

RESEARCH ARTICLE

Copper tetrazolate based metal-organic frameworks as highly efficient catalysts for artificially chemical and electrochemical CO₂ conversion

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Abstract

Development of efficient catalyst for CO₂ conversion is highly demanded to alleviate the CO₂ related environmental and energy crisis. Here, we develop a series of copper tetrazolate based metal-organic frameworks (MOFs) (Cu-5H, Cu-5M and Cu-5P) to promote the artificial CO₂ conversion via chemical and electrochemical route. Featuring with abundant exposed Lewis-acid Cu centers, nitrogen-rich sites, and porous architecture, Cu-5M and Cu-5P exhibit high yield (>99%) toward synthesizing cyclic carbonate via the cycloaddition reaction of CO₂ to epoxide at ambient condition. In electrochemical CO₂ conversion process, Cu-5H shows high electrocatalytic activity with a large Faradaic efficiency (91%) for formate. The ex situ scanning electron microscopy and x-ray diffraction investigations indicate the in situ generated Cu species in the MOFs structure play vital roles in promoting the high electrocatalytic activity. Our work sheds light on the facile development of metal and nitrogen-rich MOF based catalysts in chemical and electrochemical conversion CO₂ to valuable chemical and fuel.

KEYWORDS

CO₂ conversion, copper tetrazolate, cyclic carbonate, electrocatalyst, metal-organic frameworks

1 | INTRODUCTION

Nowadays, dramatically increasing anthropogenic CO₂ emission from the consumption of fossil fuels has caused

serious environmental issues associated with the global warming, climate change and ocean acidization; thus, stimulating extensive efforts into developing advanced technologies on CO₂ capture and utilization.^[1] In a

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well-designed reaction, CO₂ can act as vital C1 feedstock to fabricate the value-added chemicals and carbon-based fuels, which eventually contributes to a sustainable carbon cycle and simultaneously alleviates the current energy crisis. One promising option is cycloaddition of CO₂ to epoxide toward synthesis of cyclic carbonates that have demonstrated successful applications in petrochemicals, fine chemicals, pharmaceuticals, electrochemical electrolytes, and so on.^[2] Besides, photo/electro-chemical CO₂ conversion to small molecular fuels and chemicals, coupling with renewable energy, also offers a clean and effective approach to close the carbon loop and address the issues relevant to CO₂.^[1d,3] However, due to the highly thermodynamic/kinetic stability of CO₂, neither of these CO₂ conversion processes can be effectively proceeded toward high yields of target products when employing low energy input. Therefore, it is imperative to develop a rational catalyst system to activate the inert CO₂, expedite the conversion process and thus enhance the conversion efficiency.

Inspired from the nature, a wide range of coordination transitional metal-based (Ru, Ir, Zn, Co, Ni, Cu, etc.,) complexes have been investigated as excellent catalysts in chemical CO₂ conversion and electrochemical CO₂RR by virtue of the rich transitional/heteroatom sites, tunable chemical structure and functionalities.^[3a,4] Particularly, the maximum utilization of the catalytic sites and diversity in the coordination environment afford these homogeneous molecular catalysts with high reaction efficiency. Unfortunately, issues such as the limitation of separation and fast degradation of catalytic activity, heavily hamper the large-scale applications of homogeneous catalysts in practical industry, which highlights the importance of developing efficient heterogeneous catalysts. Metal-organic frameworks (MOFs), one class of highly ordered porous crystalline coordination polymers, build up a bridge between homogeneous and heterogeneous catalysis through their molecular-like catalytic sites on the extended structure, and hold great promise in the artificial CO₂ utilization.^[2c,5] First, the diversity and tunability in composition/structure offer MOFs catalysts with precisely tailor-made catalytic environments, which are benefited to boost the catalytic activity and high selectivity toward controllable target reaction. Next, their large surface areas and ordered porous architectures allow for exposing high density of well-defined active sites and ensuring enough mass transfer during the catalytic process. Additionally, the heteroatom-donor sites (such as amine, pyridine, imidazole, triazole, tetrazole groups, etc.,) can be easily introduced into the building blocks and enhance CO₂ affinity of MOF based catalysts.^[2e,6] More importantly, their well-defined structure can be an ideal model for fundamental mechanism studies, facilitating the rational design of high-

performance catalysts. To this end, various MOFs have shown promising progresses in CO₂ conversion, such as sulfonate-based 3D Cu(II) MOF, triazole-containing MOF, Hf-NU-1000, Al₂(OH)₂TCPP-Co, VPI-100 (Cu), phthalocyanine Cu coordinated Zn MOF, and so on.^[2d,2e,7] However, the unsatisfactory catalytic activity and selectivity, complicated synthesis steps, low energy efficiency, large energy input (high temperature, large pressure or large overpotential) are still plaguing on MOFs based catalysts in artificially chemical and electrochemical CO₂ utilization. Therefore, developing a facile way to achieve rational MOFs based catalyst with well-defined active center is high expected despite grand challenges.

Herein, copper tetrazolate based MOFs (abbreviated as Cu-5H, Cu-5M, and Cu-5P) are developed for artificial CO₂ conversion. Cu-M and Cu-5P exhibit high yield (close to 100%) of cyclic carbonate synthesis via the cycloaddition reaction of CO₂ to epoxide at ambient condition due to abundant exposed Lewis-acid Cu sites and nitrogen-rich groups. In electrochemical reduction reaction, the as-synthesis Cu-5H, shows high electrocatalytic activity with a large HCOO⁻ Faradaic efficiency (FE, 91%) at -0.8 V versus reversible hydrogen electrode (RHE). The ex situ scanning electron microscopy (SEM) and x-ray diffraction (XRD) investigations indicate the in situ generated Cu species account for the high catalytic activity in electrochemical reduction of CO₂ to HCOO⁻. Our work sheds light on the facile development of N-rich MOF based catalyst in chemical and electrochemical conversion CO₂ to valuable chemical and fuel.

2 | RESULTS AND DISCUSSION

The Cu tetrazole MOFs were synthesized by solvothermal methods (details shown in Supporting information), which were confirmed by the Fourier-transform infrared (FT-IR) spectroscopy and powder XRD measurements. The typical bands (C-N, N-N, C=N, N=N, tetrazole ring and Cu-N) are included in Figure 1A. For example, ν (C-N) and ν (N-N) absorption bands are observed at around 1300–1200 cm⁻¹ while the tetrazole ring occurs at 900–1100 cm⁻¹.^[8] Most importantly, Cu-N band is found at around 695 cm⁻¹, confirming the successful coordination of Cu and N atoms.^[8a] And the disappearance of the ligand NH signals (2500–3300 cm⁻¹) in the FT-IR spectra further demonstrate the coordination of N to Cu of Cu-5H, Cu-5M, and Cu-5P, which is also verified by the observation of Cu-N peak at 500–800 cm⁻¹ in their Raman spectra (Figure S1).^[7d,9] The intensive peaks around 5° to 20° in the XRD patterns (Figure 1B), which is similar with the reported literatures,^[8,10] further prove the successful formation of Cu tetrazole MOFs as well as their excellent

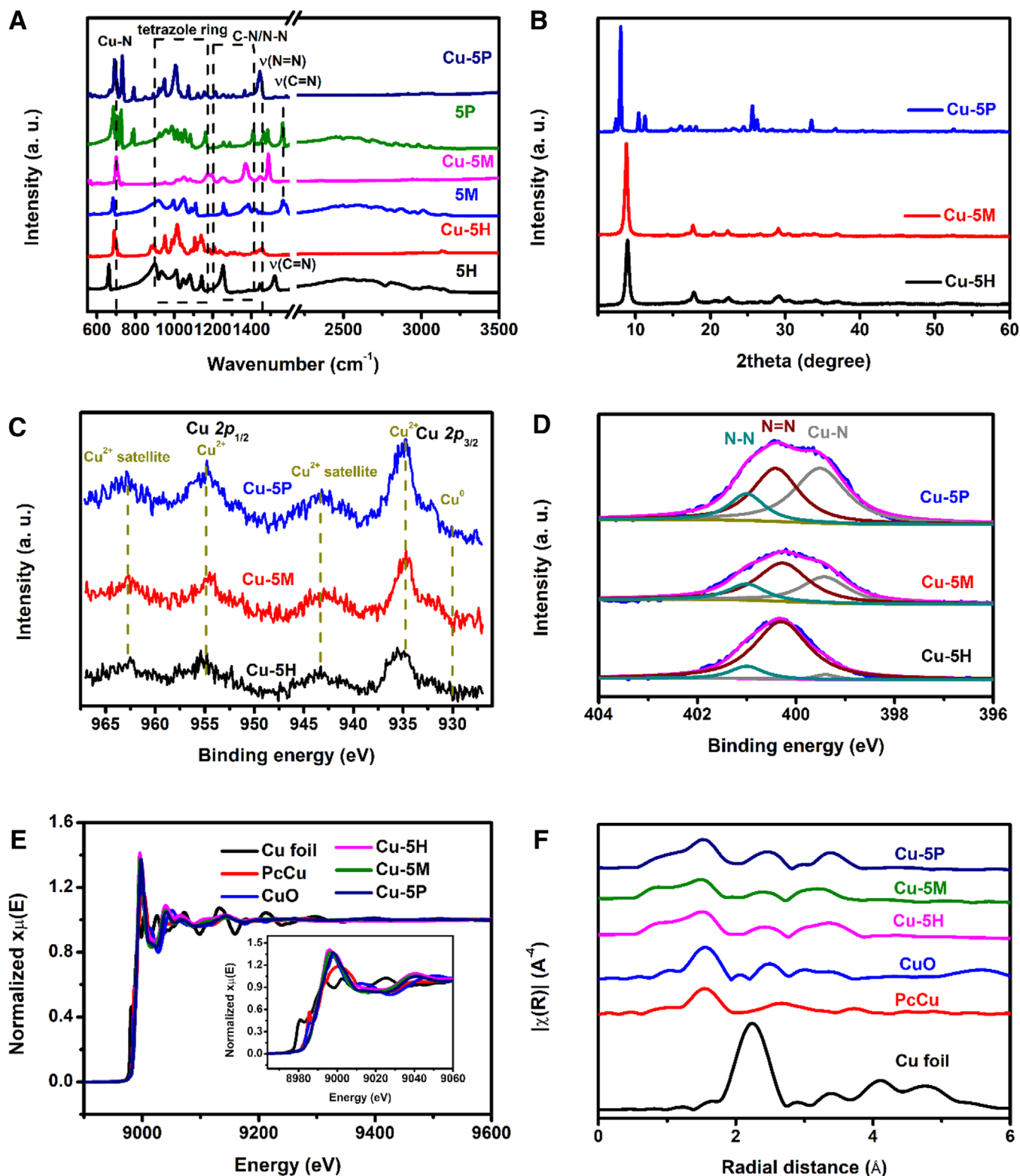


FIGURE 1 Characterizations. A, Fourier-transform infrared (FT-IR) spectra of Cu-5H, 5H (5H-tetrazole), Cu-5M, 5M (5-methyl-tetrazole), 5P (5-phenyl-tetrazole), and Cu-5P. B, X-ray diffraction (XRD) patterns of Cu-5H, Cu-5M, and Cu-5P. C, High-resolution Cu 2p XPS spectra of Cu-5H, Cu-5M, and Cu-5P. D, High-resolution N 1s XPS spectra of Cu-5H, Cu-5M, and Cu-5P. E, Cu K-edge x-ray absorption near-edge structure (XANES) spectra of Cu foil, CuO, PcCu (phthalocyanine copper), Cu-5H, Cu-5M, and Cu-5P. Inset: the enlarged figure of the XANES spectra between 8950 and 9060 eV. F, Fourier transform extended x-ray absorption fine structure (EXAFS) of Cu foil, CuO, PcCu, Cu-5H, Cu-5M, and Cu-5P

crystallinity. According to the previous reports,^[8,10] it is proposed that Cu–5P is formed with the common unit of $\text{Cu}(\text{5P})_2\text{DMSO}$ (DMSO: dimethyl sulfoxide), wherein Cu(II) center connects with two tetrazole anions via Cu–N bond and one DMSO molecule. And Cu–5M is $\text{Cu}(\text{5M})_2\text{DMSO}$ while Cu–5H is $\text{Cu}(\text{5H})_2\text{DMSO}$. It is worth noting that the introduction of methyl and phenyl groups in the tetrazolate ligand will change the solubility, the acidity constants of the tetrazole ligands, as well as bring the steric hindrance, which may influence the MOF nucleation process and promote the formation of Cu tetrazolate MOFs. Additionally, the steric hindrance of the substituents also results in different thermostability and morphology of the obtained Cu tetrazolate MOFs.^[8b,11] As shown in Figure S2, thermogravimetric analysis under air condition indicates the Cu–5M and Cu–5P are thermally stable up to 260 °C, while Cu–5H shows a gradual weight loss from 100 to 300 °C. This is likely owing to that the steric hindrance and the electronic effect of methyl and phenyl groups contribute to stabilize the MOF structures.^[11] Additionally, SEM images show that the morphology of Cu tetrazolate MOFs is varied with different substituents of ligands, which is possibly associated with the different resultant solubility and steric hindrances of the ligands. As shown in Figure S3, Cu–5H has the rice-like morphology with average length of 2.44 μm . Cu–5M shows the morphology of aggregated particles with average size of 0.3 μm , and Cu–5P possesses the nanorod morphology with average length of 6 μm . Besides, the Brunauer–Emmett–Teller (BET) surface area and pore size of the as-synthesized copper tetrazolate based MOFs are different (Figure S4). BET surface area of Cu–5P (304.7 $\text{m}^2 \text{g}^{-1}$) and Cu–5M (357.8 $\text{m}^2 \text{g}^{-1}$) are higher compared to Cu–5H (279.3 $\text{m}^2 \text{g}^{-1}$), which is favorable for exposing high density of Cu–N sites and sufficient mass transport during the catalytic process.

To investigate the chemical structure of Cu–5H, Cu–5M, and Cu–5P, x-ray photoelectron spectroscopy (XPS) measurement is performed. The survey spectra confirm the presence of Cu, C and N elements (Figure S5) in Cu–5H, Cu–5M, and Cu–5P samples. The sets of peaks at 935.2 and 954.5 eV, assigned to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, are observed in the high-resolution Cu 2p XPS spectra of Cu–5H, Cu–5M, and Cu–5P (Figure 1C), which is the typical character of Cu^{2+} .^[7d,12] Besides, the strong satellites of Cu^{2+} at 943.1 and 962.9 eV and the absent peak of metallic Cu at 931 eV further indicate the oxidation state of Cu is +2 in Cu–5H, Cu–5M, and Cu–5P MOFs.^[7d,12] And the deconvoluted N1s spectra further verifies the coordination of Cu and N (Figure 1D).^[12] To further study the chemical state of Cu in as-synthesized Cu tetrazolate MOFs, x-ray absorption spectroscopy (XAS) and extended x-ray absorption fine structure (EXAFS) analyses were carried out. As shown in the Cu K-edge

x-ray absorption near-edge structure (XANES) spectra in Figure 1E, all Cu–5H, Cu–5M, and Cu–5P MOFs exhibit a characteristic main absorption peak of $\text{Cu}(2+)$ at 8998 eV, which is similar with the reference copper(II) phthalocyanine (PcCu) and CuO; thus, confirming the existence of $\text{Cu}(2+)$ -N in as-prepared MOFs.^[7d,13] Importantly, the pre-edge peak at 8980 eV, which is typically found for metallic Cu, is absent in Cu K-edge XANES spectra of all Cu tetrazolate MOFs, excluding the impurities of metallic Cu in Cu–5H, Cu–5M, and Cu–5P MOFs.^[7d,13] The radial distribution functions for Cu atom of Cu–5H, Cu–5M, and Cu–5P is investigated by the Fourier transform EXAFS analysis. As shown in Figure 1F, an intensive peak around 1.54 Å is assigned to the Cu–N coordination in Cu–5H, Cu–5M, and Cu–5P. Moreover, the missing obvious structural peaks and the diminishment of the signal at 2.23 Å reveals that no heavy backscattering atoms (Cu) are bounding to Cu sites in Cu–5H, Cu–5M, and Cu–5P, further excluding the existence of metallic Cu in as-synthesized Cu tetrazolate MOFs. Therefore, XANES and EXAFS analysis offer solid proofs for the successful coordination of N to Cu in Cu–5H, Cu–5M, and Cu–5P.

Taking the advantages of MOFs, Cu–5H, Cu–5M, and Cu–5P MOFs are first investigated as heterogeneous catalysts for the cycloaddition of CO_2 to epichlorohydrin for chloropropene carbonate synthesis in combination with *tetra-n-tert*-butylammonium bromide as the co-catalyst (Figure 2A). As shown in Figure 2B, Cu–5P harvests a high yield (>99.9%) for chloropropene carbonate synthesis under ambient condition when the reaction time is prolonged to 24 h, which is higher than that for most of the MOF related catalysts (Table S1). And Cu–5M also obtains a high yield (>99%) for cyclic carbonate synthesis under identical condition (Figure 2C). However, Cu–5H shows only 68% yields for this cyclic carbonate, which is probably due to its lower CO_2 absorption capacity (Figure S6) and relatively lower ratio of exposed Cu–N sites (Figure S7). The high catalytic activity of Cu–5P and Cu–5M originates from the abundant exposed Cu(II) Lewis acidic sites and accessible N-donor sites (the possible mechanism is shown in Figure S8). As the critical parameters for the practical application, the stability of Cu–5P is also evaluated. No distinct degradation in yields of cyclic carbonate is discovered for the recycled Cu–5P catalysts (Figure S9), suggesting its robust stability and easier recyclability. No obvious changes in the structure of Cu–5P after chemical CO_2 conversion reaction are verified by the FT-IR spectra and XRD patterns (Figure S10 and S11), implying the excellent stability of Cu–5P during the chemical CO_2 conversion reaction.

Here, we also investigate the electrochemical CO_2 RR performance of Cu–5H, Cu–5M, and Cu–5P in a gas-tight two-compartment electrochemical cell with a standard electrode system, wherein the carbon paper loading with

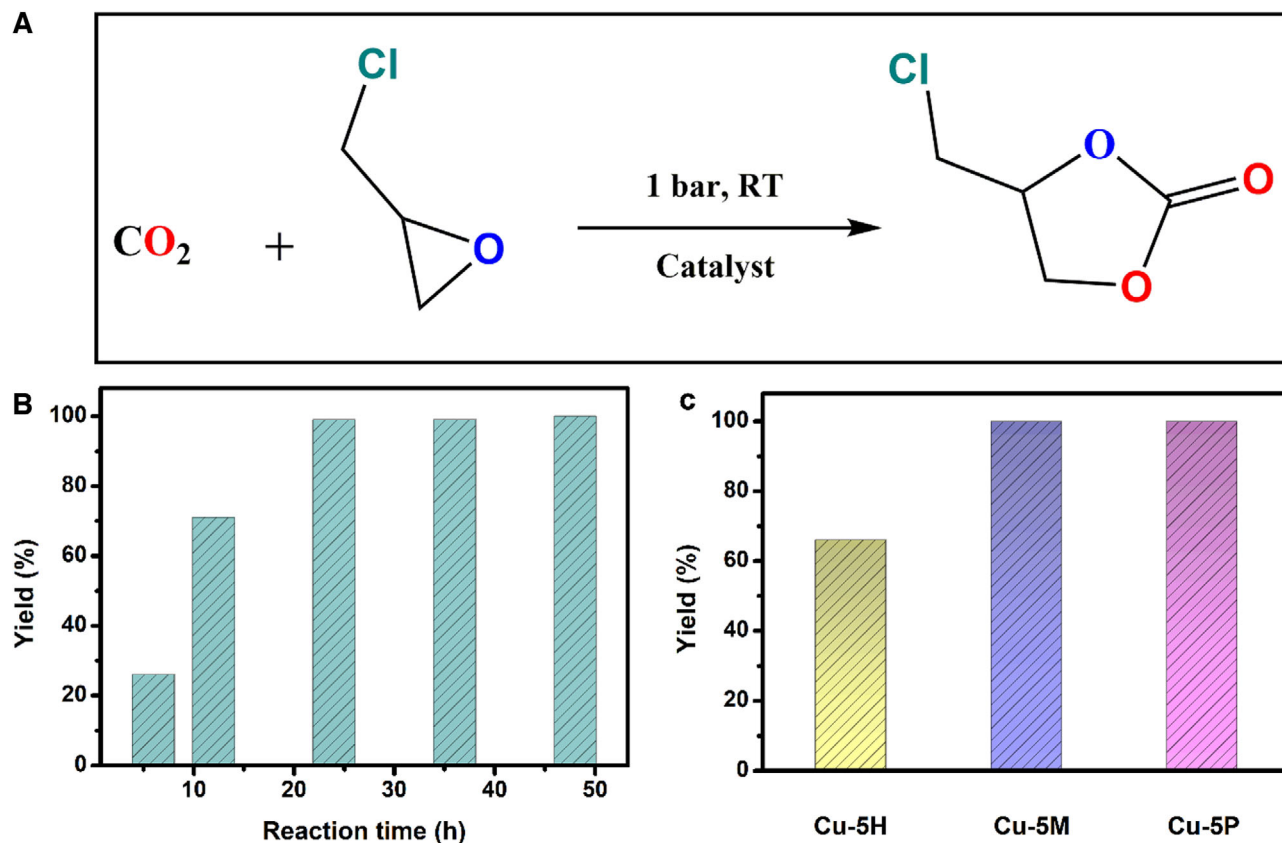


FIGURE 2 Chemical catalytic performance of Cu-5H, Cu-5M, and Cu-5P. A, Schematic synthesis process of chloropropene carbonate from cycloaddition of 1-chloro-2,3-epoxypropene and CO_2 at room temperature (RT) and 1 bar pressure. B, Yields of chloropropene carbonates versus reaction time using Cu-5P catalysts. C, Yields of chloropropene carbonates from the cycloaddition of 1-chloro-2,3-epoxypropene and CO_2 using Cu-5H, Cu-5M, and Cu-5P catalysts

catalysts, Ag/AgCl, Pt mesh, and 0.1M KHCO_3 solution are used as working electrode, reference electrode, counter electrode and electrolyte, respectively. After the electrochemical activation in 0.1M KHCO_3 solution, stable cyclic voltammetry curves are obtained for Cu-5H, Cu-5M, and Cu-5P. It is worth noting that Cu-5H and Cu-5M tend to collapse into smaller particles after the electrochemical activation as shown in the SEM images (Figure S12), which is due to the reconstructing of Cu MOFs and in situ generation of Cu species, and thus benefits for CO_2RR .^[13a,14] As shown in the linear sweep voltammetry (LSV) curves in CO_2 -saturated 0.1M KHCO_3 electrolyte (Figure 3A), Cu-5H delivers a larger current density compared to Cu-5M and Cu-5P due to its high electron transfer kinetics and larger electrochemical surface area (ECSA). To verify that the currents originate from the catalytic CO_2RR , constant potential electrolysis was performed. The products were detected via gas chromatography and nuclear magnetic resonance measurements.^[15] Cu-5H displays a high selectivity for CO_2 conversion to formate with high FE which is more than 85% over the entire applied potentials only accompany with trace of H_2 and CO (Figure S13) and

total FE of $99 \pm 0.7\%$. At -0.8 V versus RHE, Cu-5H harvests the maximum formate FE up to 91% which is higher than that of Cu-5M (87%) and Cu-5P (80%) as well as superior to other similar Cu electrocatalysts (Table S2–3). And the electrochemical double-layer capacitance (C_{dl}) were estimated to reflect the ECSA of Cu-5H, Cu-5M, and Cu-5P.^[16] As displayed in Figure 3C and S14, the larger value C_{dl} of Cu-5H demonstrates its higher ECSA compared to Cu-5M and Cu-5P, facilitating the exposing more electrochemically active sites. Electrochemical impedance spectroscopy (EIS) results (Figure 3D, S15, and Table S4) indicate that Cu-5H exhibits smaller contract and transfer resistance and thus faster electron kinetics than those of Cu-5M and Cu-5P,^[17] which will greatly contribute to the high CO_2RR catalytic activity of Cu-5H. To assess the stability, long-term electrolysis at -0.8 V versus RHE of the as-synthesized samples is carried out. All Cu-5H, Cu-5M, and Cu-5P catalysts display the long-term catalytic durability over the operating condition. Both current density and FE of Cu-5H (FE: 91%), Cu-5M (FE: 84%), and Cu-5P (FE: 80%) are maintained without apparent degradation after constant potential electrolysis for 32 h (Figure 3E,F),

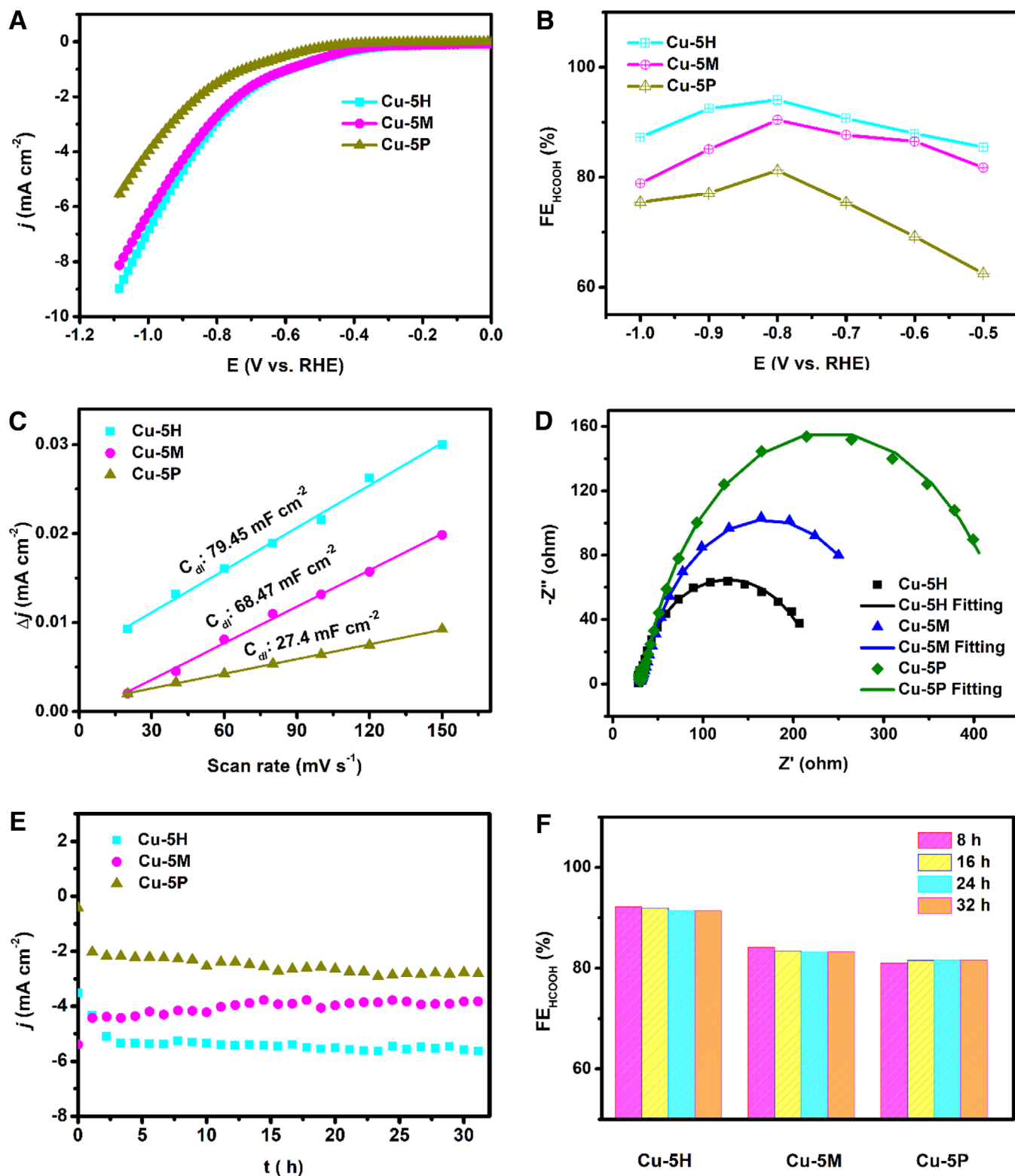


FIGURE 3 Electrochemical performances of Cu-5H, Cu-5M, and Cu-5P in CO₂-saturated 0.1M KHCO₃ solution. A, LSV curves. B, Faradic efficiency of HCOO⁻ at different potentials. C, Charging current density differences plotted against scan rates plots. D, EIS plots at -0.5 V versus reversible hydrogen electrode (RHE); E, Time-dependent current density curve at -0.8 V versus RHE. F, Faradic efficiency of HCOO⁻ at -0.8 V versus RHE with various electrolysis time

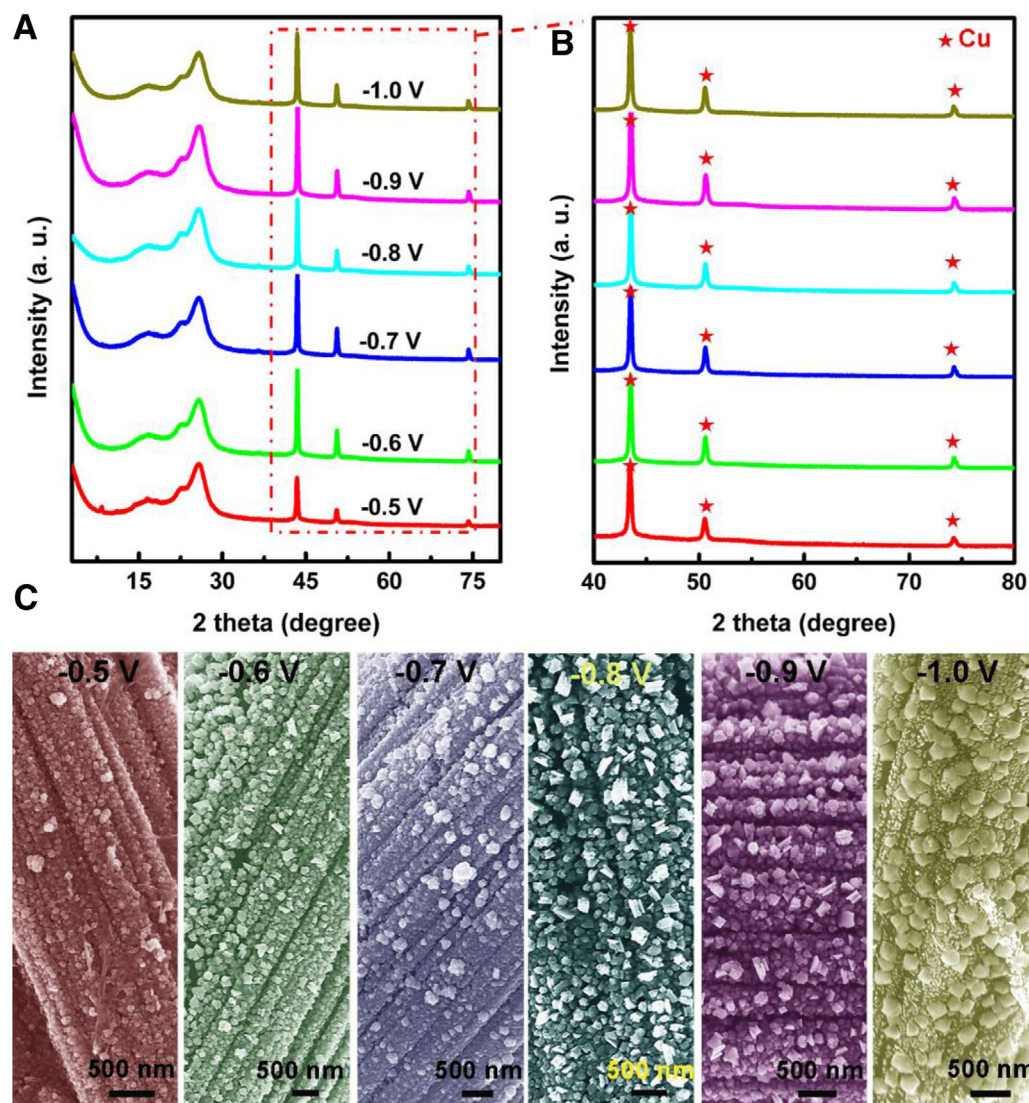


FIGURE 4 Ex situ characterizations. X-ray diffraction (XRD) patterns (A, B) and scanning electron microscopy (SEM) images (C) of Cu-5H catalysts on carbon paper after electrolysis at different potentials (-0.5 to -1.0 V vs. RHE) in CO_2 -saturated 0.1M KHCO_3 solution

highlighting the feasibility of Cu-5H, Cu-5M, and Cu-5P catalyst in electrocatalysis CO_2 RR application.

Furthermore, ex situ XRD and SEM measurements were conducted to unveiling the active sites. XRD patterns (Figure 4A,B) show the structure changes of Cu-5H over the applied potentials. At -0.5 V versus RHE, the diffraction peaks of Cu-5H MOFs as well as the metallic Cu are both observed for the Cu-5H electrode. When the applied potentials are reduced from -0.6 to -1.0 V versus RHE, the diffraction peaks of Cu-5H MOFs disappear accompany with the increasing intensity of metallic Cu peaks, suggesting that metallic Cu rather than the Cu-N would be the active center in electrocatalysis CO_2 RR, which is consistent with the literature.^[13a] SEM images of Cu-5H electrode after electrolysis at different potentials show the conversion of the morphology into smaller particles that may be associated with the generation of metallic

Cu. Similarly, a gradual reduction of the intensity of the diffraction signals of Cu-5M MOFs and simultaneously more sharper Cu peaks are observed for Cu-5M electrode when shifting the potential more negatively (Figure S16). Differently, no obvious change in the intensive peaks and morphology of Cu-5P MOFs are detected in the XRD patterns and SEM images when the electrolysis potentials are decreased from -0.5 to -1.0 V versus RHE (Figure S17). And only weak signal of metallic Cu is observed in the enlarged XRD patterns of Cu-5P electrode. This is because the substitute groups (such as phenyl group) of the tetrazolate ligands contribute to stabilize the Cu-N sites in MOFs backbone against the applied potential, which will lead to the different degree of in situ generating metallic Cu among of Cu-5H, Cu-5M, and Cu-5P samples during the catalytic process and thus the distinction in the catalytic performance. Notably, despite possessing

higher BET surface areas, the electrochemical catalytic performances of Cu–5P and Cu–5M are inferior compared to that of Cu–5H. Therefore, the high density of in situ generated Cu species, faster electron transfer kinetics and larger ECSA play more important roles in determining the high catalytic performance of Cu–5H MOFs in electrocatalysis CO₂RR to formate.

3 | CONCLUSION

In summary, we successfully use a facile strategy to develop a series of Cu tetrazolate MOFs in promoting artificial CO₂ conversion process. Merging with abundant exposed Cu active sites, high surface area and ordered porous structure, the as-synthesized Cu tetrazolate MOFs demonstrate an outstanding achievement in both chemical and electrochemical CO₂ conversion reaction. When catalyzing the cycloaddition reaction of CO₂ into epoxide to fabricate the cyclic carbonate, Cu–5M and Cu–5P show remarkably high selectivity (>99%) at ambient condition owing to the high density of exposed Lewis acidic sites and abundant pores. Meanwhile Cu–5H exhibits high catalytic activity in electrochemical CO₂RR to formate with high FE (up to 91%), associated with plenty of in situ generated Cu sites. In electrochemical CO₂RR process, the degree of reconstructed Cu in the MOFs plays a vital role in determining the catalytic activity of Cu tetrazolate MOFs. These results shed new light on developing metal and nitrogen-rich heterogeneous catalyst with well-defined active sites in artificial CO₂ conversion and pave the way toward developing practical application.

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SUPPORTING INFORMATION

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