Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal–Organic Framework mmen-Mg\(_2\)(dobpdc)

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1. INTRODUCTION

The concentration of CO\(_2\) in the Earth’s atmosphere is presently 390 ppm,\(^1\) an increase of approximately 110 ppm since the start of the Industrial Revolution.\(^2\) The combustion of fossil fuels is largely responsible for this increase,\(^3\) yet fossil fuels will continue to be heavily utilized for energy production during the 21st century. Currently, there is significant interest in the development and implementation of technologies that slow CO\(_2\) emissions and thus forestall the most severe consequences of global warming. For limiting future CO\(_2\) emissions from large, stationary sources like coal-fired power plants, carbon capture and sequestration (CCS) has been proposed.\(^4\) The CCS process involves the selective removal of CO\(_2\) from gas mixtures, the compression of pure CO\(_2\) to a supercritical fluid, transportation to an injection site, and finally permanent subterranean or submarine storage.\(^5\) For the retrofit of existing power plants, post-combustion CO\(_2\) capture is a likely configuration. In this design, fuel is burned in air and CO\(_2\) is removed from the flue. For coal-fired power plants, the largest flue gas components by volume are N\(_2\) (70–75%), CO\(_2\) (15–16%), H\(_2\)O (5–7%), and O\(_2\) (3–4%), with total pressures near 1 bar and temperatures between 40 and 60 °C.\(^6\) Aqueous amine solutions are currently the most viable absorbents for carbon capture under the aforementioned conditions, and they are presently used for the removal of CO\(_2\) from industrial commodities like natural gas.\(^7\) While a variety of advanced amines are available, 30% monoethanolamine (MEA) in water is the benchmark solvent against which competing technologies are generally compared. The low solvent cost and proven effectiveness make MEA an attractive absorbent for many applications. However, if MEA were to be utilized for CCS, electricity prices are projected to increase by 86%.\(^8\) The U.S. Department of Energy has targeted a maximum 35% increase for the cost of electricity produced from a coal power plant that captures 90% of the CO\(_2\) it generates. The diversion of steam from the electricity generation cycle to the solvent regeneration cycle sharply reduces the net electricity output of the plant, drastically increasing electricity costs. Previous work has demonstrated that plant efficiency is highly dependent on the solvent regeneration energy.\(^9\)

Presently, there is significant interest in the development of solid absorbents that selectively absorb CO\(_2\) at partial pressures applicable to CCS.\(^10\) Solid absorbents are promising candidates because the significantly smaller heat capacities of solids may reduce the sensible heat required for regeneration. In addition, solvent loss and corrosion issues resulting from the use of aqueous amines would be minimized if solids absorbents were instead utilized.\(^9\)
While CCS is perhaps unlikely to be widely implemented within the next decade, a number of current industrial processes utilize liquid or solid adsorbents to remove CO₂ from gas mixtures. These processes could benefit greatly from the next generation of adsorbents that are currently being proposed for CCS applications. Currently, aqueous amines are used industrially to separate CO₂ from gas mixtures with high CO₂ partial pressures like natural gas, while solid adsorbents are used to remove CO₂ from mixtures with very low CO₂ partial pressures.

Among the most challenging CO₂ separations is the removal of CO₂ directly from air. Prior to the cryogenic distillation of air for N₂, O₂, and Ar production, CO₂ is removed from the air to minimize solid CO₂ formation on heat exchangers. To maximize the capacity of zeolite 13X for CO₂ adsorption, the air stream is dried over alumina, cooled to 5 °C, and pressurized to 5–7 bar. The effective capacity of zeolite 13X, the most widely used adsorbent for this process, under these conditions is ca. 0.35 mmol/g, which corresponds to a volumetric capacity of approximately 0.5 mmol/cm³. In this “pre-purification” step, the CO₂ concentration in the air is reduced to less than 1 ppm. New higher-capacity adsorbents could potentially eliminate the costs associated with pre-cooling feed air and reduce the adsorbent regeneration energy.

Carbon dioxide scrubbers are critical life support systems in confined spaces with limited air exchange, such as spacecraft, submarines, and breathing suits. Because of the very low capacity of solid adsorbents for 390 ppm CO₂ in unpressurized gas streams, weight and volume limitations prevent the implementation of systems capable of maintaining CO₂ concentrations at atmospheric levels. Thus, the average CO₂ concentration aboard the International Space Station ranges from 3000 to 7000 ppm, which approaches the currently established safe limit for chronic CO₂ exposure. Improved adsorbents could potentially reduce CO₂ concentrations within confined spaces to significantly lower and potentially safer levels, while simultaneously reducing the adsorbent mass and volume.

In addition to current processes that remove CO₂ from air, proposed technologies may benefit greatly from improved air capture adsorbents. For example, alkaline fuel cells (AFCs) require CO₂-free O₂ sources to avoid electrolyte side reactions. It has been previously suggested that improved CO₂ adsorbents could solve many issues associated with the operation of AFCs because air purification imposes considerable engineering and financial burdens on the system.

Lastly, directly adsorbing CO₂ from the atmosphere combined with geologic sequestration has been proposed as a potential solution for offsetting CO₂ emissions from mobile or diffuse generators. Direct air capture, if widely implemented, could also theoretically reduce atmospheric CO₂ concentrations by capturing historic emissions rather than simply abating future emissions. Significant obstacles remain for direct air capture including its substantially higher cost compared to traditional CCS. Yet many estimates rely on the use of traditional inorganic bases, which require the construction of very large physical structures to ensure sufficient surface area for air to contact the adsorbent. Porous solid adsorbents with high surface areas could potentially drastically reduce the large capital costs associated with air capture.

Recently, amine-functionalized porous solids have been proposed as superior adsorbents for air capture compared to inorganic bases and zeolites. For example, amine-modified porous polymers have been tested for use aboard spacecraft. Silica, alumina, and carbon adsorbents functionalized with amines have also been analyzed for their efficacy as air capture adsorbents, as have ammonium ion-exchange membranes. The primary advantage of amine-functionalized adsorbents is their high capacity for 390 ppm CO₂ in some cases in excess of 2 mmol/g. However, existing materials of this type frequently require hours to reach saturation because of slow adsorption kinetics.

Metal–organic frameworks are a class of porous, crystalline adsorbents that have recently attracted much attention for use in gas separations. The high tunability of their design may enable greater functionality with reduced adsorbent mass and volume compared to traditional solid adsorbents. Among the most interesting features of some metal–organic frameworks is the presence of coordinatively unsaturated metal centers (open metal sites) along the pore surfaces. These five-coordinate metal cations, known to behave as Lewis acids that strongly polarize gas adsorbents, are further amenable to post-synthetic functionalization.

In chemically robust metal–organic frameworks with well-separated open metal sites, one amine of a diamine molecule can bind to a metal cation as a Lewis base, while the other amine remains available as a chemically reactive adsorption site. The modification of open metal sites within the metal–organic framework Cu-BTTr with the secondary amine N,N'-dimethylethenediamine (mmen) was recently reported. Upon grafting mmen onto the exposed Cu sites of the framework, a 3.5 times enhancement in CO₂ capacity at 0.15 bar and 25 °C was realized. We believe that the incorporation of very basic alkylamines into framework pores will be a promising strategy for increasing the capacity of metal–organic frameworks for CO₂ uptake at low partial pressures.

The high concentration of open metal sites within the M₂(dobdc) (M = Mg, Mn, Fe, Co, Ni, Zn; dobdc⁺ = 2,5-dioxido-1,4-benzenedicarboxylate; M-MOF-74 or CPO-27-M) series of metal–organic frameworks makes them attractive candidates for diamine functionalization. To date, however, we have been unable to synthesize promising amine functionalized derivatives of the M₂(dobdc) series. We hypothesized that the relatively narrow, one-dimensional channels (~11 Å diameter) may be hindering effective diffusion of the diamines into the framework. Thus, we sought to synthesize expanded analogues of the M₂(dobdc) structure via a ligand extension. Larger pores should enable more facile functionalization, enhance gas diffusion, and potentially unlock unrealized functionality within this interesting structural topology replete with open metal sites.

Herein, we report the first expanded analogues of the M₂(dobdc) structure type, featuring 18.4Å-wide channels and exhibiting exceptional CO₂ adsorption properties upon functionalization with mmen.

2. EXPERIMENTAL SECTION

General. All reagents were obtained from commercial vendors at reagent grade purity or higher and used without further purification. 4,4'-Dihydroxybiphenyl-1,1',3-biphenyl)-3,3'-dicarboxylic Acid (H₄dobdc). The compounds 4,4'-dihydroxybiphenyl (1.16 g, 6.24 mmol), KHCO₃ (2.00 g, 20.0 mmol), and 1,2,4-trichlorobenzene (3 mL) were added to a PTFE insert within a steel acid digestion bomb (23 mL) and heated at 255 °C for 17 h. After cooling to room temperature, the mixture was collected via vacuum filtration and washed with diethyl ether. The solid was suspended in 300 mL of...
distilled water and filtered again. To the filtrate, neat HCl was slowly added until a pH between 1 and 2 was reached. The resulting crude product was collected via filtration. Recrystallization using 50 mL of acetone and 50 mL of water per gram of crude material afforded 0.68 g (40%) of pure product as a white powder. Anal. Calcd for C14H10O6: C, 51.66; H, 3.54; O, 44.80. Found: C, 51.71; H, 3.47; O, 44.86.

A sample of fully activated Mg2(dobpdc) (24 mg, 0.088 mmol), MgBr2 (8.9 mg, 0.034 mmol), and 0.5 mL of mixed solvent (1:1 DEF:EtOH) were loaded and sealed with a PTFE cap. The mixture was irradiated in a microwave reactor (CEM Discover) for 30 min at 120 °C. After 30 min, the solution was cooled, and the resulting solid was collected via filtration and washed with hot DEF. The solid was dried under vacuum to yield 57.5 mg (95%) of Mg2(dobpdc)(DEF)-2.


diffractionometer using Cu Kα radiation (λ = 1.5406 Å). The unit cell dimensions of DEF-2 and mmen-2 were determined by performing a full-pattern decomposition using the Le Bail method, as implemented in TOPAS-Academic.13 Owing to the isomorphism with Zn4(dobpdc), the trigonal space group P3121 was used for the refinements. Crystal data for DEF-2: a = 21.761(2) Å, c = 6.9721(7) Å, V = 2859.1(5) Å3 (Rg = 0.093, Rp = 0.067). Crystal data for mmen-2: a = 21.500(2) Å, c = 6.8725(9) Å, V = 2733.2(6) Å3 (Rg = 0.042, Rp = 0.033).

Gas Adsorption Measurements. Gas adsorption data for pressures in the range 0–1.1 bar were obtained by volumetric methods using a Micromeretics ASAP2020 instrument. All gases were 99.99% purity or higher. Isotherms at 77 K were measured in liquid nitrogen baths. Isotherms at 25, 35, 45, 50, and 75 °C were measured using water circulators to maintain a constant temperature. Isotherms at 100 and 120 °C were measured using a heated sand bath controlled by a programmable temperature controller. BET surface areas were calculated from N2 adsorption at 77 K. DFT pore size distributions and pore sizes were calculated from N2 adsorption at 77 K with the Micromeretics DFT Plus Models Kit (Ver. 2.02) software suite with cylinder pore geometries for an oxide surface. The calculated mmen-2 was regenerated at 100 °C under dynamic vacuum for 4 h after measurement of each isotherm.

Isotherm analysis was performed using the Micromeritics ASAP2020 instrument. Gas adsorption data for CO2 adsorption at 25, 50, and 75 °C for mmen-2 in the region before the step in the isotherms.

Here, q is the amount of CO2 adsorbed (mmol/g), p is the pressure (bar), qsat is the saturation capacity (mmol/g), b is the Langmuir–Freundlich parameter (bar−1), and α is the Langmuir–Freundlich exponent (dimensionless) for two adsorption sites A and B. In order to model the CO2 adsorption in the region after the step, a modified Langmuir–Freundlich equation (eq 2) was employed.

\[
q = \frac{q_{\text{sat},A}b_A(p - p^*)^{\frac{1}{b_A}}}{1 + b_A(p - p^*)} + \frac{q_{\text{sat},B}b_B(p - p^*)^{\frac{1}{b_B}}}{1 + b_B(p - p^*)} + \frac{q_{\text{sat},C}b_C(p - p^*)^{\frac{1}{b_C}}}{1 + b_C(p - p^*)}
\]

Here, adsorption is considered at three sites, A, B, and C, and the extra parameter p* is used to account for the pressure at which the step in the isotherm occurs and the strongest adsorption sites are first populated. After carefully refining the parameters in eqs 1 and 2, excellent agreement was achieved between the experimental isotherm data and the corresponding isotherm fits (see Figures S10–S13). Using the appropriate isotherm fits, Mathemtica software was used to solve for the exact pressures, p, corresponding to constant amounts of CO2 adsorbed, q, at 25, 50, and 75 °C. The Clausius–Clapeyron equation (eq 3) was then used to calculate the isosteric heats of adsorption, Qst, by determining the slope of the best-fit line for ln p versus 1/T at each loading.

\[
\ln(p) = \ln\left(\frac{Q_{\text{st}}}{R}\right) + \frac{\Delta H_{\text{st}}}{RT} + C
\]

As indicated by the residual sum of square values, R2, of close to 1 (see Figure S14), the isotherm data were consistent with the Clausius–Clapeyron equation across the entire loading range considered, even with the changes in the location of the step in the isotherms.

The isosteric heats of adsorption for CO2 in the unmodified Mg4(dobpdc) were determined by fitting the adsorption isotherms at 25, 35, and 45 °C with a dual-site Langmuir–Freundlich equation (eq 1). Each temperature was fit independently, and the Clausius–Clapeyron equation was used to determine Qst as a function of loading. All fit parameters for Mg4(dobpdc) and mmen-Mg4(dobpdc) are specified in Tables S2–S4.
Model CO₂ Isotherms. Isotherms for CO₂ uptake in mmen-2 at other temperatures were predicted from the experimental isotherm at 75 °C via application of a Clausius–Clapeyron relation (eq 4).

\[
\ln p_2 = \frac{Q_a + \ln p_1}{T_2 - T_1} 
\]

Calculated pressures \((p_2)\) at constant loadings \((q)\) were determined assuming an isosteric heat of adsorption \((Q_a)\) of 71 \(kJ/mol\) for all loadings. Here, \(p_1\) is a pressure experimentally measured at 75 °C, \(T_1\) is the universal gas constant, \(T_1\) is 75 °C, and \(T_2\) is the temperature for which a model isotherm is desired.

CO₂ Selectivity Calculations. Here, the adsorption capacities of component \(n\) \((q_n)\) are defined to be molar excess adsorption capacities determined experimentally without correction for absolute adsorption, and \(p_n\) is defined to be the pressure of component \(n\) as experimentally measured. Selectivity \((S)\) is defined according to eq 5, while purity is defined according to eq 6.

\[
S = \frac{q_{CO_2}/q_1}{P_{CO_2}/P_2} 
\]

\[
\text{purity} = \frac{q_{CO_2}}{q_{CO_2} + q_2} \times 100\%
\]

Thermogravimetric Analysis and Gas Cycling Measurements. Thermogravimetric analyses (TGA) were carried out at ramp rates between 5 and 10 °C/min under a nitrogen flow with a TA Instruments TGA Q5000 (Ver. 3.1 Build 246) or a Scinco TGA N-1000.

Carbon dioxide cycling experiments were performed on the aforementioned TA Instruments analyzer using 15% CO₂ in N₂ (Praxair 99.99%), 390 ppm CO₂ in air (Praxair 99.99%), and N₂ (Praxair 99.99%). A flow rate of 25 ml/min was employed for all gases. Prior to cycling, the sample was activated by heating at 150 °C for 1 h. For Figure 6, sample mass was normalized to be 0% at the adsorption temperature (25 °C for 390 ppm CO₂; 40 °C for 15% CO₂) under flowing N₂. For Figure 7, sample mass was normalized to be 0% at 150 °C under flowing 100% CO₂. Masses were uncorrected for buoyancy effects. In Figure 6, the difference between the quantity of N₂ adsorbed at the tare temperature and the regeneration temperature likely accounts for the negative apparent mass of mmen-2 at high temperatures.

Differential Scanning Calorimetry. Thermal analysis was performed on a TA Instruments Q200 differential scanning calorimeter equipped with a refrigerated cooling system (RCS40). Through the sample cell, 15% CO₂ in N₂ or N₂ was flowed over T-Zero aluminum pans that were not hermetically sealed. An empty, aluminum T-Zero pan provided the reference sample for thermal analysis. The calorimeter was calibrated with the TA Instruments software package; the melting point of indium (156.60 °C) was utilized for the temperature calibration. Sample and pan masses were determined after activation at 150 °C for 60 min on a TA Instruments TGA Q5000 via the readout from the internal balance under flowing N₂. Identical aliquots of mmen-2 were utilized for TGA and DSC measurements to approximate heats of adsorption. Integrated heats were calculated with TA Instruments Universal Analysis software suite.

Other Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Sogang University or the Microanalytical Laboratory of the University of California, Berkeley. ¹H spectra were obtained using a 300 MHz Varian instrument. Infrared spectra were obtained from KBr pellets with a Bomen MB-104 spectrometer or on a Perkin-Elmer Spectrum 400 FTIR spectrometer equipped with an attenuated total reflectance (ATR) accessory. For diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra, the Perkin-Elmer spectrometer was equipped with a Harrick Praying Mantis Diffuse Reflectance accessory and a temperature-controlled high-pressure gas cell with Swagelok valves connecting 5% CO₂ in He (Praxair certified standard HE CDSC-K) and an oil-free vacuum.

3. RESULTS AND DISCUSSION

Synthesis, Structure, and Activation. Reaction of H₄dobpdc with ZnBr₂·2H₂O or MgBr₂·6H₂O in 1:1 DEF:EtOH afforded DEF-1 and DEF-2, respectively (see Figure 1). The coordination environment of the divalent metal cations within 1 and 2 are analogous to those in the M₄(dobdc) series. In the crystal structure of DEF-1, four different dobdc⁻⁻ ligands and one DEF molecule are bonded to each Zn⁴⁺ ion in a distorted octahedral geometry. There are three unique O donor types from the dobdc⁻⁻ ligand: bridging (µ₂) aryloxide O atoms (O1), bridging (µ₃) carboxylate O atoms (O2), and nonbridging carboxylate O atoms (O3). The equatorial plane of each Zn⁴⁺ is composed of two trans-disposed O1 ligands from different linkers, one O3 donor atom, and one O2 donor atom. An O2 donor atom occupies one axial coordination site, while the other axial site is occupied by an O donor atom from DEF, the reaction solvent. This coordination
mode results in the formation of helical chains of Zn$^{2+}$ atoms running along the c axis of the crystal. The resulting framework consists of a honeycomb lattice of hexagonal, one-dimensional channels approximately 18.4 Å in width. Bound DEF molecules occupy the Zn$^{2+}$ coordination sites along the corners of hexagonal channel walls. As shown in Figure S1, powder X-ray diffraction (PXRD) data indicate DEF-2 to be isostructural with DEF-1.

Heating DEF-2 at 420 °C for 65 min under dynamic vacuum, removed the DEF molecules bound to the metal atoms, completely activating the material and generating open Mg$^{2+}$ coordination sites. Such extreme thermal treatment was necessary because soaking in methanol at 100 °C for 20 h did not lead to exchange of the bound DEF molecules. The porosity of activated 2 was confirmed via N$_2$ adsorption at 77 K (see Figure S4), resulting in a BET surface area of 3270 m$^2$/g. Note that, in line with the expanded structure, this is significantly greater than the BET surface area of 1495 m$^2$/g reported for Mg$_2$(dobdc).36

The synthesis and structure of mmen-2 is depicted schematically at the right of Figure 1. An activated sample of 2 was suspended in hexanes and an excess of mmen was added. As shown by powder X-ray diffraction (see Figure S3), framework crystallinity was not significantly affected by activation or subsequent amine functionalization. A much reduced BET surface area of 70 m$^2$/g was calculated for mmen-2, while DFT pore size distributions indicated a reduction in average pore size (see Figures S5–S7).

Upon exposure of DEF-2 to atmospheric air, the white powder turns blue and a loss of crystallinity occurs, as observed via powder X-ray diffraction measurements. Amine functionalization, however, appears to enhance framework stability, because no similar degradation was observed for mmen-2 upon exposure to air for one week.

**CO$_2$ Adsorption Isotherms.** The CO$_2$ adsorption data obtained for 2 are depicted in Figure S8. Isosteric heats of adsorption were calculated to approach $\sim$44 kJ/mol at low coverage, as shown in Figure S9. This value is similar to those previously reported for the analogous Mg$_2$(dobdc) framework.37 The adsorption capacity of 2 at 25 °C is 4.85 mmol/g (17.6 wt %) and 6.42 mmol/g (22.0 wt %) at 0.15 and 1 bar, respectively. The gravimetric capacity of 2 for CO$_2$ at 0.15 bar exceeds the capacity of all metal–organic frameworks except for Mg$_2$(dobdc)$_3$,38 which adsorbs 6.1 mmol/g (21.2 wt %) at 25 °C and 0.15 bar.36

The alkylamine-functionalized metal–organic framework mmen-2 displayed an extremely high affinity for CO$_2$ at extraordinarily low pressures. The CO$_2$ adsorption isotherms obtained at 25, 50, and 75 °C are presented in Figure 2. At 25 °C and 0.39 mbar, near the current partial pressure of CO$_2$ in Earth’s atmosphere, the compound adsorbed 2.0 mmol/g (8.1 wt %), which is 15 times the capacity of 2. At the much higher pressure of 5 mbar, the median partial pressure of CO$_2$ within the International Space Station, the framework adsorbed 2.6 mmol/g (10.3 wt %). For comparison, zeolite SÅ, which is currently used aboard the station to adsorb CO$_2$, has a 0.85 mmol/g (3.6 wt %, crystallographic volumetric capacity 1.3 mmol/cm$^3$) at 5 mbar.12

At 25 °C, the CO$_2$ adsorption in mmen-2 reaches 3.13 mmol/g (12.1 wt %) at 0.15 bar and 3.86 mmol/g (14.5 wt %) at 1 bar. Remarkably, its CO$_2$ uptake at 1 bar and 25 °C exceeds the amount of N$_2$ adsorbed at 77 K. Thus, the low surface area measured at 77 K does not appear to accurately reflect the surface area accessible to CO$_2$, and the pore size distribution calculated from N$_2$ adsorption at cryogenic temperatures likely does not accurately represent the true pore size distribution within mmen-2. On a per mass basis, the amine-functionalized framework adsorbed less CO$_2$ than 2 at pressures higher than 20 mbar. The large density difference between the two frameworks is primarily responsible for the lower gravimetric capacity of mmen-2. Crystallographic densities of 0.58 and 0.86 g/cm$^3$ were calculated for 2 and mmen-2, respectively. At 0.15 bar, 2 and mmen-2 adsorb 2.8 and 2.7 mmol/cm$^3$, respectively.

Based upon the calculated number of dangling amine groups in mmen-2, a loading of 3.4 mmol/g would correspond to one CO$_2$ per amine, yet uptake of only ca. 2.2 mmol/g was observed. Here, pore blockages, hydrogen bonded amines, or cooperative binding mechanisms between two amines and one CO$_2$ may be limiting the accessible stoichiometry of mmen-2. Thus, significant additional capacity improvements might be realized in the material if conditions can be identified for appending one mmen per magnesium and binding one CO$_2$ molecule per dangling amine.

Isosteric heat of adsorption calculations were hindered by the presence of a prominent step in the isotherms at low pressures and convex to the pressure axis. Generally, continuous mathematical functions are used to model experimental isotherms, which then become the input parameters for the Clausius–Clapeyron relation. Since we were unable to mathematically model the CO$_2$ isotherms of mmen-2 with continuous equations over the entire pressure range, each isotherm was modeled with two Langmuir-Freundlich equations. Data sets corresponding to the adsorption regions before and after the steps were compiled and then modeled individually.

As shown in Figure 3, isosteric heats of adsorption for mmen-2 were calculated from the 25, 50, and 75 °C isotherm models. At low loadings, heats significantly lower than those expected for chemical adsorption of CO$_2$ onto an amine were calculated. However, calculated heats quickly approached and maintained a value of $\sim$71 kJ/mol, which likely corresponds to the chemical adsorption of CO$_2$ onto the free amine of mmen. Here, a carbamate with a weak C–N bond is probably formed.
through interaction the lone pair of the free amine of mmen and the electrophilic carbon of CO2.

**In situ** diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed to probe the chemical nature of adsorbed CO2. At 75 °C, 1 bar of 5% CO2 in He was introduced into an airtight gas cell containing a sample of activated mmen-2. The difference spectrum between mmen-2 under a 1 bar atmosphere and the activated framework under vacuum is shown in Figure 4. The prominent loss peak at 3316 cm⁻¹, assigned to the NH stretch of free mmen-2, is indicative of chemical adsorption of CO2 onto amines.

Recent work on alkylamine-grafted silica surfaces has suggested that chemical adsorption of CO2 onto alkylamines is not possible without neighboring amines or surface hydroxyl groups to stabilize the resulting carbamates; ammonium carbamates or surface-bonded carbamates are formed, respectively. The formation of surface-bonded carbamates in mmen-2 is unlikely due to a lack of surface hydroxyl groups, and the broad NH stretches expected for ammonium cations are not definitively resolvable from the DRIFTS difference spectrum. Furthermore, the slow reversibility of mmen-2 at room temperature (see Figure S15) appears to preclude the formation of ammonium carbamates, which have been reported to desorb CO2 from primary amines readily at room temperature. Additional experiments are necessary to ascertain whether adjacent functional groups are necessary for CO2 adsorption within such alkylamine-functionalized metal–organic frameworks.

The step in each isotherm marks the pressure at which CO2 adsorption becomes dominated by chemisorption. Interestingly, the step moves to significantly higher pressures as the adsorption temperature increases. As shown in Figure S16, the location of the step at 75 °C was reproduced four times with little variation. Thus, the step cannot be attributed to slow kinetics, but appears to be an inherent characteristic of mmen-2 CO2 adsorption isotherms. All batches of mmen-2 have exhibited steps at approximately the same pressures, even when functionalized with different amounts of amines. Figure S17 presents the 75 °C CO2 adsorption isotherm of Mg₂(dobpdc)(mmen)₁.₇₅(H₂O)₀.₂₅.

The location of the step is modeled well by a simple Clausius–Clapeyron relation (see eq 4), which predicts how isotherms move as a function of temperature. In Figure 5, the isosteric heats of CO2 adsorption onto mmen-2, as calculated using the Clausius–Clapeyron relation. The calculated values indicate that chemical adsorption of CO2 onto the amines did not occur at very low coverage.
pressures at which the steps arise. Thus, it seems that thermodynamics alone account for the movement of the step to higher pressures at higher temperatures.

The existence of the step, however, is unexpected in a strongly adsorbing material with large pores. The amines, as the strongest adsorption sites, should preferentially adsorb CO$_2$ before other, weaker adsorption sites adsorb significant quantities of CO$_2$. To explain the nonclassical adsorption behavior of mmen-2, we presently hypothesize that adsorption of CO$_2$ onto mmen is disfavored at low adsorptive concentrations (the density of gas phase CO$_2$ in the pores) because of the large positive entropy associated with reorganization of the amines, as required to form a chemical bond with CO$_2$. Before the chemical potential necessary for amine reorganization is achieved, CO$_2$ adsorption is dominated by non-amine or weak amine-CO$_2$ adsorption sites. The minimum chemical potential required for amine reorganization increases as thermal motion increases, in line with the shift of the step to higher pressures at higher temperatures. Additional experiments and modeling will be required to test this hypothesis and to understand the relationship between pore filling and adsorption in mmen-2. However, the shift of the step to higher pressures at higher temperatures could afford the opportunity for unique regeneration conditions, whereby a weak vacuum could nearly fully regenerate the material at moderate temperatures.

**CO$_2$ Selectivity.** Adsorption isotherms for N$_2$ and O$_2$ in mmen-2 at 25 °C are shown in Figure S18. The uptake capacities for these gases relative to CO$_2$ suggest that it would be a highly selective adsorbent. Since we were unable to mathematically model the CO$_2$ isotherms of mmen-2 with a meaningful, single equation to the entire pressure range of interest, ideal adsorbed solution theory (IAST) selectivities could not be calculated. Table 1 therefore instead presents the approximate molar selectivities of mmen-2 for relevant gas mixtures, as calculated according to eq 5 above using the excess quantities of CO$_2$.

The selectivity of mmen-2 for CO$_2$ over N$_2$ in air is thus estimated to be at least 49 000. However, the purity of gas adsorbed is perhaps a more physically meaningful value than selectivity, and is an important criterion for evaluating adsorbents if captured CO$_2$ is to be transported or sequestered. The purity of CO$_2$ adsorbed onto mmen-2, calculated according to eq 6, would likely be more than 96% or 98% for capture from air or flue gas, respectively.

While the purity of gas adsorbed within individual mmen-2 crystallites is very high, as shown in Table 1, the purity of gas adsorbed within a bed of adsorbent will be affected by the composition of gas phase molecules that fill the pore and intercrystalline spaces. For carbon capture applications, the high concentration of N$_2$ in these pore volumes will negatively affect the selectivity and purity values of real adsorbent beds. However, the approximate selectivity and purity values calculated in Table S6 indicate that the while the purity of CO$_2$ decreases within increasing void space, any adsorbent bed with less than 80% void space should be capable of achieving CO$_2$ purity in excess of 90%. From these calculations, we believe mmen-2 to be a promising, high-capacity adsorbent for removing high-purity CO$_2$ from dry gas mixtures containing N$_2$ and O$_2$.

**CO$_2$ Capture from Air.** To evaluate the performance of mmen-2 as a regenerable adsorbent, thermogravimetric analysis (TGA) was utilized to monitor sample mass under dynamic environments. The top panel of Figure 6 plots changes in sample mass (normalized to the mass of the framework under flow) for different CO$_2$ concentrations (the density of gas phase CO$_2$ in the pores) while simulated air containing 390 ppm CO$_2$ was flowed over the sample. Despite the very low concentration of CO$_2$, a 4.6%$_{\text{mo}}$ (%$_{\text{mo}}$ = percent mass change) 1.05 mmol/g; 4.4 wt %) was realized after 60 min. The adsorbent was then regenerated under flowing N$_2$ at 150 °C for 30 min and the cycle repeated 10 times with no apparent loss of capacity.

To the best of our knowledge, no studies evaluating the efficacy of air capture within metal–organic frameworks have yet been reported. The equilibrium capacity (2.0 mmol/g; 1.72 mmol/cm$^3$) of mmen-2 is similar to the capacities of the very best amine-grafted silica and alumina adsorbents reported to...
date. However, the kinetics of adsorption appear to be significantly faster in mmen-2 than for amines deposited via evaporation or polymerization methodologies. For example, while the pseudo-equilibrium capacity of an outstanding poly(ethyleneimine) impregnated silica gel was reported to be ca. 2.4 mmol/g, it took nearly 200 min for the silica based adsorbent to realize 4.6% \text{m/m} the capacity of mmen-2 for CO\textsubscript{2} after only 60 min.\textsuperscript{26} The easily accessed amines within mmen-2 appear to enhance adsorption rates greatly, enabling rapid adsorption–desorption cycles to be utilized.

CO\textsubscript{2} Capture from Dry Flue Gas. The capabilities of mmen-2 as an adsorbent for removing CO\textsubscript{2} from the flue gas of coal-fired power stations were also investigated. The bottom panel of Figure 6 presents the dynamic cycling behavior of mmen-2 under the relevant, dry conditions: 15% CO\textsubscript{2} in N\textsubscript{2} flowing over the solid at 40 °C. After adsorbing CO\textsubscript{2} for 15 min, the sample was heated at 120 °C for 15 min under N\textsubscript{2}. A capacity of 11.1% \text{m/m} (2.52 mmol/g, 9.9 wt %) relative to the sample mass of mmen-2 under N\textsubscript{2} at 40 °C was realized. After 50 cycles, only a 0.2% \text{m/m} capacity loss was observed. Longer adsorption and desorption times did not significantly improve the cycling capacity of the material, nor did higher desorption temperatures. Note that the apparent capacity of mmen-2 greatly exceeds the ca. 2 wt % working capacity\textsuperscript{43} of aqueous monoethanolamine (MEA) scrubbers, which would likely swing between the same adsorption and desorption temperatures.

If captured CO\textsubscript{2} is to be sequestered, high-purity CO\textsubscript{2} is essential. To desorb the ca. 98% pure CO\textsubscript{2} adsorbed onto mmen-2, a N\textsubscript{2} or air purge cannot be utilized to strip the adsorbent bed. Hence, to approximate the working capacity of mmen-2 using a temperature swing without a N\textsubscript{2} purge, a pure CO\textsubscript{2} purge was utilized instead. A 7.8% \text{m/m} (1.8 mmol/g, 7.2 wt %) was realized when 15% CO\textsubscript{2} in N\textsubscript{2} at 40 °C was desorbed with 100% CO\textsubscript{2} at 150 °C. In Figure 7, 15% CO\textsubscript{2} was introduced over a sample of mmen-2 activated at 150 °C under N\textsubscript{2}, an exothermic heat flow of −153 J/g was observed (event A). After 15 min, mmen-2 was heated to 120 °C under N\textsubscript{2} (event B). Lastly, the regenerated material was cooled under N\textsubscript{2} to 40 °C (event C). The integrated heats calculated for each event are given in the legend.

![Figure 8](image1.png)

Figure 8. Heat flows from mmen-2, as determined via differential scanning calorimetry. First, 15% CO\textsubscript{2} in N\textsubscript{2} was adsorbed at 40 °C (event A). After 15 min, mmen-2 was heated to 120 °C under N\textsubscript{2} (event B). Lastly, the regenerated material was cooled under N\textsubscript{2} to 40 °C (event C). The integrated heats calculated for each event are given in the legend.

introduced over the sample at 150 °C (point A). The change in atmosphere from 100% to 15% CO\textsubscript{2} partially activated the framework, resulting in a negative effective mass (point B). As the sample cooled to 40 °C under the 15% atmosphere, CO\textsubscript{2} was adsorbed. After 15 min at 40 °C (point C), 100% CO\textsubscript{2} was introduced and the sample was heated at 10 °C/min. The increase in CO\textsubscript{2} concentration at low temperatures temporarily
Approximate heat capacities ($C_p$) were calculated for mmen-2. Over the 80 °C temperature range, the average heat required to regenerate CO$_2$-loaded mmen-2 was 3.3 J/g·K. The regenerated framework released an average of 1.3 J/g·K upon cooling, a reasonable approximation of the heat capacity of mmen-2. For comparison, the heat capacity of a 30 wt % MEA solution without CO$_2$ is $\sim$3.8 J/g·K over the same 80 °C range. The lower regeneration energy of mmen-2 is thus attributable to its lower heat capacity. In addition, the significantly greater working capacity of mmen-2 means that a smaller mass is required to adsorb the same amount of CO$_2$. The heat required to desorb CO$_2$ from the amines is similar for mmen-2 and MEA solutions.

4. CONCLUSIONS AND OUTLOOK

With the new metal–organic frameworks $M_2$(dobpdc) ($M = \text{Zn (1), Mg (2)}$), an expanded variant of the $M_2$(dobdc) (MOF-74) structure type has been achieved, leading to enlarged, 18.4-Å-wide channels lined with open metal coordination sites. Functionalization of 2 with mmen, afforded a remarkable new CO$_2$ adsorbent, mmen-Mg$_2$(dobpdc). The large capacity, high selectivity, and fast kinetics of this material for adsorbing CO$_2$ from dry gas mixtures with N$_2$ and O$_2$ make it an attractive new adsorbent for applications in which zeolites and inorganic bases are currently used, including the removal of CO$_2$ from air.

Future work will focus on evaluating the efficacy of alkylamine-appended metal–organic frameworks such as mmen-2 under humid conditions. Whether the presence of water in gas mixtures will significantly affect the stability, capacity, selectivity, or regeneration energy of mmen-2 is presently unknown. In addition, the peculiar CO$_2$ isotherm shapes warrant further investigation, since a detailed understanding of the adsorption behavior within mmen-2 may enable the synthesis of even better materials for CO$_2$ capture. Finally, efforts are also underway to improve the separation performance of the material through use of various other polyamines in place of mmen.

ASSOCIATED CONTENT

Supporting Information

Powder X-ray diffraction patterns and fits, additional CO$_2$, N$_2$, and O$_2$ isotherms and fits, FTIR spectra, TGA traces, and additional purity and regeneration energy calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(5) DOE/NETL Carbon Dioxide Capture and Storage RD&D Roadmap; National Energy Technology Laboratory, 2010.
(8) Fout, T.; Murphy, J. T. DOE/NETL’s Carbon Capture & R&D Program for Existing Coal-Fired Power Plants; DOE/NETL 2009/1356; National Energy Technology Laboratory, 2009.
(9) Carbon Dioxide Capture from Existing Coal Fired Power Stations; Revision Nov 2007; DOE/NETL 401/110907; National Energy Technology Laboratory, 2007.
isotherm data for mmen-2. At each temperature independently, unsuitably large numbers of parameters were required for good fits to be obtained.