation of bioethanol to acetaldehyde as important renewable platform chemical.

Finally, the hydrogenation of CO_2 to formate is used as a model reaction to demonstrate the benefits of the concept of microporous macroligands for the immobilization of molecular catalysts in solid support materials to combine the advantageous properties such as high activity and selectivity with the separability and the option for continuous processing in fixed-bed reactors. We report a systematic study of the structure-activity-relationship of solid molecular Ru catalysts based on polyphosphine nanoporous hyper-crosslinked polymers (HCPs) as macroligands for the selective hydrogenation of CO_2 to formate [6-8].

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Femtosecond Absorption Spectroscopy to Elucidate Elementary Mechanisms of Molecules in Complex Environments

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Abstract

Understanding the ultrafast dynamics of photoexcited molecules in complex environments is essential for advancing photochemistry, photocatalysis, and material design [1]. This presentation explores how femtosecond broadband absorption spectroscopy, in combination with stationary spectroscopic techniques, can reveal elementary processes such as internal conversion, intersystem crossing, and charge transfer—often mediated by conical intersections and influenced by solvent dynamics. We demonstrate the power of this approach through case studies ranging from vision-related isomerization to photocatalytic systems involving Cu(I)[2] and Al(III)[3] complexes. These systems highlight the role of non-innocent ligands and the impact of environmental factors such as solvent polarity, viscosity, and temperature on excited-state behavior.

A particular focus is placed on the Red-Edge effect, originally observed in photophysics (fluorescence) and recently extended to photochemistry. Here, excitation wavelengthdependent reactivity challenges traditional assumptions—such as excitation-independent fluorescence spectra and the expectation of maximum conversion efficiencies at peak absorption. Action plots and ultrafast measurements reveal that electronic transitions like fluorescence or intersystem crossing can critically influence quantum yields when they ocur much faster than solvent reorganization times [4]. By correlating femtosecond spectroscopy with quantum chemical calculations and longertimescale techniques (e.g., NMR, EPR), we gain mechanistic insights into excited-state lifetimes, quantum yields, and spectral shifts. This enables a deeper understanding of how molecular structure and environment govern photoreactivity [5]. Our findings underscore the importance of carefully selecting reference systems, ligands, solvents, and excitation conditions. Ultimately, this knowledge paves the way for the rational design of photoactive materials with tailored properties.

Keywords: Femtosecond spectroscopy, Ultrafast dynamics, Photoexcited states, Red-Edge effect, Fundamentals of photocatalysis

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Metal-Ligand Interactions in Catalysis

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Abstract

Transition metals are particularly effective in catalyzing many industrially important processes under mild conditions and providing high selectivity for the processes where the formation of special products is targeted. In the catalytic processes the transition metal can be attacked by all kind of Lewis bases present in the medium or deliberately added to the system. All the Lewis bases including substrates, solvents, and impurities are considered as ligands which can interact with metal. The design of catalysts as well as the implementation of catalysis are strongly affected by the metal-ligand interaction. Therefore, the knowledge on metal-ligand interaction is vital in understanding the catalysis. Herein, metal-ligand interaction is discussed in the following basic groups: (i) only σ−donor ligands, (ii) ligands which act as σ−donor as well as π−donor, (iii) ligands having both the σ−donating and π−accepting abilities. In each group, the metal-ligand interaction is conversed by considering the simplest members, which can easily be elaborated for the heavier homologues.

Keywords: Transition metal, Catalysis, Metal-ligand interaction, Metal-metal bond, Catalytic activity, Reusability of catalyst

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