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Microwave-assisted fabrication of a mixed-ligand $[Cu_4(\mu_3\text{-}OH)_2]$-cluster-based metal–organic framework with coordinatively unsaturated metal sites for carboxylation of terminal alkynes with carbon dioxide

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The development of efficient and stable metal–organic framework (MOF) catalysts with coordinatively unsaturated metal sites for modern organic synthesis is greatly important. Herein, a robust $[Cu_4(\mu_3\text{-}OH)_2]$-cluster-based MOF (Cu-MOF) with a mixed-ligand system was successfully fabricated by a microwave-assisted method under mild conditions. The as-prepared Cu-MOF catalyst possessing unsaturated Cu (II) sites exhibited excellent catalytic activity toward the direct carboxylation of 1-ethynylbenzene with CO_2, and various propiolic acid derivatives were synthesized in moderate to good yields under optimized reaction conditions. Furthermore, the catalyst remained stable and could be easily recycled for five sequential runs without incredible decrease in catalytic efficiency.

KEYWORDS

alkyne carboxylation, carbon dioxide, copper (II)-based MOF, microwave synthesis

1 | INTRODUCTION

During the past two decades, carbon dioxide (CO_2) has garnered significant attention as an abundant, low-cost, nontoxic and renewable C1 source in organic synthesis.[1–3] Although CO_2 is chemically inert and difficult to activate for bond formation, there have also been noteworthy advances in the development of efficient methods that enable the transformation of CO_2 into value-added chemicals.[4–9] In particular, the direct C–H carboxylation of terminal alkynes with CO_2 has been recognized as a highly valuable strategy for the synthesis of alkynyl carboxylic acids, because the products are key intermediates for the synthesis of a variety of biologically active compounds such as falvones, coumarins, arylidene oxindoles, and alkynylarenes.[10] To date, many homo- and heterogeneous catalyst systems for terminal alkyne carboxylations have been reported in the literature,[11–15] and most attention has been focused on noble metal Ag. For the construction of truly sustainable systems, the replacement of heterogeneous Ag-based catalysts by cheaper ones is highly desirable.[13–15] Several Cu-based homogeneous catalytic systems using Cu(I) salts (CuI, CuCl, and CuBr) have been reported in this research area[16–19]; however, further application was severely impeded by either the recycling problems or the metal contamination of the products. Recently, use of Cu-based heterogeneous catalytic systems has also proved to be effective in activating the triple bonds of alkynes for the carboxylation with CO_2. For example, He and Li with their co-workers reported CuBr loaded on activated carbon (CuBr@C) as recyclable catalyst for the carboxylation with ethylene carbonate as solvent.[20] Kim's group recently reported that $CuCl_2$ incorporated in polyvinyl imidazolium tri-cationic ionic liquid ($CuCl_2$@Poly-GLY (1-Vim)$_3$(OMs)$_3$) demonstrated an improved catalytic efficiency for coupling of alkyne and CO_2,[21] but the catalyst synthetic route limits its further application. Therefore, the exploration of efficient, inexpensive, easily prepared and robust heterogeneous catalysts for this type of reaction is still a challenge.

Metal–organic frameworks (MOFs), built from the assembly of metal centers and multifunctional organic ligands through metal–ligand coordination bonds, are a relatively new class of crystalline porous materials, which can be directly adopted as heterogeneous catalysts or as catalyst supports/precursors in many important organic transformations.[22–26] Recently, a few MOFs, such as MIL-101[13] UiO-66,[27] and ZIF-8,[28] have been used as support of reactive silver nanoparticles to construct MOF-supported silver nanoparticle catalysts for the coupling of alkynes with CO_2. In contrast, the contribution involving the direct catalysis of such conversions by MOF catalysts is still scarce.[29,30] For example, Zhao et al. chose the N,O-donor ligand isonicotinic acid (HIN) to synthesize two cluster-based Gd-Cu heterometallic coordination frameworks $\{[Gd_4Cu_4I_3(CO_3)_2(IN)_9(HIN)_{0.5}(DMF)(H_2O)]\cdot DMF\cdot H_2O\}_n$ and $\{[Gd_3Cu_{12}I_{12}(IN)_9(DMF)_4]\cdot DMF\}_n$ that possess active catalytic sites $[Cu_{12}I_{12}]$ and $[Cu_3I_2]$, which could catalyze the alkyne carboxylation in the presence of *n*-BuI.[29] Very recently, Verpoort and co-workers presented the first example of Cu-based MOF $\{[Cu\ (IN)_2]\cdot DMF\cdot H_2O\}_n$ (Cu (IN)-MOF) applied for the direct carboxylation of terminal alkynes with CO_2.[30] Therefore, it is expected that many Cu-based MOFs could endow them with the ability for this type of reaction, and thus need further developments.

Developing a fast and efficient approach for the preparation of MOF-based catalysts is of great significance. In the majority of cases, MOF materials can be produced through conventional synthetic techniques such as solvothermal, hydrothermal or diffusion methods over a period of several days to weeks.[31] For a long time, microwave-assisted method has been widely applied in the synthesis of a great variety of nanomaterials, since microwave dielectric heating possesses the merits of large reduction of reaction time, high yields of products, controllable of crystal nucleation and growth, and better reproducibility.[32–34] So far, some landmarked MOFs including MOF-5,[35] UiO-66,[36] and HKUST-1,[37] have been prepared by the microwave methodology. Very recently, we have also shown the application of microwave synthesis to rapidly prepare a series of crystalline blue luminescent coordination polymers with diverse structures.[38]

With the above considerations in mind, a 3-D tetranuclear Cu-based MOF (Cu-MOF) has been synthesized rapidly by the reaction of copper (II) nitrate, 4-amino-1,2,4-triazole, and sodium 5-sulfoisophthalate in aqueous solution under microwave irradiation under mild conditions (Scheme 1). The Cu-MOF featuring a tetranuclear unit of $[Cu_4(\mu_3\text{-}OH)_2]$ possessed good chemical and thermal stability, and was shown to be a highly active, readily recovered and reused catalyst for the carboxylation of terminal alkynes with CO_2. This work demonstrates that the potential of using acid–base mixed-ligand MOFs with high-nuclearity Cu (II) clusters as a non-precious metal-based heterogeneous catalyst for CO_2 fixation.

2 | EXPERIMENTAL SECTION

2.1 | Materials and methods

All reagents and solvents were commercially available and were used as received. Microwave synthesis was performed in MDS-6G (SINEO). Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/max-2500 diffractometer at 40 kV and 100 mA for a Cu-target tube ($\lambda = 1.5406$ Å). The calculated PXRD patterns were obtained from the single-crystal diffraction data using the PLATON software.[39] Thermogravimetric analysis (TGA) experiments were carried out in the temperature range of 25–800°C on a Dupont thermal analyzer under an air atmosphere at a heating rate of 10°C min^{-1}. Scanning electron microscopy (SEM) images were taken by a VEGA 3 TESCAN. The transmission electron microscopy (TEM) images were obtained on a JEM-2100F microscope with a limited line resolution capacity of 1.4 Å at an accelerating voltage of 200 kV. Brunauer–Emmett–Teller (BET) surface area analysis was performed on a Micromeritics ASAP 2460 surface area analyzer at 77 K. ^1H NMR and ^{13}C NMR spectra were recorded on 300- and 500-MHz NMR spectrometers (Bruker AVANCE). Fourier transform-infrared (FT-IR) spectra of samples in KBr pellets were recorded utilizing a Nicolet ESP 460 FT-IR spectrometer in the range of 4000–400 cm^{-1}. X-ray photoelectron spectra (XPS) were conducted on a PHI 5000 Versa Probe X-ray photoelectron spectrometer equipped with Al Kα radiation (1486.6 eV).

2.2 | Preparation of cu-MOF

The synthesis of Cu-MOF was performed in a microwave reactor. A mixture of Cu $(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1.0 mmol), 4-amino-1,2,4-triazole (0.040 g, 0.5 mmol), sodium 5-sulfoisophthalate (0.161 mg, 0.6 mmol), NaOH (0.048 g, 1.2 mmol), and distilled water (30 ml) was placed in a 100-ml Teflon-lined container. The container was sealed and then irradiated at 60°C in microwave oven with power 300 W for 15 min. The reaction product of Cu-MOF (0.238 g) in the form of a precipitate was centrifuged, washed with distilled water (10 ml) for three times and dried in vacuum with a yield of 94% based on Cu. Selected FT-IR data (KBr, cm^{-1}): 3368 br, 3113 m, 1608 s, 1561 m, 1476 w, 1436 m, 1369 s, 1278 w, 1,177 w, 1076 w, 1047 w, 928 w, 758 m, 712 m, 614 m.

2.3 | General procedure for carboxylation of the terminal alkynes

In a typical experiment, a 50-ml stainless steel autoclave, equipped with a magnetic stirring bar, was charged with Cu-MOF (40.6 mg, 1 mol%), Cs_2CO_3 (1.955 g, 6 mmol), 1-ethynylbenzene (0.408 g, 4.0 mmol) and DMF (20 ml). Once added, CO_2 (0.3 MPa) was introduced into the reaction mixture under stirring at 100°C for 16 hr. After the reaction, the mixture was cooled to room temperature and monitored by high-performance liquid chromatography (Shimadzu LC-VP) with a UV detector at 241 nm, a Hypersil ODS2 column (250 mm × 4.6 mm, 5 μm), and a mixture of methanol and H_2O (3/1, v/v) as eluent with a flow rate of 0.8 ml min^{-1}. The concentration of 1-ethynylbenzene and product were calibrated by external standard method with standard samples.

The Cu-MOF catalyst was recovered in the solid residue after centrifugation and separation from the organic layer (DMF solution). For the other terminal alkynes, after the reaction, the solid residue was separated via centrifugation, and the filtrate was diluted with water (30 ml). The mixture was washed with CH_2Cl_2 (20 ml × 3) and the aqueous layer was acidified with concentrated HCl (6 moL L^{-1}) to pH = 1, then extracted with CH_2Cl_2 (20 ml × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and then evaporated. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate/formic acid (200/100/1, v/v/v) as the eluent to afford the propiolic acids.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization of catalyst

Compared with the conventional hydro/solvothermal syntheses, the microwave-assisted approach is a facile and ultrafast method. However, microwave-assisted fabrication of MOFs at room temperature is scarcely reported. Previously, the single-crystal structure of Cu-MOF was firstly reported by Wang and co-workers,[40] where Cu-MOF was hydrothermally synthesized by the reaction of Cu $(NO_3)_2 \cdot 3H_2O$, 4-amino-1,2,4-triazole (atrz), sodium 5-sulfoisophthalate (NaH_2SIP) and NaOH under hydrothermal synthetic conditions at 120°C for 3 days, and the yield was about 60%. Besides, the chemical properties of Cu-MOF for potential catalytic applications are not yet explored, and are of considerable interest since the acid-based mixed-ligand Cu-MOF contains robust and coordinatively unsaturated tetranuclear $[Cu_4(\mu_3\text{-}OH)_2]$ clusters.[24] In this work, Cu-MOF could be successfully obtained by microwave irradiation at 60°C for 15 min to give a yield of 94%. Moreover, Cu-MOF could also be isolated under the microwave heating conditions, using $CuCl_2$, Cu $(OAc)_2$ and $CuSO_4$ as source of metal atoms (confirmed by PXRD, IR spectra and elemental analyses). The morphology and size of the Cu-MOF prepared using the microwave method were investigated using scanning electron microscopy (SEM). Figure 1a shows that the Cu-MOF material is mainly consisted of microparticles formed from packing of nanosheets. As depicted in Figure 1b, TEM images revealed that such prepared Cu-MOF nanoparticles have an ultrathin morphology. The Brunauer–Emmett–Teller (BET) surface area and pore size distribution have been measured (Figure S1). The results indicated that the Cu-MOF has a very small surface area of 42.2 m^2 g^{-1} and the pore size is very small. The synthetic reproducibility is high. PXRD patterns (Figure 1c) confirmed the phase purity of the as-prepared Cu-MOF. Bulk elemental analysis of Cu-MOF was consistent with the molecular formula of $\{[Cu_4(\mu_3\text{-}OH)_2(atrz)_2(SIP)_2] \cdot 4H_2O\}_n$. For the IR spectra (Figure 1d), a strong and broad band in the range of 3600–3150 cm^{-1} indicates the O–H stretching frequencies. The medium intensity peaks at ~1561 and ~1436 cm^{-1} are in agreement with the existence of a triazole ring. The typical strong peaks at ~1608 and ~1369 cm^{-1} can be attributed to the ν_{as} (COO^-) and ν_s (COO^-) vibrations, respectively. The characteristic vibrations of ν_{as} (SO_3^-) in Cu-MOF are in the range of 1278–1177 cm^{-1}, whereas the ν_s (SO_3^-) absorptions are in the range of 1076–1047 cm^{-1}.

SCHEME 1 Microwave-assisted synthesis of $[Cu_4(\mu_3\text{-}OH)_2]$-cluster-based metal–organic framework (Cu-MOF)

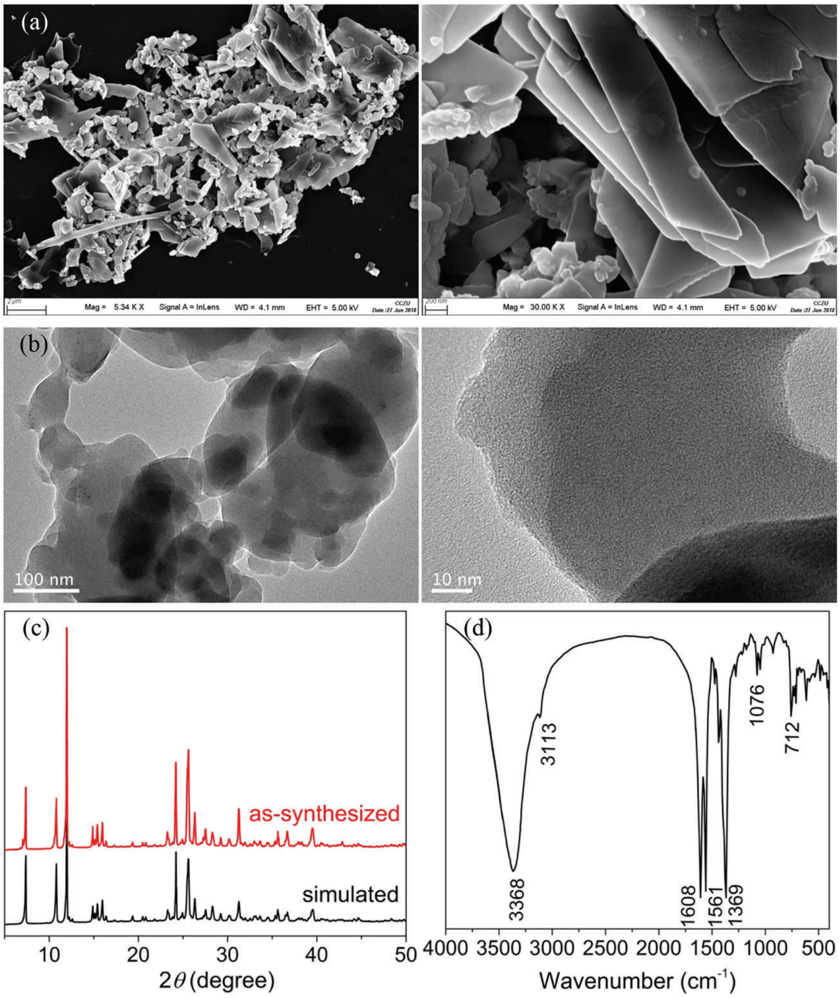


FIGURE 1 (a) Scanning electron microscopy (SEM) images of $[Cu_4(\mu_3\text{-}OH)_2]$-cluster-based metal–organic framework (Cu-MOF) prepared under microwave irradiation, (b) transmission electron microscopy (TEM) images of Cu-MOF prepared under microwave irradiation, (c) powder X-ray diffraction (PXRD) patterns for as-prepared and simulated Cu-MOF, and (d) Fourier transform-infrared (FT-IR) spectrum of Cu-MOF

Cu-MOF is thermally and chemically stable. TG analysis showed that the decomposition temperature of Cu-MOF is about 280°C (Figure 2a). PXRD patterns revealed that the robust structure of Cu-MOF was retained after the crystalline sample was heated at 250°C in air for 6 hr (Figure 2b). Cu-MOF is also stable in various chemical environments (Figure 2c,d), such as being suspended in dilute acidic or basic aqueous solution (pH = 2 or 13) at room temperature, in boiling water, and in various hot organic solvents.

3.2 | Catalytic activity

Stable copper-based MOFs containing coordinatively unsaturated copper centers, acting as Lewis acid sites, can be utilized as effective heterogeneous catalysts in many important organic transformations. Notably, each tetranuclear $[Cu_4(\mu_3\text{-}OH)_2]$ cluster in Cu-MOF possesses two available unsaturated metal sites, and the activation process is indeed not required. The catalytic activities of the as-prepared Cu-MOF were tested using the direct

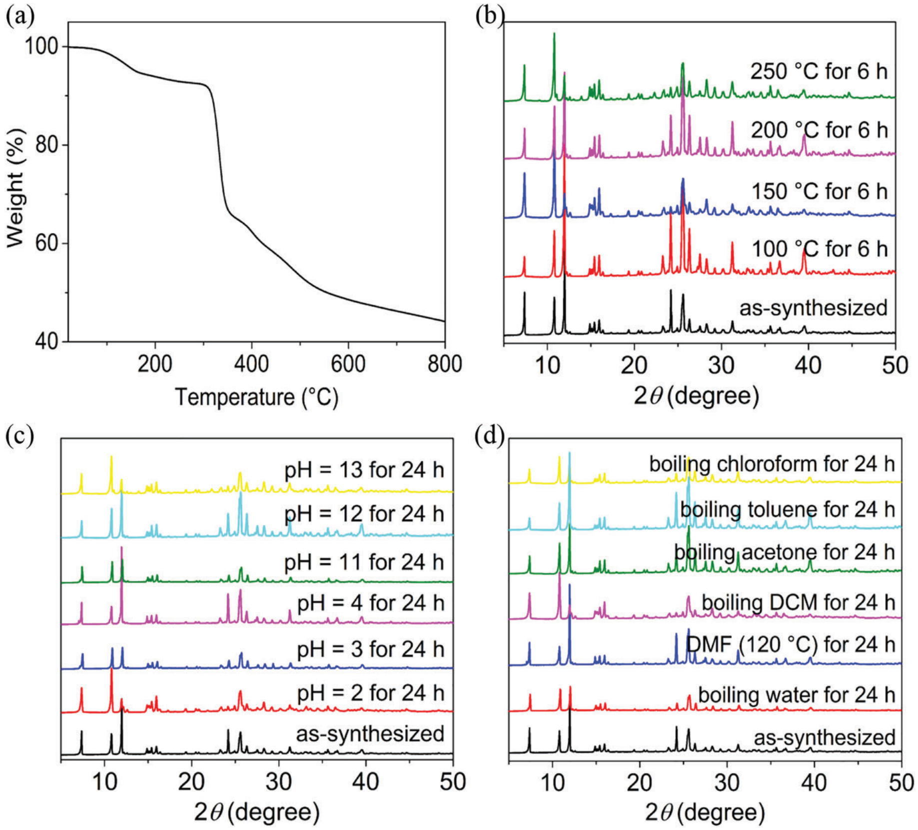


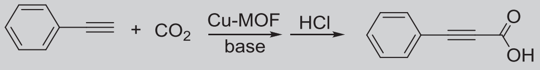
FIGURE 2 (a) The thermogravimetric analysis (TGA) profile of [$Cu_4(\mu_3\text{-}OH)_2$]-cluster-based metal–organic framework (Cu-MOF). (b) Thermal stability tests for Cu-MOF monitored by powder X-ray diffraction (PXRD) analysis after the crystalline samples of Cu-MOF were heated at 100°C, 150°C, 200°C, and 250°C in air for 6 hr, respectively. (c) PXRD patterns of Cu-MOF after immersing in aqueous solutions of HCl and NaOH with different pH values at room temperature for 24 hr. (d) PXRD patterns of as-synthesized Cu-MOF and treated Cu-MOF by immersing in boiling water and organic solvents, including boiling chloroform, toluene, acetone, dichloromethane (DCM), and in hot DMF at 120°C for 24 hr

carboxylation of 1-ethynylbenzene with CO_2 as a model reaction. In order to obtain the optimized reaction conditions, we have varied different parameters such as solvent, base, amount of base (Table 1), temperature, reaction time, catalyst loading, and pressure (Figure 3). All of these parameters play major roles in the carboxylation reaction as shown in Table 1 and Figure 3.

Initially, various solvents were used to understand the influence of solvent system on the carboxylation reaction. The reaction was performed in solvents like DMF, DEC, NMP, DMAC, DMSO, CH_3CN, dioxane and MB (Table 1, entries 1–8). Among these solvents, DMF was found to be most effective, which may be due to the fact that DMF is a better solvent for both Cs_2CO_3 and CO_2 (DMF is a weak base) than the other organic solvents.[41] It is noteworthy that the replacement of Cs_2CO_3 by other bases such as Na_2CO_3 and K_2CO_3 under otherwise identical conditions resulted in low conversion (Table 1, entries 9 and 10), while CsF and CsOAc were inactive to this reaction (Table 1, entries 11 and 12), indicating that Cs_2CO_3 is a suitable base for the deprotonation of terminal alkynes. The amount of Cs_2CO_3 was varied (Table 1, entries 1 and 13–17) and the highest 1-ethynylbenzene conversion of 91% and high target product selectivity of 97% were obtained by using 6 mmol Cs_2CO_3 (Table 1, entry 1). It can also be observed that a negligible amount of the propiolic acid product was obtained in the absence of any base (Table 1, entry 13). Entries 1 and 18–21 show the influence of the catalyst loading on the reaction. Catalyst loading could not be decreased to 0.5 mol% because of noticeable decline in the conversion and selectivity.

Figure 4 shows the dependence of the conversion and selectivity on the reaction temperature, reaction time, catalyst loading and pressure. The conversion markedly increased at higher temperature and 100°C was found to be a relatively optimized temperature (Figure 3a). Under lower temperature (40°C to 80°C), the carboxylation reaction became slow and cannot be completed. As the reaction temperature was raised to 120°C, a gradual decrease in the 1-ethynylbenzene conversion and the product selectivity was observed, which might be related to the stability of the propiolic acid product at higher temperature. It may decompose to 1-ethynylbenzene through de-carboxylation process when it is over heated. Meanwhile, the reaction showed moderate conversion in 4 hr of reaction time (Figure 3b). With increasing time of the reaction, the conversion increases and 16–20 hr are required to complete reactions. However, a small decrease in selectivity of propiolic acid product was observed after prolonging the reaction time to 24 hr, probably being ascribed to the occurrence of homo-coupling of 1-ethynylbenzene (side-reaction).[30] Figure 3c displays the effect of catalyst loading on the

TABLE 1 Optimization of the reaction conditions[a]



Entry	Solvent[b]	Base	Base amount (mmol)	Conv.[c](%)	Select.[c](%)
1	DMF	Cs_2CO_3	6	91	97
2	DEC	Cs_2CO_3	6	5	5
3	NMP	Cs_2CO_3	6	35	87
4	DMAC	Cs_2CO_3	6	38	85
5	DMSO	Cs_2CO_3	6	72	91
6	CH_3CN	Cs_2CO_3	6	16	32
7	dioxane	Cs_2CO_3	6	5	27
8	MB	Cs_2CO_3	6	3	8
9	DMF	Na_2CO_3	6	19	33
10	DMF	K_2CO_3	6	27	42
11	DMF	CsF	6	3	5
12	DMF	CsOAc	6	2	7
13	DMF	—	—	7	12
14	DMF	Cs_2CO_3	2	33	42
15	DMF	Cs_2CO_3	4	58	73
16	DMF	Cs_2CO_3	8	88	93
17	DMF	Cs_2CO_3	10	85	91
18	DMF	Cs_2CO_3	6	0	10
19	DMF	Cs_2CO_3	6	0.5	51
20	DMF	Cs_2CO_3	6	1.5	91
21	DMF	Cs_2CO_3	6	2	90

[a] Reaction conditions: catalyst ([$Cu_4(\mu_3\text{-}OH)_2$]-cluster-based metal–organic framework, Cu-MOF, 1 mol%), 1-ethynylbenzene (4 mmol), solvent (20 ml), CO_2 (0.3 MPa), 100°C, 16 hr.

[b] Solvent: DMF (N,N-dimethylformamide), DEC (diethyl carbonate), NMP (1-methyl-2-pyrrolidinone), DMAC(N,N-dimethylacetamide), and DMSO (dimethylsulfoxide), MB (methylbenzene).

[c] Conversion and selectivity were determined by liquid chromatography (LC) analysis.

reaction. When the catalyst loadings was reduced from 2 mol% to 1 mol%, good to excellent conversion and selectivity were still obtained. Furthermore, the influence of pressure on the carboxylation reaction was also surveyed on the catalytic system (Figure 3d), which confirmed that the catalyst system proved to be efficient at a low CO_2 pressure (0.3 MPa).

Subsequently, the substrate scope for the Cu-MOF-catalyzed carboxylation reaction was investigated with various terminal alkynes under the above-optimized reaction conditions (Table 2). It was found that the Cu-MOF catalyst is not sensitive to the functionality of the terminal alkynes. Good yields (71%–88%) were achieved for aromatic alkynes with both electron-donating and electron-withdrawing groups (Table 2, entries 1–16). Additionally, the heterocycle-containing substrates 2-ethylnylthiophene and 3-ethylnylthiophene were also examined, and the corresponding products were obtained in good yields (Table 2, entries 17 and 18). Moreover, the aliphatic alkyne 1-hexyne underwent the reaction to give 71% of the desired product (Table 2, entry 19).

To demonstrate the stability and reusability of the Cu-MOF catalyst, five recycles were carried out. After finishing each reaction, the Cu-MOF catalyst was recovered from the reaction mixture by centrifugation and washed before the next catalytic run. As shown in Figure 4a, the results revealed that the recovered Cu-MOF catalyst could maintain its high activity with no obvious decrease after five consecutive cycles. Furthermore, the PXRD pattern of fifth used catalyst indicated that the Cu-MOF could retain its crystallinity (Figure 4b). The FT-IR spectra (Figure 4c) and X-ray photoelectron

FIGURE 3 Effect of reaction temperature (a), reaction time (b), catalyst loading (c), and the pressure (d) on reaction conversion and product selectivity

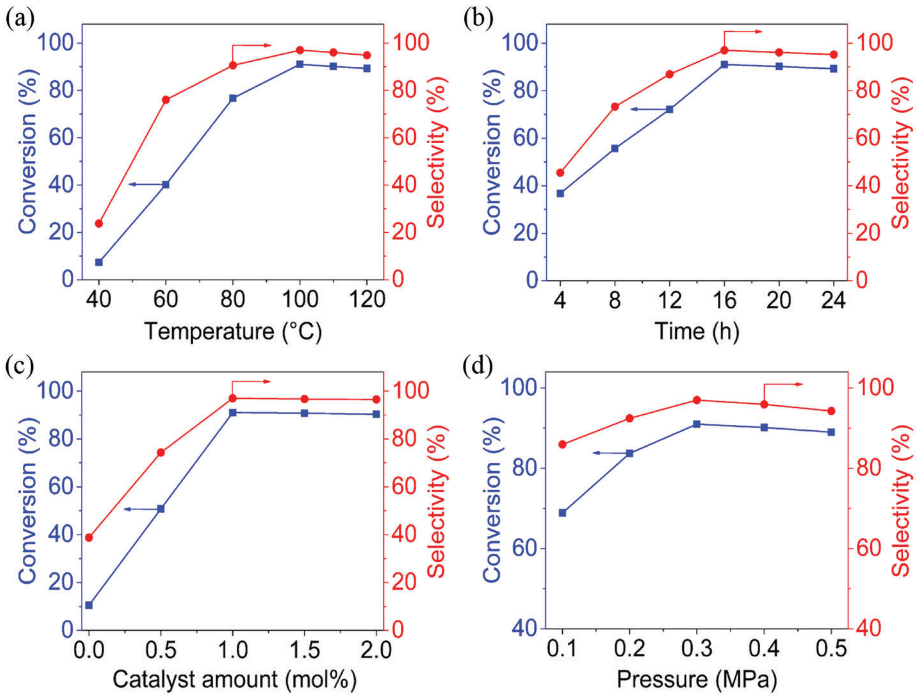
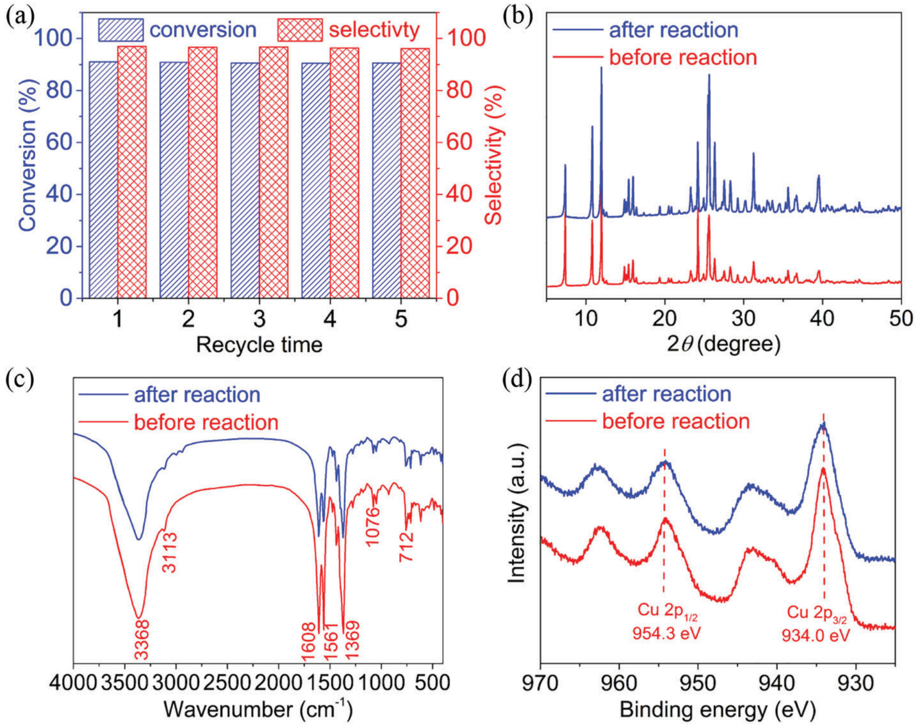


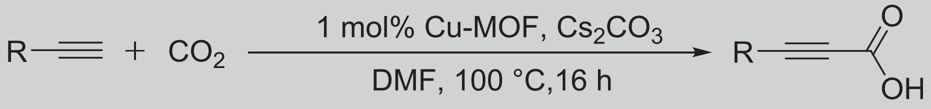
FIGURE 4 (a) Recyclability of $[Cu_4(\mu_3\text{-}OH)_2]$-cluster-based metal–organic framework (Cu-MOF) for the synthesis of propiolic acid under standard reaction conditions. (b) Powder X-ray diffraction (PXRD) patterns of Cu-MOF before and after catalysis. (c) Infrared (IR) spectra of Cu-MOF before and after catalysis. (d) X-ray photoelectron spectra (XPS) patterns of Cu-MOF before and after catalysis

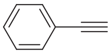
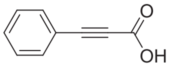
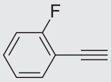
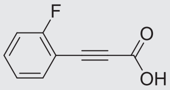
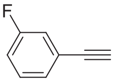
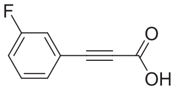
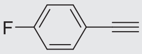
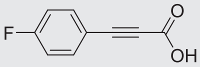
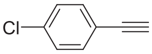
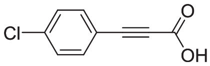
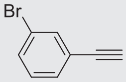
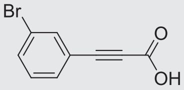
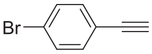
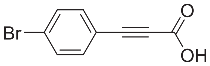
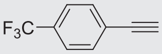
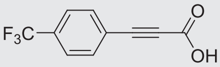
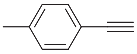
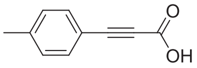


spectroscopy (XPS) spectra (Figure 4d) of the recovered Cu-MOF sample are almost identical to those of the as-synthesized one. It was observed that the ground Cu-MOF catalyst with a smaller particle size (60–400 mesh) could accelerate the rate of the carboxylation. Because the surface area and pore size of the Cu-MOF catalyst is very small, this reaction should be catalyzed by the active sites on the surface of Cu-MOF.

To gain insight into the catalytic mechanism, some control experiments were further conducted (Table 3). In the absence of the Cu-MOF catalyst, a negligible amount of the 1-ethynylbenzene conversion was observed (Table 3, entry 1). The introduction of ligand atrz or 1,3-H_2BDC did not promote the reaction at all (Table 3, entries 3 and 4). Metal salts such as Cu $(NO_3)_2$ and Cu $(OAc)_2$ were found to catalyze the reaction with

TABLE 2 Various terminal alkynes used for the carboxylation with CO_2 using the Cu-MOF catalyst[a]



Entry	Reactant	Product	Yield (%)
1			88
2			73
3			75
4			80
5			72
6			77
7			81
8			79
9			85

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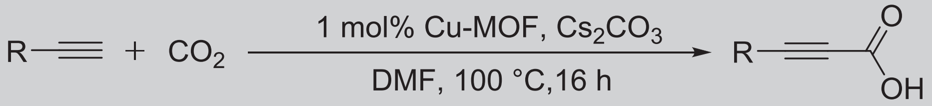

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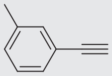
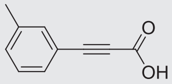
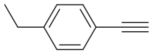
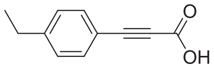
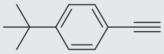
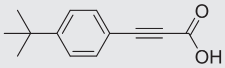
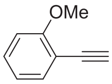
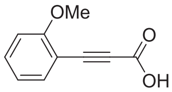
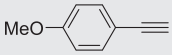
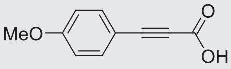
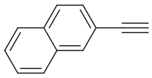
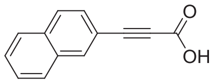
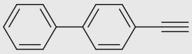
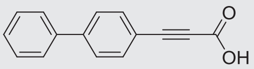
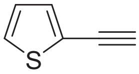
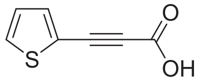
10			82
11			81
12			78
13			76
14			83
15			76
16			80
17			72

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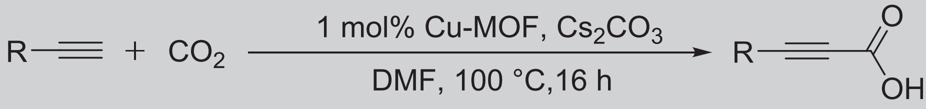
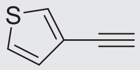
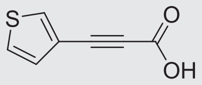
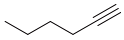
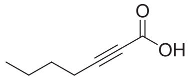
TABLE 2 (Continued)

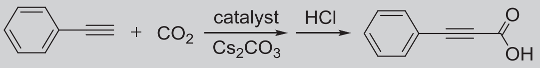


Entry	Reactant	Product	Yield (%)
18			75
19			71

[a]Reaction conditions: catalyst ($[Cu_4(\mu_3\text{-}OH)_2]$-cluster-based metal–organic framework, Cu-MOF, 1 mol%), substrate (4 mmol), Cs_2CO_3 (6 mmol), DMF (20 ml), CO_2 (0.3 MPa), 100°C, 16 hr.

[b]Isolated yield.

TABLE 3 The carboxylation of 1-ethynylbenzene with CO_2 with different catalysts[a]



Entry	Catalyst	Conv.[b](%)	Select.[b](%)
1	—	11	38
2	Cu-MOF	91	97
3	atrz	12	37
4	1,3-H_2BDC	14	39
5	Cu $(NO_3)_2 \cdot 3H_2O$	44	88
6	Cu $(OAc)_2 \cdot H_2O$	69	91
7	Cu-BTC	86	93
8	Cu-FMOF	78	85
9	Cu-X	14	30
10	Cu-Beta	33	52
11	Cu-ZSM-5	50	62
12	Cu_2O	16	44
13	CuO	42	56

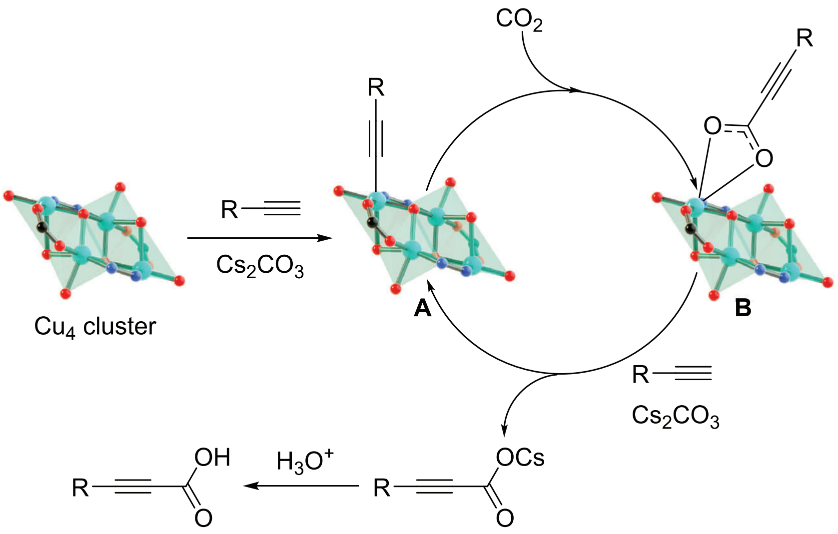
[a]Reaction conditions: catalyst (1 mol%), 1-ethynylbenzene (4 mmol), Cs_2CO_3 (6 mmol), solvent (DMF, 20 ml), CO_2 (0.3 MPa), 100°C, 16 hr.

[b]Conversion and selectivity were determined by liquid chromatography (LC) analysis.

moderate conversion (Table 3, entries 5 and 6), which implied that the metal Lewis acidic catalysts are favorable. For further comparison, we also tested the catalytic activities of the heterogeneous Cu-based catalysts in the carboxylation reaction, including Cu-based MOFs (Cu-BTC and Cu-FMOF), Cu-doped zeolites (Cu-X, Cu-Beta and Cu-ZSM-5) and copper oxides (Cu_2O and CuO) (Table 3, entries 7–13). The results revealed that the MOF-based catalysts are more efficient than the metal-doped zeolites and metal oxides as well as metal salts. Obviously, the catalytic activity of Cu-MOF is slightly higher than Cu-FMOF and Cu-BTC as well as the Cu (IN)-MOF system.[30] It should be noted that Cu-MOF is constructed from tetranuclear $[Cu_4(\mu_3\text{-}OH)_2]$ clusters, whereas Cu-BTC is based on dinuclear paddle-wheel Cu_2 clusters, while both Cu-FMOF and Cu (IN)-MOF are composed of mononuclear Cu unit. Meanwhile, these MOF-based catalysts all have coordinatively unsaturated Cu (II) sites. Therefore, the different catalytic activity for these MOF-based catalysts might be caused by the difference in their coordination environments of the Cu (II) center, and Cu-MOF containing high-nuclearity unsaturated Cu (II) clusters would be beneficial for such carboxylation reaction.

On the basis of the above results and some previous reports,[21,30,42] a possible mechanism over the Cu-MOF catalyst was proposed and schematically depicted in

SCHEME 2 Proposed reaction mechanism for the $[Cu_4(\mu_3\text{-}OH)_2]$-cluster-based metal–organic framework (Cu-MOF)-catalyzed carboxylation of terminal alkynes with CO_2



Scheme 2. First, the terminal alkyne coordinates to a nearby unsaturated copper (II) center of the tetranuclear unit of Cu-MOF, and the acidity of the alkyne C–H bond is enhanced. Then, the deprotonation reaction of terminal alkyne by Cs_2CO_3 leads to the copper (II) acetylide intermediate A. Meanwhile, the insertion of CO_2 into sp-hybridized carbon–copper bond results in the formation of the copper propiolate intermediate B, which subsequently reacts with another terminal alkyne and Cs_2CO_3 releasing cesium propiolate, simultaneously regenerating copper (II) acetylide intermediate A. At the end of the reaction, the acidification of cesium propiolate affords the propiolic acid product.

4 | CONCLUSIONS

In summary, we have prepared a robust tetranuclear cluster-based Cu (II)-organic framework Cu-MOF through a simple and fast method assisted by microwave irradiation. The Cu-MOF material acts as an effective catalyst for the direct carboxylation of the terminal alkynes with CO_2 with high catalytic activity and selectivity. A wide substrate scope and a good functional groups tolerance could survive the reaction conditions to afford the propiolic acids in good to excellent yields. This catalyst also exhibits good stability and could be readily recycled for five times without significant decrease in catalytic activity. This work therefore provides a promising strategy for preparing other high-nuclearity MOF-based catalysts for CO_2 conversion, C–C, and C–heteroatom bond formation, and this approach is currently underway in our laboratory.

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AUTHOR CONTRIBUTIONS

Wen-Jing Wang: Data curation; formal analysis; investigation; methodology. **Zhong-Hua Sun:** Data curation; methodology. **Sheng-Chun Chen:** Conceptualization; methodology; project administration; resources; software. **Jun-Feng Qian:** Investigation; resources. **Ming-Yang He:** Formal analysis; software. **Qun Chen:** Funding acquisition; project administration.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supporting information of this article.

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SUPPORTING INFORMATION

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