

Direct Air Capture of CO₂ Using Amine Functionalized MIL-101(Cr)

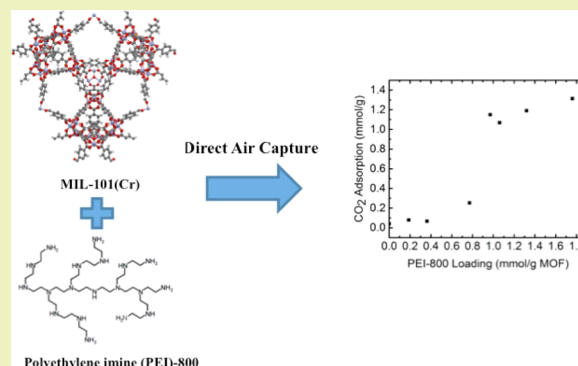
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S Supporting Information

ABSTRACT: Direct adsorption of CO₂ from ambient air, also known as direct air capture (DAC), is gaining attention as a complementary approach to processes that capture CO₂ from more concentrated sources such as flue gas. Oxide-supported amine materials are effective materials for CO₂ capture from dilute gases, but less work has been done on metal organic framework (MOF) supported amine materials. Use of MOFs as supports for amines could be a versatile approach to the creation of effective amine adsorbents because of the tunability of MOF structures. In the present work, MIL-101(Cr) materials functionalized with amine species are evaluated for CO₂ capture from simulated air. Two amines are loaded into the MOF pores, tris (2-amino ethyl) (TREN) and low molecular weight, branched poly(ethylene imine) (PEI-800), at different amine loadings. The MIL-101(Cr)-TREN composites showed high CO₂ capacities for high loadings of TREN, but a significant loss of amines is observed over multicycle temperature swing adsorption experiments. In contrast, MIL-101(Cr)-PEI-800 shows better cyclic stability. The amine efficiency (mol CO₂/mol amine) as a function of amine loading is used as a metric to characterize the adsorbents. The amine efficiency in MIL-101(Cr)-PEI-800 showed a strong dependence on the amine loading, with a step change to high amine efficiencies occurring at ~0.8 mmol PEI/g MOF. The kinetics of CO₂ capture, which have important implications for the working capacity of the adsorbent, are also examined, demonstrating that a MIL-101(Cr)-PEI-800 sample with a 1–1.1 mmol PEI/g MOF loading has an excellent balance of CO₂ capacity and CO₂ adsorption kinetics.

KEYWORDS: Metal organic frameworks, Amine efficiency, Cyclic stability, Open metal sites, Poly(ethylene imine)



INTRODUCTION

Anthropogenic CO₂ emissions have been identified as a primary cause of the increase in average global temperature due to greenhouse effects.¹ Almost half of the CO₂ emissions in the US are from point sources such as industrial installations and power plants.² Most carbon capture technologies developed to date focus on CO₂ capture from these large point sources. However, for widespread adoption, the energy use of these processes must be reduced and the cost effectiveness of the technologies must be improved. Today, the benchmark technology for postcombustion CO₂ capture is the aqueous monoethanol amine (MEA) based absorption technology, which suffers from a high-energy penalty in part due to the high heat capacity of water.^{3,4} A complementary and much less studied approach to carbon capture is to capture CO₂ directly from the air, also denoted as direct air capture (DAC), originally proposed by Lackner.⁵ DAC has the advantage of location flexibility and the input gas stream, ambient air, is relatively clean, as the concentrations of SO_x and NO_x are low.^{6,7} However, DAC has the disadvantage of having a very dilute input stream, with air today containing about 400 ppm of CO₂.⁸ This necessitates the need for a high capacity adsorbent that can reversibly capture CO₂ at low net energy use.

Solid adsorbents have received considerable attention in recent years as alternatives to liquid amine solutions because of their lower heat capacities compared to aqueous amines.⁹ Generally speaking, a lower energy penalty during the adsorption–desorption process is expected to create a lower cost of CO₂ capture. Amine functionalization of solid materials is one way of creating adsorbents for CO₂ capture.¹⁰ Through the zwitterionic mechanism of CO₂ capture analogous to liquid amines,¹¹ the functionalization of solids with amine sites can lead to a significant increase of the heat of adsorption of CO₂ on various materials, leading to elevated adsorption capacities. Significant uptake of CO₂ is possible at very low CO₂ partial pressures in materials functionalized with amines due to the steep adsorption isotherm created by amine-functionalization. This makes such materials promising adsorbents for air capture applications.^{10,12,13}

One of the most important metrics used to analyze the effectiveness of amine-based sorbents for applications in CO₂ capture is amine efficiency, defined as the moles of CO₂ adsorbed normalized by the moles of amine present in the

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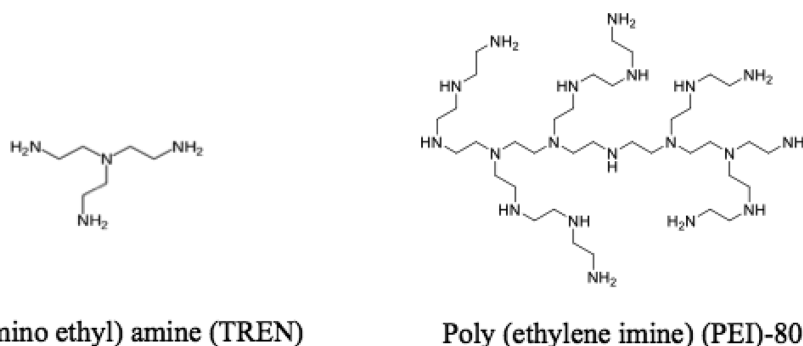


Figure 1. Polyamines for the air capture studies.

material. The zwitterionic mechanism suggests a maximum chemisorptive amine efficiency of 0.5 for dry sorption conditions, as two amines are required to capture one CO_2 molecule.¹¹ Amine efficiencies observed during practical direct air capture conditions are often much lower than the theoretical maximum.¹⁴ High amine efficiencies have been achieved by use of amine molecules or polymers that place many amines in close proximity to each other, and by developing sorbents that allow sufficient accessibility to the various amine sites. Xu et al.¹⁵ introduced the concept of “molecular basket” sorbents, where CO_2 was packed inside the pores of a mesoporous SBA-15 support using a polymer containing many amine groups. They observed that confinement of the polymer improved the effectiveness of the composite toward CO_2 capture. Poly-(ethylene imine) (PEI) has been commonly used as the preferred polymer because of its high amine content, low volatility (relative to low molecular weight amines like MEA) and commercial availability.^{16–19} Amine efficiencies associated with PEI have been found to be dependent on the loading of PEI in the material,¹⁵ and the morphology of the PEI polymer in the porous support has been found to play a role as well.²⁰ In another approach, small molecules such as tetraethylene pentamine (TEPA),²¹ diethyl tetramine (DETA)²² and other small amines have been impregnated in supports such as mesoporous silica SBA-15 and activated carbon to enhance CO_2 capture, because of their high amine density and the improved packing of these small molecules in the pores. For a given support, it is not always straightforward to predict which amines will yield the most efficient adsorbents, and it is important to establish a structure–property relationship to identify optimum adsorbent designs.

Recently, metal organic frameworks (MOFs) have emerged as potential CO_2 sorbents as well as supports for amine-based CO_2 capture.^{23,24} MOFs are hybrid materials with metal nodes connected by organic linkers to create two or three-dimensional crystalline structures. There are over 20 000 metal organic frameworks reported in the open literature with a variety of combinations of metals and organic linkers.^{25,26} There are a few potential advantages of MOFs compared to other commonly used substrates such as silica. High BET surface areas and tunable pore characteristics make many MOFs attractive supports for a variety of gas separation applications. Also, a variety of open metal sites in some families of MOFs such as $\text{M}_2(\text{dobpdc})$ ²⁷ ($\text{dobpdc}^{4-} = 4,4'$ -dioxido-3,3'-biphenyldicarboxylate, $\text{M} = \text{Mg}, \text{Mn}, \text{Zn}, \text{Ni}, \text{Co}, \text{Fe}$) offer an opportunity for selective postsynthetic functionalization to enhance the selectivity of gas adsorption. Stability under a wide range of conditions, high pore volume and a high density of open metal

sites are some desired features in a MOF framework for further functionalization with amines.²⁸ Two materials with these characteristics are $\text{MIL-101}(\text{Cr})$ ²⁹ and $\text{Mg}_2(\text{dobpdc})$.²⁷

The MOF $\text{MIL-101}(\text{Cr})$ has a 3D framework, large pore volume and high BET surface area ($2600\text{--}4500 \text{ m}^2/\text{g}$), with open chromium metal site densities of up to 3 mmol/g MOF framework.³⁰ $\text{MIL-101}(\text{Cr})$ is stable in boiling water, and over a wide range of pH conditions.²⁹ Liu et al.³¹ observed good regenerability of $\text{MIL-101}(\text{Cr})$ after exposure to SO_2 and NO , further demonstrating good stability of the framework. Both the Cr open metal sites and the open space within the porous framework can be loaded with various amine species for CO_2 capture applications. Hwang et al.³⁰ first reported the postsynthetic modification of $\text{MIL-101}(\text{Cr})$ with ethylene diamine (ED) and studied the resulting materials for catalytic applications. Subsequently, the framework was studied for CO_2 capture after functionalization with triethylenepentamine (TEPA)³² or pentaethylenehexamine (PEHA)³³ for CO_2 capture under simulated flue gas conditions. Jiang et al.³⁴ utilized ED, diethylene triamine (DETA) and diaminodipropylamine (DADPA) to the open metal sites in $\text{MIL-101}(\text{Cr})$ and observed that DETA showed the best adsorption capacity for flue gas capture conditions. Chen et al.^{35,36} loaded $\text{MIL-101}(\text{Cr})$ using PEI-300, PEI-1800 and PEI-10000 and found that PEI-300, at higher loadings, demonstrated the highest CO_2 capacities for conditions similar to flue gas applications. They also demonstrated CO_2/N_2 selectivity ~ 2000 for partial pressures of (0.1 mbar) of CO_2 .

$\text{M}_2(\text{dobdc})$ ($\text{M} = \text{Mg}, \text{Ni}, \text{Co}, \text{Zn}$; $\text{dobdc}^{4-} = 1,4$ -dioxido-2,5-benzenedicarboxylate) is another MOF with a high density of open metal sites. Choi et al.^{37,38} modified $\text{Mg}_2(\text{dobdc})$ with ethylene diamine and demonstrated improved CO_2 capture and stability of the material under ultradilute conditions. In another study, diamine functionalized $\text{Mg}_2(\text{dobpdc})$ was demonstrated to have exceptional performance for CO_2 capture.²⁷ Planas et al.³⁹ McDonald et al.⁴⁰ and Drisdell et al.⁴¹ provided data supporting an unconventional CO_2 adsorption mechanism in this system, whereas the $\text{MIL-101}(\text{Cr})$ family of materials is presumed to adsorb CO_2 via conventional amine- CO_2 binding mechanisms. Although water stability of $\text{Mg}_2(\text{dobpdc})$ has not been systematically studied, breakdown of $\text{Mg}_2(\text{dobdc})$ under humid conditions has been reported.⁴²

Considering the excellent stability of $\text{MIL-101}(\text{Cr})$, the goal of this work is to systematically study CO_2 adsorption from simulated air with a focus on understanding how the equilibrium adsorption capacity and uptake kinetics are affected by the composition of a family of $\text{MIL-101}(\text{Cr})$ -amine materials. High CO_2 equilibrium adsorption capacities and

rapid kinetics are important to assess the possible merit of these adsorbents for future practical applications. For the present study, we have functionalized MIL-101(Cr) with both small and large polyamine molecules, as shown in Figure 1. Tris (2-amino ethyl)amine (TREN) is a small polyamine with a high density of primary amines. Branched poly(ethylene imine) with a molecular weight of 800 (PEI-800) is among the most commonly used polyamines in studies of amine-functionalized mesoporous oxides such as SBA-15 and MCM-41.⁹ The CO₂ uptake and corresponding amine efficiencies (mol CO₂/mol amine) for different loadings of TREN and PEI-800 in MIL-101(Cr) are measured. The temperature dependence of CO₂ adsorption over MIL-101(Cr)-PEI-800 adsorbents has also been explored.

EXPERIMENTAL SECTION

Material Synthesis. Chemicals. All the chemicals were used as purchased. Cr(NO₃)₃ (99%) and benzene dicarboxylic acid (H₂BDC) were purchased from Acros Chemicals. Dimethylformamide (DMF), tris (2-amino ethyl) (TREN) (96%, Reagent grade) and poly(ethylene imine) (PEI) (Mw 800, Mn 600) were purchased from Sigma-Aldrich. Methanol (ACS grade) and Toluene were purchased from BDH Chemicals.

MIL-101(Cr) was synthesized with a modified recipe from Hatton et al.⁴³ First, 800 mg of Cr(NO₃)₃ and 332 mg of H₂BDC were mixed in 10 mL of deionized (DI) water. Acetic acid was used at the modulator in the synthesis to adjust the crystal size. Different ratios of acetic acid/ligand were used in the synthesis. Finally, based on the crystal size analysis, 1.5 mL of 36% acetic acid was used as a modulator in the synthesis. About 5 mg of MIL-101(Cr) crystals were used as a seed in the synthesis to obtain a uniform crystal size distribution. The solution was heated in a Teflon lined reactor at 200 °C for 12 h followed by cooling with 1 °C ramp to obtain large BDC crystals. The resultant slurry was washed repeatedly with MeOH, DMF and MeOH. The obtained powder was dried under vacuum at 150 °C.

MIL-101(Cr)-TREN (Grafted). MIL-101(Cr) was activated at 150 °C by heating under 20 mTorr vacuum for 12 h. 200 mg of activated MIL-101(Cr) and a stoichiometric amount of TREN were added to toluene and heated at 110 °C under reflux in N₂ atmosphere overnight. The solution was filtered and repeatedly washed with MeOH and then dried under 20 mTorr vacuum overnight.

MIL-101(Cr)-TREN; MIL-101(Cr)-PEI (Impregnated). MIL-101(Cr) was activated at 150 °C by heating under 20 mTorr vacuum for 12 h. A stoichiometric amount of TREN/PEI was dissolved in 10 mL of MeOH, and 200 mg of activated MIL-101(Cr) was added to the solution followed by stirring under N₂ atmosphere for 24 h. The methanol was removed by rotary evaporation, and pale green MIL-101(Cr)-amine composites were later dried overnight under 20 mTorr vacuum.

Characterization. Nitrogen Physisorption. N₂ physisorption experiments at 77 K were performed using a Quantachrome Quadrasorb surface area analyzer. 50 mg of powder was activated at 60 °C under vacuum for 3 h. Microporous surface area was estimated using the BET method following criteria outlined by Walton et al.⁴⁴ in the P/P_0 range of 0.05–0.2. Pore volumes were estimated by N₂ physisorption at partial pressure of 0.995. Surface area and pore volumes for MIL-101(Cr) and MIL-101(Cr)-amine samples were normalized to per gram of MIL-101(Cr) in the material.

Elemental Analysis. C, H, N contents of the MIL-101(Cr) and amine impregnated samples were measured at Atlantic Microlabs (Norcross, GA). The N content was used to ascertain the amine loadings in the composite materials.

Powder X-ray diffraction (PXRD) measurements were made using a PANalytical X'Pert diffractometer using Cu K α radiation.

CO₂ Adsorption Experiments. CO₂ adsorption experiments were performed using thermogravimetric analysis (TGA) using a TA Instruments, Q 500 apparatus. In a typical experiment, 30 (\pm 3) mg of sample was pretreated with helium (flow rate: 90 mL/h) for 3 h at 110

°C followed by thermal equilibration at 25 °C. Subsequently the sample was exposed to 400 ppm of CO₂ in helium at the same temperature and flow rate for 6 h. Measurement in helium offers a direct way to compare adsorption capacities with single gas adsorption isotherm data. For subsequent cycles, samples were reactivated in helium at 110 °C. A Micromeritics ASAP 2020 was used to measure CO₂ adsorption isotherms. Samples were activated at 60 °C under vacuum for 3 h prior to analysis. Amine efficiencies were calculated by normalizing CO₂ adsorption capacities with the moles of amine determined by elemental analysis.

Scanning Electron Microscopy. A Hitachi SU 8230 cold field emission microscope was used to estimate crystal size of MIL-101(Cr). Measurements were made using an accelerating voltage of 1 kV/10 kV and 10 μ A current. Particles were coated with gold–palladium before the measurement.

RESULTS AND DISCUSSION

A number of synthesis conditions was initially explored for the synthesis of MIL-101(Cr). Because introduction of polyamines is expected to increase diffusional resistance for CO₂ uptake, a small crystal size is desired. Figures S1 and S2 show scanning electron microscope images of MIL-101(Cr) materials made with different ratios of acetic acid/BDC (4, 12.5 respectively). Bipyramidal crystals with crystal size ~150–200 nm and ~600–800 nm were obtained. Similar results have been observed with monocarboxylic acids in the case of MIL-101(Cr)⁴⁵ and Cu-BTC,⁴⁶ where it was postulated that a high concentration of acid controls the deprotonation of benzene dicarboxylic acid and can change the rate of crystal nucleation. MIL-101(Cr) with a small crystal size is expected to aid in the insertion of PEI in the crystals. To this end, further experiments were done with small crystals synthesized using an acetic acid/BDC ratio of 4.

TREN as the Amine Component. Two types of amine-loaded samples were prepared. Those labeled “grafted” have a sufficiently limited amount of amine such that each molecule could, in principle, graft to an open Cr coordination site. Samples labeled “impregnated” have additional amine added such that some of the molecules must be physically contained within the pore space without grafting on an open Cr coordination site. Figure 2 shows the CO₂ adsorption isotherms for MIL-101(Cr)-TREN (grafted) and MIL-101(Cr) at 298 K. As expected, the CO₂ adsorption is greatly improved as a result of functionalizing the framework with TREN. However, the adsorption at a CO₂ partial pressure of 0.4 mbar, the pressure of relevance for DAC, is only ~0.35 mmol/g. CO₂ capacities in a similar range were obtained by Hu et al.³⁴ for MIL-101(Cr)

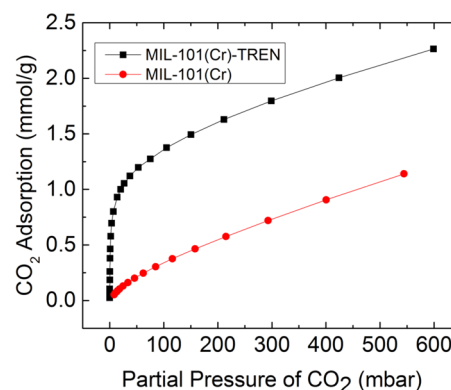


Figure 2. CO₂ adsorption as a function of CO₂ partial pressure for MIL-101(Cr)-TREN (grafted) and the bare MOF.

loaded with smaller amine molecules such DETA and DADPA. The TREN loading for the material used in Figure 2 was 2.63 mmol/g MOF, so the amine efficiency at a CO₂ partial pressure of 0.4 mbar is only ~4%. Thus, despite the improved CO₂ adsorption as a result of functionalization with TREN, the material is unlikely to be effective for DAC. To improve CO₂ adsorption at the partial pressure of 0.4 mbar, a further increase in amine loading was sought through wet impregnation, whereby additional TREN molecules were deposited in the MOF pores, beyond the loading that can chemically bind to open metal coordination sites. As shown in Figure 3, observed

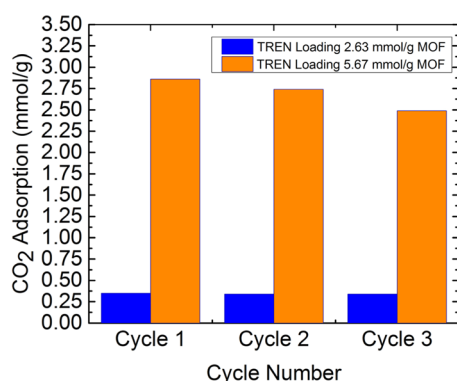


Figure 3. Cyclic CO₂ uptake at partial pressure of 0.4 mbar for MIL-101(Cr)-TREN (grafted) and MIL-101(Cr)-TREN (impregnated).

CO₂ adsorption at 0.4 mbar partial pressure is 2.8 mmol/g, which corresponds to an improved amine efficiency of ~17% for the sample with an amine loading of 5.67 mmol/g MOF.

Stable cyclic CO₂ adsorption with rapid kinetics is important for economical application of adsorbents. Here we first report cyclic adsorption of CO₂ for MIL-101(Cr)-TREN system for three adsorption–desorption cycles using a TGA flowing 400 ppm of CO₂ (0.4 mbar partial pressure) in helium. The material was regenerated at 110 °C for 3 h between the cycles before adsorption at 25 °C. Different trends were observed for the two samples with different TREN loadings. The grafted TREN sample (Figure 3, blue) showed a stable cyclic performance over three cycles, whereas the impregnated TREN sample (Figure 3, orange) showed a significant decline in the capacity in subsequent cycles despite a superior initial adsorption capacity (~2.8 mmol/g). This is attributed to the high volatility of TREN (boiling point 265 °C), leading the weakly adsorbed TREN species to evaporate under the desorption conditions. This can be observed via the change in the baseline in Figure S6. Despite the stable cyclic adsorption capacity of 0.35 mmol/g, the MIL-101(Cr)-TREN (grafted) sample was not considered for further air capture studies, as the capacity is likely too low for practical use.⁴⁷

PEI as the Amine Component. Because some of the lack of cyclic stability in the material discussed above is likely associated with the volatility of the low molecular weight amine (TREN) that was used, the use of less volatile PEI-800 was explored to test whether this would yield a material with improved cyclic adsorption stability. MIL-101(Cr)-PEI-800 samples were made with different loadings of PEI. Specifically, PEI loadings were varied from 0.18 to 1.8 mmol/g MOF to explore whether there was an optimal loading of PEI for CO₂ adsorption under air capture conditions. Table 1 captures the

results of elemental analysis, relating the PEI loadings corresponding to the nitrogen content in the material.

Table 1. Amine Loadings and Elemental Analysis Results for MIL-101(Cr)-PEI-800 Samples

amine loadings (mmol/g MOF)	C %	H %	N %
0.18	40.5	4.5	4.2
0.36	42.3	5.2	7.5
0.77	43.3	6.2	12.8
0.97	43.8	6.7	14.6
1.06	44.8	6.6	15.4
1.32	41.9	7.6	17.2
1.76	46.7	7.5	19.6

Table S2 lists the BET surface area reduction as a function of amine loading. Figures S4 and S5 show powder XRD patterns and N₂ physisorption isotherms for these materials. At higher loadings of PEI, a progressive decrease in intensity of the lower angle XRD peaks was observed. This is attributed to an increase in the organic matter in the material. All the materials showed a characteristic MIL-101(Cr) N₂ physisorption isotherm with secondary uptake around $P/P_0 = 0.2$, but the N₂ physisorption decreased progressively as the amine loadings increased.

Figure 4 depicts the pore volume of the sorbents as a function of the PEI-800 loading. The red points represent the

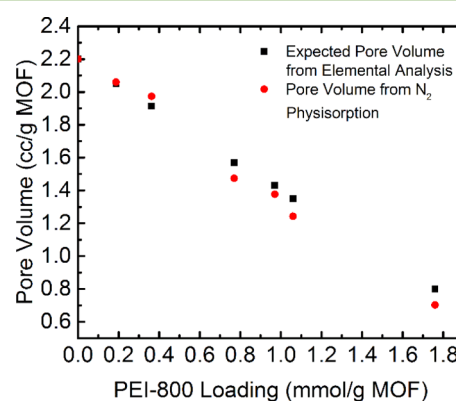


Figure 4. Comparison of pore volumes measured by nitrogen physisorption and calculated based on elemental analysis for MIL-101(Cr)-PEI-800 samples with different loadings of PEI.

pore volume calculated from the cryogenic nitrogen physisorption isotherm at $P/P_0 = 0.995$. The black points, representing the theoretical pore volume, are the calculated pore volumes based on the PEI loadings obtained from elemental analysis. This represents the total pore volume minus the volume occupied by the mass of PEI determined by elemental analysis, using the liquid density of PEI for the mass to volume conversion. Close agreement between the physisorption and theoretical pore volumes strongly supports the hypothesis of effective insertion of PEI-800 inside the pores of MIL-101(Cr).

Figure 5 presents CO₂ adsorption uptakes measured on the TGA using 400 ppm CO₂ by MIL-101-PEI (800) samples with different loadings of PEI-800. At lower PEI loadings, despite relatively higher pore volumes, low CO₂ adsorption capacities were obtained (0.2–0.3 mmol/g), representing only 1–3% amine efficiency (Figure 6). As the PEI loading was increased further, despite a continual decrease in the pore volume, the

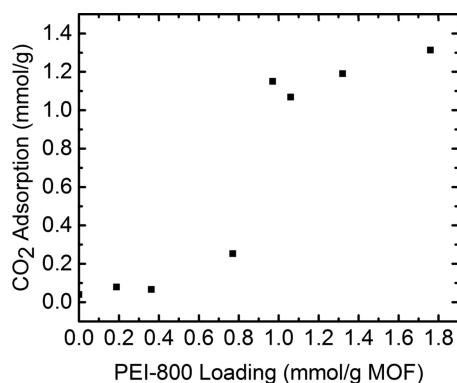


Figure 5. Gravimetric CO₂ uptake at 400 ppm for MIL-101(Cr)-PEI-800 at different loadings of PEI.

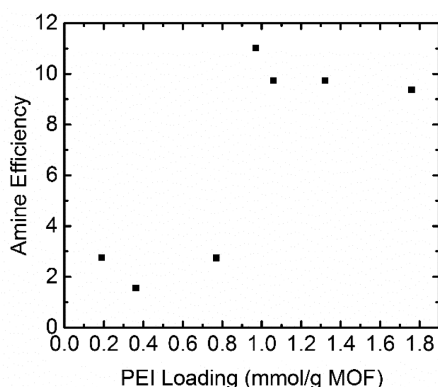


Figure 6. Amine efficiencies for MIL-101(Cr)-PEI-800 samples with different PEI loadings at 400 ppm of CO₂ concentration.

CO₂ adsorption (1.1–1.35 mmol/g) and amine efficiency (~10%) increased dramatically. The relatively high amine efficiency (~11%) observed with the MIL-101(Cr)-PEI-800 sample with amine loading of 0.97 mmol/g MOF is attributed to the relatively high pore volume of the sample. Improvements in amine efficiency with increasing amine loading have also been observed for mesoporous silica MCM-41/SBA-15 supported PEI samples.^{15,48} This has recently been attributed to changes in the morphology of PEI as the loading increases.²⁰ We hypothesize that at lower loadings of PEI, the polymer interacts strongly with the MOF framework and many amine sites are not available for CO₂ capture, resulting in a low amine efficiency. It has also been widely empirically observed that amine efficiencies increase with amine loading up to a point where steric constraints prevent effective access to all the amine sites in oxide-supported amine sorbents.^{15,48}

Although superior capacities were obtained for MIL-101(Cr)-PEI-800 at higher loadings of PEI, it is also worthwhile to compare the best adsorption capacity (1.35 mmol/g) achieved here with other adsorbents for air capture applications. Examples from the literature include 0.98 mmol/g (TRI-PE-MCM-41⁴⁹), 1.39 mmol/g (nanofibrillated cellulose (NFC) functionalized with *N*-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (AEAPDMS)¹⁸), 1.72 mmol/g (SBA-15 functionalized with hyper branched amino silica¹⁰), 1.72 mmol/g (Fumed silica functionalized with PEI-25000⁷), 2.2 mmol/g (SBA-15-PEI-800⁵⁰) and 3 mmol/g (Mg₂(dobpdc) functionalized with *N,N'*-dimethylethylenediamine (mmen)⁴⁰). For similar amine loadings of PEI (45 wt %) in SBA-15-PEI-800, Choi et al.¹⁰ obtained higher capacities (2.2 mmol/g) and

amine efficiencies (22%) air capture studies. This suggests the importance of the interaction of the aminopolymer with the substrate in affecting the sorption accessibility of amine sites for CO₂ adsorption.

Adsorbents with CO₂ adsorption capacities of more than 1 mmol/g at 400 ppm of CO₂ concentration were explored further via isotherm studies at multiple temperatures, cyclic adsorption/desorption studies and kinetic studies, as reported below (Figure 7).

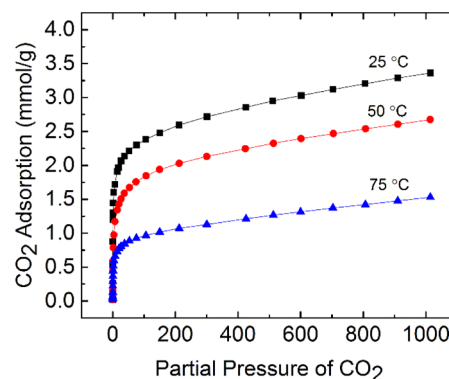


Figure 7. CO₂ uptake as a function of temperature for MIL-101(Cr)-PEI-800 with an amine loading of 1.06 mmol/gMOF.

CO₂ adsorption isotherms for a representative high adsorption capacity sample with PEI loading of 1.06 mmol/g MOF were measured at multiple temperatures. An isosteric heat of adsorption ~70 kJ/mol of CO₂ adsorbed at very low coverage was obtained using the Clausius–Clapeyron equation. As expected thermodynamically, as the temperature increased, the CO₂ adsorption progressively decreased. This is in contrast with sorbents based on PEI loaded into some other supports such as mesoporous silica SBA-15, where it has been reported that modest increases in temperature enhanced CO₂ capture due to kinetic effects.^{15,51,52}

Cyclic adsorption/desorption studies for MIL-101(Cr)-PEI (800) with a PEI loading of 1.06 mmol/g MOF (Figure 8) demonstrated that this material had less loss of capacity during cycling than the MIL-101(Cr)-TREN materials described above (Figure 3). The CO₂ uptake dropped 2.7% and 1.9% after the first and second cycles, respectively. This is attributed to lower volatility associated with the higher molecular weight of PEI-800 compared to TREN. It should also be noted that no

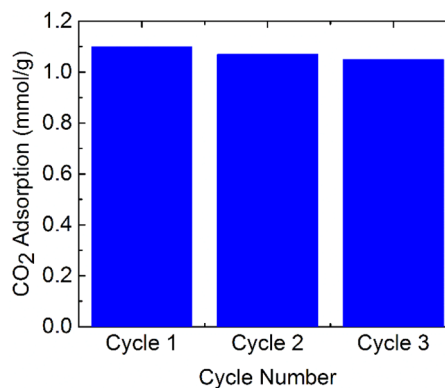


Figure 8. Cyclic CO₂ adsorption capacities for MIL-101(Cr)-PEI with a PEI loading of 1.06 mmol/gMOF.

adverse effects (Table S3) were observed for CO₂ adsorption after exposure of the materials to 32% relative humidity, again suggesting that this material might offer good stability.

Figure 9 shows the kinetic performance of three MIL-101(Cr) samples with different loadings of PEI-800 via plots of

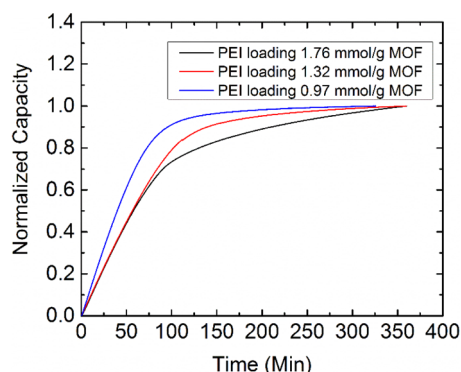


Figure 9. Kinetic representation of CO₂ adsorption. Normalized CO₂ uptake (capacity at t /capacity at t_{∞}) as a function of time for MIL-101(Cr)-PEI at different PEI loadings.

normalized capacity as a function of time. Despite the increase in the CO₂ capacity from 1.1 to 1.35 mmol CO₂/g-adsorbent as a result of higher PEI-loadings, the time required to reach adsorption equilibrium increased significantly with higher PEI loadings. Table 2 lists the CO₂ adsorption as a function of time

Table 2. CO₂ Adsorption (mmol/g) in MIL-101(Cr)-PEI-800 as a Function of Time (min)

time (min)	MIL-101(Cr)- PEI-0.97 (mmol/g)	MIL-101(Cr)- PEI-1.32 (mmol/g)	MIL-101(Cr)- PEI-1.76 (mmol/g)
25	0.42	0.27	0.29
50	0.70	0.52	0.58
75	0.93	0.76	0.80
100	1.04	0.95	0.98
pseudoequilibrium	1.15 (237 min)	1.20 (306 min)	1.35 (341 min)

for different PEI loadings (from 0.97 to 1.76 mmol/g MOF). The sample with PEI loading 0.97 mmol/g MOF achieved pseudoequilibrium CO₂ adsorption of 1.15 mmol/g in ~240 min vs sample with PEI loading of 1.76 mmol/g MOF, which took ~340 min to achieve adsorption of 1.35 mmol/g. The difference in the kinetics of the samples with PEI loadings of 1.32 and 1.76 mmol/g MOF was quite significant, with a long tail for the sample with the higher PEI loading representing increased diffusion resistance encountered by CO₂ because of the high loading of PEI. Bollini et al. made similar observations for high loadings of aminopropyl silane in mesoporous silica SBA-15.⁵³

Even though high capacities are achievable at higher loadings, the trade-offs between adsorption uptake and adsorption kinetics put practical limits on possible cyclic adsorption-desorption cycles. Considering these trade-offs between adsorption capacity and kinetics, a PEI loading of 1.0–1.1 mmol/g MOF (~85 wt %) is suggested to be most useful for MIL-101(Cr) under the conditions employed.

CONCLUSION

The CO₂ adsorption uptake capacity and kinetics, along with the associated amine efficiencies for different masses of TREN and PEI-800 loaded into MIL-101(Cr), have been reported. MIL-101(Cr) grafted with TREN demonstrated enhanced CO₂ capture over the original, amine-free framework, but the amines were not very effective for CO₂ capture. Higher loadings of TREN obtained by physical impregnation of additional amine into the pore space improved the amine efficiency and CO₂ adsorption uptake, but the amines were labile and could be lost during thermal cycling because of the relatively high volatility of TREN. Similar CO₂ capacities³⁴ at 400 ppm using other small molecules such as DETA, DADPA indicate that these adsorbents are not very effective for air capture applications. MIL-101(Cr) functionalized with PEI showed low amine efficiencies at low loadings of PEI, but amine efficiencies improved substantially as the loading of PEI-800 was increased. At the highest amine loadings, kinetic limitations associated with pore blockage led to only modest increases in uptake and substantially slowed adsorption kinetics. This suggests there is compositional window where a balance of the CO₂ uptake and kinetics will be optimized for this family of materials. The amine-modified MOF adsorbents were also evaluated in a cyclic CO₂ adsorption/desorption cycles under simulated air capture conditions, demonstrating that the optimal MIL-101(Cr)-PEI material had relatively good stability under lab scale temperature swing adsorption conditions and on exposure to humidity.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b01692.

MIL-101(Cr) crystal size for acetic acid/BDC ratio 4 (Figure S1), MIL-101(Cr) crystal size for acetic acid/BDC ratio 12.5 (Figure S2), degradation data for MIL-101(Cr)-TREN samples (figure S3), powder XRD patterns for MIL-101(Cr) and MIL-101(Cr)-PEI(800) (Figure S4), N₂ physisorption isotherms for MIL-101(Cr) and MIL-101(Cr)-PEI(800) (Figure S5), elemental analysis for MIL-101(Cr) functionalized with TREN and PEI-800 (Table S1), BET surface areas for MIL-101(Cr)-PEI(800) samples as a function of PEI loading (Table S2), weight of adsorbent (mg) vs time (min), with loss in the baseline indicating leaching of amine in the adsorbent (Figure S6), effect of exposure to humidity on CO₂ adsorption at 400 ppm (Table S3) (PDF)

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Notes

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