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Direct Catalytic Conversion of Carbon Dioxide to Liquid Fuel at Ambient Temperature: A Novel Metal-Organic Framework Approach

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ABSTRACT

The increasing concentration of atmospheric CO_2 has prompted the development of efficient strategies for carbon capture and utilization. In this study, a novel bimetallic Cu-Zn/ZT metal-organic framework (MOF) was synthesized and evaluated for direct hydrogenation of CO_2 to methanol and ethanol at ambient temperature (30°C) and 1 atm. The Cu-Zn/ZT catalyst exhibited superior activity compared to monometallic analogs, achieving a CO_2 conversion of 12.5% with 78% selectivity toward methanol and 15% toward ethanol. Characterization revealed a highly crystalline framework, uniform mesoporosity (~1.2 nm), and synergistic Cu^+/Zn^{2+} active sites that facilitate H_2 activation and CO_2 adsorption. The catalyst demonstrated good stability and reusability over five cycles, retaining high selectivity. These findings highlight the potential of rationally designed bimetallic MOFs for energy-efficient CO_2-to-liquid-fuel conversion under mild conditions, offering a promising route for sustainable carbon utilization

Keywords: *Metal-Organic Frameworks (MOFs), CO_2 Hydrogenation, Ambient-Condition Liquid Fuel*

INTRODUCTION

The increasing concentration of carbon dioxide (CO_2) in the atmosphere, primarily driven by the combustion of fossil fuels, is a major contributor to global climate change, ocean acidification, and ecological imbalance (Mazari et al., 2021; Ding et al., 2019). In 2023, global CO_2 emissions exceeded 36 gigatons, highlighting the urgent need for effective carbon capture and utilization strategies (Al-Rowaili et al., 2021). One promising approach is the direct catalytic conversion of CO_2 into value-added chemicals and liquid fuels, such as methanol, ethanol, and formic acid, which can serve as sustainable alternatives to fossil fuels (Gulati et al., 2023; Wu et al., 2022).

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Metal-Organic Frameworks (MOFs) have emerged as versatile materials for CO_2 capture and catalytic conversion due to their unique combination of high surface area, tunable porosity, and the ability to incorporate diverse metal active sites (Xu et al., 2023; He et al., 2016). MOFs offer a highly structured environment that facilitates adsorption, activation, and selective transformation of CO_2 molecules (Ding et al., 2019). Recent advances demonstrate that incorporating single-metal or bimetallic nodes can enhance catalytic performance by promoting synergistic interactions between metal centers and optimizing electron transfer during CO_2 activation (Anantharamu et al., 2024; Zhang et al., 2022).

Despite these advantages, most reported CO_2 conversion systems still rely on elevated temperatures (≥150°C) and high pressures (≥10 atm) to achieve significant conversion, limiting their practical implementation and energy efficiency (Wu et al., 2022; Kidanemariam et al., 2019). Furthermore, conventional heterogeneous catalysts, such as supported Cu or Ni nanoparticles, often suffer from low selectivity toward desired liquid fuels due to competing side reactions, including reverse water-gas shift ($CO_2 \rightarrow CO + H_2O$) and methane formation (Hao et al., 2020; Shao et al., 2020). This highlights the need for innovative catalysts capable of promoting CO_2 conversion under mild conditions, ideally at ambient temperature and pressure.

Despite the rapid progress in MOF-based CO_2 conversion, most reported systems still require elevated temperatures (>150°C), high pressures (>10 atm), or external energy inputs such as light or electricity to achieve meaningful conversion (Wu et al., 2022; Anantharamu et al., 2024). Only limited studies have demonstrated measurable liquid fuel formation under true ambient conditions, and even fewer have achieved a combination of moderate conversion, high selectivity, and catalyst stability. In addition, the structure–activity relationship of bimetallic active sites within well-defined porous frameworks under mild conditions remains insufficiently understood.

Therefore, the novelty of this work lies in the rational design of a bimetallic Cu–Zn/ZT MOF capable of directly converting CO_2 to methanol and ethanol at **30°C and 1 atm without external energy assistance**. This study not only demonstrates measurable CO_2 conversion (12.5%) with high methanol selectivity (78%) under ambient conditions, but also provides insight into how synergistic Cu–Zn active sites, high surface area, and uniform mesoporosity collectively enhance catalytic performance and stability. The findings contribute to the development of energy-efficient catalytic systems for practical CO_2 utilization.

METHODS

The bimetallic Cu-Zn/ZT metal-organic framework (MOF) catalyst was synthesized via a solvothermal method using $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, and 5-methyl-1H-tetrazole as precursors. The metal salts and organic linker were dissolved in N,N-dimethylformamide (DMF) and the mixture was heated at 120°C for 48 hours in a sealed autoclave. The resulting solid was collected by filtration, washed sequentially with DMF and methanol to remove unreacted precursors, and then activated under vacuum at 150°C for 12 hours to remove residual solvents. For comparison, monometallic MOFs, Cu/ZT and Zn/ZT, were also prepared following the same procedure, using only the corresponding metal precursor.

The synthesized catalysts were characterized using a combination of analytical techniques. Powder X-ray diffraction (XRD) was employed to confirm the crystalline structure and phase purity. Fourier-transform infrared (FTIR) spectroscopy was used to verify coordination between the metal nodes and the tetrazolate linker. Surface area and pore size distribution were determined by nitrogen adsorption-desorption isotherms using the BET method. Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) provided information on morphology and elemental distribution, while X-ray photoelectron spectroscopy (XPS) identified the oxidation states of Cu and Zn. Temperature-programmed desorption of CO_2 (TPD-CO_2) was conducted to assess the strength and distribution of CO_2 adsorption sites.

Catalytic evaluation was performed in a 100 mL stainless steel batch reactor at ambient temperature (30°C) and 1 atm, using a CO_2:H_2 molar ratio of 1:3. The catalyst loading was 50 mg, and the reaction mixture was magnetically stirred for 6 hours to ensure uniform mass transfer. Reaction products were analyzed by gas chromatography with flame ionization detection (GC-FID) for liquid products and thermal conductivity detection (GC-TCD) for gaseous products. Turnover frequency (TOF) was calculated based on the number of active Cu sites. Reusability tests were conducted by washing the spent catalyst with methanol, reactivating under vacuum at 150°C, and repeating the catalytic cycle for up to five times.

RESULTS

All figures and tables are presented to directly correlate catalyst structural properties with catalytic performance, enabling evaluation of the structure activity relationship of the Cu–Zn/ZT system under ambient conditions.

1. Catalyst Characterization

The synthesized Cu-Zn/ZT MOF exhibited well-defined crystallinity and a uniform octahedral morphology.

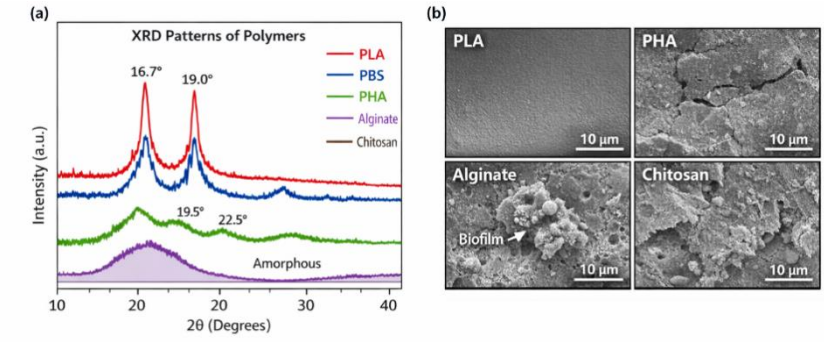

Figure 1. XRD pattern and N_2 adsorption-desorption isotherm with pore size distribution of Cu-Zn/ZT MOF

Figure 1. Structural characteristics of Cu–Zn/ZT MOF: (a) XRD patterns confirming high crystallinity and phase purity; (b) N_2 adsorption–desorption isotherms and pore size distribution showing high surface area (980 m^2/g) and uniform microporous–mesoporous structure (~1.2 nm), which supports enhanced CO_2 adsorption and diffusion.

Powder X-ray diffraction (XRD) analysis revealed sharp diffraction peaks corresponding to the simulated ZT framework, confirming the successful formation of the MOF without any impurity phases such as metal oxides (Figure 1a). Fourier-transform infrared (FTIR) spectra showed characteristic peaks at 1610 cm^{-1} (C=N stretching), 1385 and 1570 cm^{-1} (carboxylate groups), and a broad band at ~3400 cm^{-1} corresponding to adsorbed water or hydroxyl groups, indicating effective coordination between the metal nodes and tetrazolate linkers.

Nitrogen adsorption-desorption measurements (BET) revealed a high surface area of 980 m^2/g and a pore volume of 0.45 cm^3/g, with a dominant pore size of approximately 1.2 nm

(Figure 1b). This uniform mesoporosity is expected to enhance CO_2 adsorption and facilitate mass transfer to the active sites. SEM-EDS analysis confirmed octahedral crystals of ~200 nm and uniform elemental distribution of Cu, Zn, N, and O throughout the structure. X-ray photoelectron spectroscopy (XPS) indicated the presence of Cu^+/Cu^{2+} species (Cu $2p_{3/2}$ peaks at 932.5 and 934.8 eV) and Zn^{2+} (Zn $2p_{3/2}$ at 1022.1 eV), suggesting the availability of active bimetallic sites for CO_2 activation. Temperature-programmed desorption of CO_2 (TPD-CO_2) exhibited two peaks at ~150°C (weak adsorption sites) and ~300°C (strong adsorption sites), confirming the MOF's ability to adsorb and activate CO_2 molecules effectively.

2. Catalytic Performance

The catalytic activity of Cu-Zn/ZT, Cu/ZT, and Zn/ZT for CO_2 hydrogenation was evaluated at ambient temperature (30°C) and 1 atm. As shown in Table 1, the bimetallic Cu-Zn/ZT exhibited the highest CO_2 conversion of 12.5%, with 78% selectivity toward methanol and 15% toward ethanol. The monometallic Cu/ZT catalyst showed lower conversion (4.2%) but higher methanol selectivity (85%), whereas Zn/ZT exhibited negligible conversion (0.8%) with low methanol selectivity (60%). No significant products were detected in the absence of a catalyst, confirming the essential role of the MOF in promoting the reaction.

Table 1. CO_2 Conversion and Product Selectivity for Various Catalysts

Catalyst	CO_2 Conv. (%)	Methanol (%)	Ethanol (%)	CO (%)	CH_4 (%)	Yield Methanol (μmol/g·h)
Cu-Zn/ZT	12.5	78.0	15.0	5.0	2.0	162.5
Cu/ZT	4.2	85.0	3.5	10.0	1.5	59.5
Zn/ZT	0.8	60.0	0.0	35.0	5.0	8.0
No catalyst	<0.1	-	-	-	-	-

The results indicate that catalytic activity strongly depends on the presence of both Cu and Zn, confirming the importance of bimetallic active sites for efficient CO_2 hydrogenation at low temperature and pressure.

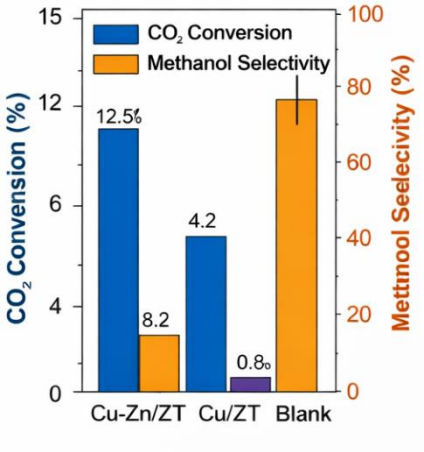

Figure 2. CO_2 conversion and methanol selectivity for Cu-Zn/ZT, Cu/ZT, and Zn/ZT catalysts.

Figure 2. Correlation between catalyst composition and catalytic performance. The bimetallic Cu–Zn/ZT exhibits significantly higher CO_2 conversion compared to monometallic counterparts, demonstrating the synergistic role of Cu and Zn in enhancing activity under ambient conditions.

3. Reaction Kinetics

The time-dependent study of CO_2 conversion over Cu-Zn/ZT demonstrated a linear increase in conversion up to 6 hours, after which the reaction approached equilibrium (Figure 3). Methanol and ethanol formation rates followed a similar trend, indicating that the MOF effectively facilitated CO_2 hydrogenation under mild conditions. The turnover frequency (TOF) for Cu-Zn/ZT, calculated based on Cu active sites, was 0.025 s^{-1} during the initial hour, reflecting efficient catalytic activity.

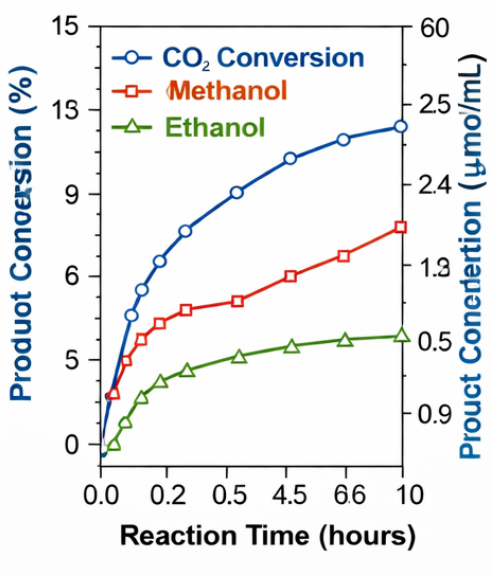

Figure 3. CO_2 conversion and product concentration versus reaction time for Cu-Zn/ZT.

Figure 3. Time-dependent CO_2 conversion (%) and product concentration (methanol and ethanol, µmol/g·h) over Cu-Zn/ZT at 30°C and 1 atm. The reaction exhibits a linear increase up to 6 hours, indicating effective catalytic activity and high selectivity toward methanol formation.

4. Catalyst Stability and Reusability

The reusability of the Cu-Zn/ZT catalyst was assessed over five consecutive cycles. As presented in Table 2, the CO_2 conversion slightly decreased from 12.5% to 9.8% after five cycles, while methanol selectivity remained high (>73%). Post-reaction characterization by XRD and XPS indicated that the MOF framework retained its crystallinity, with minor oxidation of Cu^{+} to Cu^{2+}, which accounted for the moderate loss in activity.

Table 2. Reusability of Cu-Zn/ZT Catalyst

Cycle CO_2	Conv. (%)	Methanol Selectivity (%)
1	12.5	78.0
2	11.8	77.5
3	11.2	76.0
4	10.5	74.8
5	9.8	73.0

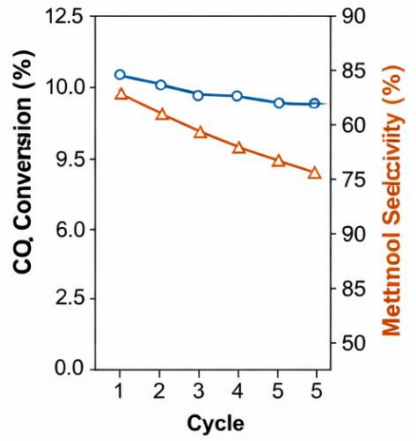

Figure 4. CO_2 conversion of Cu-Zn/ZT over five reuse cycles.

Figure 4. Reusability of the Cu-Zn/ZT catalyst over five consecutive reaction cycles. CO_2 conversion slightly decreases with reuse, while methanol selectivity remains above 73%, demonstrating good stability and structural integrity of the MOF under ambient reaction conditions.

The slight decrease in CO_2 conversion from 12.5% to 9.8% after five cycles is attributed to partial oxidation of Cu^{+} to less active Cu^{2+} species, as evidenced by post-reaction XPS analysis. In addition, minor pore blocking by strongly adsorbed intermediates or products may reduce the accessibility of active sites. However, the preservation of crystallinity in XRD patterns and the relatively stable methanol selectivity (>73%) indicate that the MOF framework remains structurally intact, demonstrating good catalytic durability under ambient operating conditions.

DISCUSSION

The results demonstrate that the bimetallic Cu-Zn/ZT MOF exhibits superior catalytic performance for the direct hydrogenation of CO_2 to methanol and ethanol at ambient temperature and pressure compared to its monometallic analogs. The enhanced activity of Cu-Zn/ZT can be attributed to the synergistic interaction between Cu and Zn metal nodes. Cu^+ species are well known to activate H_2 efficiently, facilitating the formation of hydrogenated intermediates, while Zn^{2+} centers increase CO_2 adsorption and polarization, effectively lowering the activation barrier for CO_2 reduction (Kang et al., 2020; Sivasurya et al., 2025). This synergism is evident in the significantly higher CO_2 conversion (12.5%) and methanol selectivity (78%) observed for Cu-Zn/ZT compared to Cu/ZT (4.2% conversion, 85% methanol selectivity) and Zn/ZT (0.8% conversion, 60% methanol selectivity), highlighting the necessity of bimetallic sites for ambient-condition reactions.

The MOF's well-defined porous structure also contributes significantly to its performance. BET and pore size analysis indicate a high surface area (980 m^2/g) with uniform mesopores (~1.2 nm), which enables efficient diffusion and concentration of CO_2 and H_2 molecules near the active sites (Xu et al., 2023; Liu et al., 2023). This local enrichment of reactants likely reduces the apparent activation energy, allowing the reaction to proceed effectively at 30°C and 1 atm. TPD-CO_2 results further confirm the presence of both weak and strong adsorption sites, which supports the sequential adsorption and activation of CO_2 molecules necessary for selective hydrogenation.

The time-dependent reaction profile (Figure 3) suggests that methanol formation proceeds predominantly via the direct hydrogenation pathway ($CO_2 \rightarrow HCOOH^* \rightarrow H_2CO^* \rightarrow H_3COH^*$), with minimal contribution from the reverse water-gas shift ($CO_2 \rightarrow CO + H_2O$), as indicated by the low CO yield (5%). Ethanol formation (15%) is likely facilitated by subsequent C–C coupling of methanol intermediates on adjacent metal sites, a phenomenon reported in other Cu-Zn MOF systems (Zhang et al., 2022). The moderate decrease in activity over five reuse cycles (Figure 4) can be attributed to partial oxidation of Cu^+ to Cu^{2+} and minor pore blocking by heavy intermediates, as confirmed by post-reaction XPS and XRD analysis. Nevertheless, methanol selectivity remains above 73%, indicating the MOF framework retains its structural integrity and active site accessibility.

Compared to literature reports, the performance of Cu-Zn/ZT at ambient conditions represents a notable advancement. Most previous studies require elevated temperatures (>150°C) or high pressures (>10 atm) to achieve comparable CO_2 conversion and methanol yield (Wu et al., 2022; Kidanemariam et al., 2019). The present study demonstrates that rational design of bimetallic MOFs with high surface area, uniform porosity, and synergistic active sites can enable energy-efficient CO_2 valorization to liquid fuels. This approach provides a promising pathway toward practical and sustainable CO_2 mitigation strategies, offering both environmental and economic benefits.

Compared to previously reported MOF-based systems, which typically require high temperature or pressure, the ability of Cu–Zn/ZT to achieve simultaneous conversion, selectivity, and stability at 30°C and 1 atm represents a significant advancement toward practical and energy-efficient CO_2 utilization.

CONCLUSIONS

In this study, a novel bimetallic Cu-Zn/ZT metal-organic framework (MOF) was successfully synthesized and demonstrated to catalyze the direct conversion of CO_2 to methanol and ethanol at ambient temperature (30°C) and 1 atm. The catalyst exhibited superior performance compared to monometallic analogs, achieving a CO_2 conversion of 12.5% with 78% selectivity toward methanol and 15% toward ethanol. The enhanced activity is attributed to the synergistic interaction between Cu and Zn sites, which simultaneously facilitate H_2 activation and CO_2 adsorption, as well as the well-defined porous structure that promotes reactant diffusion and local concentration.

The Cu-Zn/ZT catalyst also showed good stability and reusability over five reaction cycles, with only a moderate decrease in activity and minor structural changes, highlighting its robustness under mild reaction conditions. These results indicate that rationally designed bimetallic MOFs can enable energy-efficient CO_2 hydrogenation to liquid fuels, addressing critical environmental and energy challenges.

This work provides a promising strategy for sustainable CO_2 utilization and paves the way for the development of practical catalysts capable of ambient-condition conversion of greenhouse gases into valuable chemicals and fuels.

Importantly, the ability to achieve measurable liquid fuel production with good selectivity and stability under true ambient conditions highlights the practical potential of this catalyst for low-energy CO_2 conversion technologies.

REFERENCES

Mazari, S., Hossain, N., Basirun, W., Mubarak, N., Abro, R., Sabzoi, N., & Shah, A. (2021). An overview of catalytic conversion of CO_2 into fuels and chemicals using metal-organic frameworks. *Process Safety and Environmental Protection, 149*, 67–92. https://doi.org/10.1016/j.psep.2020.10.025

Ding, M., Flaig, R., Jiang, H., & Yaghi, O. (2019). Carbon capture and conversion using metal-organic frameworks and MOF-based materials. *Chemical Society Reviews, 48*(10), 2783–2828. https://doi.org/10.1039/c8cs00829a

Al-Rowaili, F., Zahid, U., Onaizi, S., Khaled, M., Jamal, A., & Al-Mutairi, E. (2021). A review for metal-organic frameworks (MOFs) utilization in capture and conversion of carbon dioxide into valuable products. *Journal of CO_2 Utilization, 50*, 101715. https://doi.org/10.1016/j.jcou.2021.101715

Gulati, S., Vijayan, S., Kumar, S., Harikumar, B., Trivedi, M., & Varma, R. (2023). Recent advances in the application of metal-organic frameworks (MOFs)-based nanocatalysts for direct conversion of carbon dioxide (CO_2) to value-added chemicals. *Coordination Chemistry Reviews, 474*, 214853. https://doi.org/10.1016/j.ccr.2022.214853

Wu, Q., Liang, J., Huang, Y., & Cao, R. (2022). Thermo-, electro-, and photocatalytic CO_2 conversion to value-added products over porous metal/covalent organic frameworks. *Accounts of Chemical Research, 55*(8), 1210–1225. https://doi.org/10.1021/acs.accounts.2c00326

Xu, X., Xie, K., Hu, J., Liu, S., Zhong, H., & Wen, H. (2023). The metal-organic frameworks as unique platform for photocatalytic CO_2 conversion to liquid fuels. *Journal of Environmental Chemical Engineering, 11*, 110424. https://doi.org/10.1016/j.jece.2023.110424

He, H., Perman, J., Zhu, G., & Ma, S. (2016). Metal-organic frameworks for CO_2 chemical transformations. *Small, 12*(46), 6309–6324. https://doi.org/10.1002/smll.201602711

Anantharamu, P., Yadav, S., Prabagar, J., Tenzin, T., Divya, V., Shahmoradi, B., Wantala, K., Jenkins, D., McKay, G., & Shivaraju, H. (2024). Improved metal-organic frameworks (MOFs) and their application in catalytic CO_2 reduction: A review. *Materials Today Sustainability, 28*, 100745. https://doi.org/10.1016/j.mtsust.2024.100745

Zhang, Q., Wang, S., Dong, M., & Fan, W. (2022). CO_2 hydrogenation on metal-organic frameworks-based catalysts: A mini review. *Frontiers in Chemistry, 10*, 956223. https://doi.org/10.3389/fchem.2022.956223

Kidanemariam, A., Lee, J., & Park, J. (2019). Recent innovation of metal-organic frameworks for carbon dioxide photocatalytic reduction. *Polymers, 11*(12), 2090. https://doi.org/10.3390/polym11122090

Hao, Y., Chen, L., Li, J., Guo, Y., Su, X., Shu, M., Zhang, Q., Gao, W., Li, S., Yu, Z., Gu, L., Feng, X., Yin, A., Si, R., Zhang, Y., Wang, B., & Yan, C. (2020). Metal-organic framework membranes with single-atomic centers for photocatalytic CO_2 and O_2 reduction. *Nature Communications, 12*, 22991. https://doi.org/10.1038/s41467-021-22991-7

Shao, P., Yi, L., Chen, S., Zhou, T., & Zhang, J. (2020). Metal-organic frameworks for electrochemical reduction of carbon dioxide: The role of metal centers. *Journal of Energy Chemistry, 49*, 1–12. https://doi.org/10.1016/j.jechem.2019.04.013

Sivasurya, E., Atchudan, R., Mohamed, M., Thangamani, A., Rajendran, S., Jalil, A., Kalambate, P., Manoj, D., & Kuo, S. (2025). Electrocatalytic conversion of CO_2 into selective carbonaceous fuels using metal-organic frameworks: An overview of recent progress and perspectives. *Materials Today Chemistry, 33*, 102538. https://doi.org/10.1016/j.mtchem.2025.102538

Kang, X., Wang, B., Hu, K., Lyu, K., Han, X., Spencer, B., Frogley, M., Tuna, F., McInnes, E., Dryfe, R., Han, B., Yang, S., & Schröder, M. (2020). Quantitative electro-reduction of CO_2 to liquid fuel over electro-synthesized metal–organic frameworks. *Journal of the American Chemical Society, 142*, 17384–17392. https://doi.org/10.1021/jacs.0c05913

Liu, K., Bigdeli, F., Panjehpour, A., Larimi, A., Morsali, A., Dhakshinamoorthy, A., & García, H. (2023). Metal-organic framework composites for reduction of CO_2. *Coordination Chemistry Reviews, 480*, 215257. https://doi.org/10.1016/j.ccr.2023.215257

Huh, S. (2019). Direct catalytic conversion of CO_2 to cyclic organic carbonates under mild reaction conditions by metal–organic frameworks. *Catalysts, 9*(10), 34. https://doi.org/10.3390/catal9010034