Highly Effective Carbon Fixation *via* Catalytic Conversion of CO_2 by an Acylamide-Containing Metal-Organic Framework

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ABSTRACT: On the way toward a sustainable low-carbon future, in addition to physical capture and permanent underground deposition of anthropogenic emitted CO_2, an alternative and much attractive way should be carbon fixation *via* catalytically chemical conversion of CO_2 into value-added chemicals and reusable materials. A metal-organic framework (MOF) incorporating accessible nitrogen-rich groups and unsaturated metal sites was successfully constructed *via* solvothermal assembly of an acylamide-containing tetracarboxylate ligand and Cu(II) ions. Characterizations including structural analysis, gas adsorption and Raman spectral detection were carried out to reveal that the MOF presents not only a high porosity with exposed Lewis-acid metal sites, but also a high CO_2-adsorbing capability. Such inherent structural features make the MOF a highly promising candidate as a heterogeneous catalyst for CO_2 chemical conversion, which was confirmed by its high efficiency on the CO_2 cycloaddition with small size epoxides. Due to the size control of the open porous windows, catalytic activity of the MOF shows a sharp difference between small and large epoxides. Remarkably high efficiency and size selectivity on CO_2 catalytic conversion enable the MOF to be an advanced heterogeneous catalyst for carbon fixation.

Introduction

Sharply increasing anthropogenic greenhouse gas emission since the beginning of industrial revolution has been considered as the leading culprit in recently average temperature increase of the global surface and subsequently climate changes.[1-4] Carbon dioxide (CO_2) has been cited as the primary greenhouse gas. Therefore, developing innovative strategies to reduce the anthropogenic CO_2 emission becomes an imperative task to the worldwide scientists. Actually, the CO_2 emitted from the fossil fuel consumption can be taken as an abundant carbon source. In addition to physical capture and permanent underground deposition,[1-4] an alternative way to achieve a sustainable low-carbon future should be carbon fixation *via* catalytically chemical conversion of CO_2 into value-added chemicals and reusable materials.[5-10] Such an approach is not only a reliable way to reduce the anthropogenic greenhouse gas emission, but also a much attractive strategy to achieve the carbon recycling and to further decrease our dependence on petrochemicals. Diverse catalysts have been developed for the purpose of carbon fixation *via* catalytically chemical conversion of CO_2. Some heterogeneous catalysts have shown their superiority in the product purifications and catalyst recycling as compared with their homogeneous analogues.[5-7]

Owing to their high porosity and large surface area, metal–organic frameworks (MOFs) are a group of highly promising materials for wide applications.[11-18] Numerous fascinating porous MOFs have been constructed so far, and great efforts have been dedicated to investigating their applications toward gas or small molecules.[11-13] Recently, MOFs have also been taken as highly efficient heterogeneous catalysts or catalyst carriers in various reactions.[14-18] Although some MOFs have been employed as heterogeneous catalysts in the CO_2 chemical conversion, it is still necessary to construct more effective MOFs for such a purpose especially under mild reaction conditions in order to lower the energy consumption and production costs. In addition, factors such as the framework affinity to CO_2 still need to be investigated during the process of CO_2 catalytic conversion.[19-24] Theoretical and experimental studies have demonstrated that accessible nitrogen-rich units, such as amine, imidazole, pyridine, triazole, and tetrazole, in porous materials could significantly increase the capability of CO_2 adsorption.[25-32] Since acylamide as a typical nitrogen-rich group also shows a high affinity to CO_2, acylamide-containing MOFs with open metal sites should be highly promising candidates for CO_2 chemical conversion.[30-32]

Herein, we present the successful construction of a highly porous MOF, $\{Cu_2[(C_{20}H_{12}N_2O_2)(COO)_4]\}_n$ (**1**), which incorporates both accessible acylamide groups and exposed Cu sites exhibiting a high CO_2-adsorbing capability. Further investigations on the CO_2 catalytic cycloaddition with propylene epoxide and other small substrates show its remarkably high efficiency on catalytic conversion of CO_2. Moreover, the pore-size effect of MOFs on reaction substrates should still be investigated in order to examine the generality of catalytic activity toward CO_2 cycloaddition reactions. When extended the reaction to larger substrates, sharp decreases of catalytic activity from MOF **1** were observed, indicating that the MOF has a high selectivity toward molecular size of the substrates. The remarkably high efficiency and size selectivity on CO_2 catalytic conversion make the constructed MOF a highly promising heterogeneous catalyst for carbon fixation.

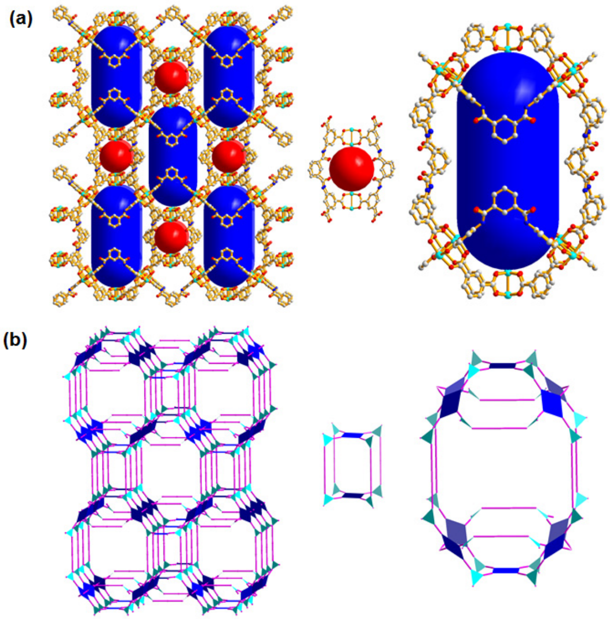


Figure 1. (a) Perspective view of the porous framework of **1** showing the incorporation of accessible nitrogen-rich acylamide groups and unsaturated Cu_2 sites with two kinds of pores (red and blue balls). (b) Illustration of the topological network of **1** showing judicious combination of planar tetratopic paddlewheel Cu_2 clusters and triangle-pair formed **L1** linkers.

Results and Discussion

For constructing nitrogen-rich MOF **1**, an acylamide-containing tetracarboxylate ligand, bis(3,5-dicarboxyphenyl) isophthal amide (**H_4L1**), was designed and successfully synthesized (see the experimental section in the Supporting Information (SI)). In addition to have a close interaction with CO_2 molecule, the incorporated unsaturated metal sites in MOFs could act as Lewis-acid catalytic centers in catalytic reactions.[33,34] Cu(II) ions incorporated in MOFs are usually in a typical paddlewheel form with two exposed sites, which can achieve the functions of both framework affinity and catalytic activity toward CO_2.[35-38] Thus, Cu(II) cation was chosen for the construction of the MOF with synthesized **H_4L1**, and high quality blue crystals of **1** were successfully obtained after solvothermal reactions (Figure S1 in SI).

Structural determination reveals that **1** has a three-dimensional (3D) porous framework with a formula of $[Cu_2(\mathbf{L1})]_n$ (Figures 1 and S2 in SI). As shown in Figure 1a, a pair of neighboring Cu(II) ions were coordinated by four distributed carboxylate groups from four different **L1** ligands, resulting in the formation of expected typical paddlewheel Cu_2 cluster.[35-38] From the viewpoint of the organic ligand, each terminal isophthalate moiety of **L1** bridges two paddlewheel Cu_2 clusters that are then extended by the 1,3-phenylenediamide group of **L1** to form two kinds of crab-like chelating units (Figure S2a,b in SI). The combination of four **L1** with two paddlewheel Cu_2 clusters gives the formation of a cage with a diameter of 0.87 nm (point to point distance without considering the atom radius, cage with a red ball in Figure 1a), while twelve isophthalate moieties and eight **L1** ligands connect ten paddlewheel Cu_2 clusters to afford another cocoon-like cage with a diameter of 1.4 nm and a length of 2.6 nm (cage with a blue ball in Figure 1a). These two kinds of cages then accumulate regularly to give the final formation of a 3D porous framework of **1**. Taking typical paddlewheel Cu_2 cluster as a simple planar tetratopic node and **L1** as a triangle-pair linker formed by two connected triangles,[39-41] the 3D porous framework of **1** can be reduced to an network consisting of two types of cages, a square pillar and a dodecahedron (Figure 1b). After removing the coordinated and discrete solvents in the pores of the structure, the calculation on its porosity was carried out by using PLATON/VOID program, showing that its total solvent-accessible volume is 70.9% and the density of the desolvated framework is 0.591 g cm^{-3}.[42] The structural analysis and calculations clearly indicate that **1** possesses a high porosity

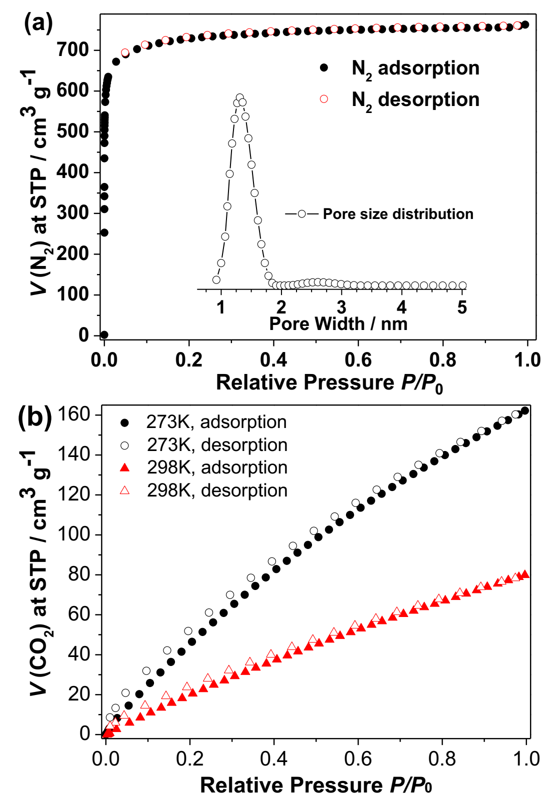


Figure 2. (a) N_2 adsorption/desorption isotherms of activated **1** at 77 K and its calculated pore-size distribution. (b) CO_2 adsorption isotherms of activated **1** at 273 K and 298 K, respectively.

In order to further confirm the porosity, N_2 sorption investigations were conducted. After the activation process, the stability of the framework was confirmed by powder X-ray diffraction (PXRD) measurement (Figure S3 in SI). N_2 sorption at 77 K for the activated sample of **1** was then carried out. As shown in Figure 2a, typical reversible type I sorption isotherm with a quickly increased step prior to the plateau was exhibited, indicating that **1** has a microporous feature.[43] The activated **1** shows an overall N_2 uptake of 762.8 $cm^3\ g^{-1}$ at 1 atm with a Brunauer-Emmett-Teller (BET) surface area of 2878.9 $m^2\ g^{-1}$ (Figures 2a and S5 in SI). The surface area is comparable with some reported MOFs possessing similar frameworks, such as ZJU-72 and NTU-113.[37,38] Based on non-local density functional theory, the pore size distribution of activated **1** was calculated from its N_2 sorption isotherm at 77K, demonstrating that the pore size ranges from 1.0 to 1.8 nm with a peak focused at 1.3 nm (Figure 2a). Its high surface area and narrow pore size distribution present a good agreement with the observations from the crystal structure.

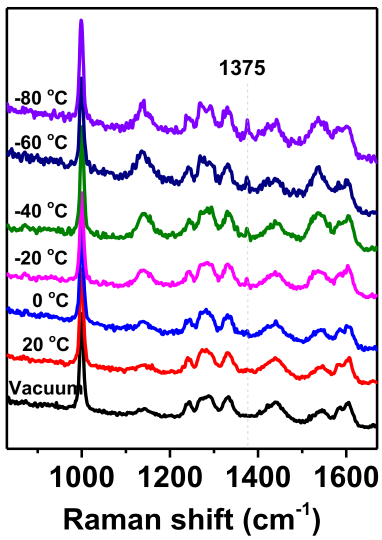
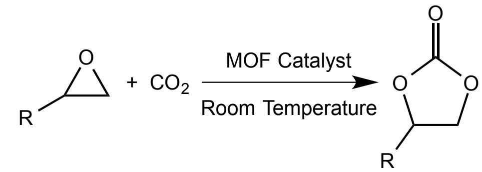


Figure 3. Temperature-dependent Raman spectra of MOF **1** (Vacuum) and CO_2-adsorbed **1** (20 to –80 °C), showing obvious spectroscopic changes before and after the CO_2 adsorption.

The inherent structural feature of incorporating nitrogen-rich acylamide units and exposed metal sites within the framework together with the high porosity inspired us to investigate its adsorption capability toward CO_2. As illustrated in Figure 2b, at 273 K and 1 atm, MOF **1** gives a total CO_2-uptake value of up to 162.2 $cm^3\ g^{-1}$, which is comparable and even higher than some reported MOFs having similar surface areas, such as ZJU-72 and NTU-113.[37,38] Such high CO_2-uptake capability should be ascribed to the rational introduction of both CO_2-philic acylamide units and exposed metal sites into the framework of **1**. According to the adsorption isotherms at 273 and 298 K (Figures 2b and S6 in SI), the isosteric heat of adsorption (Q_{st}) for CO_2 was calculated *via* the Clausius-Clapeyron equation. MOF **1** presents a Q_{st} value of ~36.7 kJ mol^{-1} for CO_2 sorption at low loading range. When converging into a pseudo-plateau at relatively high CO_2 uptake, the Q_{st} value was ~25.6 kJ mol^{-1}. The Q_{st} values of MOF **1** are comparable to some reported nitrogen-rich MOFs such as NTU-180 (~32.2 kJ mol^{-1} at low loading range and ~25.8 kJ mol^{-1} at relatively high uptake),[23] confirming that the constructed acylamide-containing MOF has a high affinity to CO_2.

Scheme 1. Catalytic CO_2 cycloaddition with epoxides to produce cyclic carbonates.



Raman spectroscopy has been employed to study gas adsorption behavior of MOF materials *via* spectroscopic changes before and after the adsorption.[44,45] In order to monitor the framework affinity of **1** toward CO_2, *in-situ* Raman spectral investigations were implemented upon temperature changes. As illustrated in Figure 3, a new peak at 1375 cm^{-1} appears after **1** adsorbs CO_2 especially at lower temperatures, while no such peak was observed from MOF **1** in vacuum without CO_2 under the same conditions (Figure S7 in SI). At lower temperatures, this peak becomes much clearer and sharper. According to the literature descriptions,[44,45] the generated peak should correspond to symmetric C=O stretch mode of adsorbed CO_2 in the framework of MOF **1**. Comparing with literature reported value for gaseous CO_2 at 1388 cm^{-1}, a visible red shift of ~13 cm^{-1} was observed, which should be due to the interaction between adsorbed CO_2 and the activated framework. Raman spectroscopic measurements clearly indicate that the framework of **1** has a strong interaction with CO_2 molecule.

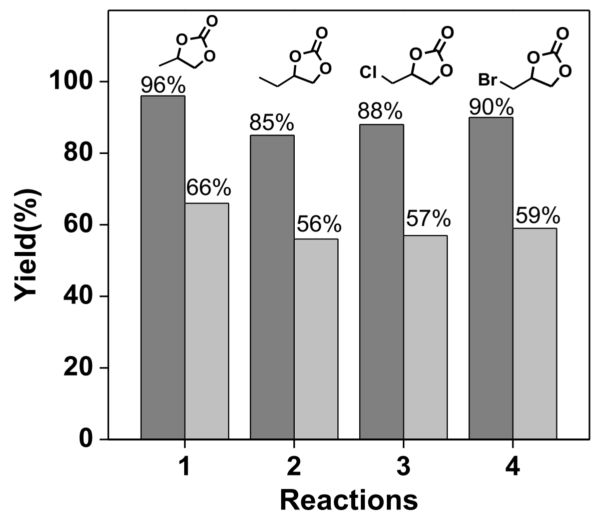
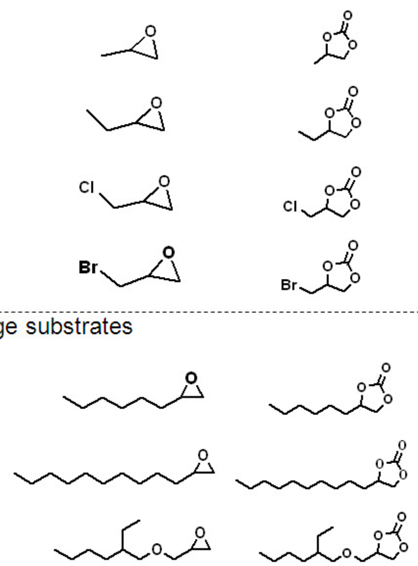


Figure 4. Yields of various cyclic carbonates generated from the CO_2 cycloaddition with related epoxides catalyzed by **1** (black) and HKUST-1 (gray).

Above analyses reveal that **1** possesses a highly porous framework with the incorporation of CO_2-philic nitrogen-rich acylamide units and exposed Lewis-acid metal sites (Figure S8 in SI). Such unique inherent structural features make the constructed MOF a highly promising candidate as a heterogeneous catalyst for CO_2 chemical conversions. Among CO_2 related reactions, catalytic CO_2 cycloaddition with epoxides (Scheme 1) has been intensively investigated owing to wide applications of the produced carbonates in pharmaceutical and electrochemical industries.[46-48] Thus, CO_2 cycloadditions with various epoxides were selected to investigate the catalytic activity of the fabricated MOF **1** in the chemical conversion of CO_2. HKUST-1, as a benchmark Cu-based MOF, was also selected as a catalyst for control experiments, since it has the same embedded Lewis-acid metal sites.[35]

Table 1. Yields of various cyclic carbonates generated from 1 catalyzed CO_2 cycloadditions with small/large-size epoxides.

Entry	Epoxides	Products	Yields
Small substrates			
1			96
2			85
3			88
4			90
Large substrates			
5			10
6			7
7			6



Four typical liquid epoxides, *i.e.*, propylene oxide (1), 1-butene oxide (2), 2-(chloromethyl)oxirane (3), and 2-(bromomethyl) oxirane (4), were selected (Figure 4 and Table 1) as substrates, and the reactions were carried out in a Schlenk tube. In a typical reaction, 20 mmol propylene oxide and 0.5 g co-catalyst of tetrabutyl ammonium bromide (TBAB) were introduced into the Schlenk tube containing activated MOF catalyst with 0.08 mmol Cu sites (0.2 mol% based on paddlewheel Cu_2 units), and the mixture was stirred under 1 atm of CO_2 at room temperature for 48 h. The reaction was conducted under anhydrous condition. Yields of the generated cyclic carbonates from CO_2 cycloaddition with related epoxides were then determined. As shown in Figure 4, yields of generated cyclic carbonates catalyzed by **1** are 96% for propylene oxide, 85% for 1-butene oxide, 88% for 2-(chloromethyl)oxirane, and 90% for 2-(bromomethyl)oxirane with corresponding turnover frequency (TOF) values of 10.0, 8.9, 9.2, and 9.4 mol carbonate per mol Cu_2 cluster per hour. However, the related cyclic carbonates generated through the same processes catalyzed by HKUST-1 are only 66%, 56%, 57%, and 59% with TOF values of 6.9, 5.9, 6.0, and 6.2 mol carbonate per mol Cu_2 cluster per hour, respectively. The comparison of the yields for all four generated cyclic carbonates clearly demonstrates that the constructed **1** presents remarkably higher catalytic activity than HKUST-1 for CO_2 catalytic cycloadditions with related epoxides under the same reaction conditions.

The catalytic mechanism was further investigated according to the literature reports.[19-24] As aforementioned, the catalytic activity of the constructed MOF on CO_2 conversion is ascribed to its exposed Lewis-acid Cu sites in the activated framework of **1**. The unsaturated orbital of Cu can accept the electrons from donators such as the O atom of propylene oxide as shown in Figure 5. Part of electron transfer from O atom of epoxide to Cu after binding to Cu results in the weakness of C-O bond of epoxide. Meanwhile, the less-hindered C atom of epoxide is attacked by the Br^- from $^tBu_4NBr$ and the epoxy ring opens. Then, the positive charged carbon of epoxide is attacked by the O atom from adsorbed CO_2 cooperating with the attraction of O atom in epoxide to C atom in CO_2. Finally, a ring closed step is achieved with the generation of cyclic carbonate. Given the same embedded Lewis-acid metal sites and similar pore size in both MOFs, higher catalytic activity of **1** should be assigned to the increase of the CO_2 affinity *via* the introduction of the acylamide groups into the framework.

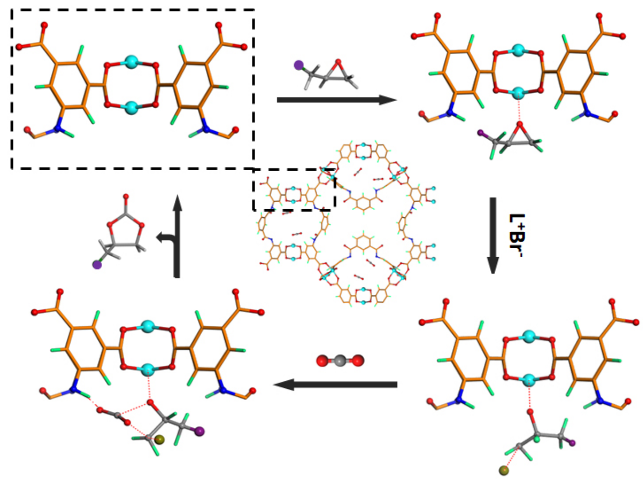


Figure 5. Schematic representation of the catalytic mechanism for the reaction of epoxide and CO_2 into cyclic carbonate catalyzed by MOF **1**. Peacock blue sphere: open Cu site; L^+ = *tetra*-n-butylammonium; violet sphere in the epoxide: functional group such as H, CH_3, Cl, or Br.

As propylene carbonate shows the highest yield, the catalyst recyclability was then tested by taking **1** catalyzed CO_2 cycloaddition with propylene oxide as an example. The results indicate that no significant decrease in the catalytic activity was observed even after 5 cycles of reactions (Figure S9 in SI). The PXRD patterns of the recycled **1** are also consistent very well with the calculated ones from the crystal data (Figure S10 in SI), indicating that the framework of **1** was well maintained during the catalytic reactions.

In order to study the size effect of substrates on such CO_2 cycloaddition reactions, we extended this work to larger epoxide substrates. Three large liquid substrates, 1,2-epoxyoctane (5), 1,2-epoxydodecane (6) and 2-ethylhexyl glycidyl ether (7), were selected (Table 1) for carrying out the experiments at the aforementioned solvent-free conditions. However, when they were subjected to the same reaction process, sharp decreases of the product yields were observed.

As shown in Table 1, their yields were just 10%, 7% and 6% respectively, indicating that large substrates cannot easily enter into the pores of **1** to participate in the catalytic reactions on account of the pore-size confinement of the constructed MOF. These observations also confirm that the CO_2 cycloadditions with small substrates (entries 1-4 in Table 1) are performed within the pores of **1**, and the MOF exhibits size selectivity to small and large substrates during the reactions.

Conclusions

In summary, by artfully extending the backbones of tricarboxylate ligands *via* click chemistry, a highly porous MOF with large pores has been successfully assembled. The dye-probed large-molecule related investigations clearly indicate that the constructed MOF is a highly promising porous material for large-molecule based applications including imaging, delivery, pollutant removal as well as size-dependent separation. On account of the easy and efficient approach for the generation of porous frameworks with large pore sizes for large organic molecule based applications, the present method of constructing MOFs with large pores *via* click-extension of the organic backbones could serve as a general protocol for developing more MOFs with large pores for desired applications.

ASSOCIATED CONTENT

Supporting Information.

Synthesis and characterization details, crystal structure and data, powder XRD, TGA, BET surface area, gas adsorption/desorption isotherms, Raman spectra, FT-IR spectra, and catalytic recyclability. CCDC 1532419.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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