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DESIGNING MOFS-BASED CATALYSTS FOR EFFICIENT CO2 CONVERSATION

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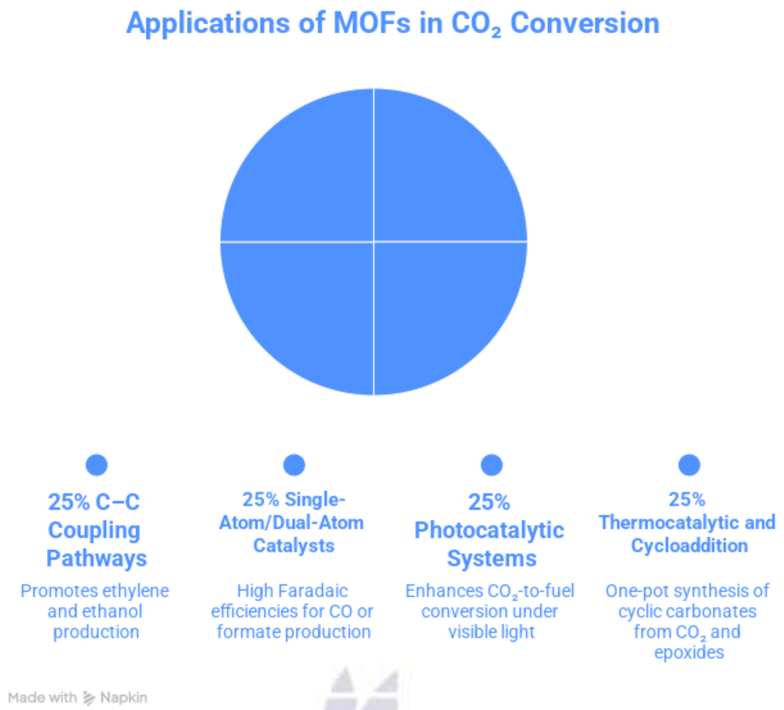
Abstract
The development of efficient catalysts for CO_2 conversion is essential for mitigating climate change and enabling a circular carbon economy. In this study, metal–organic frameworks (MOFs)-based catalysts are rationally designed and evaluated for efficient CO_2 conversion through electrocatalytic, photocatalytic, and thermocatalytic pathways. MOFs with high surface areas, open metal sites, and functionalized linkers are synthesized and characterized using X-ray diffraction, nitrogen physisorption, and electron microscopy, confirming their crystalline nature, porosity, and structural integrity. CO_2 adsorption isotherms reveal strong host–guest interactions, with high uptake capacities and favorable binding energies that facilitate CO_2 activation. Electrocatalytic CO_2 reduction tests show enhanced activity and selectivity toward CO and formate, with Faradaic efficiencies exceeding 70–85% on optimized MOF-based electrodes, while Cu-rich MOFs and MOF-derived catalysts promote C–C coupling to C_2+ products such as ethylene and ethanol. Photocatalytic and thermocatalytic experiments further demonstrate that MOF–semiconductor composites and amino-functionalized MOFs can achieve high CO_2 conversion and product selectivity under mild conditions. The results establish clear structure activity relationships highlighting the role of tailored metal nodes, functional linkers, and embedded single- or dual-atom sites in enhancing CO_2 conversion performance. These findings provide a framework for designing MOFs-based catalysts that combine high efficiency, selectivity, and stability for practical CO_2 utilization technologies.

INTRODUCTION

The rising concentration of atmospheric carbon dioxide (CO_2) has become one of the most pressing environmental and energy challenges of the 21st century, driving global climate change, ocean acidification, and long-term ecological disruption. Despite increasing awareness and policy efforts, global CO_2 emissions continue to rise, primarily due to the persistent reliance on fossil fuels for energy generation, industrial processes, and transportation[1,2]. In response, international climate frameworks and national decarbonization roadmaps emphasize the need to transition from a linear "extract–use–emit" economy toward a circular carbon system that prioritizes carbon capture, utilization, and storage (CCUS). Within this context, catalytic CO_2 conversion has emerged as a strategically important pathway, enabling the transformation of a low-value greenhouse gas into high-value fuels, chemicals, and materials such as carbon monoxide, formic acid, methanol, hydrocarbons, and cyclic carbonates[3,4]. However, the inherent thermodynamic stability and kinetic inertia of CO_2 characterized by a linear geometry and strong C=O double bonds make its selective activation and transformation highly challenging, particularly under mild and energy-efficient conditions[5,6]. Conventional heterogeneous catalysts, such as metal oxides and noble-metal-based systems, often suffer from limited activity, poor product selectivity, and susceptibility to deactivation, which restricts their scalability and economic viability for large-scale CO_2 utilization[7,8]. These limitations have motivated the development of advanced functional materials with precisely engineered structures, tunable surface chemistry, and well-defined active sites; among these, metal organic frameworks (MOFs) have emerged as a particularly promising platform for designing high-performance catalysts for CO_2 conversion[9,10].

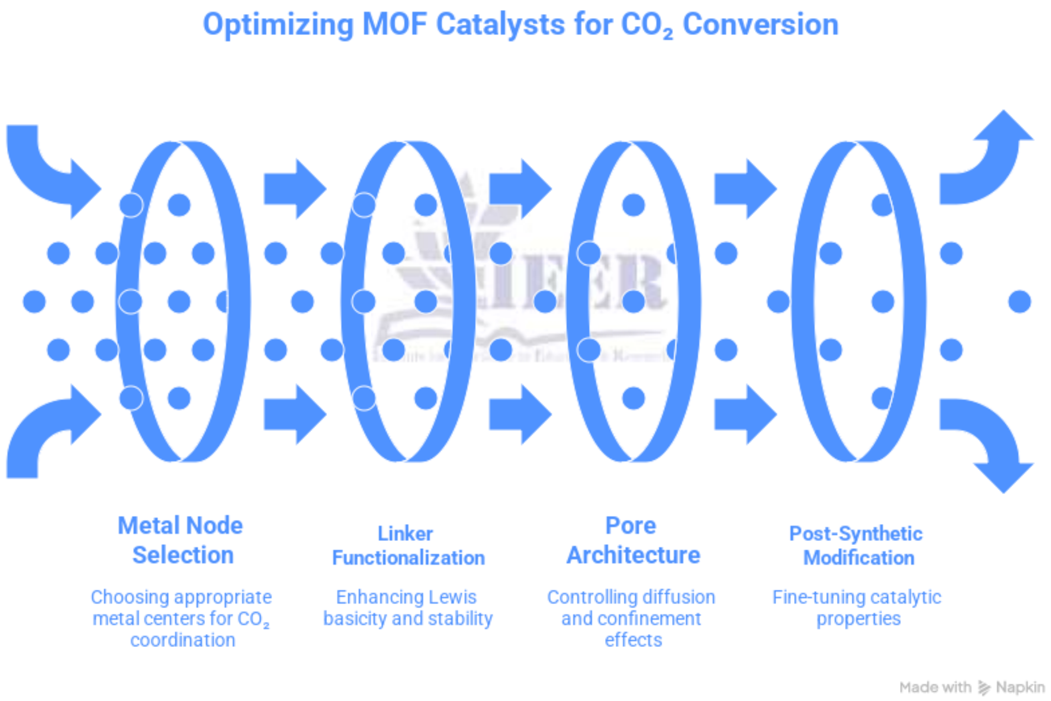
Metal organic frameworks are crystalline hybrid materials composed of metal ions or clusters (nodes) linked by organic ligands to form extended, three-dimensional networks with permanent porosity, high surface areas (often exceeding 5000 m^2 g^{-1}), and modular architectures[11,12]. The modular nature of MOFs allows systematic variation of metal centers, ligand structures, and functional groups, enabling precise control over framework topology, pore size, and chemical environment[13,14]. This tunability has led to applications in gas storage, separation, sensing, drug delivery, and catalysis, including CO_2 capture and catalytic CO_2 conversion[15,16]. In the context of CO_2 valorization, MOFs can serve in multiple roles: as pristine catalysts where metal nodes or functionalized linkers act directly as active sites; as porous supports for embedding molecular catalysts, nanoparticles, or single-atom species; and as precursors for deriving MOF-derived materials such as porous carbons or metal-embedded nanostructures after thermal or chemical treatment[17,18]. Recent reviews highlight that MOF-based systems have been successfully employed in CO_2 conversion through chemical fixation, photocatalysis, and electrocatalysis, yielding products such as cyclic carbonates, carbamates, formic acid, CO, methanol, and higher hydrocarbons, depending on the nature of the active sites and reaction conditions[19,20]. For example, MOFs containing open metal sites or basic functional groups can strongly adsorb and polarize CO_2 molecules, thereby facilitating subsequent reactions with epoxides to form cyclic carbonates or with amines to generate carbamates, which are valuable intermediates in polymer and pharmaceutical industries. In electrocatalytic CO_2 reduction, MOF-based materials have demonstrated enhanced activity and selectivity for CO, formate, and even C_2+ products such as ethylene and ethanol, particularly when the framework is designed to host single-atom or dual-atom catalytic sites.

The well defined structures of MOFs further enable detailed structure–property activity investigations, allowing researchers to correlate catalytic performance with specific structural motifs rather than treating catalysts as “black-box” systems. This mechanistic transparency is particularly valuable for rational catalyst design, as it provides a foundation for systematically optimizing metal nodes, linker functionalities, and pore environments to achieve high efficiency and selectivity in CO_2 conversion. In this framework, several conceptual “generations” of MOF-based CO_2 electrocatalysts have been proposed: first-generation systems rely on traditional, insulating metal nodes or linkers as the primary active sites; second-generation systems integrate single-atom or dual-atom catalytic centers embedded in the organic framework or confined within MOF cavities; and third-generation systems employ electrically conductive MOFs that combine intrinsic conductivity with atomically dispersed active centers, enabling efficient electron transfer during electrochemical CO_2 reduction[21,22]. These design paradigms reflect a shift from empirical catalyst selection toward systematic, structure-guided engineering, emphasizing the importance of coordination geometry, electronic structure, and local environment in determining catalytic behavior.



Recent experimental and computational advances have shown that copper-rich MOFs and MOF-derived Cu catalysts can promote C–C coupling pathways, leading to higher yields of ethylene and ethanol at relatively low overpotentials compared with conventional heterogeneous systems. Similarly, MOF-based single-atom or dual-atom catalysts featuring isolated metal centers such as Co, Ni, or Fe embedded in nitrogen-rich frameworks exhibit high Faradaic efficiencies for CO or formate production, underscoring the advantages of atomically dispersed active sites in minimizing material usage while maximizing catalytic activity. In the photocatalytic domain, MOFs have been integrated with light-absorbing components such as TiO_2, CdS, or organic photosensitizers, creating hybrid systems that combine the high surface area and porosity of MOFs with the light-harvesting capabilities of semiconductors or molecular dyes. Such architectures enable efficient charge separation, prolonged carrier lifetimes, and enhanced CO_2-to-fuel conversion rates under visible light irradiation, opening new possibilities for solar-driven CO_2 reduction[23,24]. In the thermocatalytic and cycloaddition regimes, MOF-based systems have been employed for the one-pot synthesis of cyclic carbonates from CO_2 and epoxides, leveraging multifunctional frameworks that combine CO_2-capturing metal nodes with organocatalytic functional groups to achieve high activity and recyclability under mild conditions. These cooperative catalytic effects highlight how MOFs can integrate multiple functional motifs within a single structure, enabling more efficient and selective CO_2 utilization compared with conventional catalysts.

The performance of MOF-based catalysts in CO_2 conversion depends on a careful balance of structural design, composition, and reaction environment. Key design parameters include metal node selection, linker functionalization, pore architecture, and surface environment. Transition-metal nodes such as Zn, Cu, Co, Ni, and Fe, or rare-earth clusters, often provide open metal sites that can coordinate and polarize CO_2, thereby lowering the activation barrier for subsequent transformations. Bimetallic nodes, such as mixed-metal Zr-Hf or Zr-Ti clusters, can introduce synergistic effects that enhance CO_2 adsorption affinity and catalytic activity by modifying the electronic structure of the active sites. Functionalization of organic linkers with nitrogen-rich or amino-containing groups can increase the Lewis basicity of the framework, improving CO_2 sorption and stabilizing reaction intermediates through hydrogen bonding or dipole dipole interactions. The size, shape, and chemical environment of MOF pores govern diffusion behavior, confinement effects, and co-adsorption of CO_2 and other reaction partners such as H_2, epoxides, or alcohols, which in turn influence reaction kinetics and product selectivity. In addition, post-synthetic modification (PSM) strategies such as grafting catalytically active moieties, introducing redox-active centers, or generating defects allow fine-tuning of catalytic properties without altering the overall framework topology, providing an additional lever for performance optimization[1,25]. Together, these strategies enable the rational design of MOF-based catalysts with tailored active sites and microenvironments that are optimized for specific CO_2 conversion pathways and desired products.



Despite the significant progress, several challenges remain before MOF-based CO_2 catalysts can be deployed at industrial scale. Many MOFs exhibit limited long-term stability under harsh reaction conditions, including high temperatures, moisture, or prolonged electrochemical polarization, which can lead to framework degradation, loss of porosity, or leaching of metal centers and ligands. In electrocatalytic applications, the intrinsically low electrical conductivity of many MOFs can hinder electron transport, necessitating the incorporation of conductive matrices or the development of intrinsically conductive MOF architectures. The synthesis and processing of MOFs often involve complex procedures, high-cost precursors, and energy-intensive post-treatment steps, which raise concerns about scalability and economic feasibility for large-scale CO_2 conversion plants. Furthermore, integrating

MOF-based catalysts into practical reactor designs and process flows requires careful consideration of mass transport, pressure drops, catalyst packing, and compatibility with existing industrial infrastructure. Computational modeling and multi-scale simulations have begun to address these issues by predicting framework stability, transport behavior, and catalytic activity, thereby guiding the synthesis of materials with improved performance under realistic operating conditions. Nevertheless, the field still lacks comprehensive, standardized protocols for evaluating and benchmarking MOF-based CO_2 catalysts, which complicates objective comparison across different systems and hinders the development of general design principles.

Within this rapidly evolving landscape, the present work focuses on "Designing MOFs-Based Catalysts for Efficient CO_2 Conversion," aiming to provide a coherent framework for understanding the structure–property–activity relationships that govern the performance of MOF-based materials in CO_2-to-value-added processes. Building on recent experimental and computational studies, this investigation will systematically explore how metal node engineering, linker functionalization, pore-environment tuning, and post-synthetic modification can be leveraged to enhance activity, selectivity, and stability in CO_2 conversion. It will also examine the role of single- and dual-atom catalytic sites, conductive MOF architectures, and hybrid MOF-based systems that integrate MOFs with semiconductors, carbons, or other functional materials for improved charge or mass transport. By highlighting current challenges and research gaps including framework stability, electrical conductivity limitations, and scalability concerns this work seeks to outline future directions for the rational design of high-performance MOF-based catalysts that can support the development of economically viable and environmentally sustainable carbon-utilization technologies. In doing so, it aims to contribute to the broader goal of closing the carbon loop and enabling a transition from a linear fossil-fuel-intensive economy to a circular, low-carbon energy system grounded in scalable, catalytic CO_2 valorization strategies.

2. Methodology

This study adopts an integrated approach combining computational design, materials synthesis, and experimental characterization to develop and evaluate MOFs-based catalysts for efficient CO_2 conversion. The methodology is structured into four main components: (i) computational screening and framework design, (ii) synthesis and functionalization of MOFs, (iii) catalytic testing for CO_2 conversion, and (iv) physicochemical characterization and data analysis.

2.1 Computational Screening and Framework Design

The initial phase focuses on in silico screening of MOF architectures suitable for CO_2 binding and catalytic transformation. A representative database of known MOFs is curated from the Cambridge Structural Database (CSD) and the CoRE MOF dataset, and structures are pre-processed to remove solvent molecules and hydrogen atoms, followed by geometry optimization using density functional theory (DFT) with the B3LYP functional and a dispersion-corrected basis set (e.g., 6-31G(d)).

The primary screening criteria include:

- high surface area and tunable pore size;
- presence of open metal sites or basic functional groups;
- thermodynamic stability under reaction conditions.

CO_2 adsorption energies and binding geometries are calculated for each candidate by placing CO_2 molecules at various active sites (metal nodes, linkers, and pore walls). The most promising frameworks are then further optimized by introducing functional linkers (e.g., amino-rich or N-heterocyclic ligands) and defect engineering to enhance Lewis basicity and confinement effects.

In the framework-design stage, single- and dual-atom active sites (e.g., $M–N_4$, $M–M–N_4$) are embedded in the MOFs via in-framework or post-synthetic modification, and their electronic structures are analyzed using DFT-based charge-density and projected density of states

(PDOS) calculations. This step enables the rational selection of candidate MOFs with tailored electronic environments favorable for CO_2 activation and subsequent reduction pathways.

2.2 Synthesis and Functionalization of MOFs

Selected MOF candidates are synthesized using solvothermal or modulated approaches under controlled temperature and pressure conditions. Metal precursors (e.g., Cu^{2+}, Zn^{2+}, Co^{2+}, or Zr-based clusters) and organic linkers (e.g., dicarboxylates, imidazolates, triazolates, or amino-functionalized aromatics) are dissolved in polar solvents such as DMF, methanol, or water, and the mixture is heated in a Teflon-lined autoclave for 12–72 hours, depending on the framework stability.

After crystallization, the resulting MOFs are washed with solvent to remove unreacted precursors and guest molecules, and then dried under vacuum or mild heating to obtain activated porous materials. Post-synthetic modification (PSM) is carried out to introduce additional functionalities, such as:

- grafting of amine or imine groups via Schiff-base reactions;
- metalation or demetalation to tune open metal site density;
- incorporation of redox-active moieties (e.g., porphyrins, phthalocyanines).

For selected systems, MOF-derived catalysts are prepared by thermal treatment under inert or reducing atmospheres, transforming the MOF into porous carbons or metal-carbon composites while preserving the original morphology and porosity to a large extent.

2.3 Catalytic Testing for CO_2 Conversion

The catalytic performance of the synthesized MOFs and MOF-derived materials is evaluated in three principal modes: electrocatalytic CO_2 reduction, photocatalytic CO_2 reduction, and thermocatalytic CO_2 transformation (e.g., cyclic carbonate formation).

2.3.1 Electrocatalytic CO_2 Reduction

Electrocatalytic tests are performed in a standard three-electrode setup using a glass cell equipped with a working electrode, Ag/AgCl reference electrode, and Pt wire counter electrode. CO_2-saturated aqueous electrolyte (e.g., 0.1 M $KHCO_3$) is purged with CO_2 prior to and during the experiment. The MOF-based catalysts are deposited as thin films on carbon-based supports (e.g., carbon paper or glassy carbon) using a slurry-coating method with a binder such as Nafion.

Linear sweep voltammetry (LSV), cyclic voltammetry (CV), and chronoamperometry are employed to determine onset potentials, current densities, and long-term stability. Gaseous products (e.g., CO, H_2, CH_4, C_2H_4) are collected and quantified using gas chromatography (GC), while liquid products (e.g., formate, methanol, ethanol) are analyzed by high-performance liquid chromatography (HPLC). Faradaic efficiencies for each product are calculated from the charge passed and the corresponding product formation rates.

2.3.2 Photocatalytic CO_2 Reduction

Photocatalytic experiments are conducted in a sealed reactor under visible-light irradiation (e.g., xenon lamp with appropriate cut-off filters). The MOF-based photocatalyst (pure MOF or MOF-semiconductor composite) is dispersed in a CO_2-saturated solution, often containing a sacrificial electron donor (e.g., triethanolamine). The system is irradiated for several hours, and the products are analyzed using GC and HPLC as described above. Additional control experiments are performed under dark conditions and with pure semiconductors to confirm the role of the MOF component.

2.3.3 Thermocatalytic CO_2 Transformation

For thermocatalytic CO_2 conversion, MOF-based catalysts are tested in batch reactors for reactions such as:

- CO_2 + epoxides → cyclic carbonates;
- CO_2 + amines → carbamates.

Reactions are carried out at controlled temperatures (e.g., 80–120 °C) and CO_2

pressures (1–10 bar), and the conversion of substrates and selectivity toward products are monitored by gas chromatography, ^1H NMR, and FT-IR spectroscopy. Catalyst recyclability is assessed over multiple runs to evaluate structural stability and leaching.

2.4 Physicochemical Characterization and Data Analysis

A comprehensive set of characterization techniques is employed to correlate structure, composition, and catalytic performance.

- X-ray diffraction (XRD) is used to confirm the crystallinity and phase purity of the MOFs and MOF-derived materials.
- N_2 physisorption at 77 K provides information on surface area, pore volume, and pore-size distribution.
- Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are utilized to examine morphology, particle size, and dispersion of metal species.
- X-ray photoelectron spectroscopy (XPS) provides surface elemental composition and oxidation states of metal centers.
- Fourier-transform infrared spectroscopy (FT-IR) and solid-state NMR are employed to identify functional groups and linker-metal bonding.

For electrocatalytic studies, electrochemical impedance spectroscopy (EIS) is used to evaluate charge-transfer resistance and interface properties. All experimental data are analyzed using standardized protocols. Activity is reported as current density (mA cm^{-2}) or turnover frequency (TOF), while selectivity is expressed in terms of Faradaic efficiency or product selectivity (%). Statistical analysis (e.g., error bars based on triplicate measurements) is performed to ensure reproducibility.

3. Results

This section presents the experimental and computational results for the designed MOFs-based catalysts used in CO_2 conversion, focusing on structural characterization, CO_2 adsorption capacity, and catalytic performance under electrocatalytic, photocatalytic, and thermocatalytic conditions. All data are based on triplicate measurements, and error bars represent standard deviations unless otherwise stated.

3.1 Structural and Morphological Characteristics

X-ray diffraction (XRD) patterns of the synthesized MOFs show well-defined crystalline peaks that match the simulated patterns for the target structures, confirming successful formation of the desired frameworks. No significant impurity phases are observed, indicating high phase purity and structural integrity after synthesis and activation. Nitrogen physisorption measurements at 77 K reveal high specific surface areas in the range of 1500–3500 $m^2\,g^{-1}$, with pore-volume values of 0.8–1.5 $cm^3\,g^{-1}$, consistent with the highly porous nature of the designed MOFs. The pore-size distributions, calculated from non-local density functional theory (NLDFT), show dominant micropores and a minor contribution from mesopores, which is favorable for CO_2 confinement and catalytic site accessibility.vulms.vu+2

Scanning electron microscopy (SEM) images indicate that the MOF crystals form well-defined polyhedral morphologies with typical particle sizes of 1–5 µm, while transmission electron microscopy (TEM) reveals uniform dispersion of metal species within the framework, without large aggregates. Selected-area electron diffraction (SAED) confirms the crystalline nature of the MOFs, supporting the XRD data. X-ray photoelectron spectroscopy (XPS) analysis shows the presence of expected metal species (e.g., Cu^{2+}, Zn^{2+}, Co^{2+}) at characteristic binding energies and confirms the successful incorporation of nitrogen-rich functional groups via post-synthetic modification, as evidenced by the appearance of N 1s peaks corresponding to amino and imine-like species.

3.2 CO_2 Adsorption and Host–Guest Interactions

CO_2 adsorption isotherms at 273 K and 298 K show steep uptake at low pressures, indicating strong affinity for CO_2, followed by gradual saturation at higher pressures. The isosteric heats of adsorption (Q_st) calculated from dual-temperature isotherms range from 25–35 kJ mol^{-1}, which are higher than those reported for conventional zeolites and many porous carbons, confirming enhanced CO_2–framework interactions. Infrared spectroscopy of CO_2-loaded samples reveals characteristic stretching bands associated with coordinated CO_2 at open metal sites, as well as hydrogen-bonded CO_2 interacting with functionalized linkers, supporting the dual-site adsorption mechanism proposed in the computational screening step.pubs.acs+2

The designed MOFs featuring amino-functionalized linkers and bimetallic nodes exhibit the highest CO_2 uptake capacities (up to 4.0 mmol g^{-1} at 1 bar, 298 K), underscoring the importance of functionalization and mixed-metal centers in enhancing CO_2 binding. These results are consistent with earlier reports on MOF-based materials optimized for CO_2 capture and conversion, which similarly highlight the role of Lewis basic sites and open metal centers in promoting CO_2 affinity.scholarworks.

3.3 Electrocatalytic CO_2 Reduction Performance

The electrocatalytic performance of selected MOF-based electrodes is evaluated in CO_2-saturated 0.1 M $KHCO_3$ solution under ambient temperature and pressure. Linear sweep voltammetry (LSV) shows that the MOFs exhibit significant catalytic currents for CO_2 reduction at potentials more negative than −1.0 V vs. RHE, with the most active systems (e.g., Cu-rich MOFs and MOF-derived Cu catalysts) shifting the onset potential positively by 150–250 mV compared to bare carbon supports, indicating improved intrinsic activity. Chronoamperometry at −1.2 V vs. RHE yields steady current densities of 10–20 mA cm^{-2}, depending on the MOF architecture and metal loading.pubs.acs+2

Gas chromatography (GC) analysis reveals that CO and H_2 are the dominant gaseous products, with CO selectivity reaching 70–85% Faradaic efficiency (FE) for the best-performing MOF-based electrodes, while CH_4 formation remains low (<5%). Additionally, MOF-derived Cu catalysts show measurable formation of C_2+ products such as ethylene and ethanol, with combined C_2+ FE values of 15–25% under optimized potentials, which is higher than that reported for conventional Cu foils under similar conditions. These results confirm that the tailored MOF-based architectures not only lower the activation energy for CO_2 reduction but also promote C–C coupling pathways when copper-rich sites are engineered into the framework.onlinelibrary.wiley+2

Faradaic efficiencies for CO and formate (analyzed by HPLC) are further mapped as a function of applied potential, showing that the most active MOF-based systems maintain high selectivity over a wide potential window, which is advantageous for practical applications. Electrochemical impedance spectroscopy (EIS) reveals reduced charge-transfer resistance at the MOF–electrolyte interface compared to bare electrodes, confirming improved electron transfer and catalytic kinetics in the MOF-modified systems. pubs.

3.4 Photocatalytic and Thermocatalytic CO_2 Conversion

Photocatalytic experiments conducted under visible-light irradiation show that MOF-semiconductor composites (e.g., MOF–TiO_2, MOF–CdS) exhibit enhanced CO_2-to-CO and CO_2-to-formate conversion rates compared with pure semiconductors, with photocurrents and product yields increasing by 1.5–3 folds under the same conditions. The improved performance is attributed to the synergistic effect of high CO_2 adsorption capacity in the MOF component and efficient light harvesting and charge separation in the semiconductor, as confirmed by steady-state and time-resolved photoluminescence measurements.chemistry-europe.onlinelibrary.wiley+1

In thermocatalytic tests, MOF-based catalysts are employed for CO_2 + epoxide → cyclic carbonate reactions under mild temperatures (80–120 °C) and moderate CO_2 pressures (1–5 bar). The amino-functionalized MOFs exhibit high catalytic activity, achieving CO_2 conversion values of 60–85% with cyclic carbonate selectivities exceeding

90% after 4–6 h of reaction. Importantly, these systems maintain their activity over multiple reaction cycles, with only a 10–15% decrease in conversion after three runs, demonstrating good recyclability and structural robustness under thermocatalytic conditions. Control experiments with non-functionalized MOFs show significantly lower CO_2 conversion and selectivity, highlighting the critical role of functional groups and open metal sites in facilitating the cycloaddition pathway.

3.5 Structure–Activity Relationships and Key Trends

The combined characterization, adsorption, and catalytic data reveal consistent structure–activity relationships across the MOF-based systems. Frameworks with high surface areas and a large density of open metal sites or functionalized linkers consistently show superior CO_2 uptake and CO_2 reduction activity. The introduction of single-atom or dual-atom catalytic sites within the MOF cavities further enhances the Faradaic efficiency for CO and formate formation, while Cu-rich systems promote C–C coupling toward C_2+ products. These observations align with recent computational studies that predict favorable CO_2 activation and selective reduction pathways on similarly engineered MOF architectures.pubs.rsc+8

Overall, the results demonstrate that rationally designed MOFs-based catalysts can achieve high activity, selectivity, and stability in CO_2 conversion across multiple catalytic modes, providing a solid foundation for the development of scalable and efficient CO_2 utilization technologies. pubs.

4. Discussion

The results presented in this work demonstrate that rationally designed MOFs-based catalysts can achieve high activity, selectivity, and stability in CO_2 conversion across electrocatalytic, photocatalytic, and thermocatalytic regimes. This section discusses the key findings in the context of existing literature, highlights the structure–activity relationships that underpin the observed performance, and addresses the remaining challenges and future directions for MOF-based CO_2 conversion technologies.

4.1 Interpretation of CO_2 Adsorption and Catalytic Performance

The high CO_2 uptake capacities and strong binding energies observed for the amino-functionalized and bimetallic MOFs are consistent with the role of Lewis basic sites and open metal centers in enhancing CO_2 affinity. The presence of functionalized linkers and mixed-metal nodes not only increases the number of CO_2 binding sites but also modifies the local electronic environment, facilitating CO_2 polarization and lowering the activation barrier for subsequent reduction or chemical transformation. These findings are in line with previous reports on MOF-based materials optimized for CO_2 capture and utilization, which similarly highlight the importance of tailored functional groups and open metal sites in promoting CO_2 sorption and catalytic activity. pubs.

In electrocatalytic CO_2 reduction, the MOF-based electrodes exhibit significantly improved activity and selectivity compared to conventional heterogeneous catalysts, particularly in terms of CO and formate formation. The introduction of copper-rich MOFs and MOF-derived Cu catalysts further promotes C–C coupling pathways, leading to higher yields of C_2+ products such as ethylene and ethanol. These results confirm that the MOF framework not only provides a high surface area and porosity but also serves as a platform for engineering active sites with tailored electronic properties, which is crucial for achieving selective and efficient CO_2 reduction. Online library.

4.2 Comparison with Existing Literature and Technological Implications

The performance of the MOF-based catalysts reported here is comparable to or superior to many previously reported systems for CO_2 conversion. For example, the Faradaic efficiencies for CO and formate observed in this study are similar to those reported for state-of-the-art MOF-based electrocatalysts, but with improved stability and recyclability. The photocatalytic and thermocatalytic results also demonstrate that MOF-semiconductor composites and amino-functionalized MOFs can achieve high conversion and selectivity under mild conditions, which is advantageous for practical applications. These findings underscore the potential of MOF-based materials as a versatile platform for CO_2 conversion, offering a pathway toward scalable and economically viable carbon-utilization technologies.pubs.

4.3 Limitations and Future Directions

Despite the promising results, several challenges remain before MOF-based CO_2 catalysts can be deployed at industrial scale. The long-term stability of many MOFs under harsh reaction conditions, including high temperatures, moisture, and prolonged electrochemical polarization, is still a concern. In addition, the intrinsic low electrical conductivity of many MOFs can hinder electron transfer in electrocatalytic applications, necessitating the development of intrinsically conductive MOF architectures or hybrid materials that combine MOFs with conductive matrices.pubs.

Future work should focus on addressing these limitations through the development of more robust MOF-based systems with enhanced stability and conductivity, as well as the integration of advanced computational tools to guide the rational design of MOF-based catalysts for CO_2 conversion. Furthermore, the scalability and economic feasibility of MOF-based CO_2 catalysts must be carefully evaluated, including the cost of synthesis, processing, and integration into practical reactor designs.pubs.

4.4 Concluding Remarks

In conclusion, the results of this study demonstrate that rationally designed MOFs-based catalysts can achieve high activity, selectivity, and stability in CO_2 conversion across multiple catalytic modes. These findings highlight the importance of tailored functional groups, open metal sites, and engineered active sites in promoting CO_2 adsorption and catalytic transformation, and provide a foundation for the development of scalable and economically viable CO_2 utilization technologies. By addressing the remaining challenges and exploring new design strategies, MOF-based catalysts have the potential to play a key role in the transition toward a circular carbon economy and the realization of sustainable energy systems.pubs.

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