Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites

David Britt, Hiroyasu Furukawa, Bo Wang, T. Grant Glover, and Omar M. Yaghi[1]

Center for Reticular Chemistry at the California NanoSystems Institute, Department of Chemistry and Biochemistry, University of California, 607 Charles E. Young Drive East, Los Angeles, CA 90095

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Selective capture of CO_2, which is essential for natural gas purification and CO_2 sequestration, has been reported in zeolites, porous membranes, and amine solutions. However, all such systems require substantial energy input for release of captured CO_2, leading to low energy efficiency and high cost. A new class of materials named metal-organic frameworks (MOFs) has also been demonstrated to take up voluminous amounts of CO_2. However, these studies have been largely limited to equilibrium uptake measurements, which are a poor predictor of separation ability, rather than the more industrially relevant kinetic (dynamic) capacity. Here, we report that a known MOF, Mg-MOF-74, with open magnesium sites, rivals competitive materials in CO_2 capture, with 8.9 wt. % dynamic capacity, and undergoes facile CO_2 release at significantly lower temperature, 80 °C. Mg-MOF-74 offers an excellent balance between dynamic capacity and regeneration. These results demonstrate the potential of MOFs with open metal sites as efficient CO_2 capture media.

carbon dioxide capture | dynamic adsorption | reticular chemistry

Selective removal of CO_2 from gaseous mixtures is of paramount importance for the purification of fuel gases such as methane and acetylene and because of the imminent problem of anthropogenic CO_2 emissions. Effective systems for CO_2 removal must combine high selectivity and capacity with minimal energetic input to liberate the captured CO_2. Materials presently used are amine solutions, zeolites, and porous membranes, but all fall short in one or more of these categories (1). To date, metal-organic frameworks (MOFs) have been shown to exhibit exceptional CO_2 storage capacity under equilibrium conditions where pure CO_2 is introduced into the pores (2–6). However, their capacities are dramatically reduced when exposed to mixtures of gases under dynamic conditions, as would be the case in power plant flue gas and methane mining applications. A useful measure of dynamic separation capacity is obtained by exposing the material to mixed gas streams and detecting the appearance or "breakthrough" of CO_2 from the material. Here, we report that a MOF replete with open magnesium sites, Mg-MOF-74 [Mg_2(DOT); DOT: 2,5-dioxidoterephthalate], has excellent selectivity, facile regeneration, and among the highest dynamic capacities reported for CO_2 in porous materials. Specifically, when Mg-MOF-74 is subjected to a gas stream containing 20% CO_2 in CH_4, a percentage in the range relevant to industrial separations, it captures only CO_2 and not CH_4. The pores retain 89 g of CO_2 per kilogram of material before breakthrough, a value higher than any other achieved in MOFs, and that rivals the highest capacities in zeolites. Remarkably, 87% of the captured CO_2 can be liberated at room temperature, and the remaining amount can be completely removed by mild heating (80 °C). Based on this favorable performance, we assert that MOFs represent a competitive class of materials for efficient CO_2 capture, and that Mg-MOF-74 strikes the right balance between high capacity and heat of adsorption, notwithstanding the great opportunities available for functionalizing such MOFs for even further improved performance.

In previous work, it has been shown that coordinatively unsaturated (open) metal sites in MOFs can be prepared by removal of coordinated solvent molecules (7, 8). Whereas flexible molecular or polymeric structures rearrange or aggregate to occlude such reactive sites, the rigidity of MOFs ensures that open metal sites remain accessible to incoming guests. MOF-74, a prototypical example, has one-dimensional hexagonal channels with 5-coordinate zinc(II) ions decorating the edges of each channel (Fig. 1) (9). This material was found to have exceptional separation capacity for gases such as sulfur dioxide, ammonia, and ethylene oxide (10), and H_2 storage capacity (11). Subsequent to this initial discovery, a series of MOFs in which the 5-coordinate zinc(II) ions of MOF-74 are substituted for various divalent metal ions, including nickel, cobalt, manganese, and magnesium, has been described in various reports (12–15). Studies of equilibrium gas uptake in these materials have demonstrated the key role of the metal ion in determining uptake properties (16–18). One study on the nickel-containing analog presents an X-ray single crystal structure of CO_2 bound "end-on" to the open nickel sites in the MOF, clearly demonstrating the role of the metal in binding (19). The CO_2 uptake of another member of the series, Mg-MOF-74 (alternatively labeled CPO-27-Mg), was found to be exceptionally high at low-pressure (<0.1 atm) in equilibrium isotherm experiments performed at room temperature (14). Indeed, we have calculated the initial isosteric heat of adsorption to be 39 kJ mol^{-1}. This value reflects a strong physisorption interaction but remains well below the energy of a chemical bond, which is desirable for facile CO_2 release. Another encouraging feature of this MOF is that the ratio of the Henry's Law constant for CO_2 and CH_4 adsorption is as high as 330 [see supporting information (SI) *Appendix* Section S1 for details of selectivity calculations]. This value, which is >1 order of magnitude higher than the best reported in MOFs, indicates that this material has the thermodynamic selectivity necessary for effective separation (20). Therefore, we surmised that these attributes make this MOF an excellent candidate for substantial binding of CO_2 from an incoming gas stream without prohibitive energetic requirements for its removal.

Results

We performed "breakthrough" separation experiments on Mg-MOF-74 to determine its CO_2 separation capacity. The

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[1] To whom correspondence should be addressed. E-mail: yaghi@chem.ucla.edu.

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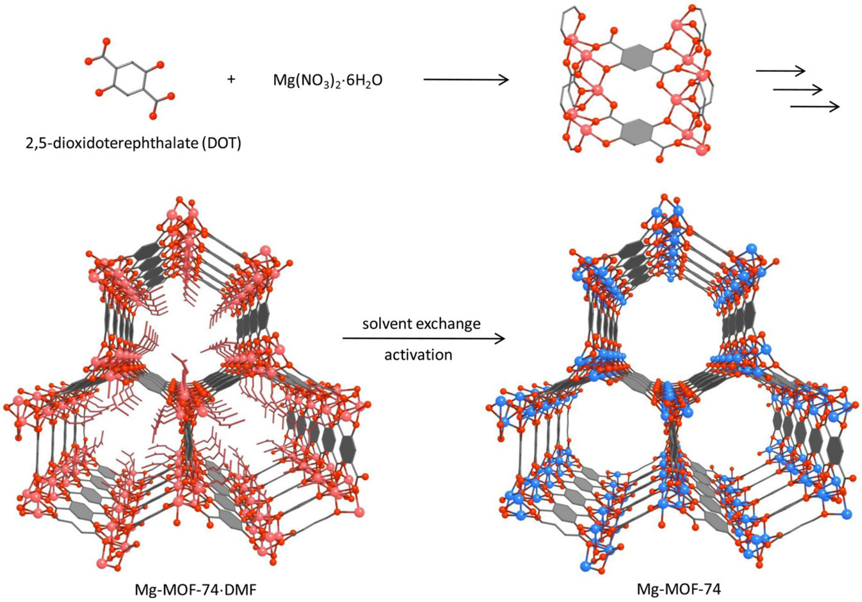

Fig. 1. Single crystal structure of Mg-MOF-74, formed by reaction of the DOT linker with $Mg(NO_3)_2 \cdot 6H_2O$. The structure consists of 1D inorganic rods linked by DOT to form linear hexagonal channels. C atoms are shown in gray, O atoms in red, 6-coordinate Mg atoms and terminal ligands in pink, and 5-coordinate Mg atoms in blue. H atoms and terminal ligands on the fragment at top right are omitted for clarity.

activated adsorbent was purged with CH_4 until no other gases were detected in the effluent and exposed to a 10-mL min^{-1} flow of a 20% mixture of CO_2 in CH_4. The effluent from the bed was monitored by mass spectrometry. The resulting "breakthrough curve" (Fig. 2) demonstrates that Mg-MOF-74 provides complete separation of CO_2 from the CH_4 stream. We note that no rise or "roll-up" of CH_4 effluent concentration is observed before CO_2 saturation, indicating that the framework does not adsorb CH_4 significantly. Furthermore, CH_4 breakthrough during the initial purge is essentially instantaneous. It is clear that no significant amount of CH_4 remains adsorbed to the framework after saturation with CO_2.

From these breakthrough data, we calculate that Mg-MOF-74 takes up 8.9 wt. % CO_2 before breakthrough, corresponding to 0.44 molecules of CO_2 per magnesium ion. This equates to a volumetric capacity of 81 g of CO_2 per liter of adsorbent based on a calculated density of 0.91109 g mL^{-1} (see *SI Appendix* Section S2 for details of the volumetric capacity calculation). Because these values are obtained from breakthrough experiments and thus reflect both the kinetic and thermodynamic aspects of separation, they provide clear evidence that Mg-MOF-74 represents a major advance in CO_2 separation capacity in MOFs.

To test the importance of the metal ion in CO_2 adsorption, we performed CO_2 breakthrough measurements on Zn-MOF-74 (see *SI Appendix* Section S3). Zn-MOF-74 is an exact structural analog to the Mg-MOF-74 structure, differing only by substitution of the metal. Zn-MOF-74 takes up just 0.35 wt. % of CO_2, a reduction of 96% from Mg-MOF-74. This result clearly implicates the metal ion as the primary factor in CO_2 binding. Furthermore, CO_2 adsorbed in the nickel analog to these structures was determined in previous work via infrared spectroscopy and X-ray diffraction to be bound end-on to the metal ion (19). It is apparent that the interaction between CO_2 and the magnesium ion in Mg-MOF-74 is responsible for its high capacity.

Essential to any CO_2 capture material is the energy required for CO_2 release. Indeed, this step is a primary factor in the cost of current separation processes (1). To test the regeneration properties of the MOF, a sample saturated with CO_2 was subjected to a CH_4 purge flow at 25 mL min^{-1} for 10 min at room temperature. Successive breakthrough experiments (Fig. 3) reveal that Mg-MOF-74 retains a capacity of 7.8 wt. % after this room temperature regeneration process, >87% of its intrinsic capacity. Further cycling does not lead to further reduction of capacity. The full capacity of the MOF can be regained by purging at just 80 °C. Although regeneration methods in an industrial process would likely involve some combination of flow, pressure, and temperature modulation, these tests signify that Mg-MOF-74 provides high-capacity separation with very mild conditions for regeneration.

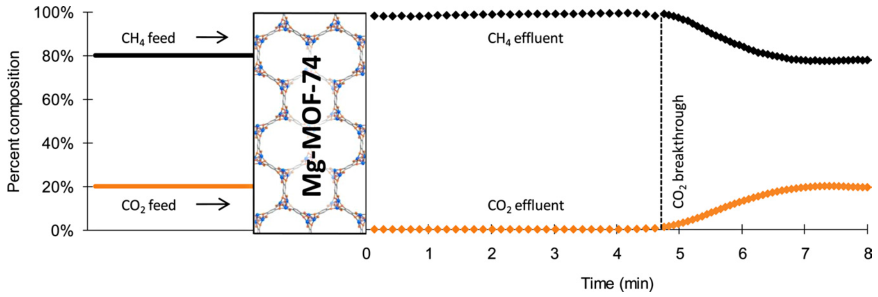

Fig. 2. A 20% mixture of CO_2 in CH_4 is fed into a bed of Mg-MOF-74. Effluent concentrations are shown, indicating complete retention of CO_2 until saturation. CO_2 breakthrough occurs at the dashed line.

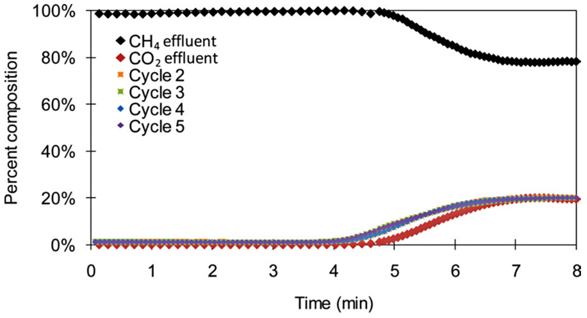

Fig. 3. Breakthrough cycling in Mg-MOF-74. CO_2 and CH_4 effluent from fully regenerated Mg-MOF-74 and CO_2 effluent for four repeat cycles after 10-min purge at 25-mL min^{-1}, indicating facile regeneration.

The intrinsic adsorption properties of Mg-MOF-74 are not adversely affected by water vapor. After exposure to ambient atmosphere for 2 days, Mg-MOF-74 was fully regenerated under nitrogen flow and elevated temperature. The MOF does not suffer from permanent loss of capacity due to reaction with water. The thermal stability of Mg-MOF-74 was tested previously by thermal gravimetric analysis, during which it was found to be stable above 400 °C (14). Although complete study of the stability of the MOF over time in operative conditions is necessary, the framework is sufficiently robust to withstand temperatures far above those encountered in separation processes, which typically do not exceed the range of 140 °C (1, 21, 22).

Discussion

Comparison of the separation properties of Mg-MOF-74 with standard CO_2 capture materials shows that this material represents a breakthrough for high-capacity storage with moderate regeneration conditions. The dynamic separation capacity, initial heat of interaction, and regeneration conditions for Mg-MOF-74 and several standard materials are compared in Table 1. We include data for two MOFs previously reported to take up CO_2 selectively, the rigid zeolitic imidazolate framework ZIF-78 [Zn(nbIm)(nIm); nbIm: 5-nitrobenzimidazolate, nIm: 2-nitroimidazolate] and the "breathable" amino-MIL-53 [AlOH(AT); AT: 2-aminoterephthalate] frameworks. Although dynamic separation capacity depends on experimental parameters such as flow rate and sample dimensions, Mg-MOF-74 is clearly a landmark among MOFs, with a separation capacity more than twice the nearest candidate and far milder regeneration conditions in breakthrough experiments run under similar conditions. NaX zeolite is among the most effective porous adsorbents considered for CO_2 separation (22, 24). Breakthrough experiments performed on NaX under identical conditions to those performed on Mg-MOF-74 show that the MOF material, with dynamic capacity of 8.9 wt. % CO_2, takes up more CO_2 than NaX, which has a dynamic capacity of 8.5 wt. %. Moreover, after a 10-min purge at 25-mL min^{-1}, NaX regains 71% of its capacity (6.4 wt. %), whereas Mg-MOF-74 regains 87% of its capacity (7.8 wt. %). The temperature required to achieve full regeneration in Mg-MOF-74 is also significantly reduced. Among the best porous adsorbents available for CO_2 separation, Mg-MOF-74 offers the best balance between separation capacity and ease of regeneration, making it a strong candidate for energy-efficient CO_2 capture.

Although a direct comparison between Mg-MOF-74 and amine solutions is difficult because the mechanism of absorption differs completely from adsorption in porous solids, amine solutions are far more widely used in industrial natural gas purification than porous adsorbents (1, 21). Thus, it is necessary to make some assessment of the potential of Mg-MOF-74 relative to these solutions. A 30% monoethanolamine (MEA) solution, the most prevalent absorbent in commercial amine treatment of natural gas, takes up 13.4 wt. % CO_2 under typical operating conditions (21). Mg-MOF-74 takes up two-thirds as much by comparison but with initial heat of interaction diminished by more than a factor of two, 39 kJ mol^{-1} in the MOF to 84 kJ mol^{-1} in MEA. The effect of the lower heat of interaction is evident in the far milder regeneration conditions for Mg-MOF-74. As such, it is expected that removal of CO_2 from the MOF material will require less energy in any separation process. Needless to say, MEA solutions are toxic and highly corrosive and present an additional environmental challenge.

Materials and Methods

Mg-MOF-74 was synthesized and activated according to reported procedures (see *SI Appendix* Section S4). Its structure and porosity were confirmed by powder X-ray diffraction and N_2 adsorption isotherm, respectively. The compound was stored in ambient atmosphere and regenerated on the breakthrough apparatus under N_2 atmosphere at at least 250 °C before use. NaX zeolite beads, 8–12 mesh, were regenerated before use at at least 250 °C under purge flow or vacuum, overnight. N_2, CO_2, and CH_4 gases were obtained with 99.999%, 99.995%, and 99.999% purity, respectively. Nitrogen isotherms for confirmation of surface area were collected on a Quantachrome Instruments NOVA 4200e surface area and pore-size analyzer. CH_4 and CO_2 isotherms were collected on Quantachrome AUTOSORB-1 automatic volumetric adsorption instrument. Breakthrough experiments were performed on a 0.4- × 5.0-cm bed of adsorbent inside stainless steel Swagelok tubing. Volume not occupied by the adsorbent bed was filled with stainless steel beads. The flow rate and composition of the gases were determined by MKS Alta digital mass flow controllers. The pressure was held at 762 Torr by an MKS Type 640 pressure controller. The above were monitored by using an MKS Type 247 4 channel readout. The gaseous effluent from the sample bed was monitored for CO_2, CH_4, N_2, and O_2 by using a Hiden Analytical HPR20 mass spectrometer (see *SI Appendix* Section S5 for full details of the experimental apparatus and conditions). The sample cell was heated for regeneration by using an Omegalux HT-WAT051–002 heating mantle. Powder X-ray diffraction was performed on a Bruker D8 Discover θ-2θ diffractometer in reflectance Bragg–Brentano geometry at 40 kV, 40 mA (1,600 W) for Cu Kα_1 radiation (λ = 1.5406 Å).

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Table 1. Adsorption and separation properties of Mg-MOF-74, other MOFs, and standard CO_2 separation materials

Material	Mg-MOF-74	NaX	30% monoethanol-amine (MEA)[21,23]	Amino-MIL-53[6]	ZIF-78[5]
Separation capacity (wt. %)*	8.9 (7.8)	8.5 (6.4)	13.4	3.7	1.4
Initial heat of ab- or adsorption (kJ mol^{-1})	39	43	84†	–	29
Full regeneration conditions	80 °C, purge flow	118 °C, purge flow[22]	120 °C, recirculation	159 °C, purge flow	–

*Values in parentheses represent capacity regained after 10-min purge at 25 mL min^{-1}, indicating facile regeneration in Mg-MOF-74.
†Value determined at 313 K.

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