A microporous Cu-MOF with optimized open metal sites and pore spaces for high gas storage and active chemical fixation of CO$_2$†

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A microporous Cu-MOF with optimized open metal sites and pore spaces was constructed based on a designed bent ligand; it exhibits high-capacity multiple gas storage under atmospheric pressure and efficient catalytic activity for chemical fixation of CO$_2$ under mild conditions.

CO$_2$, as an anthropogenic greenhouse gas, is considered to be one of the greatest environmental concerns of our age.$^1$ Such a serious issue mainly stems from the burning of fossil fuels, which bear around 86% of all energy used globally.$^2$ Solving this problem relies on alternative green sources$^3$ with low carbon consumption as well as carbon capture and sequestration.$^4$ H$_2$ is believed to be the ultimate fuel with water as the only by-product; CH$_4$ produces lower CO$_2$ emission and is seen as a transitional fuel; CO$_2$ capture is an immediate solution to the on-going climate change.$^5$ Consequently, storage of H$_2$, CH$_4$ and CO$_2$ has been an unfailing research hotspot in chemistry and material science for the last few decades.$^6$ Amongst various porous candidate groups of absorption materials, metal-organic frameworks (MOFs) hold the greatest potential for effective gas storage due to the modification of pore size/shape and surface area by elaborate selection and design of the linkers.$^7$ Although great progresses in gas storage capacity have been made based on MOF-adsorbents, most materials dominate high volumetric storage using a special gas uptake,$^8$–$^{10}$ such phenomenon of which can be attributed to different kinetic diameters, quadrupole moments and polarizabilities of H$_2$, CH$_4$ and CO$_2$. Realization of high-capacity multiple gas storage materials is essential to meet the urgent demand for clean energy and carbon capture, however, involved reports are very few especially under ambient pressure.$^{11}$

Meanwhile, CO$_2$ being an inexpensive and abundant renewable C1 building block provides an alternative feedstock to fossil fuels. Converting CO$_2$ into high-value chemicals undoubtedly helps to mitigate global warming and conforms to green and sustainable chemistry. One of the most promising technologies is the coupling reaction of CO$_2$ and epoxides to form cyclic carbonates, which are widely applied in pharmaceutical and fine chemical industries.$^{12}$ What is more, the cycloaddition of CO$_2$ to an epoxide produces no side products in accordance with green chemistry and atomic economy.$^{13}$ Although homogeneous catalysis has been industrialized in the formation of cyclic carbonate, the process requires high temperatures and pressures as well as rigorous separation and purification of products.$^{14}$ For this application, it is desirable to develop efficient heterogeneous catalysts that operate under mild conditions.

With the above considerations in mind, our attention was paid to the creation of open metal sites in a MOF-material, which can be generated by removing metal-bound solvent molecules, as coordinatively unsaturated metal centers not only strengthen the gas–MOF interaction$^{15}$ but can also be utilized as heterogeneous Lewis acid catalysts for the efficient transformation of CO$_2$ into cyclic carbonate.$^{16}$ Herein, a semi-rigid tetracarboxylic acid ligand 5,5′-(dimethylsilanediyl) diisophthalic acid (H$_4$L in Fig. 1a, left) was designed and synthesized. The phenyl rings face each other and form an angle at the Si atom; such a conformation is conducive to the formation of cavity space so that the density of open metal sites of each gas-hosting void can be increased. To the best of our knowledge, the ligand H$_4$L is among never documented examples. Based on the bent ligand, a microporous MOF with a [Cu$_2$(CO$_2$)$_4$]–type paddlewheel cluster, [Cu$_2$L(H$_2$O)$_2$]•4H$_2$O·2DMF 1 was successfully synthesized and structurally characterized. Remarkably, the activated phase 1a displays high multiple gas uptake (H$_2$, CH$_4$ and CO$_2$) under atmospheric pressure and high catalytic activity for chemical fixation of CO$_2$ under mild conditions.
Interestingly, six paddlewheels and three L4 ligands form a secondary building unit (SBU) with one formula unit per unit cell. The framework is built from four-coordinated nodes shown as green squares (Fig. 1a, right) and the latter can be simplified as a bent linker shown as a pair of red outstretched triangles (Fig. 1a, left). Such an arrangement extends infinitely to give rise to a (4,4)-connected network of ssa topology with a Schlafli symbol of \{4/2\} \{4\} \{8\} (Fig. 1c).17 There are hexagon channels with methyl groups hanging inward-facing running along the c-axis (Fig. 1b) and the apertures of which are about 9.5 Å at the widest and 7.0 Å at the narrowest spacing. Interestingly, six paddlewheels and three L4 ligands form a cage with an approximate pore diameter of 8.0 Å (taking the van der Waals radii of atoms into consideration) (Fig. 1d and Fig. S9, ESI†); such cage voids afford beneficial circumstances for more favourable gas access and consequent host-guest interaction. The total effective free volume of 1 with removal of solvent molecules is 63.6% (3640.9 Å³ out of the 5727.3 Å³ unit cell volume) calculated by PLATON analysis.18

To confirm the porosity of the activated phase 1a, N2 sorption–desorption isotherms were measured at 77 K and 1 bar, and showed a reversible type-I behaviour, characteristic of permanent microporous materials, with an uptake of 392 cm³ g⁻¹; there is a slight hysteresis between the sorption and desorption traces (Fig. S8, ESI†), which may be due to the cage effect of the network.19 The Brunauer-Emmett-Teller (BET) surface area was calculated to be 1145.9 m² g⁻¹ with a pore volume of 0.998 cm³ g⁻¹. Such porosity is moderate and even lower than those of early reported MOFs.20 However, 1a takes up a significant amount of H2, CH4, and CO2 under atmospheric pressure.

The H2 adsorption capacity of the activated phase 1a was measured at 77 K and 87 K. As shown in Fig. 2, the H2 sorption isotherms show no hysteresis on adsorption and desorption, indicating that H2 sorption is reversible physisorption. The H2 uptake capacity of 1a reaches 209.3 cm³ g⁻¹ (9.35 mmol g⁻¹, 1.87 wt%) at 87 K and 1 bar, and its H2 adsorption capability is up to 303.6 cm³ g⁻¹ (13.6 mmol g⁻¹, 2.7 wt%) at 77 K and 1 bar, being among the highest values known to date and significantly higher than those of some highly porous MOFs with much larger surface areas, such as MOF-177 (4526 cm² g⁻¹, 1.23 wt%),21 IRMOF-6 (2476 cm² g⁻¹, 1.46 wt%),22 and PCN-68 (5109 cm² g⁻¹, 1.87 wt%).23 The above results indicate that the optimized pore size plays a dominant role in reducing the fraction of under-utilized void space, which consequently increases the high density of open metal sites and attractive adsorbate–adsorbent interactions.24 Noticeably, there is only a small number of MOFs which exhibit over 2.0 wt% H2 uptake under the same conditions (Table S3, ESI†).25,26

The sorption behaviours of 1a toward CH4 and CO2 were studied at 273 and 298 K at 1 bar, all of which are fully reversible and do not reach saturated adsorption (Fig. 2). 1a shows a maximum CH4 uptake of 18 cm³ g⁻¹ (0.8 mmol g⁻¹, 1.29 wt%) at 298 K, and 69 cm³ g⁻¹ (3.1 mmol g⁻¹, 4.9 wt%) at 273 K. These values are much higher than most of those reported at 1 bar, such as CPM-33b (41.3 cm³ g⁻¹, at 273 K), L1-Cu (36.97 cm³ g⁻¹, 273 K) and [Zn(btz)] (0.57 at 273 K and 1.57 mmol g⁻¹ at 298 K),27 and even higher than or comparable to some well-known MOFs such as MOF-200 (41 cm³ g⁻¹, at 290 K and 35 bar) and MOF-210 (53 cm³ g⁻¹, at 290 K and 35 bar) measured at high pressures.28 It is interesting that 1a exhibits a high CO2 uptake capacity of 149 cm³ g⁻¹ (6.65 mmol g⁻¹, 29.3 wt%) at 273 K and 115 cm³ g⁻¹ (5.2 mmol g⁻¹, 22.7 wt%) at 298 K; such uptake values at both temperatures are impressive as there are few MOFs exhibiting a
CO₂ uptake of more than 20.0 wt% under ambient conditions,²⁹ even though numerous MOF structures have been reported. The CO₂ absorption amount of Zn-MOF-74 (17.6 wt%), Cu₃(BTC)₂ (18.4 wt%) and PCN-6 (15.9 wt%) at 273 K and 1 bar is higher among reported MOFs,³⁰ which are lower than that of 1a. The superior CO₂ capture of 1a may be attributed to the overlap of potential fields of the pore walls and high density of open metal sites in small pores.

High CO₂ uptake together with the exposed copper metal sites within the framework of 1a inspired us to investigate its heterogeneous catalytic activity for the cycloaddition reaction of CO₂ with epoxides (Table 1). Typically, the reactions were carried out using the epoxide (20 mmol) and carbon dioxide in the presence of a co-catalyst, tetrabutylammonium bromide (TBAB, 0.3 mmol), at 373 K and 1 MPa; while the loading of the catalyst (0.01 mmol) is a 0.5 mol% ratio based on the Cu₂ cluster. Remarkably, 1a performed with high efficiency in the CO₂ cycloaddition especially with small-sized epoxides (Table 1): the glycidol was completely converted to cyclic carbonate within 2 h with a turnover number (TON) of 2000 per mole of catalyst and a turnover frequency (TOF) as high as 1000 per mole of catalyst per hour. A small decrease in the conversion (95.2%) was observed when the hydroxyl was substituted for a chloride substituent and the corresponding TON and TOF values were 1904 and 952 h⁻¹; such values are very impressive, to the best of our knowledge, as the TON and TOF values are far greater than the previously reported values for MOF catalysts under similar conditions (Table S7, ESI†). To check the generality of the CO₂ cycloaddition in this work, larger epoxide substrates were employed and the experiment conducted under similar conditions. The reaction yields catalyzed by 1a from related epoxides are almost complete for 1,2-epoxy-3-phenoxypropane and 64.1% for styrene oxide (SO) within 6 h with corresponding TOF values of 333 and 214 h⁻¹ per Cu₂ cluster. Despite there being a certain decrease compared with values for small substrates under the same conditions, the TOF values of larger ones are still among the highest known to date (Tables S8 and S9, ESI†). To examine its recyclability, taking the CO₂ cycloaddition with glycidol as an example, the catalyst 1a was successively reused in 3 runs without significant decrease in the catalytic efficiency (Fig. S13, ESI†). Additionally, the structural integrity of 1a after catalysis was proved by powder X-ray diffraction (PXRD) measurements (Fig. S3, ESI†). Both high activity and recyclability make 1a an excellent heterogeneous catalyst for chemical CO₂ fixation.

Accordingly, a tentative mechanism for the 1a-catalyzed cycloaddition of epoxide and CO₂ into cyclic carbonate was proposed based on some previous reports,³¹ and is shown in Fig. S14 (ESI†). The coupling reaction is initiated by binding the epoxide with the Lewis acidic copper site in the activated phase. Once binding with copper, the C–O bond of the epoxide is weakened, partly due to electron transfer from the oxygen atom to copper. Subsequently, the less-hindered carbon atom of epoxide is attacked by the Br generated from nBu₄NBr, which opens the epoxy ring, as a consequence of its lower steric effect and higher positive charge. This is followed by the interaction of an oxygen atom from CO₂ with the positively charged carbon of the epoxide and that of the O atom of the epoxide with the C atom of CO₂. The succedent ring closure gives the production of cyclic carbonate.

In summary, a microporous novel Cu-MOF has been successfully designed and synthesized based on a bent silicon-centered ligand. The title compound features optimized cavity space and a high density of embedded Lewis acid metal sites; such an intrinsic structure motif endows it with excellent gas storage performance under atmospheric pressure and heterogeneous catalytic activity for chemical fixation of CO₂ under mild conditions. The generation of a high density of active metal centres within confined cages through crystal engineering has been proved to be an applicable way to develop preponderant materials for gas uptake and chemical CO₂ fixation.

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Notes and references
