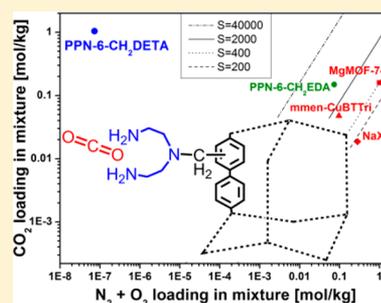


Carbon Dioxide Capture from Air Using Amine-Grafted Porous Polymer Networks

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Supporting Information

ABSTRACT: Amine-grafted porous polymer networks were investigated for CO₂ capture directly from air (400 ppm CO₂, 78.96% N₂, and 21% O₂). Under these ultradilute conditions, PPN-6-CH₂DETA has an extraordinarily high CO₂ selectivity (3.6×10^{10}) and loading capacity (1.04 mol/kg) as calculated using ideal adsorption solution theory. In addition we have shown that the material outperforms other materials based on simulated breakthrough calculations, thus showing great potential to be used in direct air capture applications.



Rising atmospheric CO₂ levels have been strongly correlated with global climate change. Current levels are about 392 ppm and rising as we continue to consume extraordinary quantities of fossil fuels to feed societies' voracious and growing appetite for energy.¹ Scientists around the world are investigating new materials and processes to mitigate CO₂ emissions by implementing capture technologies, primarily at large single-point sources such as power plants, which are generating about one-third of total CO₂ emissions in relatively high concentrations (5–20% in exhaust gas).² This focus will allow significant quantities of CO₂ to be captured, therefore slowing the rise in global levels. These new technologies are extremely important as we will continue to burn substantial quantities of fossil fuels over the next decades, despite tremendous efforts in alternate, cleaner fuel sources. It has, however, been suggested that, in addition to stalling emissions, we need to begin capturing CO₂ directly from the air.^{3,4} This would additionally address the other two-thirds of emissions that are generated from the transportation and other industries (e.g., concrete, paper, and chemical production). From a technology standpoint, direct air capture (DAC) poses an even greater challenge because of the extremely dilute CO₂ concentrations in ambient air. However, DAC provides some interesting economic benefits that may aid in making this a viable global technology. Among the largest factors are that it can be decoupled from the fossil fuel power generation, thus taking advantage of renewable energy resources to drive the regeneration process, and allowing deployment directly at sequestration sites, substantially reducing CO₂ transport costs.⁵ In fact, CO₂ capture from ambient air has already been deployed in a few scenarios and is a crucial part of daily operations. Scrubbers are being implemented as part of life

support systems in submarines, spacecrafts, and personal closed-circuit breathing systems, where CO₂ concentrations are typically below 5000 ppm, the United States Occupational Safety and Health Administration's threshold limit. If the exhaled gas is to be recycled, it is necessary to remove the CO₂ from the breathing loop to avoid its presence at concentrations considered hazardous to human health.

All of these closed systems provide added benefits over global scale DAC: they have 1 order of magnitude higher CO₂ concentrations, known and manageable contaminant levels, and the entire volume of gas can be directed through scrubber units because they are completely enclosed systems. For larger scale applications, movement of air through the scrubber units becomes an important energy consideration, although wind may be used to facilitate transport.

One well-studied DAC technology uses sodium hydroxide solutions to absorb CO₂ from air and convert it to sodium carbonate, which is further reacted with Ca(OH)₂ to form calcium carbonate (CaCO₃(s)). The CO₂ is recovered via a calcination step by heating to >900 °C, forming CaO as the solid product; this process is obviously quite energy intensive, and has been estimated by an American Physical Society report to be around \$600 per ton of CO₂.⁶ Another state of the art technology relies on amine solutions to chemically react with CO₂, forming carbamates, which has the benefit of being selective for only CO₂ over all of the other gases. In both processes, however, there are some significant drawbacks,

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particularly, large energy requirements to regenerate the system, highly corrosive solutions, and solvent boil-off, all of which can pose significant problems during extended operation.⁷

To combat the drawbacks, an alternate approach, capturing CO₂ in solid sorbents via a physical adsorption mechanism, have been proposed and developed.^{3,8–10} These systems must have high selectivities for CO₂ over other gases at the concentrations at which separation is to be performed, large working capacities, low regeneration energies, and stability toward contaminants. Recently, amine-tethered porous silica composites^{11–14} and amine-appended metal–organic frameworks (MOFs), such as mmen-Mg₂(dobpdc),^{15,16} have shown promising results to capture CO₂ from ultradilute gas streams. A detailed economic study of DAC by Kulkarni and Sholl recently reported the total system cost at several potential U.S. sites to be around \$100/ton of CO₂.⁵ The solid sorbent chosen for their study, TRI-PE-MCM-41, has a loading of 0.98 mol_{CO₂}/kg_{sorbent} and a calculated heat of adsorption of 67.3 kJ/mol.⁸ One of the conclusions they reached is that higher loading may further reduce this cost, as larger volumes of CO₂ can be extracted per adsorption cycle. The regeneration energy is largely dependent on the heats of adsorption and heat capacities of the materials.

The results presented herein focus on tethering amines to porous polymer networks (PPNs). The support structure, PPN-6, is a covalently bonded carbon scaffold with a BET surface area of 4023 m²/g, which is extremely stable toward strong acid and base. This stability and large internal pore surface have allowed us to modify the structure by introducing sulfonic acid groups¹⁷ and, in this case, amines to make this material suitable in a DAC process.

■ EXPERIMENTAL SECTION

The materials discussed herein were synthesized as previously reported.¹⁸ Experimental single-component isotherms for CO₂, N₂, and O₂ are shown in the Supporting Information (Figures S1–S5). These isotherms are first converted from excess loadings to absolute loadings, using the Peng–Robinson equation of state for estimation of the fluid density inside the pores at the relevant temperatures and pressures.

■ RESULTS AND DISCUSSION

Isotherm Fit. N₂ and O₂ adsorption isotherms of all of the structures analyzed, as well as the CO₂ isotherm of PPN-6-CH₂Cl, show no isotherm inflections, thus allowing the use of a single-site Langmuir model to fit the data. The CO₂ adsorption isotherms for PPN-6-CH₂DETA and –EDA, however are much steeper in the low-pressure regime and therefore require a multisite Langmuir model to properly fit the data. Fitting of these adsorption isotherms in the low-pressure regions are of particular importance in the context of CO₂ capture from ambient air because of the low concentrations of about 400 ppm. In our earlier work, which examined CO₂ capture from flue gases, dual-site Langmuir fits were used. The isotherms were carefully remeasured at very low pressures and revealed a second inflection point, thus indicating the need for a triple-site model:

$$q^0 \equiv q_A^0 + q_B^0 + q_C^0 = \frac{q_{\text{sat,A}} b_A p}{1 + b_A p} + \frac{q_{\text{sat,B}} b_B p}{1 + b_B p} + \frac{q_{\text{sat,C}} b_C p}{1 + b_C p} \quad (1)$$

It is vital for the isotherm fits to properly capture the steep isotherm characteristics at pressures below 1000 Pa. Each of the sites contributes to the total loading at different pressures. For CO₂ capture from ambient air, the parameters for the first site are of particular importance in determining the component loadings in mixtures with N₂ and/or O₂ because the partial pressures of CO₂ are extremely low. The fitted parameters for all isotherms are given in the respective tables in the Supporting Information.

In the context of this discussion, we would like to make a note about fitting experimental data to conform to physical models. It is important to keep in mind the chemical and structural characteristics of the system that is being modeled before adding fitting parameters. Theoretically, any isotherm can be modeled by an *n*-site Langmuir model; however, when using the Langmuir model to represent reality, structural data should be taken into account. In the case of PPN-6-CH₂DETA and –EDA a three-site model is appropriate because the chemical structure of these materials is made up of primary and secondary amines, and the backbone (phenyl) moieties, all of which have been shown to have different adsorption enthalpies with CO₂. Using more fitting parameters could increase the goodness-of-fit for each isotherm, but would chemically not make sense, thus making a three-site model the appropriate choice.

Another point, which has not been properly addressed in some published papers using multisite Langmuir models to fit CO₂ data, is the definition of the *q*_{sat} and *b* parameters. When these values are fit using minimization functions, there is the possibility of reaching a local minimum, but one that does not conform to good chemical sense. Therefore, when fitting the *q*_{sat} values over a range of temperatures, the *q*_{sat} value should be fixed. By definition, *q*_{sat} describes the quantity of gas adsorbed when exactly one layer of a given site is saturated, which is not temperature-dependent. The *b* values can be thought of as adsorption-equilibrium constants, generally decreasing with temperature, and can often be modeled by the Arrhenius equation. These minor nuances when fitting experimental data can have significant positive or negative effects on the predicted loadings and any subsequent calculations.

IAST Calculation. Ideal adsorption solution theory (IAST), developed by Myers and Prausnitz,¹⁹ has frequently been used to evaluate mixed component isotherms because it has been shown to reflect true mixed component measurements. To evaluate the efficacy of using PPN-6-CH₂EDA and –DETA for DAC, two separate IAST evaluations were performed. In both cases, CO₂ concentrations were taken to be close to the current global level of 400 ppm (40 Pa). The first set of calculations was performed using N₂ as the balance gas (100 kPa); the results are shown in Table S6. In previous studies it has been shown that O₂ can play a significant role in competing for adsorption sites against CO₂. To ensure a higher degree of accuracy, we additionally tested the effects of O₂ in our systems. The second set of calculations was performed using “air” to be composed of 78.96% N₂ and 21% O₂; the data are plotted in Figure 1. The results show that O₂ plays a larger role in competition with CO₂ than N₂ does; however, PPN-6-CH₂DETA retains significant adsorption of CO₂ in the mixture, thus indicating its efficacy for DAC. The reasons for the high selectivity over both N₂ and O₂ can be ascribed in large part to the high CO₂ loadings, particularly below 100 Pa. Other materials for CO₂ capture, Mg-MOF-74, NaX zeolite, and

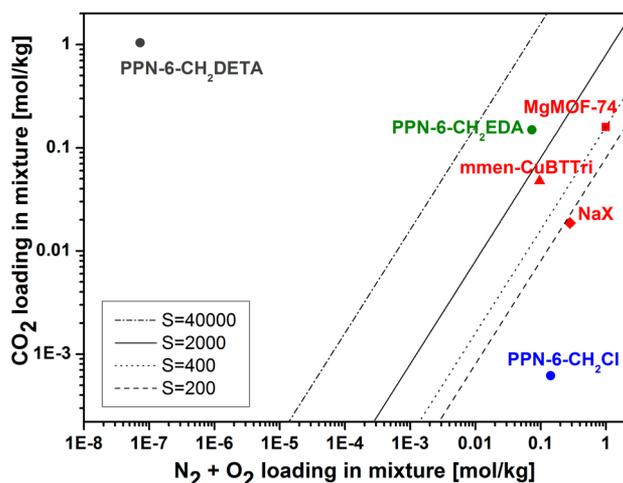


Figure 1. IAST calculations of component loadings of CO₂ and (N₂ + O₂) in the adsorbed phase with selected materials. The total bulk gas pressure is 100 kPa and contains 400 ppm CO₂, 78.96% N₂, and 21% O₂. Loadings for calculated selectivities are shown as a guide.

mmenCuBTTri are plotted for comparison, although only results using CO₂/N₂ are available.^{20,21}

Comparing the two amine-grafted PPNs reveals significant differences in CO₂ loading at these low concentrations. –EDA and –DETA have both been shown to be possible candidates for flue gas capture because of high selectivities and loading capacities in mixed component systems; however, for ambient air capture only –DETA is a viable candidate. The reasons for this have a strong basis in the chemical structure of the two materials. The –EDA structure has only short diamine chains, whereas –DETA has a third amine available to bind CO₂. This structural difference imparts –DETA with much higher loading without any pore blockage. The high loading and chemisorption-type interactions result in a boost in selectivity of 7 orders of magnitude. This difference is difficult to compare because the selectivity for –DETA is so high. A more telling number is the resultant purity of gas after separation (Table 1, eq 6 in Supporting Information). The value for –EDA is 67.0% in the N₂ + O₂ case, whereas –DETA reaches 99.999993%, which indicates that this material would be useful in a true mixed component system because the resulting CO₂ is a high enough purity to compress and store or use as a UHP grade chemical commodity. The desorption, or recovery, of this high-

Table 1. Comparison of CO₂ Loading, IAST Selectivity, and CO₂ Purity Data for CO₂ Capture from “Air” Containing 400 ppm CO₂

material	CO ₂ (mol/kg)	N ₂ ^a		N ₂ + O ₂ ^a	
		S _{IAST}	purity	S _{IAST}	purity
MgMOF-74 ²⁰	0.16	401	13.8		
Zeolite NaX ²⁰	0.02	166	6.2		
mmen-CuBTTri ²¹	0.05	1239	33.1		
PPN-6-CH ₂ Cl	0.001	11	0.4	11	0.4
mmen-Mg ₂ (dobpdc) ¹⁵	2.05	4.9 × 10 ^{1b}	96.1	4.2 × 10 ^{1b}	94.4
PPN-6-CH ₂ EDA	0.15	5078	67.0	5086	67.0
PPN-6-CH ₂ DETA	1.04	3.8 × 10 ¹⁰	99.9	3.6 × 10 ¹⁰	99.9

^aBalance gas. ^b“Molar selectivity”.

purity gas also does not require extraordinary amounts of energy, which is evidenced by the moderate heats of adsorption of 54 kJ/mol. See Figure S6 for loading-dependent adsorption enthalpies of all materials.

For PPN-6-CH₂DETA, pure component loading at 40 Pa is not as high as that for mmen-Mg₂(dobpdc);¹⁵ however, it is a decidedly better choice for CO₂ capture from ambient for several reasons: (1) The selectivity over N₂ and O₂ are substantially higher, although the values are extraordinarily high (3.6 × 10¹⁰ vs 4.2 × 10⁴) in both cases. (2) A more meaningful method of evaluating these compounds for ambient air capture is the modeled CO₂ purity after capture, reaching only 94% (below the industrial standard for pure gas) in the N₂ + O₂ case for mmen-Mg₂(dobpdc). Further comparisons are listed in Table 1. (3) Stability, primarily toward water, will also be a significant factor when extracting CO₂ from ambient air. While MgMOF-74 has been shown to be unstable toward moisture,²² amine-containing materials have been reported to enhance sorption capacities and selectivities in the presence of water.^{8,13,23,24}

Breakthrough Calculation. To determine whether –DETA is indeed a promising candidate for CO₂ removal from ambient air in fixed bed adsorbers, breakthrough calculations were performed using the methodology described in earlier works.²⁵ The breakthrough simulation used here has been validated by comparison with experimental breakthrough measurements carried out using a variety of mixtures by two different groups.^{26–28} This analysis provides crucial insights into true performance because it takes working capacity, selectivity, sorbent volume, and loading in mixed conditions into account. A schematic of a packed bed adsorber and full description of equations and methodology are given in the Supporting Information. Results of breakthrough calculations and comparison to other materials are shown in Figure 2a. The breakthrough calculations were carried out in both scenarios (using air to be 99.96% N₂, or a mixture of 78.96% N₂ and 21% O₂), keeping the constant 400 ppm inlet partial pressure of CO₂. The *x*-axis is a *dimensionless* time, τ , obtained by dividing the actual time by the contact time between the gas and the porous materials. Concentration of CO₂ in the outlet gas (ppm) is plotted along the *y*-axis. The result of a desirable material is longer breakthrough times, τ_{break} as this allows more CO₂ to be adsorbed. From a practical point of view, the best structure is the one that is capable of adsorbing the most amount of CO₂ for a given volume of material. The quantity adsorbed by the material in the packed column during the time interval 0 – τ_{break} is expressed in moles of CO₂ adsorbed per liter of adsorbent material and is plotted on the *y*-axis of Figure 2b. PPN-6-CH₂Cl has the shortest breakthrough time because it has the lowest CO₂ adsorption capacity, while –DETA has the longest breakthrough time, reflecting the highest uptake capacity of CO₂.

At the time of breakthrough, CO₂ uptake of –DETA is 0.36 mol/L, compared with 0.12 mol/L for MgMOF-74. Although MgMOF-74 has been shown to be useful for flue gas capture, in large part because the adsorption capacity at 0.15 bar is so high, at lower concentrations, such as ambient air, –DETA is, to the best of our knowledge, superior to any other materials tested by IAST and simulated breakthrough methods to date.

Working Capacity. By fitting experimental data to a multisite Langmuir model, adsorption quantities can be modeled as a function of pressure and temperature. Working capacity of a material in a TSA process can be defined as the

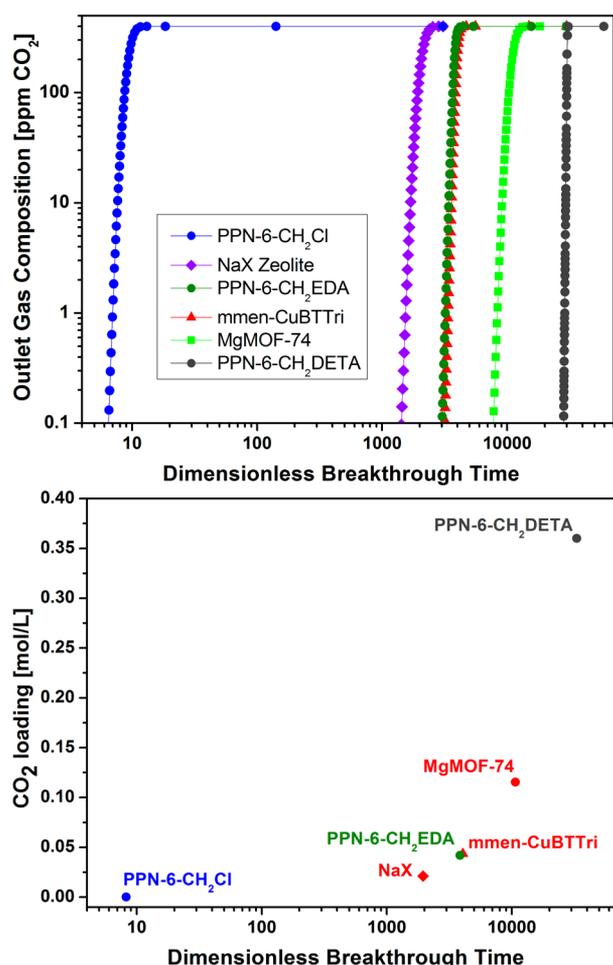


Figure 2. (a) Transient breakthrough of a $\text{CO}_2/\text{N}_2/\text{O}_2$ mixture in an adsorber bed packed with $-\text{CH}_2\text{Cl}$, $-\text{EDA}$, $-\text{DETA}$, MgMOF-74 , NaX zeolite, and mmenCuBTtri . (b) CO_2 adsorption capacities expressed as moles of CO_2 adsorbed per liter of adsorbent material as a function of the dimensionless breakthrough times.

difference in loading quantities at the adsorption and desorption state (eq 2):

$$\sum q_{\text{sat},i} \frac{b_i(T_{\text{ads}})P_{\text{ads}}}{1 + b_i(T_{\text{ads}})P_{\text{ads}}} - \sum q_{\text{sat},i} \frac{b_i(T_{\text{des}})P_{\text{des}}}{1 + b_i(T_{\text{des}})P_{\text{des}}} \quad (2)$$

where q_{sat} and b are Langmuir parameters (see Supporting Information for details) and i is the index for the CO_2 adsorption site.

Working capacities were calculated from mixed component (IAST) loadings at 295 K/400 ppm CO_2 and desorption at 1 bar over a range of temperatures. Figure 3 shows the working capacities of DAC as a function of temperature, with positive working capacities above 98 °C. Porous materials generally have low heat capacities and in the case of $-\text{DETA}$, the adsorption enthalpies are around 60 kJ/mol (see Figure S6), indicating that the regeneration energy penalty would not be very high.

CONCLUSIONS

DAC is a viable technology that should be given more consideration, as several features make it economically more feasible than it is often given credit for. The primary concerns regarding costs of DAC are driven by high regeneration

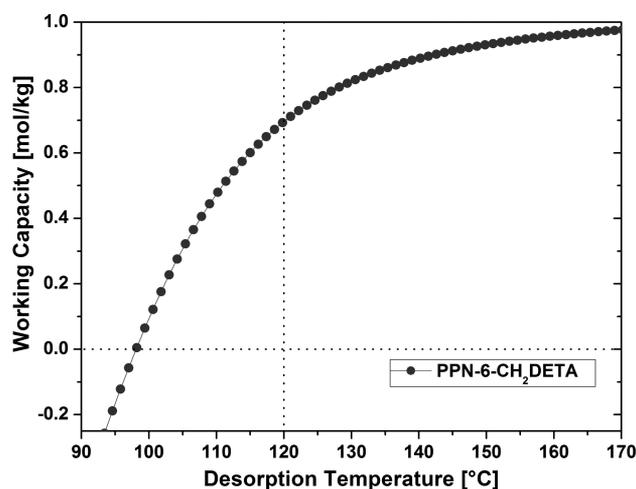


Figure 3. Working capacity as a function of desorption temperature.

energies for the state of the art technologies, in large part because of the enormous quantities of water that must be heated during regeneration. By moving to solid sorbent technologies, these energy penalties can be reduced. Amines supported on solid materials have been explored, primarily on silica supports; however, to the best of our knowledge, these amine-grafted PPNs represent the first sorbents taking advantage of highly porous three-dimensional carbon scaffold.^{3,10} Due to the stability of the base structure and large internal pore volume, many different amines can be included and amine loadings could easily be varied to tune the adsorption properties toward DAC. To the best of our knowledge, at 400 ppm, $\text{PPN-6-CH}_2\text{DETA}$ has among the highest selectivity and loading capacities using IAST and simulated breakthrough measurements of any compound reported to date. We can also conclude that the length of the amine chain is of crucial importance, as the shorter amine, $-\text{EDA}$, did not perform well under the conditions tested. $-\text{DETA}$ has a 6% higher CO_2 loading capacity than TRI-PCM-40 at 400 ppm (0.98 mol/kg) and the heat of adsorption is also evaluated to be about 25% lower (53.8 vs 67.3 kJ/mol). Both of these factors were significant parameters identified by Kulkarni and Sholl as large contributors to the capture cost in their recent report. This leads us to conclude that low costs are readily achievable with the $-\text{DETA}$ framework. Work is still being conducted on further extending the amine chains and varying loading ratios as this has been shown to affect CO_2 loading.

ASSOCIATED CONTENT

Supporting Information

Isotherm fit, IAST calculation, and breakthrough calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. W. Lu and J. P. Sculley contributed equally.

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Notes

The authors declare no competing financial interest.

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